Review Article

Hydrogen energy, economy and storage: Review and recommendation

J.O. Abe [a,b,*], A.P.I. Popoola [a], E. Ajenifuja [a,b,c], O.M. Popoola [b]

[a] Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, P.M.B. X680, Pretoria, South Africa
[b] Centre for Energy and Electric Power, Tshwane University of Technology, Pretoria, South Africa
[c] Center for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria

ARTICLE INFO

ABSTRACT

The hydrogen economy is a proposed system where hydrogen is produced and used extensively as the primary energy carrier. Successful development of hydrogen economy means innumerable advantages for the environment, energy security, economy, and final users. One major key to wholly develop hydrogen economy is safe, compact, light and cost-efficient hydrogen storage. The conventional gaseous state storage system as pressurized hydrogen gas and liquid state storage system pose safety and cost problems to onboard applications; therefore, they do not satisfy the future goals for a hydrogen economy. Fortunately, solid-state storage systems based on metal hydrides have demonstrated great potentials to store hydrogen in large quantities in a quite secure, compact, and repeatedly reversible manner and thus, becoming increasingly attractive option for hydrogen applications. However, techno-economic feasibility of hydrogen storage systems is yet to be realized as none of the current metal hydrides fulfill all the essential criteria for a practical hydrogen economy, mainly because of low hydrogen storage capacity, sluggish kinetics and unacceptable temperatures of hydrogen absorption/desorption. This article gives a brief review of hydrogen as an ideal sustainable energy carrier for the future economy, its storage as the stumbling block as well as the current position of solid-state hydrogen storage in metal hydrides and makes a recommendation based on the most promising novel discoveries made in the field in recent times which suggests a prospective breakthrough towards a hydrogen economy.

© 2019 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Contents

* Corresponding author. Department of Chemical, Metallurgical and Materials Engineering, Tshwane University of Technology, P.M.B. X680, Pretoria, South Africa.
E-mail address: johnabe.fm@gmail.com (J.O. Abe).

Introduction

Energy is an integral part of our everyday life, and it is required to perform virtually all human activities. However, we still take energy for granted someway while energy crisis is on the increase [1−3]. Fossil fuels such as petroleum, natural gas, and coal provide more than 80% of all the energy being consumed globally [3−8]. The expanding population of the world and incessant humans desire to improve their living standard continue to give rise to high energy demand far way back from 1950. The world energy consumption is projected to climax in 2035 while the world economy is projected to go into a long depression after 2040 [3,5,9−12]. To a great extent, major economies of the world today rely on fossil fuels. However, excessive dependence on fossil fuels has become a critical global challenge in today's economy, because they are diminishing apace [4−6,9,13−15]. It was speculated that current fossil fuel reserves can support a maximum of 40 years for petroleum, 60 years for natural gas and 156 years for coal [17]. The world experienced a major surprise in 2008 when oil prices skyrocketed (Hirscher, 2009) [18]. With the level of the current consumption rate, the prospect is that these fuels will continue to be high-priced and if care is not taken may be out of stock soon [4,6]. Consequently, increase in energy consumption and depletion of reserves of fossil fuel present a danger to the energy and economic security worldwide plus the fact that they are not environmentally friendly, because they release greenhouse gases and other pollutants which are major contributors to planet-warming [1,3,4,6,12,13,15,19,20].

Anthropogenically, humanity is reaching an era when if nothing serious is done to mitigate the current energy challenge life on planet earth will be unbearable economically and health-wise because of chronic health issues emanating from hazardous air contamination. Hence, the need to reappraise the current dependence on fossil fuels is now recognized [2,6,13,18,21,22]. Many scientists and engineers have come to terms with the fact that sourcing an environmentally clean, cheap and more sustainable energy on demand to replace the existing fossil fuel system could solve these global energy problems [5,6,12,16,20,23]. Therefore, the vision of the future sustainable energy calls for:

❖ ascertaining security of energy supply;
❖ introduction of the use of sustainable local energy resources;
❖ reduction of global carbon dioxide emissions;
❖ significant improvement of urban air quality; and
❖ creation of a new industrial and technological energy base, essential for the prosperity of the future economy [1,14].

After numerous considerations, hydrogen because of its outstanding properties emerged a hopeful ideal sustainable future energy carrier [10,13,21,22,25−31]. The concept of employing hydrogen as an energy carrier dates to over two centuries ago but was accentuated following the global energy crisis of 1970s with technological advances in the 1980s [30,32]. The topic of hydrogen as potential energy of the future economy has been the theme of research in the field for quite some time. The extremely low density of hydrogen makes its storage a technical issue to settle to achieve a hydrogen-oriented economy [3,10,11,14,24,31,33,34]. Generally, hydrogen can be stored as pressurized gas, cryogenic liquid, or physically or chemically bonded to appropriate solid-state material [3,21,25,31,32,40]. Among these storage systems, solid-state storage systems based on metal hydrides show greater potentials for high gravimetric capacity for hydrogen storage in a quite safe, efficient, compact and repeatedly reversible way and, therefore, gradually gaining prominence for hydrogen applications [11,21,31,34−36]. As of now, none of the metal hydrides presented has fulfilled all the necessary requirements for a hydrogen economy, mainly because of low hydrogen storage capacity, sluggish kinetics and unreasonable temperatures of hydrogen ab(de)sorption [11,31,37−45]. The present review laconically discusses hydrogen energy, hydrogen economy, hydrogen storage, the current position of solid-state hydrogen storage in metal hydrides and finally makes a recommendation based on promising new developments in the field which suggest a prospective breakthrough for hydrogen storage practical applications towards a hydrogen economy.

Hydrogen energy

Hydrogen is largely regarded as a potential cost-efficient clean fuel for the future economy owing to the proven fact that it is: (i) the most abundant element in the universe (makes up more

than 90% of all atoms), (ii) the lightest element (molecular weight = 2.016) with highest known energy content (calorific or heating value) of any fuel, (iii) sustainable, (iv) non-toxic, and (v) unlike petroleum, natural gas or coal, it is as an energy carrier, environmentally pleasant and beneficial with water as the only exhaust product at conversion to energy. Hydrogen can be generated from both renewable such as hydro, wind, wave, solar, biomass and geothermal energy sources, and non-renewable such as coal, natural gas and nuclear energy sources. It can be stored as a fuel and used in transportation, in power generation systems using fuel cells, in internal combustion engines or turbines [3,11,12,16,22,24,25,30−33,38−40,46]. Hydrogen has an awesome energy storage capacity and it has been shown from calculations that the energy contained in 1 kg of hydrogen is about 120 MJ (=33.33 kWh), which exceeds double of most conventional fuels [39,47−50]. Table 1 shows the comparison of energy contents of hydrogen and other alternative fuels.

In line with the sustainable energy vision of our future, Becherif et al. [25] discoursed more benefits derivable from hydrogen including: (i) security of energy via drop of oil imports, (ii) sustainability by maximizing renewable energy sources, (iii) reduction of pollution and improvement of urban air quality by the generation of near-zero carbon, greenhouse gases, and oxide emissions at usage, and (iv) economic feasibility for future global economy prosperity. For these reasons, hydrogen has been put forward as a key solution to the current prevailing energy challenge and planet-warming which threatens to cripple the energy security and environmental safety worldwide [7,18,24,40,52].

Hydrogen economy

A hypothetical idea of a system where hydrogen is the principal energy carrier is called the Hydrogen Economy or Hydrogen Energy System. John Bockris was the first person to use the term "hydrogen economy" during his presentation in 1970 at General Motors (GM) Technical Center. The primary aim of a hydrogen economy is that hydrogen would be produced largely from energy sources that are readily available with the view to substituting the current fossil fuels used in transport, industrial, residential and commercial sectors. Hydrogen economy has been proposed to be a very refined and lasting answer to the interconnected problems confronting the world today including: (i) global environmental issues, (ii) depletion of natural resources, (iii) food shortage and malnourishment in the third world nations, and (iv) the expanding growth of the world population. Even though the problems associated with the fossil fuel economy are indeed grave and overwhelming, successful development of the hydrogen economy means tremendous advantages for the environment, energy security, economy, and final consumers [6,8,11,13,23,24,32,46,53−55]. Despite undeniable advantages, prompt conversion from fossil fuel energy system to a hydrogen energy system has been faced with significant scientific, technological and socioeconomic roadblocks. Hydrogen's extremely low density makes its storage a critical matter in the transition [10,11,24,31,34,56,57]. Although hydrogen is typically used by refineries and chemical industries, its production, storage, and delivery costs are too high and unacceptable for most energy applications [11,27,40,58,59]. Nonetheless, the huge benefits of the hydrogen economy are so fascinating that the governments of different nations across the globe are investing immensely towards enhancing the prospects of the energy system [32]. In 2003, the European Commissions High Level Group for Hydrogen and Fuel Cells Technologies suggested that the European Union in 2050 should attain a hydrogen-based economy and estimates that 35% of newly produced vehicles will be fueled by zero carbon hydrogen in 2040 [1]. On the other hand, the U.S. Department of Energy's Energy Efficiency and Renewable Energy, Fossil Energy, Nuclear Energy, and Science Offices proposed that conversion to hydrogen-powered fuel cell vehicles should take place about 2020 [14,60,61].

Hydrogen storage

For decades hydrogen storage has been in the mainstream of research of most technologically progressive nations of the world. The motivation behind the move is the credence given to the fact that hydrogen can help to tackle the growing demand for energy and hold up global climate change [13,31,58,62,63]. Moreover, storage of hydrogen is a key enabling technology for a sustainable hydrogen energy development essential for the prosperity of the future economy [21,39,60,64,65]. The hydrogen economy requires both mobile and stationary hydrogen storage systems to thrive. The mobile division is thought to be the higher quantity consumer of hydrogen in the future hydrogen economy. Although hydrogen has decent properties to fuel internal combustion engines in automobiles, it is presumed that polymer electrolyte membrane fuel cells (PEMFCs) will substitute conventional engines at the instance of a hydrogen-based economy. Unlike an engine which converts chemical energy into heat and then heat into mechanical energy,

Table 1 − Comparison of some selected energy contents of fuels [51].		
Fuel	Energy contents [MJ/kg]	
	Lower heating value	Higher heating value
Gaseous hydrogen	119.96	141.88
Liquid hydrogen	120.04	141.77
Natural gas	47.13	52.21
Liquified Natural Gas (LNG)	48.62	55.19
Still gas (in refineries)	46.89	50.94
Crude oil	42.68	45.53
Liquefied Petroleum Gas (LPG)	46.60	50.14
Conventional gasoline	43.44	46.52
Reformulated or Low-Sulfur Gasoline (RFG)	42.35	45.42
Conventional diesel	42.78	45.76
Low-Sulfur diesel	42.60	45.56
Coal (wet basis)	22.73	23.96
Bituminous coal (wet basis)	26.12	27.26
Coking coal (wet basis)	28.60	29.86
Methanol	20.09	22.88
Ethanol	26.95	29.84

PEMFC directly and efficiently transforms the chemical energy of hydrogen fuel into electrical energy with water as the only exhaust product, and capable to lower greenhouse gases emissions, current use of energy, and reliance on fossil fuels [3,11,16,24,59,66]. However, both mobile and stationary storage systems have their peculiar requirements and challenges. Concerning stationary applications, hydrogen storage issues of weight and volume are not as much serious compared to mobile applications. Stationary hydrogen storage systems can take up more space, function at high temperatures and pressures and feature spare capacity to offset sluggish kinetics. Even so, inadequate materials for storage tanks is a major technical setback against the development of stationary hydrogen storage systems. On the other hand, mobile applications hydrogen storage requirements are way exhaustive in contrast to stationary applications [11,24,67]. The U.S. Department of Energy (DOE) goals for hydrogen storage requirements for mobile applications identifies the significance of both gravimetric and volumetric capacity of storage. Here, the gravimetric capacity of storage refers to the quantity of hydrogen gas a given weight of storage material can generate while volumetric capacity of storage conveys the quantity of hydrogen gas contained in a given volume of storage material as seen in Table 2 below. High values of both parameters are greatly desired for suitable hydrogen storage. However, if storage is too heavy, the range of the vehicle will be restricted and if storage is too voluminous, the luggage space will be restricted as well. In other words, effective balance must be ensured. Other important aspects of requirements for onboard hydrogen storage include low-operating pressure, low operating temperature between, fast kinetics of hydrogen uptake/release, low heat of formation to minimize the energy necessary for hydrogen release, low heat dissipation during the exothermic hydride formation, limited energy loss during charge and discharge of hydrogen, multicycle reversibility of hydrogen uptake/release, high stability against oxygen and moisture for long cycle life, low cost of recycling and charging infrastructures, high safety under operating conditions and public acceptance [11,14,21,24,31,59,62,68−70]. Table 2 shows an overview of some of the new DOE technical system goals for onboard hydrogen storage for light-duty fuel cell vehicles beginning from 2020.

Hydrogen stable chemistry allows room for long period storage of energy [73]. Hydrogen could be stored in multiple ways, though with their identified strengths and weaknesses [52]. There are three basic types of hydrogen storage systems available depending on the size of storage and area of application namely, gaseous, liquid and solid-state storage systems [3,25,31,32,40,74].

Gaseous state storage system

The most established hydrogen storage system is physical storage in the form of pressurized hydrogen gas. As previously stated, hydrogen has a very low density of 0.089 kg/m^3, because of this its storage requires high pressure or extremely low temperatures [11,35,39,52,59]. At present, the current fuel-cell applications require that hydrogen is pressurized between 35 MPa and 70 MPa. Hypothetically, between 11 and 13% of the hydrogen energy content is affected negatively by pressurizing [54]. Due to its extreme lightness, there are chances that under high-pressure hydrogen leakage from containing vessels may ensue. Steel and aluminium materials are used for the traditional type of storage vessels for commercial hydrogen. However, carbon fiber reinforced plastic composite vessel with adequate strength and impact resistance for safety during collisions, is a lighter solution but too expensive and generates another problem for future cost reduction in contrast to steel or aluminum vessels [18,35,52,54,61,67,68]. Moreover, the scientists and engineers are exploring other options that are more economical and practical. If the quantity of hydrogen to be stored is large or the storing time is somewhat long, compressed hydrogen could be stored in large underground storages in suitable geological formations as

Table 2 − Overview of some selected parts of the U.S. DOE technical system goals for onboard hydrogen storage for light-duty fuel cell vehicles [11,25,71,72].

Storage parameter	Unit	2020	2025	Ultimate
Storage capacities				
Gravimetric capacity				
Material-based gravimetric capacity	[kWh/kg]	1.5	1.8	2.2
System-based gravimetric capacity	[kgH$_2$/kg system]	0.045	0.055	0.065
Volumetric capacity				
Material-based volumetric capacity	[kWh/L]	1.0	1.3	1.7
System-based volumetric capacity	[kgH$_2$/L system]	0.030	0.040	0.050
Storage system cost (and fuel cost)	[$/kWh net]	10	9	8
	[$/kg H$_2$]	333	300	266
Durability/Operability				
Operating ambient temperature	[°C]	−40/60 (sun)	−40/60 (sun)	−40/60 (sun)
Min/Max delivery temperature	[°C]	−40/85	−40/85	−40/85
Cycle life (1/4 tank to full)	[cycles]	1500	1500	1500
Min. delivery pressure from tank	[bar]	5	5	5
Max delivery pressure from tank	[bar]	12	12	12
Charging/Discharging rates	[min]	3−5	3−5	3−5
System fill time (for 4−10 kg)				
Fuel purity (H$_2$ from storage)	[%H$_2$]	Meet or exceed applicable standards e.g. SAE J2719 (99.97 dry basis)		

caverns of salt domes. Hydrogen storage in salt caverns is a desirable prospect for hydrogen seasonal storage at elevated pressures and hydrogen can be released within an appropriate period. The salt caverns are extremely impervious to hydrogen, even under high pressures and effectively prevent leakage. On calm or cloudy days when solar and wind power are not so active, hydrogen could then be recovered from caverns and burned in combined-cycle power plant that generates electricity. For quite some time, there were no suitable infrastructures that can effectively burn pure hydrogen, but in recent times this kind of infrastructures are being developed [27–29,54,75–78]. One of the most recent examples is the hydrogen underground storage project in Romania, which is a part of the European assessment project given the name HyUnder project, supported by the FCH JU (Fuel Cell and Hydrogen Joint Undertaking). This project is aimed at facilitating the storage of enough hydrogen underground in salt caverns for potential use, especially in chemical industry, the transport sector and salt industry [27,29,77,78]. To date, despite promising options the relatively low hydrogen density, extremely high gas pressures, cost and system safety issues are still significant hindrances of this technically simple and fully established technology [11,31,32,35,39,61,68,70].

Liquid state storage system

Another method of physical storage of hydrogen is in the form of cryogenic liquid. Storage as liquid comes with a higher density. Liquid hydrogen has a density of about 71 g/L at its normal boiling point of 20 K, which is approximately 1.8 times the density of hydrogen pressurized up to 70 MPa at 288 K. Owing to the low boiling point of liquid hydrogen, its cooling technology requires very low temperatures which consume about 30% of its total energy content [17,33]. Thus, special double-walled vessels furnished with good insulation systems are essential to mitigate heat leakage. More compact and lighter cryogenic pressure vessels, therefore, provide better safety advantages than compressed hydrogen vessels. However, the persistent boil-off of hydrogen and too much energy required for liquefaction restrict the potential use of liquid hydrogen storage systems to applications that require high energy density as well as uses where hydrogen cost does not matter, and its consumption is within a short time, examples include air and space and automotive applications [7,17,29,30,41].

Solid-state storage system

In view of a hydrogen economy, storage systems need to be very safe, efficient, economical, light and compact [11,21,38,39,59,76,79,80]. On the other hand, it was mentioned earlier that the conventional pressurized hydrogen gas and cryogenic liquid hydrogen require a lot of space, bulky storage system and have safety issues plus high cost; therefore, they fail to satisfy the future targets for a hydrogen economy [21,34,40,57]. It is obvious that hydrogen storage needs a more technical breakthrough, probably in the most feasible option in contrast to pressurized hydrogen gas and cryogenic liquid hydrogen. Specifically, for a fuel cell vehicle, storage of enough hydrogen onboard is a major hurdle to cross. A hydrogen storage system is expected to possess high gravimetric and volumetric capacity to realize techno-economically viable hydrogen-based vehicular applications. To achieve this goal much attention is currently being given to storing hydrogen in solid-state materials. Solid-state materials can reversibly absorb and release hydrogen which positions them as a vantage option since they are not used up straight off [11,13,21,25,26,33–35,37,68]. The exploitation of hydrogen storage potentials of new solid-state systems may perhaps usher in a significant shift in the defective paradigm of hydrogen storage and have a major impact on the road to a working hydrogen economy [21,25,36,37].

In solid-state storage systems, hydrogen is stored either by physisorption or chemisorption [11,31,34,35,40,68]. In physisorption, molecular hydrogen adsorbed on surfaces of solids by van der Waals interactions such as in carbon-based materials: carbon nanotubes, fibers, fullerenes, activated carbon, zeolites, metal-organic frameworks (MOFs) as well as covalent organic frameworks (COFs) and more recently polymers of intrinsic microporosity (PIMs). The hydrogen can then be liberated whenever required by thermal stimulation or any other suitable technique. Although the reversibility and fast kinetics make these materials nice-looking options, low hydrogen storage capacity at ambient conditions and the requirement of extremely low temperatures for high hydrogen storage capacity place appalling constraints on the use of these materials as it touches on the practical application [2,11,21,31–33,35,37,39,42,70,81]. On the other hand, chemisorption is in form of atomic hydrogen chemically reacting with solids to form hydrides (metal, complex and chemical hydrides). While several prototypes of complex hydrides vessels mostly with $NaAlH_4$ and $Mg(NH_2)_2–LiH$ have been developed and tested with confirmed high energy densities, the complexity of the hydrogenation and dehydrogenation reactions of complex hydrides and the deficiency of reversibility presently hamper potential applications [31,33,37,39,81,82]. Similarly, chemical hydrides provide higher energy densities compared to other hydrides because they are typically composed of lighter elements plus the fact that they can release hydrogen easily under relatively moderate operating conditions. For example, sodium borohydride ($NaBH_4$) can provide relatively high theoretical hydrogen yield (10.8 wt%) through hydrolysis reaction, which proceeds in an aqueous medium with a catalyst. Unfortunately, the use of hydrolysis for hydrogen generation onboard is restricted by too much heat generated during the reaction and the dehydrogenation reactions are not reversible, that is, the fuels are used up straight off. Besides, the ensuing by-products must be regenerated off-board the vehicle [3,21,33,37,39,61,83–85]. However, among the hydrides, metal hydrides have been recognized as one of the most feasible solutions to store hydrogen. Metal hydrides hold the promise to link hydrogen storage with a future hydrogen economy [3,21,34,40,42,70,86,87]. Advances in metal hydride technology demonstrate that metal hydrides offer a great opportunity for hydrogen to be stored to a high degree of safety, reversibility of hydrogenation/dehydrogenation, volumetric energy densities of hydrogen, low-pressure equipment and little energy requirements for both mobile and stationary applications [3,11,45,88]. Over the past decade, governmental policies

across the world have encouraged intensive research on hydrogen storage in metal hydrides with specialized attention on the implementation of polymer electrolyte membrane fuel cells (PEMFCs) [42,61,89,90].
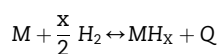
Metal hydrides

A metal hydride is technically formed via a chemical reaction but acts like a physical storage method [11,13,57]. In metal hydride tank, hydrogen molecules bond into metal under moderate temperature and pressure, usually between 3 and 30 atm, much lower than compressed gas tanks. This makes the system safer than any other solutions since hydrogen gas leakage cannot be spontaneous or the containing tank blow up by itself [13,54,59,62]. However, metal hydride tanks are comparatively very heavy, but weight should not be a challenge for stationary and some other niche applications, especially for small storages. And once their weight issue is solved by discovering novel light materials, incorporating them in mobile application will be more probable [87]. Moreover, they have comparatively high hydrogen volumetric energy densities, good storage efficiency, and can uptake/release hydrogen with a slight change in pressure, which make them one of the most promising solutions [11,13,32,54].

According to Crivello et al. [91], Züttel [70], Heung [87], Blackburn et al. [92], Prabhukhot et al. [11] and Sakintuna et al. [62], metal hydrides are produced by the interaction of hydrogen with different metals, either pure or alloy (in granular form or particles) resulting in solid-state storage under moderate temperature and pressure which gives them the crucial safety advantage above gaseous and liquid storage systems. A key contributing factor to a wide usage of metal hydrides in the field of hydrogen storage is their huge capacity to accommodate a significant amount of hydrogen in their structures [13,37,92,93]. It is possible to pack more atoms of hydrogen into a metal that forms a hydride lattice than into the same volume of liquid hydrogen because when such metal is brought in contact with gaseous hydrogen, the hydrogen molecules are first adsorbed onto the surface of the material [13,37,70,94]. If enough energy is added to the system, the hydrogen molecules dissociate into hydrogen atoms, then diffuses into the bulk and occupy the interstitial sites of the metal crystal lattice and forms a solid solution with a lesser amount of hydrogen (α phase). As more energy is added to the system, the hydrogen content increases, a hydride phase (β phase) nucleates which allows the metal to absorb hydrogen in larger amounts and grows until the metal becomes saturated with hydrogen. For example, the hydrogen storage density of magnesium hydride (6.5H atoms/cm^3) is way higher than hydrogen gas (0.99H atoms/cm^3) or liquid hydrogen (4.2H atoms/cm^3). Thus, metal hydride storage is a safe, volume-efficient storage system for onboard applications [11,22,37,62,87,89,91,95].

Ozturk and Demirbas [59], Sahaym and Norton [13] and Zaluski et al. [43] described metal hydrogenation as the formation of metal hydrides by hydrogen absorption usually accompanied by the release of heat. In this way, as hydrogen gas is absorbed in these metal particles pressure builds up in the tank. However, for decomposition and dehydrogenation

process equal amount of heat must be added to the metal hydride. These processes are continuously repeatable, and reversible metal hydrides can, therefore, be used for the storage of heat and hydrogen. Charging and discharging of the hydride tank can be performed as many times as possible in as much as the hydride material does not become contaminated [11,91,96,97].

According to Züttel [70], all the reversible hydrides operating around room temperature and atmospheric pressure comprise of transition metals. The most reactive ones are the electropositive elements such as lanthanides, actinides, and members of the titanium and vanadium groups. Depending on the thermodynamics of the reaction, different temperatures apply to different metal hydrides. A typical reversible interaction between metal/alloy and hydrogen can be written as:

$$M + \frac{x}{2} H_2 \leftrightarrow MH_X + Q$$

where M is a metal, an intermetallic alloy, or a solid solution, x is a positive whole number, MH$_x$ is the formed hydride and Q is the heat of reaction. A simplified model of hydrogen storage in a metal hydride is given in Fig. 1 below.

Prabhukhot et al. [11] and Ozturk and Demirbas [97] reported that both the thermodynamic and kinetic conditions are the essential requirement that must be met for hydrogen storage to occur. Under this circumstance, a metal exposed to hydrogen gas absorbs hydrogen until equilibrium is reached. There are various reaction steps that kinetically may prevent a hydrogen-storing system to reach its thermodynamic equilibrium of hydrogen storage within a reasonable time. The reaction rate of a metal-hydrogen system is, therefore, a function of pressure and temperature. Hydrogen storage in metal hydrides comprises a few mechanistic steps and depends on some parameters. Essentially, the surface of the metal must be able to dissociate the hydrogen molecule and permit easy mobility of hydrogen atoms to be able to store hydrogen. Different metals have different abilities to dissociate hydrogen depending on their surface structures, morphologies, and purities.

According to David [41], Lai et al. [81] and Khafidz et al. [94], metal hydrides can be categorized into low-temperature hydrides and high-temperature hydrides based on the
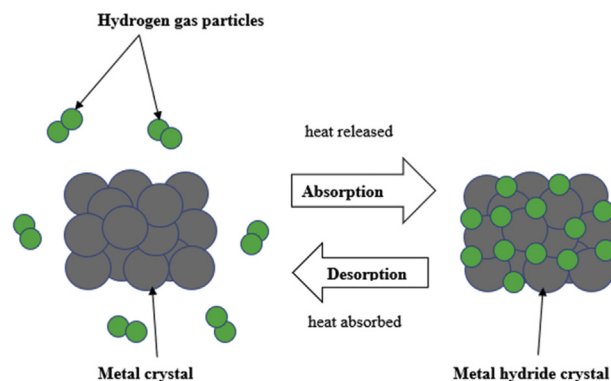

Fig. 1 – A simplified model of a metal hydride hydrogen storage.

temperature of absorption/desorption of hydrogen. Hydrogen is bound via covalent bonding in the low-temperature hydrides, and the metal hydride consists of high molecular weight material which exhibits fast kinetics and low hydrogen equilibrium pressures because of their low heat of reaction. These metal hydrides are mostly intermetallic alloy or solid solution hydrides operating at ambient to moderate temperatures. Whereas on the other hand, hydrogen is usually ionically bound in the high-temperature hydrides, and the metal hydride consists of low molecular weight material. Although the high temperature restricts the choice of high-temperature hydrides, they have been found to possess relatively higher hydrogen storage capacities than the low-temperature hydrides.

According to many authors who worked on hydrogen storage materials [2,3,11,41,43,81,98–102], the common low-temperature hydrides for hydrogen storage can be grouped based on the stoichiometries as AB_5–type (e.g. $LaNi_5$), AB_2-type (e.g. Ti–Zr alloys), A_2B-type (e.g. Sb_2Ti, Sn_2Co) and AB-type (e.g. Ti–Fe alloys), where A represents elements with high affinity for hydrogen typically rare-earth or alkaline-earth metal (e.g., Ca, Ti, Y, Zr, Hf, La, Ce, etc.) and B represents elements with low affinity for hydrogen typically a transition metal that forms only unstable hydrides (e.g., Cr, Mn, Fe, Co, Ni), but their combined hydrogen storage capacity is relatively low (below 2 wt%) because of the crystal structure and unit cell volume limitation. For instance, the intermetallic compound $LaNi_5$ is one of the most studied hydrogen storage material because it exhibits good hydrogen storage characteristics in terms of kinetics, pressure and temperature requirements. However, at a moderate temperature, the hydrogen storage capacity of $LaNi_5$ is quite low at about 1.4 wt % and it is too costly for onboard applications [3,11,26,39,45,88]. Another intermetallic compound well studied for hydrogen storage is FeTi with a maximum hydrogen storage capacity of about 1.9 wt% and due to the formation of oxide layer of titanium, activating the material is problematic which makes it unachievable to reproduce ab(de)sorption of the maximum quantity of hydrogen in the compound without high temperature and high hydrogen pressure [3,11,21,26,43–45,65]. Thus, existing metal hydride systems fail to store large quantities of hydrogen and the development of new kinds of metal hydrides is essential [41]. However, magnesium and magnesium-based alloys have been extensively investigated as hydrogen storage materials by many researchers [11,42,62,82,103–108], because of the numerous advantages of magnesium including lightness, abundant availability, resistance to heat, damping capacity and low cost. Although the alloys were found prospective and competitive

candidate for mobile hydride storage with good reversibility, recyclability and higher capacities (up to 7.6 wt%) compared to other hydrogen storage alloys, they have slow kinetics and uptake/release hydrogen at a high temperature range between 300 and 400 °C which reduce their efficiency and suitability for hydrogen storage applications. Therefore, major significant problems associated with the practical use of metal hydrides consist in weight and low hydrogen storage capacity for the low-temperature metal hydrides on the one hand, and slow kinetics and unacceptable high temperatures for relatively lightweight metal hydrides with higher hydrogen storage capacities on the other hand [11,13,26,38,40–45,64,66,110]. Table 3 shows the comparison of the hydrogen storage properties of some common hydrides.

Most of the promising hydride-forming metals and alloys such as the magnesium and magnesium-based alloys [34,110], are very reactive and form a surface passivation layer (SPL) [40,42], consisting metal oxides, hydroxides, carbon-oxygen compounds and water of various thicknesses which acts as a hydrogen barrier and must be broken for the gaseous hydrogen to diffuse into the bare surface. To enable practical applications, these materials usually need to be activated before their kinetics are improved to effectively absorb/desorb hydrogen [11,26,43,57,94,107,111,112]. This activation process requires the application of high temperatures or high hydrogen pressures to overcome the activation barrier. The higher the activation barrier the more the energy input required [43,102,110]. Homogenization by slow and complex heat treatment in a vacuum is usually conducted where fresh material surface becomes available as the SPL is broken up. However, some of the oxidation that generated the SPL may not be easily reversed, leaving a portion of the sample inactive to hydrogen uptake. Besides, the heat treatment process is done at elevated temperatures and high hydrogen pressures. This hypothetical "poisoning" effect could be more pronounced at high temperatures [43,92,93]. Hence, care is taken to avoid heat treatment as much as possible [16]. All these are shortcomings that have limited the widespread usage and commercialization of metal hydrides as hydrogen storage devices for long [11,41,43].

Recent developments in improving hydrogen storage in metal hydrides

During the past three decades, researchers and developers in the field have made great efforts towards enhancing the kinetics of hydrogen absorption/desorption of current metal hydrides with considerable hydrogen storage capacities

Type of hydride	Metal/Alloy	Hydride	Structure	Weight percent of hydrogen [wt.%]	Equilibrium pressure [bar]	Operating temperature [K]	Reference
AB_5	$LaNi_5$	$LaNi_5H_6$	Hexagonal	1.4	2 bar	298	[26,39,94,102,108–110]
BCC solid solution	TiV_2	TiV_2H_4	Cubic	2.60	10 bar	313	[102,108,109]
AB_2	ZrV_2	$ZrV_2H_{5.5}$	Hexagonal	3.01	10^{-8} bar	323	[102,108]
AB	FeTi	$FeTiH_2$	Cubic	1.89	5 bar	303	[3,94,102,108,109]
Elemental	Mg	MgH_2	Hexagonal	7.6	1 bar	600	[13,40,108–110]
A_2B	Mg_2Ni	Mg_2NiH_4	Cubic	3.59	1 bar	555	[102,108–110]

Table 3 — Common hydrides and their hydrogen storage properties.

without increasing the temperature. In this session, we will consider briefly major important feasible approaches reported, which essentially involve the addition of catalysts, alloying with other elements, nanostructuring and nano-confinement [26,33,40,42,43,45,102,107,109,113–116,121].

Catalysis

Catalysis is the process of enhancing the sorption kinetics of hydrogen of metal hydride systems that facilitates dissociation of hydrogen molecules or recombination of hydrogen atoms rapidly and effectively. Common catalysts employed to improve hydriding/dehydriding kinetics of metals/alloys include various transition metals (e.g. Ti, V, Ni, Pd, Pt, Ru, Rh), metal oxides (e.g. Nb_2O_5, Cr_2O_3, Fe_3O_4, TiO_2), non-metals (e.g. carbon) and compounds [11,13,40,57,63,102,109,113,116–119]. As an example, Adams and Chen [102] identified palladium as a good catalyst for other metal hydrides with exceptional properties required for hydrogen applications since it requires little or no activation energy and has a superior dissociative ability. Palladium can take up large volumetric amounts of hydrogen at normal room temperature and atmospheric pressure still in its primary α-phase, and then forms Pd-hydride as more quantities of hydrogen is absorbed. Based on these, the authors presented a conceptual model of clusters of MgH_2 in pure, nanocrystalline and Pd-doped forms. It was found that Pd-doped Mg takes three times faster to reach the same hydrogen capacity as pure Mg. The inherent selectivity of palladium for hydrogen, quick sorption kinetics, and reversible formation of hydride enable Pd-based alloy films to reach a high hydrogen gas quality at 99.9999% purity. Another potential catalyst is platinum. Carbon-supported platinum is often applied as an electrocatalyst in low-temperature fuel cells. The widespread application of palladium, platinum and other platinum group of metals remains unrealistic because they are prohibitively expensive. Notwithstanding, if suitable cost-efficient methods such as alloying with more economical metals and use of nanoscale materials can be employed, these elements can be very useful in hydrogen economy to purify hydrogen and harness its energy through fuel cells. Fetcenko et al. [120] carried out an interesting investigation where cheap coated alloy capable of high hydrogen storage capacity and excellent room temperature kinetics was discovered. The authors produced Mg–Ni based alloys with Mg content ranging between 40 and 65 atomic percent of the alloy by melt spinning and mechanical alloying. The alloy was coated with a catalytically active metal film (Fe or Pd) approximately 20 nm thick deposited on a minimum of a part of a surface of the Mg–Ni based alloy. It was observed that these catalytic treatments play a significant role in influencing the excellent properties of the alloys. Hydrogen storage capacity up to 4.86 wt % at pressures of about 10 bar with a high degree of absorption rate at low temperatures of about 30 °C in 2 min. Interestingly, the alloy could as well desorb fully the stored hydrogen below 250 °C, beginning at temperatures as low as 90 °C. Shan and co-authors [57] showed a significant improvement of the hydrogen uptake and release performances of AB₅ type intermetallic alloy $LaNi_{4.7}Al_{0.3}$ treated with small amounts of palladium and platinum. The authors attributed the finding to enhanced spillover and reverse

spillover of hydrogen respectively. The treated alloys could as well be activated at very low hydrogen pressure at room temperature and uptake and release hydrogen at quicker rates (up to hundred times), even after more than two years of air exposure. Prabhukhot et al. [11] also reported that the addition of nanoparticles of palladium, platinum, and ruthenium as catalysts has been studied and a substantial improvement in the ab(de)sorption kinetics was observed. Khafidz and co-authors [94] also stated that the catalytic effects of transition-metal oxides and pure or as-received metals, such as titanium, nickel, and other catalysts, have received considerable attention due to their positive influence on the kinetic properties of light metal-based materials. Other catalysts such as intermetallic compounds, carbon materials, mesoporous materials, such as aerogels and silica materials have also been investigated. These elements and their related compounds have the promise of high, reversible, and practical hydrogen storage capacity for large-scale and distributed energy storage for stationary applications, and mobile applications, including vehicles and portable power equipment [2,81,107,121–124]. For instance, Daryani et al. [125] studied the combined effect of TiH_2 and TiO_2 particles on the kinetics of hydrogen desorption of nanostructured magnesium hydride. It was reported that adding the titanium-based catalysts to MgH_2 brought about improved uptake kinetics of hydrogen of 4.5 wt% H_2 within a short period after 60s and led to a substantial enhancement of release kinetics of hydrogen also. The authors claimed that the catalysts addition to MgH_2 was responsible for the improved sorption kinetics of hydrogen by weakening the Mg–H bond, increasing hydrogen diffusion into the particles surface enabled by the MgH_2 particles high specific surface area and the presence grain boundaries. The active species of the catalysts enter the MgH_2 compact and improves the hydride phases growth and nucleation. In another work, Barkhordarian et al. [126] investigated the catalytic mechanisms of various transition-metal oxide on magnesium-based hydrides sorption reaction. The researchers found that catalytic activity was strongly affected by four distinct physico-thermodynamic properties of the transition-metal compound: multiple structural defects, low stability of the compound, a high valence state of the transition-metal ion the compound contains, and very strong attraction between the transition-metal ion and hydrogen. Based on the observation, the authors concluded that further optimization with various catalysts for sorption properties enhancement of magnesium-based hydrides is possible and should be considered. The same authors investigated the efficiency of Nb_2O_5 as a catalyst for hydrogen sorption reaction of magnesium and compared the result with other metal oxide catalysts (Fe_3O_4, V_2O_5, Mn_2O_3, TiO_2, Cr_2O_3, Sc_2O_3, Al_2O_3, CuO, SiO_2) [121]. It was found that niobium pentoxide (Nb_2O_5) gave the highest catalytic effect on the MgH_2 with fastest hydrogen absorption rate within 60s for 7 wt% H_2 and 130 s at 300 °C for desorption. Sabitu et al. [127] also confirmed the outstanding catalytic effect of Nb_2O_5 by comparing the effects of four different transition-metal oxides (Fe_3O_4, ZrO_2, Nb_2O_5, and CeO_2) on the desorption kinetics of hydrogen of MgH_2. The results showed that MgH_2 with Nb_2O_5 additive exhibited the fastest kinetics in 16 min and the lowest desorption temperature of 205 °C in contrast to other metal oxides. The rates of

hydrogen desorption of MgH_2 mixed with the transition metal oxides declined in the following order: Nb_2O_5, Fe_3O_4, CeO_2, and ZrO_2 to pure MgH_2. Consequently, Barkhordarian et al. [126] and Sabitu et al. [127] suggested that the catalytic effect from Nb_2O_5 lead to improved desorption properties of MgH_2 by accelerating the pathway of hydrogen diffusion in the presence of surface barriers in the reaction. Likewise, Kimura et al. [128] demonstrated the hydrogen absorption of Mg catalyzed by 1 mol% Nb_2O_5 under temperature condition as low as −50 °C. The thermodynamic and kinetic properties were examined for MgH_2 with and without Nb_2O_5. The activation energy of hydrogen absorption for the catalyzed Mg was found to be 38 kJ/mol, which was appreciably lower than that of MgH_2 without the catalyst. The kinetic improvement was also observed on the hydrogen desorption process. Although the thermodynamic properties were not affected by the catalyst, the Nb_2O_5 addition mainly influenced the reaction rates between Mg and hydrogen and revealed the exceptional catalytic effects. Nonetheless, intensive research is still ongoing about finding appropriate catalysts for enhancing the absorption/desorption properties of hydrogen in different metal hydrides.

Alloying with other elements

According to Khafidz et al. [94], Rahman et al. [111], Wang and Wang [56], Kimura et al. [128] and Rahmaninasab et al. [107], alloying is a conventional and well-organized technique for improving the thermodynamics and hydrogen sorption kinetics of metal hydrides. Among various categories of composites based on alloys with different stoichiometries, AB_5, AB, A_2B, and AB_2 (as earlier stated) are found useful for hydrogen storage applications. These compounds are also regarded as interstitial hydrides owing to their hydrogen ab(de)sorption ability under moderate temperature and pressure. Despite the presence of stable oxide/hydroxide layers or species that are defective in the hydrogen gas, the kinetic reaction of hydrogen at the alloy-based surfaces is achievable in contrast to hydride materials. Furthermore, the crystal lattice structure of the metal hydrides has much to do with their thermal stability and hydrogen ab(de)sorption kinetics because hydrogen atoms can occupy the interstitial sites of the crystal lattice. Alloying has some specific effects on materials structures and hydrogen storage. It may destroy the metal hydride formed to develop different structures which affect the mechanical properties of the material, and in effect improve its absorption and desorption kinetics. The hydrogen sorption properties of light metals can be improved by adding other elements where the hydrogen-metal bond strength reduces and the interphase boundary between the different interactions of the composite constituents plays a major role. During the past few years, researchers have reported alloying with transition metals as a useful technique. Transition metals have been recognized to promote the dissociation and recombination of hydrogen and the addition of small quantities of such metals could enhance limited ab(de)sorption reactions and kinetics [33,86]. As an example, Liang et al. [129] studied the catalytic effect of transition metals (Ti, V, Ni, Fe, and Mn) additions on hydrogen sorption in nanocrystalline MgH_2. In the process, the authors ball milled 5% of the

transition metals with the MgH_2 alloy for 20 h. It was observed that all the transition metals additions brought about a decrease in the activation energy of hydrogen desorption from MgH_2. Vanadium addition exhibited the fastest desorption kinetics with a very small activation energy (62.3 kJ/mol) compared to that of MgH_2 (120 kJ/mol). On the other hand, titanium addition showed the fastest kinetics of absorption. Similarly, Fruchart et al. [130] reported that one of the most promising nanocrystalline compounds basically based on Mg and other element or elements selected in minor quantities such as vanadium, titanium and niobium, with vanadium additive giving one of the best trade-offs between ab(de)sorption kinetics and reversible storage capacity. Remarkable improvements in hydrogen ab(de)sorption kinetics have been made by additives like these on magnesium. Based on this, the authors worked on improving the activation issue of Mg-based hydrogen storage alloys for effective hydrogen uptake and release. First, the magnesium-based powder was hydrided. Then suitable proportions of BCC alloy powders based on Ti, V and one other metal chosen between Cr and Mn were added, mixed thoroughly and milled. The hydrogen absorption process executed at 240 °C and 10 bar gave up to 5.2 wt % capacity. It was observed that hydrogen capacity of 4.5 wt % was absorbed in about 2.5 min. On the other hand, hydrogen desorption was somewhat slower where 4.5 wt % of hydrogen was released in 5 min at 260 °C. Based on the result, the authors assumed that the issue of slow kinetics in the Mg-based alloys was mostly resolved, while that of the very high temperatures remains unresolved yet. According to Jia [31], transition metal alloys such as $LaNi_5$, FeTi (Mn), and Mg_2Ni, have been demonstrated to be effective metal-based additives. These alloys enable quick and effective hydrogen molecules dissociation for absorption or Mg−H bond destabilization for desorption, leading to improved hydrogenation kinetics or reduced desorption temperatures in Mg/MgH2 system because of low enthalpy of MgH_2 formation. For instance, Rahmaninasab et al. [107] studied the possibility of reducing the hydrogenation reaction enthalpy by alloying other elements with magnesium. The authors found that in the formation of Mg_2NiH_4 from the reaction of hydrogen with Mg_2Ni alloy, the enthalpy of Mg_2NiH_4 formation (−64.5 kJ/mol) was less than the enthalpy of MgH_2 formation (−75 kJ/mol). In another work by Morinaga and co-authors [131], it was discovered that the binding energy between nickel and hydrogen is stronger than that between magnesium and hydrogen in the metal hydride Mg_2NiH_4. However, this Ni−H bond in Mg_2NiH_4 is weaker compared to the Mg−H bond in pure MgH_2, which led to the low formation enthalpy of Mg_2NiH_4. Likewise, in a review by Zhu et al. [132], thermodynamics tuning of Cu_2Mg alloy was reported. As hydrogen is absorbed, Cu_2Mg decomposed into MgH_2 and $MgCu_2$ and the equilibrium temperature of hydrogen desorption under 1 bar H_2 pressure declines to 240 °C. According to Vajo and co-workers [133], significant achievements have been made in the modification of the thermodynamics of hydrogenation and dehydrogenation reactions using additives that form alloys or compounds with magnesium in hydrogenated or dehydrogenated states. For example, after Mg_2Ni was hydrogenated, Mg_2NiH_4 formed was determined with 3.6 wt% hydrogen and the process occurred at an equilibrium pressure

of 1 bar at 245 °C. In 2017, Young et al. [119] reported some results obtained by Pd additives in metal hydride alloy systems involving Mg, C, AB, A_2B, AB_2, AB_5, and BCC solid solutions. The authors discovered major improvements in the rates of absorption and desorption of hydrogen, electrochemical discharge capacity, high-rate discharge-ability, activation, and cycle life performance. Prabhukhot et al. [11] also reported the hydrogen storage behavior of other magnesium-based alloys (Mg–Ni and Mg–Co) other than MgH_2, tested because of their storage potentials. The results showed that Mg_2Ni intermetallic demonstrated good kinetics and about 3 wt% of hydrogen storage capacity but $MgNi_2$ failed to absorb any hydrogen. The Mg_2CoH_5 and Mg_3CoH_5 phases of the Mg–Co system gave hydrogen storage capacities of 4.5 and 5.4 wt% respectively. It was also found that the rate of absorption of the Mg–Co system was much higher compared to Mg alone. Some other authors also worked on improving the poor activation characteristics of TiFe. For instance, Jain et al. [117] studied the hydrogenation properties of TiFe using Zr_7Ni_{10} alloy additive with the aim to enhance the first hydrogenation behavior of TiFe alloy. Two different processing routes namely, single-melt and co-melt were investigated comparatively. In single-melt, the alloys of TiFe and Zr_7Ni_{10} were mixed and melted together, and in co-melt, the alloys were melted separately and thereafter melted together. The microstructure of the as cast samples revealed the presence of a Zr-rich intergranular phase decorating the grains of TiFe-rich matrix and Ni particles uniformly distributed within the sample. It was observed that addition of Zr_7Ni_{10}, even in small quantity resulted in a significant improvement in the hydrogenation behavior of TiFe alloy. Therefore, the authors concluded that the results of hydrogen absorption are not determined by the production route, whereas, by the addition of Zr_7Ni_{10} to TiFe alloy, an improved intermetallic material with better hydrogenation performance can be achieved easily.

Nanostructuring

According to Chen and Zhu [109], Yu et al. [114], Fichtner [134], Zhao-Karger et al. [135] and Sadhasivam et al. [40] and Shao et al. [64], metal clusters stability and reactivity are a function of their size, especially in the nanoscale range, which presents a new area of practical solid-state hydrogen storage. Nanomaterials generally have substantially distinct properties in contrast to the coarse-grained counterparts because of their increased surface area, shorter diffusion distances and multiplied grain boundary atoms. Nanostructuring is conventionally achieved by high-energy ball milling. Babu et al. [82] mentioned that ball milling method is a cost-effective process applied to metal hydrides to obtain good surface properties. According to Prabhukhot et al. [11], nanostructuring has been proven to benefit thermal and mechanical stability, hydrogen sorption kinetics and thermodynamic properties. Development of various nanocrystalline structures with enhanced hydrogen absorption/desorption properties has been achieved [42,67,81,107,109,114,134,136]. In a recent work by Rahmaninasab et al. [107], it was stated that one of the commonest techniques for enhancing hydrogen sorption of magnesium hydride is high-energy ball milling. Based on

this, the authors synthesized magnesium hydride + mischmetal nanostructured composite from magnesium hydride plus 6 and 10 wt% of mischmetal by ball milling at various times. It was reported that the ball milling was effective to produce nanostructured composite with increased free surface, decreased grain sizes, increased grain boundaries, porous surface structure with high active sites for the adsorption and desorption of hydrogen, micro-strains generated, and defects created on the surface and within the magnesium hydride + mischmetal crystals and grains. These defects facilitated the diffusion of hydrogen into the material by decreasing the diffusion activation energy, and the altered structure and reduced crystallite sizes improved kinetics and greatly influenced the hydrogen sorption properties. Generally, smaller crystallite sizes are proportional to more grain boundaries. The presence of multiple grain boundaries and interfaces in the nanocrystalline materials give favourable pathways for hydrogen diffusion and speeds up the kinetics of hydrogen ab(de)sorption. Callini and co-workers [136] reviewed some works on solid-state hydrogen storage using nanostructured materials. The authors mentioned that particle size reduction is a novel strategy to improve the thermodynamic and kinetic properties of hydride materials. It is an established fact that the physicochemical properties of materials are influenced when particles size reaches the nanoscale regime. As particles size reduces, hydride materials typically show faster kinetics of hydrogen sorption because of shorter diffusion paths and more surface area exposed to hydrogen. Prabhukhot et al. [11] also mentioned that the rate of hydrogen desorption from MgH_2 was enhanced by ball milling in a planetary ball mill. Wagemans and co-authors [42] studied the effect of crystal grain size on the thermodynamic stability and hydrogen desorption properties of magnesium and magnesium hydride using quantum mechanical calculations. The authors found that nanostructured MgH_2 clusters had a significantly lower desorption enthalpy than the bulk MgH_2. So, the nanostructured magnesium clusters (~0.9 nm in size) released hydrogen at a lower temperature of only 200 °C. It was also reported that ball-milling effectively increased the hydrogen absorption/desorption rate of MgH_2 by eliminating the oxide layer on the surface. In another work by Shan et al. [57], it was reported that mechanical grinding of small amounts of palladium with the intermetallic alloys $LaNi_{4.7}Al_{0.3}$, $CaNi_5$ and Mg_2Ni in air significantly improved their hydrogen storage performances. Similarly, Rahman et al. [111] investigated the influence of $MgNb_2O_6$, $Mg_4Nb_2O_9$ and $Mg_3Nb_6O_{11}$ on hydrogen ab(de)sorption reactions in MgH_2 promoted by ball milling. The milling of MgH_2 and the oxide additives was done for 12 h under a high purity argon atmosphere. It was found that the presence of the Mg–Nb oxides greatly increased the sorption kinetics of the hydrogen ab(de)sorption processes. Tajima et al. [137] also investigated the hydrogen sorption kinetics of FeTi alloy with nanostructured surface layers. The alloy sample was prepared via mechanical milling. The nanostructured FeTi exhibited much higher initial rate of hydrogen absorption than the bare FeTi alloy. It was found that the rate controlling step shifted from the dissociation of hydrogen molecules on the surface to the permeation of hydrogen atoms through grown surface oxide layers as the surface oxidation of the nanostructured FeTi

ensued. It was also confirmed that the nanostructured FeTi surface exhibited a much lower value for the work function of electrons than the bare surface. Therefore, the authors suggested that the results revealed that the nanostructured surface layers promoted hydrogen dissociation by easy exchange of electrons with the hydrogen molecules, and hence, hydrogen absorption rate was enhanced. In addition to various benefits of high-energy ball milling in the synthesis of metal hydrides, it has also been shown that it plays a substantial role in the synthesis of catalysts alloys/composites, creating a good interface between hydride and catalyst and promoting the proper distribution of the catalyst.

Nanoconfinement

As earlier mentioned, an established technique for enhancing the sorption kinetics of hydrogen is nanostructuring. More recently, a new strategy of nanoconfinement technique is attracting more interest in energy storage to produce nanomaterials and has been practised on diverse metal hydride systems. Nanoconfinement can be accomplished by constricting the active material within porous scaffold hosts that are light (for the sake of gravimetric hydrogen storage capacity), with very high surface area/porosity (to allow high loadings), not reactive (to prevent unnecessary reactions), cheap and abundant with suitable purity such as carbon-based materials and ordered mesoporous silicas. Other scaffold materials being studied for supporting active storage include ordered mesoporous oxides, zeolites, and metal-organic frameworks, as well as thin-film systems but with little progress because of their weight and cost factors. On the other hand, nanoscale carbon-based materials (e.g. nanofibers, nanotubes, nanowires, nanorods, and nanoribbons) have gained prominence for quite some years now because of their high surface areas which promote physisorption kinetics, surface interactions, bulk adsorption, desorption temperature, and hydrogen dissociation. Nanoconfinement technique has shown great potential to favourably influence the thermodynamics and enhance dehydrogenation kinetics of metal hydrides essential for reversibility of hydrogen storage for onboard applications. Added to the general effects of nanostructuring, nanoconfinement could as well prevent agglomeration of the particles and segregation of phases for the composite system by suppressing particles movement within the scaffold hosts. The hydrogen sorption kinetics of lightweight solid-state materials can be enhanced by doping them on carbon-based materials. Due to the unique electrical nature of carbon and the prominent C–H interaction, the carbon-based materials exert strong catalytic influence on the light metal hydrides either via nanosizing or close contact with carbon nanostructures [7,65,81,94,102,109,133,138–140]. Zhang and Qu [86] also mentioned that the carbon scaffold does not only provide the edge active sites for the hydrogen atoms in MgH_2 system, but also hinders the sintering and growth of MgH_2 nanoparticles. Zhao-Karger [140] investigated the effect of nanoconfinement on the kinetic and thermodynamic properties of MgH_2 in microporous scaffold. By direct hydrogenation of Bu_2Mg within the pores of the carbon microporous scaffold, MgH_2 nanoparticles with a size range of about 3 nm were formed. The dehydrogenation activation

energy was reduced by 52 kJ/mol compared to the bulk material, and a much lower enthalpy (63.8 ± 0.5 kJ/mol) and entropy (117.2 ± 0.8 J/mol) of reaction were found for the nanoconfined system. Wu et al. [141] reported that several investigations have been done on the effects of various carbon-based materials on MgH_2. Breathtakingly, all the carbon-based materials effectively enhanced the kinetics of Mg, mostly in hydrogen absorption capacity. It was also observed that more than 6.0 wt% H_2 was absorbed by all Mg–C composites within 5 min. However, Mg/SWNT demonstrated the greatest hydrogen storage properties in all, as shown by improved hydrogen capacity, enhanced kinetics of absorption/desorption, and significantly decreased desorption temperature. Prabhukhot et al. [11] and de Jongh and Adelhelm [7] also reported several advantages of nanoconfinement including heat transport/mechanical stability, improvement in hydrogen sorption kinetics, thermodynamic properties, and reversibility. Likewise, Callini and co-workers [136] mentioned in a review solid-state hydrogen storage with nanostructured materials that nanoconfinement plays an active role in collecting individual nanoparticles for model studies of hydrogen absorption. For instance, nanoconfined MgH_2 particles released hydrogen at 200 °C instead of 400 °C for bulk magnesium, and within 5 min most of the hydrogen content could be absorbed at 300 °C compared to 60 min for ball-milled magnesium. Recently, Zhang et al. [142] reported a new approach to nanoconfine MgH_2 into a carbon aerogel material with pore size range of about 13 nm by infiltrating soluble dibutylmagnesium ($MgBu_2$) as a precursor into a carbon aerogel, and then hydrogenated the incorporated $MgBu_2$ to MgH_2. It was found that the MgH_2 based composite had over 5 times more dehydrogenation kinetics than the ball-milled activated MgH_2. Based on this, Nielsen et al. [143] later investigated the effects of carbon aerogel pore size on hydrogen storage properties of MgH_2. Results revealed that the smaller pore sized aerogel material would uptake the fewer MgH_2, and the nanoconfined MgH_2 in smaller pores facilitated the fast desorption rate of hydrogen because of the size reduction of the confined hydride. Therefore, it is generally realized that nanoconfining active hydrogen storage materials through porous supports or scaffolds, particularly the carbon-based nanomaterials offers a significant improvement in both the kinetic and thermodynamic properties.

Conclusion and recommendation

Hydrogen is a prominent candidate for ideal cost-efficient clean and sustainable energy carrier for the future energy and global economic security. The persistent obstacle to prompt integration of hydrogen into the world economy remains its storage. Among several options presented so far, solid-state storage systems based on metal hydrides have been recognized as one of the most feasible solutions to store hydrogen in hydrogen-powered systems. Most metal hydrides have not been able to store large quantities of hydrogen, and those which do are plagued with slow kinetics and unable to release hydrogen at low temperatures. Therefore, it continues to be a challenge for scientists and engineers in the field to investigate properties of metal hydrides to develop new kinds

of metal hydride systems with large hydrogen storage capacities and favourable kinetics at low temperatures of uptake and release respectively. Currently, there is enough proof from the literature and research findings to support the viability and enormous benefits of storing hydrogen in current metal hydrides. Then the most significant focus of intensive research in hydrogen storage would be enhancing the kinetics of the promising hydrides and investigating new materials and/or methods combinations to produce high hydrogen density storage with fast kinetics at reasonably low temperatures. In this review, most promising novel achievements by researchers in the field to have greatly benefited hydrogen sorption kinetics and thermodynamic properties in recent times have been reported, viz. the use of catalysts, alloying with other elements, nanostructuring via high-energy ball milling and nanoconfinement by supporting active hydrogen storage materials with porous scaffold hosts. Accordingly, the authors recommend that more focused work should be done based on the discoveries with great opportunities to pave the road to a hydrogen economy.

Acknowledgment

REFERENCES

[1] European Commission. Hydrogen energy and fuel cells: a vision of our future. Luxembourg: Office for Official Publications of the European Communities; 2003.

[2] Chamoun R, Demirci UB, Miele P. Cyclic dehydrogenation—(Re)hydrogenation with hydrogen-storage materials: an overview. Energy Technol 2015;3:100—17. 2015.

[3] Rusman NAA, Dahari M. A review on the current progress of metal hydrides material for solid-state hydrogen storage applications. Int J Hydrogen Energy 2016;41:12108—26.

[4] Sun Y, et al. Tailoring magnesium based materials for hydrogen storage through synthesis: current state of the art. Energy Storage Mater 2018;10:168—98.

[5] Veziroglu TN, Sahin S. 21st Century's energy: hydrogen energy system. Energy Convers Manag 2008;49:1820—31.

[6] Veziroglu TN. Conversion to hydrogen economy. Energy Procedia 2012;29:654—6.

[7] de Jongh PE, Adelhelm P. Nanosizing and nanoconfinement: new strategies towards meeting hydrogen storage goals. ChemSusChem 2010;3:1332—48.

[8] Iordache I, Gheorghe AV, Iordache M. Towards a hydrogen economy in Romania: statistics, technical and scientific general aspects. Int J Hydrogen Energy 2013;38:12231—40.

[9] Luo X, Wang J, Dooner M, Clarke J. Overview of current development in electrical energy storage technologies and the application potential in power system operation. Appl Energy 2015;137:511—36.

[10] Ren J, Musyoka NM, Langmi HW, Mathe M, Liao S. Current research trends and perspectives on materials-based hydrogen storage solutions: a critical review. Int J Hydrogen Energy 2017;42:289—311.

[11] Prabhukhot PR, Wagh MM, Gangal AC. A review on solid state hydrogen storage material. Adv Energy Power 2016;4(2):11—22.

[12] Rand DAJ. A journey on the electrochemical road to sustainability. J Solid State Electrochem 2011;15:1579—622.

[13] Sahaym U, Norton MG. Advances in the application of nanotechnology in enabling a 'hydrogen economy'. J Mater Sci 2008;43:5395—429.

[14] Durbin DJ, Malardier-Jugroot C. Review of hydrogen storage techniques for on board vehicle applications. Int J Hydrogen Energy 2013;38:14595—617.

[15] Mueller-Langer F, Tzimas E, Kaltschmitt M, Peteves S. Techno-economic assessment of hydrogen production processes for the hydrogen economy for the short and medium term. Int J Hydrogen Energy 2007;32:3797—810.

[16] Marbán G, Valdés-Solís T. Towards the hydrogen economy? Int J Hydrogen Energy 2007;32:1625—37.

[17] Midilli A, Ay M, Dincer I, Rosen M. Hydrogen and hydrogen energy strategies I: current status and needs. Renew Sustain Energy Rev 2005;9:255—71.

[18] Hirscher M. Handbook of hydrogen storage: new materials for future energy storage. Weinheim, Germany: WILEY-VCH Verlag GmbH & Co. KGaA; 2009.

[19] Chiari L, Zecca A. Constraints of fossil fuels depletion on global warming projections. Energy Policy 2011;39:5026—34.

[20] Sahlberg M. Light-metal hydrides for hydrogen storage. Digital comprehensive summaries of uppsala dissertations from the faculty of science and technology 666. Uppsala: Acta Universitatis Upsaliensis.; 2009. p. 1—56.

[21] Zhang Y, et al. Development and application of hydrogen storage. J Iron Steel Res Int 2015;22(9):757—70.

[22] Jain IP. Hydrogen the fuel for 21st century. Int J Hydrogen Energy 2009;34:7368—78.

[23] Bossel U, Eliasson B. Energy and hydrogen economy. Alternative Fuels Data Center; 2003.

[24] Edwards PP, Kuznetsov VL, David WI. Hydrogen energy. Philos Trans A Math Phys Eng Sci 2007, April 15;265(1853):1043—56.

[25] Zhang B, Wu Y. Recent advances in improving performances of the lightweight complex hydrides Li-Mg-N-H system. Prog Nat Sci: Mater Int 2017;27:21—33.

[26] Johnson SR, et al. Chemical activation of MgH2; a new route to superior hydrogen storage materials. Chem Commun 2005:2823—5.

[27] Iordache I, Schitea D, Gheorghe AV, Iordache M. Hydrogen underground storage in Romania, potential directions of development, stakeholders and general aspects. Int J Hydrogen Energy 2014:1—11.

[28] Deveci M. Site selection for hydrogen underground storage using interval type-2 hesitant fuzzy sets. Int J Hydrogen Energy 2018;43:9353—68.

[29] Schitea D, et al. Hydrogen mobility roll-up site selection using intuitionistic fuzzy sets based WASPAS, COPRAS and EDAS. Int J Hydrogen Energy 2019;44:8585—600.

[30] Mazloomi K, Gomes D. Hydrogen as an energy carrier: prospects and challenges. Renew Sustain Energy Rev 2012;16:3024—33.

[31] Jia Y, et al. Combination of nanosizing and interfacial effect: future perspective for designing Mg-based nanomaterials for hydrogen storage. Renew Sustain Energy Rev 2015;44:289—303.

[32] Niaz S, Manzoor T, Pandith AH. Hydrogen storage: materials, methods and perspectives. Renew Sustain Energy Rev 2015;50:457—69.

[33] Webb CJ. A review of catalyst-enhanced magnesium hydride as a hydrogen storage material. J Phys Chem Solids 2015;84:96—106.

[34] Eftekhari A, Fang B. Electrochemical hydrogen storage: opportunities for fuel storage, batteries, fuel cells, and supercapacitors. Int J Hydrogen Energy 2017;42:25143–65.

[35] Salameh CM. Synthesis of boron or aluminum based functional nitrides for energy applications (hydrogen production and storage). du Languedoc-Roussillon: material chemistry. Université Montpellier II Sciences et Techniques; 2014.

[36] Crabtree GW, Dresselhaus MS, Buchanan MV. The hydrogen economy. Phys Today 2004;57:39–44.

[37] Lim KL, Kazemain H, Yaakob Z, Daud WRW. Solid-state materials and methods for hydrogen storage: a critical review. Chem Eng Technol 2010;33(2):213–26.

[38] Edalati K, et al. Design and synthesis of a magnesium alloy for room temperature hydrogen storage. Acta Mater 2018;149:88–96.

[39] Hwang HT, Varma A. Hydrogen storage for fuel cell vehicles. Curr Opin Chem Eng 2014;5:42–8.

[40] Sadhasivama T, et al. Dimensional effects of nanostructured Mg/MgH2 for hydrogen storage applications: a review. Renew Sustain Energy Rev 2017;72:523–34.

[41] David E. An overview of advanced materials for hydrogen storage. J Mater Process Technol 2005;162–163:169–77.

[42] Wagemans RW, van Lenthe JH, de Jongh PE, van Dillen AJ, de Jong KP. Hydrogen storage in magnesium clusters: quantum chemical study. J Am Chem Soc 2005;127:16675–80.

[43] Zaluski L, Zaluska A, Strom-Olsen JO. Nanocrystalline metal hydrides. J Alloy Comp 1997;253(254):70–9.

[44] Reilly JJ, Wiswall RH. Formation and propertiesof iron titanium hydride. Inorg Chem 1974;13(No. 1):218–22.

[45] Bououdina M, Grant D, Walker G. Review on hydrogen absorbing materials-structure, microstructure, and thermodynamic properties. Int J Hydrogen Energy 2006;31:177–82.

[46] Rosen MA, Koohi-Fayegh S. The prospects for hydrogen as an energy carrier: an overview of hydrogen energy and hydrogen energy systems. Energy Ecol Environ 2016;1(1):10–29.

[47] Anthony JC. Hydrogen storage for aircraft: applications overview. Ohio: Analex Corporation; 2002. Brook Park.

[48] Becherif M, Ramadan HS, Cabaret K, Picard F, Simoncini N, Bethoux O. Hydrogen energy storage: new techno-economic emergence solution analysis. Energy Procedia 2015;74:371–80.

[49] Pudukudy M, Yaakob Z, Mohammad M, Narayanan B, Sopian K. Renewable hydrogen economy in Asia–Opportunities and challenges: an overview. Renew Sustain Energy Rev 2014;30:43–757.

[50] Teichmann D, Arlt W, Wasersche P. Liquid organic hydrogen carriers as an efficient vector for the transport and storage of renewable energy. IJHE 2012;37(18):118–32.

[51] https://h2tools.org/hyarc/calculator-tools/lower-and-higher-heating-values-fuels.

[52] Sheriff SA, Yogi GD, Stefanakos E, Steinfeld A. Handbook of hydrogen energy. CRC Press; 2014.

[53] Bockris JOM. The hydrogen economy: its history. Int J Hydrogen Energy 2013;38:2579–88.

[54] Pesonen O, Alakunnas T. Energy storage: a missing piece of the puzzle for the self-sufficient living. Lapland: Lapland University of Applied Sciences; 2017. UAS publication series B: research reports and compilations.

[55] Scheer R, Nielson T, Glickson D. In: Hydrogen storage "think tank". Washington, DC: U.S. Department of Energy, Office of Hydrogen, fuel cells and infrastructure Technologies; 2003.

[56] Wang Y, Wang Y. Recent advances in additive-enhanced magnesium hydride for hydrogen storage. Prog Nat Sci: Mater Int 2017;27:41–9.

[57] Shan X, Payer JH, Jennings WD. Mechanism of increased performance and durability of Pd-treated metal hydriding alloys. Int J Hydrogen Energy 2009;34:363–9.

[58] Balema V. Hydrogen storage materials. Mater Matters 2007;2(2):2.

[59] Ozturk T, Demirbas A. Boron compounds as hydrogen storage materials. Energy Sources, Part A 2007;29(15):1415–23.

[60] Chalk SG, Miller JF. Key challenges and recent progress in batteries, fuel cells, and hydrogen storage for clean energy systems. J Power Sources 2006;159:73–80.

[61] Jorgensen SW. Hydrogen storage tanks for vehicles: recent progress and current status. Curr Opin Solid State Mater Sci 2011;15:39–43.

[62] Sakintuna B, Lamari-Darkrim F, Hirscher M. Metal hydride materials for solid hydrogen storage: a review. Int J Hydrogen Energy 2007;32:1121–40.

[63] Yang Z, Weil KS, Michael PB. Materials in clean power systems: applications, status and challenges. Int J Hydrogen Energy 2007;32:3609.

[64] Shao H, et al. Nanotechnology in Mg-based materials for hydrogenstorage. Nano Energy 2012;1:590–601.

[65] Ruse E, et al. Hydrogen storage kinetics: the graphene nanoplatelet size effect. Carbon 2018;130:369–76.

[66] Wang Y, Chen KS, Mishler J, Cho SC, Adroher XC. A review of polymer electrolyte membrane fuel cells: technology, applications, and needs on fundamental research. Appl Energy 2010;88:981–1007.

[67] Janot R, Latroche M, Percheron-Guégan A. Development of a hydrogen absorbing layer in the outer shell of high pressure hydrogen tanks. Mater Sci Eng B 2005;123:187–93.

[68] Mazzolai G. Perspectives and challenges for solid state hydrogen storage in automotive applications. Recent Pat Mater Sci 2012;5:1–12.

[69] Hua TQ, et al. Technical assessment of compressed hydrogen storage tank systems for automotive applications. Int J Hydrogen Energy 2011;36:3037–49.

[70] Züttel A. Materials for hydrogen storage. Mater Today 2003, September:24–33.

[71] https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-storage-light-duty-vehicles.

[72] https://www.energy.gov/sites/prod/files/2017/05/f34/fcto_targets_onboard_hydro_storage_explanation.pdf.

[73] Schiller M. Hydrogen energy storage: a new solution to the renewable energy intermittency problem. Renewable Energy World; 2014.

[74] Zhang F, Zhao P, Niu M, Maddy J. The survey of key technologies in hydrogen energy storage. Int J Hydrogen Energy 2016;41:14535–52.

[75] Wolf E. Large-scale hydrogen energy storage. In: Moseley PT, Garche J, editors. Electrochemical energy storage for renewable sources and grid balancing. Amsterdam: Elsevier; 2015. p. 129–42.

[76] Ozarslan A. Large-scale hydrogen energy storage in salt caverns. Int J Hydrogen Energy 2012;37:14265–77.

[77] Iordache, I., Schite, D., Buga, R., Marinoiu, A., Balan, M., & Stefanescu, I. Hydrogen underground storage in Romania, the potential, actors and relevant circumstances. The 20th World Hydrogen Energy Conference (WHEC 2014), Gwangju, South Korea, 15–20 June 2014.

[78] Iordache M, Schiteaa D, Deveci M, Akyurt IZ, Iordache I. An integrated ARAS and interval type-2 hesitant fuzzy sets method for underground site selection: seasonal hydrogen storage in salt caverns. J Pet Sci Eng 2019;175:1088–98.

[79] Zhang Y, Li J, Zhang T, Wu T, Kou H, Xue X. Hydrogenation thermokinetics and activation behavior of non-stoichiometric Zr-based Laves alloys with enhanced hydrogen storage capacity. J Alloy Comp 2017;694:300–8.

[80] Sleiman S, Huot J. Microstructure and hydrogen storage properties of Ti1V0.9Cr1.1 alloy with addition of x wt % Zr (x = 0, 2, 4, 8, and 12). Inorganics 2017;5(86):1–12.

[81] Lai H, Paskevicius M, Sheppard DA, Buckley CE, Thornton AW, Hill MR, Aguey-Zinsou K. Hydrogen storage materials for mobile and stationary applications: current state of the art. ChemSusChem 2015;8:2789–825.

[82] Babu AR, Devunuri N, Manisha DR, Prashanthi Y, Merugu R, Teja AJ. Magnesium hydrides for hydrogen storage: a mini review. Int J Chem Tech Res 2014;6(No.7):3451–1.

[83] Umegaki T, et al. Boron- and nitrogen-based chemical hydrogen storage materials. Int J Hydrogen Energy 2009;34:2303–11.

[84] Retnamma R, Novais AQ, Rangel CM. Kinetics of hydrolysis of sodium borohydride for hydrogen production in fuel cell applications: a review. Int J Hydrogen Energy 2011;36:9772–90.

[85] Marrero-Alfonso EY, Gray JR, Davis TA, Matthews MA. Hydrolysis of sodium borohydride with steam. Int J Hydrogen Energy 2007;32:4717–22.

[86] Zhang J, Yan S, Qu H. Recent progress in magnesium hydride modified through catalysis and nanoconfinement. Int J Hydrogen Energy 2018;43:1545–65.

[87] Heung L. Using metal hydride to store hydrogen. 2003.

[88] Demircan A, Demiralp M, Kaplan Y, Mat MD, Veziroglu TN. Experimental and theoreticalanalysis of hydrogen absorptionin LaNi5–H2 reactors. Int J Hydrogen Energy 2005;30:1437–46.

[89] Rönnebro EC, Majzoub EH. Recent advances in metal hydrides for clean energy applications. Mater Res Soc 2013;38:452–8.

[90] Abdessameud S, Medraj M. Understanding the hydrogen storage behavior of promising Al–Mg–Na compositions using thermodynamic modeling. Mater Renew Sustain Energy 2016;5(7):1–29.

[91] Crivello JC, Denys RV, Dornheim M, Felderhoff M, Grant DM, Huot J, Yartys VA. Mg-based compounds for hydrogen and energy storage. Appl Phys A 2016;122(85):1–17.

[92] Blackburn JL, Parilla PA, Gennett T, Hurst KE, Dillon AC, Heben MJ. Measurement of the reversible hydrogen storage capacity of milligram Ti–6Al–4V alloy samples with temperature programmed desorption and volumetric techniques. J Alloy Comp 2008;454(2008):483–90.

[93] Lopez-Suarez A. Influence of surface roughness on consecutively hydrogen absorption cycles in Ti-6Al-4V. Int J Hydrogen Energy 2010;35:10404–11.

[94] Khafidz NZ, Zahira Y, Lim KL, Timmiati SN. The kinetics of lightweight solid-state hydrogen storage materials: a review. Int J Hydrogen Energy 2016;41:13131–51.

[95] Bullock RM. Metal-hydrogen bond cleavage reactions of transition metal hydrides: hydrogen atom, hydride, and proton transfer reactions. A J Crit Discussion Curr Lit 2006;12(Issue 1):1–33.

[96] Paskevicius M, Sheppard DA, Williamson K, Buckley CE. Metal hydride thermal heat storage prototype for concentrating solar thermal power. Energy 2015;88:469–77.

[97] Demirbas A. Fuel properties of hydrogen, liquefied petroleum gas (LPG), and compressed natural gas (CNG) for transportation. Energy Sources 2002;24:601–10.

[98] van der Berg AW, Areán CO. Materials for hydrogen storage: current research trends and perspectives. Chem Commun 2008:668–81.

[99] Motyka T, Zidan R, Summers WA. Aiken, SC, 29808. In: Hydrogen storage: the key challenge facing a hydrogen economy. USA: Hydrogen Technology Laboratory, Savannah River Technology Center, Westinghouse Savannah River Co; 2018.

[100] Zadorozhnyy VY, Milovzorov GS, Klyamkin SN, Zadorozhnyy MY, Strugova DV, Gorshenkov MV, Kaloshkin SD. Preparation and hydrogen storage properties of nanocrystalline TiFe synthesized by mechanical alloying. Prog Nat Sci: Mater Int 2017;27:149–55.

[101] Shashikala K, Kumar A, Betty CA, Banerjee S, Sengupta P, Pillai CG. Improvement of the hydrogen storage properties and electrochemical characteristics of Ti0.85VFe0.15 alloy by Ce substitution. J Alloy Comp 2011;509:9079–83.

[102] Adams BD, Chen A. The role of palladium in a hydrogen economy: Review. Mater Today 2011;11(6):282–9.

[103] Ioannidou A, Makridis SS, Gjoka M, Gkanas EI. Structure, Microstructure and hydrogen storage properties of melt-spun V55Ti21Mn17Fe7 and V55Ti21Cr17Fe7. Int J Energy Res 2016:1–12. In Press.

[104] Pozzo M, Alfe D. Hydrogen dissociation and diffusion on transition metal ([Ti, Zr, V, Fe, Ru, Co, Rh, Ni, Pd, Cu, Ag)-doped Mg(0001) surfaces. Int J Hydrogen Energy 2009;34:1922–30.

[105] Ma X, Xie X, Liu P, Xu L, Liu T. Ma(2017)-Synergic-catalytic-effect-of-Ti-hydride-and-Nb-nanoparticles for improving hydrogenation and dehydrogenation kinetics of Mg-based nanocomposite. Prog Nat Sci: Mater Int 2017;27:99–104.

[106] Shao H, He L, Lin H, Li H. Progress and trends in magnesium-based materials for energy-storage research: a review. Energy Technol 2018;6:445–58.

[107] Rahmaninasab MA, Raygan S, Abdizadeh H, Pourabdoli M, Mirghaderi SH. Properties of activated MgH2+mischmetal nanostructured composite produced by ball-milling. Mater Renew Sustain Energy 2018;7(15):1–11.

[108] Møller KT, Jensen TR, Akiba E, Li H. Hydrogen – a sustainable energy carrier. Prog Nat Sci: Mater Int 2017;27:34–40.

[109] Chen P, Zhu M. Recent progress in hydrogen storage. Mater Today 2008;11(12):36–43.

[110] Jain IP, Lal C, Jain A. Hydrogen storage in Mg: a most promising material. Int J Hydrogen Energy 2010;35:5133–44.

[111] Rahman MW, et al. Effect of Mg–Nb oxides addition on hydrogen sorption in MgH2. J Alloy Comp 2011;509S:S438–43.

[112] Bloch J, Mintz M. Kinetics and mechanisms of metal hydrides formation - a review. J Alloy Comp 1997;253–254:529–41.

[113] Zhao D, Zhang Y. Research progress in Mg-based hydrogen storage alloys. Rare Met 2014;33(5):499–510.

[114] Yu X, Tang Z, Sun D, Ouyang L, Zhu M. Recent advances and remaining challenges of nanostructured materials for hydrogen storage applications. Prog Mater Sci 2017;88:1–48.

[115] Williams M, Lototsky M, Linkov V, Nechaev A, Solberg J, Yartys VA. Nanostructured surface coatings for the improvement of AB5-type hydrogen storage intermetallics. Int J Energy Res 2009;33:1171–9.

[116] Zongying H, et al. Enhancement of the hydrogen storage properties of Mg/C nanocomposites prepared by reactive milling with molybdenum. J Wuhan Univ Technol -Mater Sci Ed 2017:299–304.

[117] Jain P, et al. Hydrogenation properties of TiFe with Zr7Ni10 alloy as additive. J Alloy Comp 2015;636:375–80.

[118] Rajabpour F, Raygan S, Abdizadeh H. The synergistic effect of catalysts on hydrogen desorption properties of MgH2–TiO2–NiO nanocomposite. Mater Renew Sustain Energy 2016;5(20):1–9.

[119] Young K, Ouchi T, Nei J, Chang S. Increase in the surface catalytic ability by addition of palladium in C14 metal hydride alloy. Batteries 2017;3(26):1–24.

[120] Fetcenko MA, et al. Mg-Ni hydrogen storage composite having high storage capacity and excellent room

temperature kinetics. 2007. United State, Patent No. US 7,211,541 B2.

[121] Barkhordarian G, Klassen T, Bormann R. Catalytic mechanism of transition-metal compounds on Mg hydrogen sorption reaction. J Phys Chem B 2006;110:11020—4.

[122] Hunt, A. J., Gross, K., & Mao, S. S. (n.d.). Mesoporous oxides and their applications to hydrogen storage. Mater Matters Volume 4 Article 2.

[123] Song Y, Li B, Yang S, Ding G, Zhang C, Xie X. Ultralight boron nitride aerogels via template-assisted chemical vapor deposition. Sci Rep 2015;5:10337. https://doi.org/10.1038/srep10337. 1-9.

[124] Hamilton CW, Baker TB, Staubitz A, Manners I. B—N compounds for chemical hydrogen storage. Chem Soc Rev 2009;38:279—93.

[125] Daryani M, Simchi A, Sadati M, Hosseini HM, Targholizadeh H, Khakbiz M. Effects of Ti-based catalysts on hydrogen desorption kinetics of nanostructured magnesium hydride. Int J Hydrogen Energy 2014:21007—14.

[126] Barkhordarian G, Klassen T, Bormann R. Fast hydrogen sorption kinetics of nanocrystalline Mg using Nb2O5 as catalyst. Scripta Mater 2003;49:213—7.

[127] Sabitu ST, Goudy AJ. Dehydrogenation kinetics and modeling studies of MgH2 enhanced by transition metal oxide catalysts using constant pressure thermodynamic driving forces. Metals 2012;2:219—28.

[128] Kimura T, Miyaoka H, Ichikawa T. Hydrogen absorption of catalyzed magnesium below room temperature. Int J Hydrogen Energy 2013;38:13728—33.

[129] Liang G, Huot J, Boily S, Van Neste A, Schulz R. Catalytic effect of transition metals on hydrogen sorption in nanocrystalline ball milled MgH2—Tm (Tm = Ti, V, Mn, Fe and Ni) systems. J Alloy Comp 1999;292:247—52.

[130] Fruchart D, et al. Nanocrystalline composite storage of hydrogen. 2009. United States, Patent No. US 2009/0278086 A1.

[131] Morinaga M, Yukawa H. Nature of chemical bond and phase stability of hydrogen storage compounds. Mater Sci Eng A 2002;329:268—75.

[132] Zhu M, Lu Y, Ouyang L, Wang H. Thermodynamic tuning of Mg-based hydrogen storage alloys: a review. Materials 2013;6:4654—74.

[133] Vajo JJ. Altering hydrogen storage properties by hydride destabilization through alloy formation: LiH and MgH2 destabilized with Si. J Phys Chem B 2004;108:13977—83.

[134] Fichtner M. Properties of nanoscale metal hydrides. Nanotechnology 2009;20 204009:1—4.

[135] Zhao-Kargera Z, Witter R, Bardají EG, Wang D, Cossement D, Fichtner M. Influence of nanoconfinement on reaction pathways of complex metal hydrides. Energy Procedia 2012;29:731—7.

[136] Callini E, Aguey-Zinsou K, Ahuja R, Ares JR, Bals S, Biliskov N, Novakovic N. Nanostructured materials for solid-state hydrogen storage: a review of the achievement of COST Action MP1103. Int J Hydrogen Energy 2016;41:14404—28.

[137] Tajima I, et al. Hydrogen sorption kinetics of FeTi alloy with nano-structured surface layers. J Alloy Comp 2013;580:533—5.

[138] Lai Q, Wang T, Sun Y, Aguey-Zinsou K. Rational design of nanosized light elements for hydrogen storage: classes, synthesis, characterization, and properties. Adv Mater Technol 2018;1700298:1—43.

[139] Vajo JJ. Influence of nano-confinement on the thermodynamics and dehydrogenation kinetics of metal hydrides. Curr Opin Solid State Mater Sci 2011;15:52—61.

[140] Zhao-Karger Z, et al. Altered thermodynamic and kinetic properties of MgH2 infiltrated in microporous scaffold. Chem Commun 2010;46:8353—5. 2010.

[141] Wu CZ, Wang P, Yao X, Liu C, Chen DM, Lu GQ. Effect of carbon/noncarbon addition on hydrogen storage behaviors of magnesium hydride. J Alloy Comp 2006;414:259—64.

[142] Zhang S, et al. The synthesis and hydrogen storage properties of a MgH2 incorporated carbon aerogel scaffold. Nanotechnology 2009;20:1—6 (2009), 20(204027).

[143] Nielsen TK, et al. Confinement of MgH2 nanoclusters within nanoporous aerogel scaffold materials. ACS Nano 2009;3(11):3521—8.