



Review Solid-State Hydrogen Storage for a Decarbonized Society

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Abstract: Humanity is confronted with one of the most significant challenges in its history. The excessive use of fossil fuel energy sources is causing extreme climate change, which threatens our way of life and poses huge social and technological problems. It is imperative to look for alternate energy sources that can replace environmentally destructive fossil fuels. In this scenario, hydrogen is seen as a potential energy vector capable of enabling the better and synergic exploitation of renewable energy sources. A brief review of the use of hydrogen as a tool for decarbonizing our society is given in this work. Special emphasis is placed on the possibility of storing hydrogen in solid-state form (in hydride species), on the potential fields of application of solid-state hydrogen storage, and on the technological challenges solid-state hydrogen storage faces. A potential approach to reduce the carbon footprint of hydrogen storage materials is presented in the concluding section of this paper.

Keywords: hydrogen; hydrogen economy; hydrogen storage; metal hydrides



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1. Environmental Concerns

In the last one hundred fifty years, consequently to the second industrial revolution, the life quality of an ever-increasing fraction of the world population (excluding the periods of the 1st and 2nd world wars) has improved sensibly. This improvement has been mostly due to the growing possibility of accessing electricity, transportation, and heat. This, however, has led to an enormous increment in the world's energy demand. Although not directly, the world's energy demand is related to the world population. In the last one hundred years, the world population has increased by a factor of 4, whereas the world energy demand has increased by a factor of 24 [1]. Assuming that this trend is maintained also in the incoming decades, a further growth of the world's energy demand is expected. In fact, considering that the current world population is 7.2 billion inhabitants and is forecasted to grow to about 8.3 billion in 2030 and to 9.6 billion in 2050 [2], the word energy demand is expected to grow by a factor of 4.5. However, this value might be even higher, if the fraction of the population living in the fast-developing countries continues to grow, and if the energy demand in the already developed countries increases even further.

Nowadays, the global energy demand is almost completely supplied by fossil fuel energy sources (e.g., in the year 2016, 80% of the overall energy demand was supplied by fossil fuels, 10% by biofuels, 5% by nuclear power, and only 5% by renewable sources such as hydro, wind, solar, and geothermal) [3–5]. It is widely known that in the last century, the extensive use of fossil fuels has led to a continuous increase in the CO₂ concentration in the atmosphere. In the pre-industrial revolution period, the calculated average CO₂ level in the atmosphere oscillated between circa 180 ppm (during ice ages) and 280 ppm (during interglacial warm periods). In 1958, Charles David Keeling measured the value of CO₂ concentration at circa 317 ppm [6]. Since then, this value has increased sharply. In 2017, the CO₂ level in the atmosphere settled permanently above 400 ppm, and it is projected to reach 450 ppm by the year 2040 [7]. This, without a shadow of doubt, led to an alteration of the natural atmospheric equilibria, which in turn led to a sensible increase in the average Earth temperature.

The so-called greenhouse effect, which allows the Earth to possess a moderate temperature suitable to host life as we know it, is mainly due to the water vapor present in the atmosphere and to clouds. However, new theoretical atmosphere-ocean climate studies have shown that the planet's temperature ultimately depends on the atmospheric level of CO_2 . In fact, CO_2 (as with other greenhouse gases present in the atmosphere but in much smaller concentrations such as ozone, N2O, CH4, and chlorofluorocarbons) cannot condense and precipitate from the atmosphere under the actual temperatures, whereas water vapor can and does. The so-called noncondensing greenhouse gases (GHG) account for about 25% of the total Earth's greenhouse effect, providing a stable temperature structure that determines the current levels of atmospheric water vapor and clouds through feedback processes that control the remaining 75% of the greenhouse effect [8]. Due to the increased amount of noncondensing greenhouse gases in the atmosphere, the average global temperature has risen by approximately 0.7 °C over the last century and is expected to rise by approximately 6 °C this century. However, such an increase in the mean global temperature will lead to environmental and social scenarios that are difficult to foresee and surely not positive. It is clear at this point that, without a prompt and drastic reduction in CO₂ emissions, a remarkable and irreversible increment in the Earth's temperature is expected. This is possible only by abandoning the use of fossil fuels as the main energy supply.

2. Hydrogen Economy

The transition from a carbon-based economy to a carbon-free economy is surely the biggest challenge that humankind will face in the next century. In fact, although energy sources alternative to fossils fuels are known, their full and safe exploitation has yet to be demonstrated. Possible candidates are the so-called "renewable energy sources" (e.g., solar, wind, geothermal, wave, and hydroelectric) and nuclear sources. According to the report published by the International Energy Agency for the year 2016, the amount of electrical energy produced by renewables and nuclear sources in the countries belonging to the Organization for Economic Co-operation and Development (OECD) is equal to 24% and 18%, respectively. However, in the view of a safe and long-lasting energy solution upon which the future development of humankind can be based, the possibility of producing energy through nuclear technology must be discarded because of multiple issues. The already problematic storage of radioactive wastes must be taken into serious consideration when planning a large-scale use of this technology. Moreover, the safety of this technology after the recent Fukushima Daiichi disaster and the continuous issues with the power plants in France and Belgium are seriously debated. Last but not least, the uranium, necessary for powering the nuclear reactors' reserves, is nowadays scarcely available and not renewable. Due to the lack of harmful products resulting from their exploitation, renewable energy sources appear highly appealing from both environmental and safety points of view. However, their intermittent nature, as well as their uneven distribution on Earth, are drawbacks that necessitate the identification of a suitable energy carrier, as well as the development of (yet undeveloped) technologies that will enable their efficient and synergic utilization. In this regard, the use of hydrogen as the future energy vector within the framework of a fully integrated and sustainable hydrogen-based economy (hydrogen economy) could be the solution to the pressing environmental issue caused by the widespread use of fossil fuels as an energy source. The idea of utilizing hydrogen as an energy vector is not a recent one and dates back to the year 1874, when Jules Verne mentioned the possibility of combining hydrogen and oxygen to obtain "an inexhaustible source of heat and light" in the book The Mysterious Island. However, it was much later that the term "hydrogen economy" was coined (by John Bockris in 1970). The sustainability of such an approach is bonded to the possibility of producing hydrogen via environmentally friendly methods such as electrolysis and (in the future) photocatalytic water splitting. The possibility of producing hydrogen via electrolysis allows for utilizing the excess energy produced by renewable energy sources to produce hydrogen that, in turn, will be utilized

to produce electricity, via the use of fuel cells, when electricity cannot be directly supplied by renewable sources. The use of fuel cells for producing electricity from hydrogen is a versatile and scalable approach that can be implemented in many stationary and mobile devices [9]. In the transportation sector, the possibility to replace internal combustion engines with hydrogen-powered fuel cells is extremely interesting both from the efficiency and life quality points of view. In fact, the energetic efficiency of a fuel cell is higher than 60%, whereas, for combustion engines running on gasoline or diesel, it is only 22% or 45%, respectively. The quality of life in densely populated areas will be positively influenced by the replacement of vehicles powered by internal combustion engines with vehicles powered by hydrogen fuel cells. In fact, in a fuel cell, when hydrogen is combined with oxygen, water is the only chemical compound produced, whereas, from the combustion of gasoline and/or diesel in an internal combustion engine, a long series of harmful pollutants and particulates are released into the atmosphere (e.g., CO, CO₂, SO₂, NO_x, N₂O, VOCs, HCs, PM_{10} , and $PM_{2.5}$). Hydrogen possesses a further advantage over conventional fossil fuels. Its gravimetric energy density is considerably high (its lower heating value, i.e., LHV, is equal to 120 MJ/kg and its higher heating value, i.e., HHV, is equal to 140 MJ/kg). For example, the gravimetric energy density of hydrogen is about 3 times higher than that of gasoline. However, as hydrogen is the lightest element in the periodic table, its volumetric density in gaseous (at 20 °C and 1 bar of pressure) or liquid form (at -253 °C and 1 bar of pressure) is very low, i.e., 0.0899 g/L and 70.8 g/L, respectively [10].

3. Hydrogen Storage and Applications

Nowadays, the two most common methods commercially used to store hydrogen are in gaseous form at high pressure (350–700 bar at 20 $^{\circ}$ C) and in liquid form at cryogenic temperature (at -253 $^{\circ}$ C and 1 bar of pressure) [10]. The pressurization of hydrogen allows for improving the volumetric energy density, which, however, remains remarkably lower than those of the most common fossil fuels. In fact, gaseous hydrogen compressed to 350 bar and 700 bar possesses volumetric energy densities of 3 MJ/L and 5.6 MJ/L, respectively, whereas the volumetric energy density of gasoline is 32 MJ/L (Figure 1).



Figure 1. Comparison of specific energy (energy per mass or gravimetric density) and energy density (energy per volume or volumetric density) for several fuels based on LHV. Courtesy of the U.S. Department of Energy (DOE).

In addition, the compression to 700 bar consumes an amount of energy that is higher than the 13% of the LHV. Although dependent on the scale of the process, the liquefaction of hydrogen at -253 °C is also energy demanding, i.e., 21 to 40% of the LHV is consumed

during the condensation process. This storage method is also affected by another drawback. Due to the boil-off phenomenon, a hydrogen loss of about 1% per day is expected. Although this phenomenon can be minimized by improving the thermal insulation of the containing tank, it cannot be completely eliminated. In both the gaseous and liquid forms, hydrogen preserves its molecular structure. A further method to store hydrogen in molecular form is the physisorption on large-surface-area materials at cryogenic temperatures [11]. This storage method takes advantage of the dipolar interactions occurring between the hydrogen molecules and the surface of the absorbent material. Due to the weakness of van der Waals forces ($\Delta H = ~5 \text{ kJ/mol}_{H2}$, not considering the so-called hydrogen bonds), physisorption can occur only at cryogenic temperatures. In the past decades, several materials (e.g., zeolites, carbon-based materials, metal–organic frameworks, and polymers with intrinsic microporosity) have been investigated as potential adsorbents for hydrogen.

Interestingly, due to the high hydrogen packing density, a significant enhancement of the volumetric energy density is obtained when hydrogen is chemically bonded to other elements in solid-state. It is well known that hydrogen can form compounds with most elements in the periodic table, displaying an extremely rich chemistry. In fact, in such compounds, several different chemical bonds and interactions with the different elements can be observed. Among the elements of the periodic table, metals and a few metalloids have a high affinity for hydrogen. This high affinity leads to the breaking of the H-H bonds of the H₂ molecules and to the formation of hydride species containing M-H bonds (M = metal/metalloid) [12]. This overall process can be divided into several different steps: (1) molecular hydrogen (H_2) approaching the metal surface experiences attractive forces (van der Waals forces [13]) that confine it in a space adjacent to the metal surface (physisorption); (2) H_2 dissociates on the metal surface and forms a metal-hydrogen bond (chemisorption); (3) chemisorbed hydrogen diffuses into the bulk lattice sites and forms a solid-solution (α phase Figure 2); (4) once a certain concentration of hydrogen is reached in a certain volume of the crystal lattice, a new phase characterized by a specific atomic metal-hydrogen ratio starts to form (β phase, metal hydride) at the expense of the α phase (Figure 2); (5) the growth of the β phase at the α/β interface proceeds until the formation of the β phase is complete. The process described above can be measured and analyzed by means of pressure–composition isotherms (pcT), as depicted in Figure 2 for a typical intermetallic compound. This process ideally should occur under isobaric conditions. However, in most of the real cases, the equilibrium pressure during the α -to- β transition (and vice versa) is not perfectly constant, but spans in a small range, and the graph displays a slope (e.g., LaNi₅ [14,15]). This feature is usually attributed to a small inhomogeneity of composition in the starting material and/or the presence of small traces of contaminants. Furthermore, the equilibrium pressure for the hydrogenation process is often higher than the equilibrium pressure for the dehydrogenation process. This phenomenon is called hysteresis and, although its origin is not fully understood, state-of-the-art knowledge attributes it to the small modification of the stability of involved phases as the consequence of strain and relaxation phenomena that the metal and/or hydride lattices experience during hydrogenation and dehydrogenation [16].

The reaction of the formation of a metal hydride is accompanied by the release of a certain amount of heat (Q) that is normally expressed as kJ per mole of H_2 (kJ/mol_{H2}). This process can be summarized as follows:

$$M + (x/2)H_2 \leftrightarrow MH_x + Q \tag{1}$$

pcT-diagram



Figure 2. Schematic pcT-diagram. The α -phase is the solid-solution phase, whereas the β -phase is the hydride phase. Within the ($\alpha - \beta$) two-phase region, both the metal-hydrogen solution and the hydride phase coexist [17].

Three different types of strong chemical bonds can be found in hydride species, i.e., covalent (observed in the complex ions of borohydrides, alanates, and amides such as LiBH₄, NaBH₄, NaAlH₄, and LiNH₂) [18–20], metallic (observed in transition metalcontaining hydrides such as LaNi₅ and TiFe), and ionic (observed in alkaline and alkaline earth hydrides such as LiH, NaH, KH, CaH₂, and MgH₂). Although these bonds can be distinguished from the other, in several compounds, it is possible to observe a mixture of these types of bonds (e.g., in LiBH₄ and NaAlH₄). For these bonds, dissociation enthalpies in the range from 50 to 400 KJ/mol_{H2} are expected.

The dissociation enthalpy or enthalpy of formation (Δ H) is the key parameter that (together with the entropic variation Δ S) determines the temperature (T) and H₂ pressure (p) conditions, under which a metal hydride can exist.

Thus, the enthalpy variation associated with the dissociation or formation of a hydride also determines its theoretical operating conditions (possible variations of these parameters, due to kinetic constrains, must be considered separately). The relation between T, p, Δ H, and Δ S is described by the van't Hoff equation [21]:

$$\ln p = -\Delta H / RT + \Delta S / R \tag{2}$$

where R is the universal gas constant. For many metal hydrides, the value of ΔS is approximated to the standard entropy value of hydrogen $S_{300K} = 130.77 \text{ J/(K} \cdot \text{mol}_{H2})$. A graphical representation of the effect of ΔH on the stability of three hypothetical metal hydrides is provided in Figure 3. The regions of temperature and pressure on the left side of each p and T equilibrium curve are those conditions where the hydride phases are stable. On the contrary, the regions on the right side of the curves indicate those conditions under which the hydride phases are not stable and therefore decompose. The p and T equilibrium curves also indicate that, for a given pressure value, the increment in ΔH leads to a shift in the equilibrium temperature toward higher values.

Among the above-mentioned hydrides, MgH_2 has been one of the most studied materials for hydrogen storage purposes due to its high gravimetric and volumetric hydrogen storage capacity (i.e., $\rho m = 7.6$ wt% and $\rho v = 110$ g H/L) and to its high natural abundance (e.g., Mg is present in minerals such as magnesite, dolomite, and in salt and brine deposits) [22]. However, there are practical constraints to its employment in large-scale applications. In fact, unfavorable thermodynamics and sluggish kinetics lead to possible op-

erative conditions that are far from desired. Pure MgH₂ possesses an hydrogen equilibrium pressure of 1 bar at 283 °C (calculated considering values of enthalpy and entropy equal to 74.6 \pm 0.42 kJ/mol_{H2} and 133.4 \pm 0.7 J/(mol K), respectively). The dehydrogenation and re-hydrogenation kinetics of MgH₂ were found to be highly sensitive to the material preparation route and to the presence of additives [23–27]. In fact, the nanostructuring via ball milling, infiltration into a nanometrically structured carbon-based scaffold, as well as the addition of transition metal (TM)-based additives, oxides, and halides, significantly improve the reaction kinetics [28–31].



Figure 3. Schematic p–T diagram presenting the equilibrium line for three hypothetic metal hydrides possessing increasing dissociation enthalpy, i.e., $\Delta H_1 < \Delta H_2 < \Delta H_3$.

The issue of the high thermodynamic stability of several metal hydrides, including MgH₂, was already investigated at the end of the 1950s and during the 1960s.

In that period, Libowitz and coworkers noticed that for a fixed temperature, $ZrNiH_3$ shows a hydrogen equilibrium pressure much higher than the one measured for ZrH_2 . Thus, the use of an alloy of Ni and Zr in the stoichiometric ratio of 1:1 leads, upon hydrogenation, to the formation of a hydride species (i.e., $ZrNiH_3$) that possesses a reaction enthalpy lower than that of ZrH_2 [32]. Similarly, Reilly and Wiswall [33,34] reported the possibility of tuning the reaction enthalpy of MgH₂ by mixing Mg with other compounds in a proper stoichiometric ratio. In particular, they showed that the dehydrogenation enthalpies of $3MgH_2 + MgCu_2$ and of Mg_2NiH_4 to form $2Mg_2Cu + 3H_2$ and $Mg_2Ni + 2H_2$ are lower than those of pure MgH₂. Unfortunately, the gained reduction in the reaction enthalpy is at the expense of the system's hydrogen capacity.

Recently, owing to their high hydrogen storage capacities, "complex hydrides" have attracted considerable attention as potential hydrogen storage materials for mobile and stationary applications [18–20,35,36]. The term "complex hydrides" originates from the presence of an anionic non-metal–hydrogen complex (e.g., $[NH_2]^-$, $[BH_4]^-$, and $[AlH_4]^-$) or metal–hydrogen complex (e.g., $[CoH_5]^{4-}$, $[FeH_6]^{4-}$, $[NiH_4]^{4-}$, $[ZnH_4]^{2-}$, and $[MnH_6]^{5-}$) (often) bonded to a cationic alkali or transition metal. Based on this definition, complex metal hydrides can be divided into two main groups, i.e., non-transition metal complex hydrides (such as LiNH₂, LiBH₄, and LiAlH₄) and transition metal complex hydrides (such as Mg₂NiH₄, Mg₂CoH₅, Mg₂FeH₆, Mg₃MnH₇, and K₂ZnH₄). Complex hydrides have been known for a long time (the first report on pure metal amides was published in 1809); however, they were initially not considered as potential hydrogen storage materials but rather as a laboratory curiosity or as reducing agents in chemical syntheses. The interest in hydrogen as an energy carrier began around the 1960s, and it has grown significantly since the 1990s. However, also in this period of intensive work, non-transition metal complex hydrides were considered as unappealing hydrogen storage materials due to their apparent

irreversibility, and more generally due to the difficulty of producing them on a large scale. This scenario changed drastically in the year 1996 when Bogdanovic and Schwickardi as the first ones demonstrated the possibility to reversibly store hydrogen at moderate temperature and pressure conditions in NaAlH₄ doped with Ti-based additives [37]. Since then, many efforts have been made to investigate and optimize the kinetic properties of complex hydrides.

Despite the noticeable scientific achievements that followed the work of Bogdanovic and Schwickardi, it has been necessary to wait until the beginning of the 2000s to discover a new concept that allows the obtaining of hydrogen storage systems based on complex hydrides that are fully reversible and possess low reaction enthalpies.

In fact, the approach of Libowitz et al., and Reilly and Wiswall has been improved by Chen et al. [38], Vajo et al. [39], and Barkhordarian et al. [40]. These researchers destabilized light-weight hydrides using a second hydride or multiple hydrides. Such hydride mixtures are also called Reactive Hydride Composites (RHCs). This concept offers the advantage of obtaining a reversible hydrogen storage system with a still high theoretical hydrogen storage capacity (i.e., the weighted average of the capacities of the hydrides composing the system) that possesses a reaction enthalpy lower than those of the single hydrides composing the system. Upon dehydrogenation, the hydrides might react directly among each other (mutual or concerted reaction) or with decomposition intermediates or their respective dehydrogenation products. A schematic representation of the RHC approach for a two-component system (AH_x and BH_y) that, upon dehydrogenation, forms a single compound (AB) plus hydrogen is given in Figure 4. This approach has been successfully applied to several families of transition complex hydrides and non-transition complex hydrides.



Figure 4. Schematic enthalpy diagram depicting the RHC approach applied to a two-component system (AH_x and BH_y), which, upon dehydrogenation, forms a single compound (AB) plus hydrogen. Δ H_f[°] = standard enthalpy of formation.

In the year 2007, Nakamori et al. reported a theoretical study that underlined a linear dependency between the thermal stability of borohydrides and their formation enthalpy (Δ H). Following this work, Nakamori et al. [41] published the experimental proof of the dependency of the thermal stability of several borohydrides on the Pauling electronegativity of the metal cation. These findings opened the path to the tailoring of the thermodynamic properties of complex hydrides via either cation substitution or anion modification. In this regard, several works describing the successful thermodynamic destabilization of alanates via cation substitution, to obtain bialkali alanates, were published. Unfortunately, the application of the cation substitution approach to other complex hydrides, such as borohydrides, did not lead to significant modifications of their thermodynamic properties. The modification of the thermodynamic stability of complex hydrides via anion modifica-

tion (e.g., via the intramolecular partial replacement of F^- for H^-) is commonly referred to as the "functional anion concept" [42]. To achieve this result, complex hydrides are often mixed with metal halides. The driving force of this approach relies on the strong Pauling electronegativity of halogen atoms, which potentially weakens the force of hydrogen bonding in the complex anion, thus facilitating the hydrogen release. Although significant thermodynamic destabilizations were observed for several complex hydrides (e.g., Na₃AlH₆ and LiBH₄), the decomposition products are usually mixtures of stable halogens, and the purity of the released hydrogen is poor.

It is clear, at this point, that metal hydride-based systems display a large range of hydrogen storage properties (e.g., hydrogen storage capacity) and operating conditions (e.g., temperature and hydrogen pressures). This diversity makes it possible to imagine their employment in several different technological fields.

Considering the European energy scenario, the final energy consumption assessed by sector for the year 2017 indicates that the highest fraction of consumed energy is due to the transport sector (31%), followed by the households (27%), industry (25%), and services (15%) sectors [43]. Therefore, it is clear that the transport sector together with the household and industry sectors are the main potential fields of application for hydrogen storage technologies. Based on the requirements dictated by the Department of Energy (DoE) for solid-state hydrogen storage in mobile and stationary applications [44,45], the possibility to store hydrogen through physisorption is unlikely. On the contrary, the storage of hydrogen in metal hydrides, complex hydrides, and RHCs, owing to their high achievable hydrogen storage capacities coupled with tunable thermodynamic and kinetic properties, appears to be a suitable solution for both mobile and stationary applications.

Regarding the transportation sector, the possibility to successfully employ hydridebased materials as hydrogen storage media depends on, in addition to possessing high hydrogen storage capacity (both volumetric and gravimetric), the possibility to achieve operating conditions suitable for their use in combination with proton-exchange-membrane (PEM) fuel cells, i.e., dehydrogenation temperatures lower than 120 °C at hydrogen pressures between 1 and 10 bar [46]. For this reason, in recent decades, thorough research in identifying new hydride species capable of satisfying at once all the automotive requirements was carried out [18,19,35,47–50]. However, despite the considerable progress made, among the complex metal hydrides, NaAlH₄ (Ti-doped) is the only material that has been tested in custom-built tanks under automotive demand cycles. In this regard, the most important contributions available in the literature are those from the United Technology Center (UT), Sandia National Laboratories/General Motors (SNL/GM), and Gesellschaft für Kernenergieverwertung in Schiffbau und Schifffahrt (GKSS), now Hereon (Figure 5) [51-54]. The design of the tanks in these three cases followed different aims. The UT tank was designed to maximize tank storage capacity regardless of tank cost, while the SNL/GM tank was designed to strike a balance between storage capacity and cost, and the GKSS tank was designed to achieve rapid recharging times. The UT tank contained about 19 kg of Ti-doped NaAlH₄ loaded in an aluminum foam (to increase the heat conductivity into the powder bed) and had an overall hydrogen content of 450 g H_2 . The GKSS tank contained about 8 kg of Ti-doped NaAlH₄ mixed with graphite (divided into seven 1.4571 stainless-steel tubes) and had an overall hydrogen content of 450 g H_2 . The use of graphite has been necessary to increase the heat conductivity into the powder bed. These two tanks were constructed in a single module, whereas the storage system constructed by the SNL/GM consortium consisted of four interconnected modules, each containing 21.5 kg of Ti-doped NaAlH₄ mixed with graphite (divided into twelve 316L stainless-steel tubes). The overall hydrogen content of the SNL/GM was about 3 kg. Despite the fact that these tanks could meet automotive demand cycles, the systems' low hydrogen gravimetric capacity (around 1 wt%) precluded their utilization in commercial applications. For this to happen, the development of a better storage material that will allow solid-state tanks to reach and/or exceed the gravimetric storage capacity of modern compressed gas tanks is necessary.



Figure 5. Prototype NaAlH₄ storage tank developed in GKSS laboratories [53].

In addition to the use of NaAlH₄, the use of metal hydrides from the families AB₂ and AB₅ [55] for the development of automotive hydrogen storage tanks has been investigated in recent decades [56–59]. These hydrides are characterized by high volumetric hydrogen storage capacities but low gravimetric hydrogen storage capacities. Aimed at obtaining a metal hydride-based tank with good gravimetric hydrogen storage capacity, a hybrid high-pressure/solid-state approach was recently proposed for automotive tanks, but at the cost of the system volumetric capacity (in comparison to low-pressure metal hydride-based tanks). Using this method, metal hydrides are placed in a standard high-pressure tank. Such a concept has been pursued by a number of companies, including Toyota Motor Company, which developed a 7.3 kg hydrogen tank based on the alloy $Ti_{1.1}CrMn$ [60] that could be refilled to 80% of its capacity in only 5 min [57]. Unfortunately, using such alloys inside the high-pressure tank results in a significant increase in vehicle weight (compared to high-pressure tank vehicles), which can only be partially offset by using higher-cost, lighter-weight materials for the vehicle's other components. Furthermore, the high cost of the raw materials required for the synthesis of the best-performing alloys (e.g., Ti, Cr, V, and Mn), and the high costs for manufacturing the high-pressure vessels are barriers to the widespread use of this technology.

An additional potential field of application for hydride-based systems, closely related to the transportation sector, is that of hydrogen compression units. This technology was developed in the 1970s, and it represents a good alternative to compressing hydrogen through methods such as mechanical, electrochemical, and ionic liquid compression [61]. The advantages of using hydride-based compression units are their simplicity of design, absence of moving parts, safety, and reliability. A further advantage of this technology is that it can be operated using waste heat in an industrial application context. For understanding which kinds of metal hydride-based systems are suitable to be operated using waste heat, it should be considered that the majority of waste heat lies in the temperature range of 100–200 °C. However, industrial waste heat with a temperature lower than 100 °C is also available from the food and drink industrial sector (i.e., mostly from drying and preheating processes) [62]. Thus, hydride-based systems possessing reaction enthalpies up to about 60 kJ/mol_{H2} could be potentially used as materials for hydrogen compressing units.

The fields of application proposed thus far do not contemplate the possibility of employing hydride-based systems possessing reaction enthalpies higher than 60 kJ/mol_{H2} and/or operating temperatures higher than 200 °C. However, in the framework of a hydrogen economy based on renewable energies, these materials might find application in heat storage systems for solar and related applications [63,64]. Concentrating solar thermal power (CSP) plants successfully store thermal energy using, in most cases, a mixture of molten NaNO₃/KNO₃ salts, which possesses a latent heat of fusion of about 10 kJ/mol [65].

However, the use of such material presents some criticalities, such as the very large quantity of molten salt necessary to store energy for the night cycle, the high corrosivity, and a maximum possible operating temperature of about 565 °C [66]. These issues could be solved by replacing the NaNO₃/KNO₃ salt mixture with metal hydrides. In fact, due to the high energy density of some hydrides (e.g., formation enthalpies of MgH₂, CaH₂, and LiH are -74.6 kJ/mol_{H2} [67], -181.5 kJ/mol_{H2} [68], and -133.0 kJ/mol_{H2} [69], respectively), a significant reduction in the material mass and volume (up to 10 times) needed for the heat storage unit is possible. Moreover, using metal hydrides, operating temperatures up to almost 1000 °C can be achieved (Figure 6) [70].



Figure 6. Maximum theoretical (**A**) gravimetric and (**B**) volumetric energy storage densities of select metal hydrides compared to existing molten salt technology [66].

Hydride-based systems might also be utilized to replace diesel generators as a reliable on-demand power source in so-called "off-the-grid" applications and as a material for inter-seasonal energy storage [71]. It is well known that many facilities around the world are permanently not connected to the electric energy grid or have to continuously operate even in the event of a sudden interruption of the electrical energy supply. Despite the issues related to an adequate design and heat management, the viability of using hydride-based devices for enabling off-grid installations for power generation and energy storage was recently proved in several demonstration projects [72–75].

In the near future, owing to the possibility of using waste heat, high-energy efficiency, and environmental friendliness (i.e., use of environmentally harmless fluids), metal hydrides might find application in cooling systems. Such systems are commonly referred to as MHCSs (i.e., metal hydride cooling systems) [76]. For such a purpose, two metal hydrides possessing different thermodynamic stabilities are utilized [77,78]. Considering a given hydrogen pressure value, the metal hydride operating at a higher temperature is referred to as high-temperature hydride (A), whereas the hydride operating at a lower temperature

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is referred to as low-temperature hydride (B). The simplest MHCS operates using two reactors, one containing hydride A and the other containing hydride B. Hydride A is operated between the heat source temperature (T_{hs}) and the ambient temperature (T_{amb}), whereas hydride B is operated between T_{amb} and the cooling temperature (T_c). The overall operational process can be divided into two half cycles, namely the cooling cycle (CC) and the regeneration cycle (RC).

At the beginning of the CC operation, hydride B is fully charged, while hydride A is in the dehydrogenated state. Once the two reactors are connected, with hydride A having an equilibrium pressure higher than that of hydride B, the hydrogen flows from the reactor containing hydride B to the reactor containing hydride A. As the dehydrogenation process is endothermic, until the maximum obtainable desorbed fraction is achieved, the reactor containing hydride B provides the required cooling effect (Qc). On the contrary, as the hydrogenation reaction is an exothermic process, the heat generated in the reactor containing hydride A will have to be dispersed in the ambient environment ($Q_{amb 1}$).

During the RC, the heat provided from the available sources (Q_{hs}) is supplied to the reactor containing hydride A, causing its dehydrogenation once its equilibrium pressure rises above that of hydride B. In this case also, the heat generated by the hydrogenation of hydride B ($Q_{amb 2}$) will have to be released into the ambient environment. A schematic representation of the functioning principle of a MHCS is presented in Figure 7.



Figure 7. Schematic illustration of a MCHS operating principle using a van't Hoff plot.

Interestingly, the potential field of application of hydride-based systems as cooling systems can be extended further beyond the Earth boundaries into outer space, as demonstrated by the works of Strumpf and Bowman [79,80]. In their works, they described the possibility to provide cooling or refrigeration for a variety of space applications that require constant operating temperatures (e.g., optics cooling, detectors cooling, personal astronaut cooling during extravehicular activity, food refrigeration and freezing, extraordinary medical needs, and habitation cabin cooling) using hydride-based systems (Figure 8). These cooling devices are widely called cryocoolers and operate exploiting the Joule–Thomson (J–T) effect. In this context, the advantages provided by the use of such hydride-based technology are mostly related to the compactness of the cooling device, as well as the complete lack of vibrations that can limit the performance of highly sensitive devices to record undistorted signals.

From the discussion above, it is possible to infer that to achieve the final goal of a fully decarbonized hydrogen economy, the development of a large variety of solidstate hydrogen storage materials, each of them possessing peculiar properties suited to the targeted application, is necessary. Moreover, to sustain this epochal transition, the developed solutions must also be cost-effective, scalable, and environmentally sustainable.

The demand for metals for hydrogen storage applications is currently negligible, but it will certainly increase in the following decades, posing huge environmental and social concerns that must be handled immediately on a global scale. Deforestation, water pollution, and soil contamination are the most visible evidence of the environmental impact that metal mining has. Furthermore, mining is an energy-intensive operation that necessitates the use of significant amounts of fuel and electricity, resulting in the release into the atmosphere of large amounts of GHG emissions. Additionally, the treatment of the mined minerals, such as crushing, greening, thermal or electrochemical reduction, and so on, leads to the further release of GHG. Thus, a rethinking of the procedures used to obtain metal hydride-based hydrogen storage systems is required if we wish to consider the usage of hydrogen and its storage in solid-state as practical strategies for climate change mitigation.



Figure 8. (a) Schematic diagram of a single-stage sorption cryocooler with a metal hydride sorbent bed producing liquid hydrogen and (b) the idealized closed-loop cycle A–B–C–D that is superimposed on the isotherms for a representative metal hydride [79].

A possible solution can certainly come from the use of circular economy strategies and concepts such as recycling and by-product synergy. Although, for most of the metals used in industrial applications, well-established functional recycling processes are in place, a considerable part of the metals ends up in land fields. These scraps, once sorted, could be used to make hydrogen storage systems with a minimal carbon footprint when compared to systems made from high-purity metals and/or metal compounds. Another obstacle that prevents the widespread adoption of metal hydride-based hydrogen storage systems, namely their high-cost, will be addressed by such an approach.

Until recently, studies on the possibility of producing metal-based hydrogen storage systems from recycled metal scraps were virtually nonexistent in the literature. This lack of publications can be traced to the interest of the scientific community in deeply understanding material physicochemical properties and correlating them to specific material compositions, whereas the utilization of recycled material will inevitably introduce into the system several different contaminants. A pioneering work on the use of metal scraps for the production of hydrogen storage materials has been the one from Bergemann et al. [81]. In this work, based on the ball milling technique [82], NaAlH₄ was synthesized using aluminum obtained from a waste incineration plant and commercial NaH.

The possibility of producing Mg-based hydrogen storage materials using recycled magnesium alloy scraps was recently investigated by Pistidda et al. [24], Hardian et al. [83], and Cao et al. [84]. In these works, the materials used as magnesium sources were scraps of AZ91 alloy and Mg-10 wt% Gd alloy. The results showed that the MgH₂ formed during the hydrogenation of the milled scraps can be used to reversibly store considerable amounts of hydrogen (i.e., AZ91 up to 6 wt%) despite being stored under atmospheric conditions for a long time. Even after several dehydrogenation/hydrogenation cycles, the material showed quick reaction kinetics and complete reversibility. Surprisingly, the presence of transition metal elements in the starting alloy appears to act as dehydrogenation/hydrogenation/catalysts either alone or after generating oxide species (during exposure to the environment). Using the MgH₂ obtained from scrap AZ91 alloy, Cao et al. [84]

synthesized first Mg(NH₂)₂ and then used it in the RHC system Mg(NH₂)₂-2LiH RHC. The identical system was produced using Mg(NH₂)₂ obtained from highly pure MgH₂ as a comparison. The hydrogenation/dehydrogenation kinetics studies demonstrate that the waste material composite can reach a hydrogen capacity of 4.6 wt% in 100 min after five cycles, whereas the composite containing pure Mg(NH₂)₂ can reach a capacity of 4.4 wt% in 100 min after five cycles. Furthermore, the Mg(NH₂)₂-2LiH composites generated from waste alloy have a hydrogen desorption peak temperature of 220 °C, which is 15 °C lower than the material synthesized from pure Mg.

Although preliminary, these findings show that high-quality hydrogen storage materials can be made from metal scraps, as well as the enormous potential that using circular economy strategies could have in reducing both the carbon footprint and the cost of metal hydride-based hydrogen storage materials.

4. Conclusions

In the following decades, humankind will face enormous challenges related to climate change and energy supply. A swift transition to a more sustainable energy system is necessary, and hydrogen is the key element of this transition. In this work, it was displayed that metal hydride-based systems provide a suitable solution to store large quantities of hydrogen for mobile and stationary applications, owing to their large variety of physicochemical properties. For these reasons, in the near future, metal hydride-based materials are expected to play an important role in realizing a fully decarbonized hydrogen-based economy. However, a rethinking of the way metal hydrides are produced is necessary for avoiding issues connected to their environmental sustainability and high costs. A possible solution is the application of circular economy strategies involving the use of industrial metal scraps to be used as metal sources for the synthesis of high-quality metal hydride systems.

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