Room Temperature Metal Hydrides for Stationary and Heat Storage Applications: A Review

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Hydrogen has been long known to provide a solution toward clean energy systems. With this notion, many efforts have been made to find new ways of storing hydrogen. As a result, decades of studies has led to a wide range of hydrides that can store hydrogen in a solid form. Applications of these solid-state hydrides are well-suited to stationary applications. However, the main challenge arises in making the selection of the Metal Hydrides (MH) that are best suited to meet application requirements. Herein, we discuss the current state-of-art in controlling the properties of room temperature (RT) hydrides suitable for stationary application and their long term behavior in addition to initial activation, their limitations and emerging trends to design better storage materials. The hydrogen storage properties and synthesis methods to alter the properties of these MH are discussed including the emerging approach of high-entropy alloys. In addition, the integration of intermetallic hydrides in vessels, their operation with fuel cells and their use as thermal storage is reviewed.

Keywords: hydrogen storage, metal hydrides, stationary application, thermal storage, hydrogen tanks

INTRODUCTION

The decreasing cost of renewable energy is providing a path toward sustainable energy systems. However, the intermittency of renewables remains a major limitation. In this context, batteries have gained interest as a potential energy storage solution but the amount of possible stored energy is rather limited by current battery chemistries. In comparison, hydrogen (H₂) can provide a solution to store renewable energy with high density. H₂ is the lightest element in the universe. It has a high energy density per unit mass (142 MJ kg⁻¹) but has a very low volumetric density of 11 m³ kg⁻¹ at ambient temperature and atmospheric pressure (Züttel, 2003).

Hydrogen for stationary applications is commonly recognized as a potential power-to-power solution through the integration of electrolysers, H₂ storage tanks and fuel-cell stacks. In this case, using hydrogen for seasonal storage provides added benefit for decoupling high peak power demand from steady flow of energy in relation to batteries (Parra et al., 2019). However, owing its versatility, H₂ once produced can also enable paths toward power to gas, gas-to-gas (H₂ refueling), gas-to-heat (H₂ combustion), heat-to-gas (use of the thermal energy released upon H₂ gas storage) (Parra et al., 2019). Recently, increasing trends have been observed toward the installation of power-to-gas systems (Figure 1), and this suggests a rise in the production of H₂ gas worldwide from renewables. To date, the storage of H₂ is often achieved by compressing H₂ and this remains the preferred solution owing to the maturity and simplicity of the technology. However, the storage of H₂ can also be achieved by liquefaction or as solid state with Metal Hydrides (MH). Hydrogen liquefaction is a very energy intensive process with 30% of the energy loss through the liquefaction process (von Helmlont and Eberle, 2007). In comparison,
storage tanks using solid state hydrogen materials have the potential to store hydrogen at much higher volumetric densities than compressed and liquefied hydrogen (Table 1), while minimizing the safety risk associated with high pressure hydrogen (Züttel et al., 2010; Lototskyy et al., 2017).

Although MH have been known and studied for more than four decades (Van Vucht et al., 1970), no consensus has been reached on the optimum metal hydride to be used for hydrogen storage in stationary applications. This is because of the wide range of possible stationary applications resulting in diverse requirements in terms of hydrogen release/absorption rates, pressure and temperature operation of the metal hydride tank.

### Abbreviations

- \( \Delta H^0 \): enthalpy of formation of hydride
- \( \Delta S^0 \): entropy of formation of hydride
- \( \Delta G^0 \): change in gibbs free energy of the alloy elements
- \( \Delta H_{	ext{mix}} \): change in enthalpy from alloy elements
- \( \Delta S_{	ext{mix}} \): configurational entropy of alloy elements
- BCC: body centered cubic structure
- DCHP: double hexagonal closed packed structure
- FCC: face centered cubic structure
- HCP: hexagonal closest packed structure
- \( E_a \): activation energy
- \( K_{	ext{eff}} \): effective thermal conductivity
- \( P_{\text{eq}} \): equilibrium plateau pressure
- \( Q_m \): heat flux for the change in temperature of the reactor shell and metal hydride bed (J s\(^{-1}\))
- \( Q_{\text{reac}} \): energy produced/consumed in solid/gas reaction (J s\(^{-1}\))
- \( Q_{H_2} \): energy transferred in and out of reactor with the \( H_2 \) gas (J s\(^{-1}\))
- \( Q_W \): energy transferred in and out of reactor with the heating and cooling of water (J s\(^{-1}\))
- \( R \): Universal gas constant
- \( T \): temperature
- \( P \): pressure
- \( V \): volume
- \( \text{MH} \): metal hydride
- \( \text{MHx} \): mixed metal hydride
- \( \text{LH} \): liquefied hydrogen
- \( \text{H}_{\text{2}} \): hydrogen
- \( \text{R} \): rare earth
- \( \text{RT} \): room temperature
- \( \text{ME} \): metal hydride
- \( \text{REN} \): rare earth metal
- \( \text{PEM} \): proton exchange membrane
- \( \text{H}_{\text{2}} \): hydrogen

### Table 1

| Forms of hydrogen storage | Volumetric hydrogen density |
|--------------------------|-----------------------------|
| Compressed hydrogen at 25°C and 50 MPa | 27 |
| Liquefied hydrogen at −253°C and 0.1 MPa | 40 (71) |
| Metal hydride at 25°C and 3 MPa | 50 (110) |
For example, in the case of power-to-power systems, short-term ramp-up and down to smooth-out the effects of voltage sags and rapid changes in renewable energy generation requires very fast responding MH, i.e., fast H₂ desorption kinetics. In contrast, for seasonal storage, very cheap MH with a very high H₂ density for the bulk storage of renewable are considered more attractive. Upon the selection of appropriate hydride materials, several other important parameters should also be considered. These include the ease of activation of the hydride material toward hydrogen uptake/release, its uptake/discharge H₂ kinetics, the H₂ hysteresis effects (dictating the pressure for hydrogen uptake and release), the heat of formation of the hydride (as this will involve additional heat management issues controlling the rate of H₂ uptake/release and thus the overall efficiency), the H₂ cyclic stability and cycle life, safety associated with the hydride production, handling and operation, and its sensitivity to gas impurities as this will affect the practical H₂ storage capacity (Sandrock, 1999; Lototskyy et al., 2017). Taking this into consideration, we foresee a range of targets for hydride materials for stationary application in relation to renewable energy storage. These targets are summarized in Table 2 considering that only room temperature (RT) hydrides are relevant, i.e., no additional heat is needed to facilitate the uptake or release of hydrogen as to maximize the overall efficiency. This should be accompanied by rapid rates of H₂ (<3 min) uptake/release at the material level across a wide range of temperatures (from 50 to −40°C) that will vary depending on the location of the stationary system. From our views, relevant MH should also operate within a limited pressure range of 3 to 0.1 MPa across the temperature window state above so as to reduce the reliance on additional H₂ compressors and ensure adequate H₂ pressure is fed to the fuel cell. In addition, such stationary MH should also be capable of > 10,000 cycles with less than 30% capacity loss. This would be possible when the material undergoes minimum phase segregation or oxidation upon H₂ cycling.

The ideal scenario for stationary application would require MH to have high volumetric and gravimetric hydrogen densities. As shown in Figure 2, complex hydrides such as Mg(BH₄)₂, Al(BH₄)₃ and LiBH₄ are capable of meeting high density

| Properties                              | Values | Units |
|-----------------------------------------|--------|-------|
| Hydrogen capacity                       | >2     | wt%   |
| Enthalpy | ΔH° | 10–60 | kJ mol⁻¹ H |
| Activation method                       | ≤3 cycles at 25°C and 3 MPa |
| Absorption-desorption kinetics          | ≤3     | min   |
| Plateau pressure at −40°C               | >0.1   | MPa   |
| Plateau pressure at 100°C               | ≤3     | MPa   |
| Cycle stability with <30% capacity loss | 10,000 | cycles |

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requirements but are limited by their irreversible nature (Lai and Aguey-Zinsou, 2018). The alternative option is using RT intermetallic hydrides such as TiFe$_2$ and LaNi$_5$H$_x$ that have volumetric densities at par with complex hydrides. Such intermetallic hydrides can be expressed as $A_xB_yH_z$ where “$A$” is typically a rare-earth, alkaline earth metals or a transition metal that can easily form stable hydrides, and “$B$” is a transition metal such as Ni, Co, Mn, Cr, etc. which forms unstable hydrides (Broom, 2011). Their low gravimetric capacities, however, may pose challenges in structural support and handling of vessels containing the storage material. This design issue has been dealt with in past stationary systems where MH was used to feed hydrogen to fuel-cell systems (Table 3; Lototskyy et al., 2017).

This review explores the potential of using RT, MH for stationary applications. The types of RT, MH, their current synthesis approaches and their design challenges are reviewed below.

**BASIC PRINCIPLES OF HYDROGEN STORAGE IN MATERIALS**

Various metals (M) in the periodic table are capable of storing hydrogen in the form of hydrides through the direct dissociative chemisorption of H$_2$ gas following (1) (Figure 4B). This is particularly the case for electropositive elements such as scandium, yttrium, lanthanides, actinides and group 4 and 5 elements (Sandrock, 1999; Züttel, 2003).

$$M + \frac{x}{2}H_2 \leftrightarrow MH_x + \Delta H^\theta$$

(1)

where, M is the metal or alloy, $x$ is the hydrogen concentration and $\Delta H^\theta$ is the enthalpy of formation of hydride.

However, individual elements are usually not suitable as practical hydrogen storage materials because of their poor hydrogen storage capacity or the need of high temperatures/pressures for the uptake/release of H$_2$. For example, TiH$_2$ requires temperatures up to 800°C to fully release hydrogen (Suwanno et al., 2012).

For stationary applications, hydrogen should be reversibly stored at ambient conditions in materials with minimum energy loss. To reach suitable hydrogen storage properties, several strategies have been explored to modify hydrides of high hydrogen capacity (Lai and Aguey-Zinsou, 2018; Lai et al., 2018). In particular, alloying methods have resulted in various hydrides with hydrogen uptake/release near or at ambient conditions as summarized along the “family tree” on Figure 3. Among these various types of alloys, for the purpose of meeting the specific requirements of stationary applications, intermetallic compounds and solid solution alloys may be of prime interest because of their ability in many cases to operate close to ambient conditions and at relatively low pressures (Sandrock, 1999; Broom, 2011).

**Thermodynamics Consideration For Hydrogen Storage at Ambient Conditions**

Hydrogen bonding with hydride forming materials mainly depends on the enthalpy ($\Delta H^\theta$) of formation of hydride alloys and the associated entropy ($\Delta S^\theta$) that can be calculated theoretically using the Miedema’s model which is an atomic cell model based on semi-empirical calculations (Miedema et al., 1977; Zhang et al., 2016). $\Delta H^\theta$ determines the general operating temperature and pressure of the hydrogen storage material. While, $\Delta S^\theta$ is mainly governed by the entropy of hydrogen gas that is lost during hydrogenation, and thus for metallic hydrides this value is ~130 J mol$^{-1}$K$^{-1}$H$_2$ (Broom, 2011). For RT uptake and release of hydrogen from materials/metals a desirable hydrogen bond strength is in the range of −10 to −60 kJ mol$^{-1}$H$_2$ (Sandrock, 1999; Bérubé et al., 2007). To achieve this bond strength, elements with high and low enthalpy values are mixed together to form an alloy. In the case of LaNi$_5$, where La forms LaH$_2$ with $\Delta H^\theta = −280$ kJ mol$^{-1}$H$_2$ (Griessen and Riesterer, 1988; Liu et al., 2017) and Ni forms an unstable hydride with $\Delta H^\theta = −6$ kJ mol$^{-1}$H$_2$ (Griessen and Riesterer, 1988), alloying leads to an LaNi$_5$ intermetallic hydride that has $\Delta H^\theta = −30.8$ kJ mol$^{-1}$H$_2$ (Sandrock, 1999). Based on this alloying approach, Table 4 summarizes examples of RT MH with their thermodynamic properties.

Practically, $\Delta H^\theta$ and $\Delta S^\theta$ can be calculated from the Pressure-Composition Temperature (PCT) curves (Figure 4A-i) at varying temperatures by using the van’t Hoff plot (Sandrock, 1999). The slope of van’t Hoff plot and its y-axis intercept (Figure 4A-ii) determine $\Delta H^\theta$ and $\Delta S^\theta$, respectively, according to:

$$\ln \left( \frac{P_{eq}}{P_0} \right) = \frac{\Delta H^\theta}{RT} - \frac{\Delta S^\theta}{R}$$

(2)

where, $P_{eq}$ is the equilibrium plateau pressure, $R$ is the gas constant and $T$ is the absolute temperature.

The PCT properties of hydrides state the amount of hydrogen stored at a certain temperature and pressure (Sandrock, 1999). Typical examples of commonly known intermetallic compounds
are shown in Figure 5 (Sandrock, 1999; Broom, 2011) against the target set in Table 2 for stationary applications. In relation to favorable thermodynamic properties, alloys such as MnNi₅, TiFe, LaNi₅, TiMn₁₅ and alloys of similar composition are of interest for stationary applications. However, many of these alloys have intrinsic limitations that hinder practical application. For example, the disproportionation of LaNi₅ and MnNi₅ upon successive hydrogen cycles is a major issue because it results in a reduction of the hydrogen storage capacity upon cycling. Similarly, TiFe suffers from activation issues and thus the need of high temperatures and pressures to achieve a first hydrogen uptake. TiFe is also extremely sensitive to impurities and thus easily deactivates upon oxidation. Such a deactivation upon oxidation is also prevalent in TiMn₁₅. The latter is also highly pyrophoric.

Hydrogen absorption in metals can follow different paths along the structural formation of various hydride phases. These include the (Sahlberg et al., 2016):

(i) BCC-route where H/M = 2: BCC → distorted BCC (BCT) → FCC
(ii) RE-route (where RE = La, Ce, Pr, and Nd) with H/M > 2: dHCP → FCC → distorted FCC (BCT)
(iii) High-entropy route with H/M > 2.5: BCC → distorted FCC (BCT)

where H/M is hydrogen-to-metal atomic ratio

Transition metals such as Ti and V that have Body centered Cubic (BCC) structure have been reported to follow the BCC-route with H/M = 2 after full hydrogenation (Sahlberg et al., 2016; Lai et al., 2018). Along this route, a phase transformation is observed from the initial BCC structure to a distorted BCC (i.e., a Body centered Tetragonal phase, BCT) upon the formation of the hydride phase, and finally a Face-centered cubic (FCC) structure upon full hydrogenation, i.e., formation of TiH₂ and VH₂ (Sahlberg et al., 2016). Comparatively, rare-earth metals such as La, Ce, Pr, and Nd follows the Rare-Earth route (RE-route). Initially, these metals (H/M = 0) with a double Hexagonal Closed Packed (dHCP) structure directly forms an intermediate FCC structure (at H/M < ~2.3). Upon further hydrogenation and with H/M > 2.3, a tetragonal distortion is observed leading to distorted FCC (BCT) hydride phase (Sahlberg et al., 2016). Although higher H/M ratios are observed along the RE-route

![Family tree of metal hydrides (Sandrock, 1999).](image-url)
compared to BCC-route, the weight penalty of the rare-earth elements, e.g., La (138 g mol\(^{-1}\)), as compared to Ti (47 g mol\(^{-1}\)) leads to low gravimetric hydrogen storage capacities. This indicates a tradeoff when considering the BCC and RE-route to develop hydrogen storage materials. An alternative has been explored through the approach of the high-entropy route where a combination of transition metals is used to reach H/M > 2.3 with a distorted FCC structure. Such high-entropy based alloys are expected to display superior hydrogen properties as compared to conventional alloys while avoiding the use of rare-earth elements i.e., (i) a high storage capacity with a H/M ratio of 2.5 and (ii) a high lattice distortion leading to additional lattice strain favorable for hydride formation (Sahlberg et al., 2016). High entropy alloys tend to be based on at least five metallic elements in an equimolar ratio or with varying composition from 5 to 35%; where the entropy of mixing is larger than 1.61R (where R is gas constant) \(\approx 13.4 \text{ J.mol}^{-1} \text{ K}^{-1}\). In comparison, conventional alloys have an entropy of mixing lower than 0.69R (Zhang and Zhou, 2007). Preliminary investigations have been reported on high entropy alloys including CoFeMn-TiVZr (Kao et al., 2010), ZrTiVCrFeNi (Kunce et al., 2013), and MgZrTiFe0.5Co0.5Ni0.5 (Zepon et al., 2018). In the case of CoFeMn-TiVZr, Kao et al. (2010) demonstrated a hydrogen storage capacity of 1.8 wt% \(\text{H}_2\) at 25°C. This equates to a H/M ratio of \(\sim 1\) as compared...
to the expected >2.5. Similarly, 1.8 wt% H₂ at 50°C was observed for Zr₀.16₃Ti₀.16₂V₀.2₂₂Cr₀.1₃₅Fe₀.1₅₉Ni₀.₁₆₀ and this again corresponds to a H/M ratio of ~1. Zepon et al. (2018) used a high temperature hydride MgZrTiFe₀.₅Co₀.₅Ni₀.₅ (1.2 wt% H₂ at 350°C) to confirm the difficulty of forming the right structural phases, and in this case an incomplete transformation of the BCC phase into FCC upon hydrogenation. Comparatively, TiVZrNbHf displayed a H/M ratio of 2.5 at 300°C which is equivalent to 2.7 wt% H₂ (Sahlberg et al., 2016). TiVZrNbHf was reported to have both tetrahedral sites and ~50% of octahedral sites filled with hydrogen (Sahlberg et al., 2016). This behavior is unique compared to binary hydrides such as TiH₂ and VH₂ that store hydrogen only at tetrahedral interstitial sites (Quijano et al., 2009). Due to the high entropy alloys being recently introduced, further investigations need to be carried out on its synthesis to achieve H/M > 2.5. For example, TiVZrNbHf that achieved H/M > 2.5 and CoFeMn-TiVZr that reported H/M ~1 both were synthesized by arc-melting process suggesting further investigation on the synthesis process to achieve higher H/M (Kao et al., 2010; Sahlberg et al., 2016).

**Kinetics Consideration for Hydrogen Storage at Ambient Conditions**

For stationary applications, the kinetics of RT hydrides are expected to be fast, i.e., <3 min for full hydrogen uptake/release in order to provide fast response times in conjunction with the fuel cell. This means that at the material level the hydrogen absorption/desorption process should involve low energy barriers. At the macroscopic level, the initial hydrogen pressure and temperature can determine the various limiting rates (Figure 6A; Rudman, 1983; Bloch and Mintz, 1997). However, at a given temperature and pressure, the hydrogen absorption/release rate is dictated by the materials’ intrinsic properties. The metal-hydrogen interaction depends upon several factors (Figure 6B) associated with activation barriers including that of the H₂ physisorption (Eₚₚₜ), chemisorption (Eₐₑₜ), penetration (Eₚₑₛ), diffusion (Eₚₑ₄) and the nucleation and growth (Eₙₑ₅) of the hydride phase (Rudman, 1983; Bloch and Mintz, 1997; Lai et al., 2018). The initial physisorption of hydrogen molecules corresponds to their direct adsorption onto the alloy surface through Van der Waals forces (Eₚₚₜ ≈ 10 kJ mol⁻¹H₂) (Züttel, 2003). At the metal surface the energy required (Eₐₑₜ) for dissociation and formation of a metal-hydrogen bond via chemisorption is ≈50 kJ mol⁻¹H₂ (Züttel, 2003). The hydrogen atoms then penetrate the subsurface of metal (Eₚₑ₄) and populate the interstitial sites of the material through surface diffusion (Eₚₑ₄). Higher concentration of hydrogen atoms leads to the formation of stable metallic hydride phase (Eₙₑ₅).

The overall rate limiting step of hydrogen sorption can be determined from the reaction rate coefficient k(T), arising from the Arrhenius equation (Sun et al., 2018):

$$k(T) = Ae^{−\frac{E_a}{RT}}$$  \(3\)

where, k(T) is the rate constant, Eₐ is the activation energy and a is the pre-exponential factor.

Out of the five energy barriers stated above, one energy barrier will be much higher than others and that would determine the rate determining step while other reaction steps would perform in equilibrium (Martin et al., 1996). For example, the hydrogenation barrier is associated with the surface reactivity (Eₐₑ₅) while the desorption process is controlled by the H₂ diffusion barrier (Eₚₑ₄) (Martin et al., 1996). Studies on materials like Mg₅Ni, LaNi₅, and TiFe have also shown similar behaviors where the dissociation process at the surface affects the absorption kinetics of the alloy (Zaluzski et al., 1995a). Using catalysts like Pd, Ni, or Fe aids the dissociation of H₂ to enhance hydrogen absorption (Uchida et al., 1991). Therefore, surface segregation of metallic Ni in LaNi₅ and Mg₅Ni and Fe in TiFe were proposed as the prime mechanism for the initial activation of these alloys (Broom, 2011). Before activation, TiFe is more difficult to activate than AB₅ type alloys, and despite extensive investigations, the exact mechanism and the general rules controlling the initial activation of TiFe are still unclear (Edalati et al., 2018). Many mechanisms based on surface activation have been proposed to explain the poor activation of TiFe. This includes: (a) surface segregation of catalytically active Fe (Schlapbach et al., 1980), (b) dissolution of the surface oxide in the bulk (Schober and Westlake, 1981), and (c) poor hydrogen transport through the oxide layer (Jai-Young et al., 1983). Defects at the surface of the alloy and dissolution of the surface oxide layer are other possible approaches that have been proposed to enhance the permeability of hydrogen in the surface oxide layer (Broom, 2011; Edalati et al., 2018). Upon H₂ sorption,
several macroscopic growth regimes of the hydride phase have also been reported (Figure 6C). These includes the: (i) early particulation, (ii) grain boundary attack, and (iii) contracting envelope mechanisms. Under the contracting envelope concept, the metal hydride nuclei form a continuous layer on the surface of the alloy particles (Mintz and Bloch, 1985; Bloch and Mintz, 1997). In contrast, upon early particulation the hydride phase nucleates in an heterogeneous manner across the alloy's surface and bulk. Such a mechanism is more prevalent in brittle intermetallics and has been observed with Ti$_{1+x}$Fe alloys, for example (Lee and Perng, 1991). In the concept of grain boundary attack, the nucleation of the hydride phase is expected to occur at defected sites and grain boundaries (Bloch and Mintz, 1997). For example, in Zr above the eutectoid temperature (550°C), the formation of the initial hydride phase has been reported to exclusively occur at grain boundaries (Bloch, 1995). This particular phenomenon has also been reported in certain rare-earth metals such as Tb, Dy, Ho, and Er at high temperatures (Bloch et al., 1984; Bloch and Mintz, 1997).

Although it has been suggested that the early particulation mechanism (Figure 6C-i) for Ti-based materials is related to surface activation, many studies have also reported a grain boundary attack mechanism (Figure 6C-ii) as the main path for hydrogen sorption (Miraglia et al., 2012; Lv and Huot, 2017). In particular upon the addition of second-phases such as Zr$_7$Ni$_{10}$ in Ti$_{1-x}$V$_{1-y}$Cr$_{1+x+y}$ (x ≤ 0.4, y ≤ 0.3) (Miraglia et al., 2012) and ZrMn$_2$ in TiFe (Lv and Huot, 2017). To promote a grain boundary attack mechanism for hydrogen absorption, using mechanical treatment has also been reported to be effective (Hongo et al., 2015). For example, Edalati et al. (2013, 2014) have shown that through the application of high-pressure torsion to Mg$_2$Ni (Hongo et al., 2015), TiFe, TiFe$_{1-x}$Mn$_y$ where (x = 0.0.15 and 0.3) (Edalati et al., 2016a) and Ti-V alloys (Edalati et al., 2016b) the initial hydrogen activation was facilitated.
CURRENT ROOM TEMPERATURE HYDRIDES AND THEIR HYDROGEN PROPERTIES

Among the many RT hydrides reported to date, intermetallics and solid-solution alloys are currently the most promising for stationary applications owing to the ability of many of these alloys to store hydrogen at ambient conditions (Table 5; Rusman and Dahari, 2016; Hirsch et al., 2020). These include TiFe, TiMn$_2$-based, LaNi$_5$ and Ti-V-Cr as their parent alloys.

AB Alloys

TiFe is a low-cost well-known hydrogen storage material of the AB-type family. It releases hydrogen under ambient conditions and has a 1.9 wt% H$_2$ storage capacity (Bououdina et al., 2006). However, this alloy suffers from drawbacks with respect to hydrogen activation, i.e., the freshly prepared alloy does not form CaNi$_5$ phase.

### TABLE 5 | Examples of Metal Hydrides and their properties (Sakintuna et al., 2007).

| Type       | Material       | Hydrogen storage properties (mass%/min/°C/MPa) | Other properties                                                                 | References                      |
|------------|----------------|---------------------------------------------|---------------------------------------------------------------------------------|---------------------------------|
| AB         | TiFe + x wt% Y \(x = 4.6, 8\) | - Abs: 1.2/3/25/- | - Y with 8 wt% improved first hydrogenation kinetics                           | Gosselin and Huot, 2019         |
|            | \(Ti_1-xFeZr_2\) \(x = 0.1, 0.2, 0.5\) | - Des: 1.29/-/20/- | - Zr lowers P$_{eq}$ and narrows width of plateau                              | Rusman and Dahari, 2016         |
| FeTi       |                | - Abs: 1.92/-/25/10 | - Relaxation effects were studied by ball-milling                              | Nishimiya et al., 2020          |
| AB$_2$     | \(Ti_1-xZrCr_5 Mn_{0.2} Ni_0.8 Fe_0.3 V_0.5\) \(x = 0.05-0.45, y1 = 0.1-0.4, y2 = 0.3-1.2, y3 = 0.2-0.3, y4 = 0.05-0.5, y5 = 0-0.6\) | - Abs: 1.5/-/20/-Des: 1.5/-/20/- | - Tuning of the H$_2$ storage properties can be easily achieved by variations in content of Zr, V and Cr | Zaluski et al., 1995b            |
|            | \(Zr_{0.75}Ti_{0.25}Cr_{1.5}N_{0.5}\) | - Abs: 1.75/-/40/4.7 Des: 1.05/-/40/0.006 | - Linear relationship between lattice parameters and (Ti and Ni) parameters giving single phase with steep plateau slope | Pickering et al., 2018          |
|            | \(Ti_{1.1}CrMn\) | - Abs: 1.80/-/23/33 Des: 1.75/-/23/0.1 | - Kinetics of the alloy was similar to compressed hydrogen                       | Kojima et al., 2006             |
| TiCr$_{1.1}$V$_{0.9}$ | - Abs: 3.5/-/30/1.7 Des: 2.5/-/30/0.05 | - Maximum hydrogen capacity is reduced after melting/mechanical alloying with LaNi$_5$ addition | dos Santos et al., 2003         |
| AB$_5$     | LaNi$_5$       | - Abs: 1.3/-/25/1 Des: 1.3/-/25/0.02 | - Mechanical milling of La and Ni powder can result directly into nanocrystalline AB$_5$ phase | Liang et al., 2001a             |
|            | CaNi$_5$       | - Abs: 1.5/-/30/1.5 Des: 1.2/-/30/0.01 | - Mechanical milling of Ca and Ni powder does not form CaNi$_5$ phase            | Liang et al., 2001b             |
| Solid-solution | VZr$_2$Ti$_5$Ni$_5$ \(x = 7.4 \text{ wt}\% \text{ of V}\) | - Abs: 2.0/-/40/1 Des: 1.6/-/40/0.05 | - Zr improves hydrogen absorption in forming C14 Laves phase                     | Kuriwa et al., 1999             |
|            | \(V_{0.375}Ti_{0.25}Cr_{0.3}Mn_{0.075}\) | - Abs: 3.0/-/30/5 Des: 2.2/-/30/0.002 | - Annealing for 1 h at 1,300°C gives a uniform bcc phase solid solution with improvement in storage capacity | Seo et al., 2003                 |
|            | \(Ti_{0.25}V_{0.75}Cr_{55}\) | - Abs: 2.1/-/40/10 Des: 2.2/-/40/0.01 | - Capacity was improved by using low vanadium content and annealing treatment over 1400°C for 1 min to stabilize bcc structure | Okada et al., 2002               |
|            | \(TiCr_{1.0}Mn_{1.8}V_{27}Fe_5\) | - Abs: 3.01/-/60/3 Des: 2.0/-/60/0.003 | - Fe addition improves the activation performance, increases desorption capacity and reduces hysteresis but decreases adsorption capacity | Yu et al., 2006                  |
|            | \(TiCr_{1.2}Mn_{1.8}V_{32}\) | - Abs: 3.36/8/60/3 Des: 1.96/-/60/0.003 | - Three forms of hydride formation took place for the alloy: BCC(1.5 wt%H$_2$), Deformed FCC(3 wt% H$_2$) and FCC(full hydride) | Yu et al., 2006                  |
|            | \(TiV_{32}Cr_{10}Mn_{18}\) | - Abs: 3.98/6/20/3 Des: 2.4/-/80/0.003 | - Increase of V content changes two phase C14 Laves phase and BCC phase into a single BCC phase | Yu et al., 2004                  |

a Storage capacity (mass%)/full kinetics time (min)/operating temperature (°C)/equilibrium plateau pressure (MPa).
not absorb hydrogen at ambient conditions. TiFe is extremely sensitive to oxidation and thus one possible explanation is the formation of a Ti oxide layer at the metal alloy’s surface preventing any hydrogen penetration into the alloy (Bououdina et al., 2006). Another drawback limiting the use of TiFe is the large hysteresis between its absorption and desorption equilibrium plateau pressures, ≥1 and ≤0.7 MPa at 40°C, respectively (Reilly and Wiswall, 1974). To solve this, small substitutions with other elements, e.g., Mn, Co, Cr, or Ni, have been investigated with the aim of forming a pseudo-binary alloy TiFe$_x$M$_{1-x}$, where 0 ≤ x ≤ 0.5; and such an approach effectively results in a reduction of the hysteresis (Mintz et al., 1981).

Many efforts have also focused toward understanding the activation mechanism of TiFe based materials once exposed to hydrogen. To this aim, activation routes such as ball-milling (Emami et al., 2015), high pressure torsion (Edalati et al., 2013), cold rolling (Vega et al., 2018), and Pd doping (Davids et al., 2011) have been investigated. However, all these methods have been found to have a detrimental effect on the hydrogen storage capacity (Reilly and Wiswall, 1974; Suda et al., 2002). For example, Emami et al. (2015) reported that the H$_2$ storage capacity of TiFe dropped to 1.5 wt% after ball-milling. Edalati et al. (2013) also reported a reduction of the H$_2$ storage capacity to ~1.7 wt% upon using high pressure torsion. Similarly, a 1.4 wt% H$_2$ capacity was observed for cold rolled FeTi (Vega et al., 2018). However, upon comparing the effect of ball-milling and cold rolling on air exposed TiFe + 4% Zr, cold-rolling was found to lead to a lesser loss of hydrogen capacity (Manna et al., 2018).

**AB$_5$ Alloys**

Another intermetallic that has been extensively investigated is LaNi$_5$ (AB$_5$ based intermetallic hydride). This hydride readily forms LaNi$_5$H$_6$ hydride (1.2 wt% H$_2$) upon exposure to moderate hydrogen pressures at ambient temperature (Sandrock, 1999). The enthalpy of formation and decomposition of the hydride is −15.7 and −15.1 kJ mol$^{-1}$H$_2$, respectively (Luo et al., 1998). Some of the properties of LaNi$_5$ are summarized in Figure 7. LaNi$_5$H$_6$ has a hexagonal structure akin to the CaCu$_5$ phase (Joubert et al., 1999, 2002). In its dehydrided state, LaNi$_5$ has also a hexagonal structure with a space group of P6/mmm (Joubert et al., 1999);

![Image of LaNi$_5$ properties](image-url)

**FIGURE 7** | LaNi$_5$ properties: (A) Absorption-desorption PCT curve at 25°C (Sandrock, 1997); (B) Kinetics showing typical 1st cycle of absorption at 25°C and 0.34 MPa (Sandrock, 1997) and desorption at 30°C and 0.05 MPa (Dhaou et al., 2007); (C) Structural properties showing CaCu$_5$-type hexagonal structure (Liu et al., 2011); (D) Physical properties of LaNi$_5$ (Yang et al., 2012).

| Physical properties | Units | LaNi$_5$ |
|--------------------|-------|-----------|
| Density ($\rho$)    | kg m$^{-3}$ | 8400      |
| Specific heat ($C_p$) | J kg$^{-1}$K$^{-1}$ | 419      |
| Effective thermal conductivity ($\lambda_{th}$) | W m$^{-1}$K$^{-1}$ | 1.0      |
| Permeability ($K$)  | m$^2$ | 1.0 x 10$^{-12}$ |
| Reaction enthalpy ($\Delta H$) | J mol$^{-1}$ | 3.01x 10$^4$ |
| Porosity ($\varepsilon$) | | 0.5 |
hence LaNi₅ does not undergo any structural changes upon hydrogen absorption/release and this results in less strain induced effects during hydrogen cycling (Sahlberg et al., 2016). Mechanically milling La and Ni in a powder form has been shown to lead to the formation of nanocrystalline LaNi₅. However, the hydrogen properties of nanocrystalline LaNi₅ are relatively poor in terms of hydrogen reversibility and hydrogen capacity (0.8 wt%). Having low micro strain (∼0.05%) and relatively large crystalline grain (>28 ± 2 nm) has been found to be preferable (Liang et al., 2001a). LaNi₅ is relatively resistant to oxidation, i.e., upon oxidation the activation of the alloy can be done upon mild heating at 40°C and 1 MPa pressure with an incubation time of 20 h (Liu and Suda, 1995). However, fluorination of LaNi₅’s surface has been found to readily facilitate the re-activation of the oxidized alloy without any incubation time. In this case, the fluorinated surfaces creates a protective layer around the alloy, i.e., LaF₃, which selectively allows hydrogen to pass through it (Liu and Suda, 1995). Hence, the fluorinated alloy is immune to some extent against hydrogen impurities such as O₂, CO and CO₂ (Liu and Suda, 1995; Wang and Suda, 1995; Suda et al., 2001).

**AB₂ and Solid-Solution Alloys**

In comparison to LaNi₅ and its related systems, AB₂ alloys have relatively higher storage capacities, faster kinetics, longer cycle life and potential for lower costs (Bououdina et al., 2006). AB₂ type alloys are commonly obtained from Ti and Zr as the “A” element, while the “B” element includes 3d metals such as V, Cr, Mn, Fe, and their combination (Sandrock, 1999; Sakintuna et al., 2007). AB₂ alloys exhibit Laves phases that are classified along three crystalline structures: cubic C15, hexagonal C14 and double hexagonal C36 (Bououdina et al., 2006). An example of such AB₂ materials is TiMn₁₋₁V₀ₓ₂, which has a hydrogen storage capacity of 2.15 wt% H₂ (Sandrock, 1999). Vanadium has two hydrides VH₁₋₁ and VH₋₂ giving an appearance of two equilibrium plateau pressures (International Journal of Hydrogen Energy Reilly and Wiswall, 1970). Vanadium and vanadium-based solid-solutions with a bcc structure can absorb 3.8 wt% H₂ at RT. However, due to the lower plateau region falling below 1 Pa at ambient temperature, these hydrides can only desorb about half of the original absorption capacity (Okada et al., 2002).

To take advantage of the small hysteresis and the fast kinetics of AB₂ type alloys in combination with the higher storage capacity of solid-solution alloys, a synergetic mixture of Laves phase and BCC-type phase, i.e., Ti-V-Mn (2.1 wt% H₂ at ambient conditions) has been introduced by Akiba and Iba (1998) and (Okada et al., 2002). Such multi-phase alloys were investigated extensively by Iba and Akiba (1995, 1997) and (Akiba and Iba, 1998). Similarly, Ti-V40-Cr35% alloy that has a desorption capacity of 2.4 wt% H₂ and its related composition were studied by Okada et al. (2002) to determine any trend between the absorption capacity and the alloy composition. It was reported that even at low vanadium content (<35%), which is highly desirable due to high vanadium cost (Towata et al., 2013), high amounts of solid-solution bcc phases (primarily responsible for higher absorption capacity) were prevalent in the alloy.

**Hydrogen Cyclability of Current Room Temperature Hydrides**

Cyclic stability of MH is important when selecting an alloy for stationary applications (Wang et al., 2007; Selvaraj et al., 2018). Ideally, the hydrogen kinetics and the absorption/desorption properties of the metal hydride should not be altered during at least 10,000 cycles. Degradation of hydrogen properties after cycling can be the result of hydrogen impurities and/or a structural degradation, i.e., a disproportion of an unstable hydride phase into multiple stable phases (Broom, 2011). Disproportionation is manifested by changes in the PCT shape and/or losses in the hydrogen storage capacity (Sandrock et al., 1989). Such an effect has for example been reported to occur in LaNi₅ and Sm₂Fe₁₇ (Goodell, 1984; Sugimoto et al., 2002; Shen and Perng, 2005). For example, Sandrock et al. (1989) observed significant disproportionation when LaNi₅ was held at 180°C in its β phase. It can be minimized by the increase of the binding energy between the metal atoms (Crivello and Gupta, 2003).

To date, the most effective approach to solve the disproportion effects observed in LaNi₅ is through partial substitution of Ni with Sn, i.e., by forming LaNi₅₋ₓSnₓ, where x ∼ 0.2 (Bowman et al., 1995; Broom, 2011). La₀.₅Ce₀.₅Ni₅ has shown excellent stability throughout 20,000 cycles at 15–160°C, in comparison to LaNi₅ exhibiting >20% capacity loss due to disproportionation at the same conditions (Tarasov et al., 2018). Interestingly, Borzone et al. (2014) reported up to 1000 hydrogen cycles without any evidence of disproportionation for LaNi₅ preserving 92% of its initial capacity. This is because disproportionation occurs only when the hydrogen pressure is above the plateau pressure of the metal hydride which is then accelerated due to repeated cycling and high temperatures (Sandrock et al., 1989). In the case of LaNi₅, the effects of disproportionation at 180°C were drastically observed when the activated material was held at 13 MPa H₂ instead of 6 MPa (Sandrock et al., 1989). By cycling LaNi₅ at a lower pressure of 8 MPa H₂ at 43°C for absorption Borzone et al. (2014) observed negligible effects of disproportionation.

The AB₂ type alloy Ti₀.₉₉Zr₀.₀₂V₀.₄₈Fe₀.₉₉Sn₀.₀₅Mn₁.₅ also showed no degradation up to 42,400 cycles with cycling temperatures at 45–120°C and pressure range of 2.6–3.3 MPa while remaining its storage capacity at 1.24 wt% H₂ (Friedmeier et al., 1995). Similarly, Ti₁₋₁Cr₄Mo showed good cyclic properties with only a 6% loss in storage capacity, i.e., 1.8 wt% H₂ after 1000 cycles (Kojima et al., 2006). Also, Cho et al. (2007) showed that Ti₀.₃₂V₀.₂₅Cr₀.₄₃ afforded 1000 cycles with a steady reversible capacity of ∼2 wt% at 30°C without any signs of disproportionation. However, Selvaraj et al. (2018) reported a degradation in the hydrogen properties of Ti₃V₂₀Cr₄₈ upon 100 cycles. This was attributed to the low content of vanadium disproportionating into other stable compositions, e.g., Ti₃₂₋ₓV₂₀–βCr₄₈ where α and β are related to the amount of the intermediate TiH₀.₆₆ and VH₀.₈₁ phases formed during hydrogen cycling, respectively. The exposure of the alloy to high temperatures, e.g., >300°C, may also explain the origin of such a disproportionation.

Based on these results, it is clear that unappropriated variations in the amount of Ti and V, which form stable hydrides
precipitates in the Ti-V-Cr solid solution, can have significant effects on the disproportionation mechanisms. Based on this, Shen and Li (2015) proposed that annealing treatment could benefit the elimination of segregation.

SYNTHESIS METHODS OF ROOM TEMPERATURE HYDRIDES

Generally, the synthesis of the MH occurs along 3 recurring steps: (i) the alloy formation, (ii) annealing/chemical/mechanical treatments, and (iii) activation of the alloy. However, other aspects can also be considered as a part of the synthesis process. This includes surface treatment for oxidation resistance or catalytic additives for lowering activation barrier for H2 sorption. Hence, during the synthetic process of the alloy, the properties of MH can be tailored to meet specific hydrogen properties. Some of the synthesis processes include arc and induction melting, mechanical milling, and cold rolling/torsion process that can be scaled up for large scale manufacturing. Methods including physical and chemical vapor deposition, thermolysis, chemical reduction, and electrochemical deposition remain main lab-scale approaches (Sun et al., 2018).

Mechanically milling is among the relatively simple approaches to synthesizing alloys in large quantities (Abd.Khalim Khafidz et al., 2016). From the late 1980s, Ivanov et al. (1987) in particular, were among the first to use mechanical milling as a mean to synthesize Mg-based alloys with Co, Cr, Fe, and Ni addition (Song et al., 1987; Stepanov et al., 1987). The advantages of using mechanical milling reside in the possibility to: (i) synthesize new alloys from their respective elements and this may result in a modification of the hydrogen-metal bond strength, (ii) make nanostructures or amorphous materials, and (iii) through doping with catalytic additives improve the hydrogen kinetics (Broom, 2011; Abd.Khalim Khafidz et al., 2016). Modification by milling of the archetypal alloys and intermetallics such as LaNi5 (Corré et al., 1999; Liang et al., 2001a; Fujii et al., 2002), Mn5Ni4-based (Ares et al., 2004; Singh et al., 2004), TiFe (Abe and Kuji, 2007; Hotta et al., 2007), Ti-V-Mn (Huot et al., 2008), Ti-Cr (Takeichi et al., 2004), Ti-V-Cr (Santos et al., 2004), and Mg-Ni (Orimo and Fujii, 1998; Orimo et al., 1999; Terashita et al., 1999) have been reported. Besides mechanical milling in inert atmosphere, to combine the effects of alloy formation and activation, the concept of reactive milling has also been used, where the materials are processed under H2 atmosphere. However, such steps can also modify the crystal structure of the MH and lead to amorphous phases, which inherently affect the hydrogen storage properties (Fujii et al., 2002; Santos et al., 2004). For instance, milling LaNi5 under H2 forms two phases: LaNi5H6.15 and amorphous phase initially and further milling can also lead to nanocrystalline Ni and amorphous LaNi5H6 (γ < 5) (Fujii et al., 2002). In contrast, reactive milling of Ti-V-Cr materials leads to a hydrogenation of the alloy under hydrogen (Santos et al., 2004).

Alloys that were previously only prepared by melting methods have also now being synthesized by mechanical milling. For example, Ti50–V50 has been known to forms a BCC type structure upon arc melting. Upon ball milling Ti and V with some carbon as a process control agent, Li et al. (2019) reported a Ti50V50-10 wt% C based alloy forming a unique FCC structure with a low packing density (5.1 g cm−3) and a crystalline size of 60 nm. The packing efficiency of this FCC structure (52%) is comparatively lower than that reported for other structures such as FCC (74%), HCP (74%), or BCC (68%) and this possibly implies higher diffusion kinetics of H atoms as compared to hydrogen diffusion in the FCC lattice (Volkl and Alfeld, 1975; Li et al., 2019). TiV5Mn- and TiCr5Mn- based nano-alloys with FCC structure were also reported to form via mechanical milling (Li et al., 2018).

AB type alloys, commonly TiFe, are also synthesized conventionally using the arc-melting process. However, due to the difficulty in the activation of the alloy mainly due to the surface oxidation (Reilly and Wiswall, 1974; Jai-Young et al., 1983; Schlappbach and Riesterer, 1983; Kulshreshtha et al., 1993; Inui et al., 2002), attempts have been made in exploring other synthesizes approach for TiFe that are activation-free. For example, approaches were employed such as a mixture of O2 and H2 atmosphere to precipitate titanium oxide and iron clusters (Züchner and Kirch, 1984) and mechanical alloying to form nanostructured TiFe (Trudeau et al., 1992; Haraki et al., 2008). Alternatively, hydriding combustion synthesis is another novel approach that has been used to prepare TiFe alloys (Saita et al., 2007). This synthesis approach involves igniting the material’s precursors in pure hydrogen atmosphere and with the adiabatic flame temperature of the process as high as 1,800°C, it has been possible to synthesize TiFe alloys (Li et al., 1999). Hydriding combustion synthesis has resulted in an improvement in the activation of TiFe by shortening the activation time drastically.

INTEGRATION OF ROOM TEMPERATURE HYDRIDES IN TANKS

The design of the metal hydride tanks plays a significant role in the performance of the MH to store hydrogen effectively at RT while enabling practical hydrogen uptake and release rates. Both the metal alloy and hydrogen contribute to design challenges in enabling fully functional solid-sate hydrogen storage tanks. This includes the packing density of the tank, the overall porosity of the hydride bed, and its thermal conductivity upon hydrogen uptake and release.

Upon hydrogen absorption, the exothermic reaction of hydrogen with the absorbing alloy generates heat that raises the operating temperature. If this heat is not dissipated quickly, the absorption rate reduces and thus the charging time (Mazzucco et al., 2014). The hydrogen desorption rates are similarly impacted due to the endothermic nature of hydrogen release from metal alloys. For example, it has been observed that for Ti0.98Cr0.02V0.05Fe0.95Cr0.05Mn1.5, the operating pressure of the alloy falls below the minimum required inlet pressure of 170 kPa (absolute) for the fuel cell system, although the equilibrium plateau pressure of this alloy is high (1.1 MPa at 25°C) (Sandrock, 1999; MacDonald and Rowe, 2006; Forde et al., 2009; Melnichuk et al., 2009; Tetuko et al., 2016). Such an observation has been
attributed to problems of heat transfer within the tank that limits the desorption of hydrogen, leaving the tank full at \( \sim 60\% \).

In addition to the heat management of the metal/hydrogen reaction, additional consideration should be made in terms of the materials used for the tank itself and associated component because of the potential of hydrogen embrittlement observed in many materials (Walker, 2008).

**Managing Heat Transfer in Solid-State Tanks**

To bypass the problem of heat management, general design solutions can include: (i) oversizing the metal hydride tank and (ii) working at excessive hydrogen pressures to ensure that the hydrogen uptake still progresses despite the heat generated and subsequent increase of the equilibrium plateau pressure of the hydride and (iii) fragment the hydrogen storage tanks into multiple tanks of narrow cross section for effective heat dissipation. However, besides these simple solutions, other alternative solutions of heat integration have also been explored (Tetuko et al., 2016).

Alternatives for the desorption process such as heating the metal hydride bed above ambient temperatures by using waste heat recovered from fuel cell is often regarded as the effective approach because this is a neat way to facilitate the \( \text{H}_2 \) desorption process from metal hydride tanks (Mellouli et al., 2007; Melnichuk et al., 2009; Dhaou et al., 2010). Examples of various thermal integration systems have been investigated in the past as shown in Figure 8, using waste heat either in the form of exhaust air or closed-loop water circulation systems.

Similarly, in the case of the absorption process, the waste heat generated from the exothermic reactions of absorption of \( \text{H}_2 \) in the metal hydride bed can be effectively utilized as a thermal storage system. For example, LaNi\(_5\)H\(_6\) has an enthalpy of formation \( \approx 30 \text{ kJ mol}^{-1} \text{ H}_2 \), which gives \( \approx 15 \text{ MJ} \) of heat when 1 kg of \( \text{H}_2 \) is being absorbed (Abdin et al., 2018). This heat can be stored and redirected back to compensate for the endothermic reaction during the desorption process. For example, Jehan and Fruchart (2013) proposed McPhy-Energy system containing a self-regulating “adiabatic” type tank that can immediately deliver hydrogen to fuel-cell for electrical energy needs (Jehan and Fruchart, 2013).

The rate limiting step in the effectiveness of transferring waste heat from the metal hydride bed to the external environment is due to the poor thermal conductivity of MH. For example, a LaNi\(_5\) powder bed has a very poor effective thermal conductivity of \( \sim 1.32 \text{ W m}^{-1} \text{ K}^{-1} \) (Goodell and Rudman, 1983).

![Figure 8](image-url)
Many models have been developed in an attempt to facilitate the design of solutions for the heat management in metal hydride storage tanks. This includes 1D models to predict the weight fraction of hydrogen absorption and the metal hydride bed temperature (Mazzucco and Rokni, 2015), 3D numerical models of heat and mass transfer prediction during hydrogen uptake/release including modeling the behavior of various forms of heat exchangers such as axial heat exchanger tubes, coiled heat exchanger tubes, external cooling and transversal heat distribution fins (Satya Sekhar et al., 2015). Four different heat exchange configurations were studied i.e., by natural convection, by fins, by internal concentric circulation fluid and by concentric fins, with cylindrical metal hydride tanks. The most efficient design out of the four configurations to achieve the lowest hydrogenation/dehydrogenation time was the concentric tube for fluid flow equipped by transverse fins (Askri et al., 2009; Mohammadshahi et al., 2016).

Designing metal hydride tanks includes modeling of the interaction between metal hydride bed and its surrounding. In an equilibrium state, this interaction can be formulated in the form of an energy balance to determine the heat-transfer mechanism in the metal hydride tanks. The equations for the energy balance would differ depending on the design of the tank and the integration of heat transfer medium. To take an example of a simple setup that involves metal hydride tank integrated with water recirculation loop system would have an energy balance as shown below (Forde et al., 2009):

\[ \dot{Q}_m = \dot{Q}_{\text{react}} + \dot{Q}_{\text{H}_2} + \dot{Q}_W \]  

\[ \dot{Q}_m = c_p,\text{reactor}m_{\text{reactor}} \frac{\partial T_{\text{reactor}}}{\partial T} + c_p,\text{MH}m_{\text{MH}} \frac{\partial T_{\text{MH}}}{\partial T} \]  

\[ \dot{Q}_{\text{react}} = \dot{m}_{\text{H}_2}\Delta H \]  

\[ \dot{Q}_{\text{H}_2} = \dot{m}_{\text{H}_2}c_p,\text{MH}\left|T_{\text{surrounding}} - T_{\text{MH}}\right| \]  

\[ \dot{Q}_W = \dot{m}_Wc_p,w\left(T_{\text{w,in}} - T_{\text{w,out}}\right) \]  

where, \( c_p \) is the heat capacity, \( m \) is mass, \( T \) is temperature, \( \dot{m}_{\text{H}_2} \) is the amount of \( \text{H}_2 \) entering (absorption: “+”) or leaving (desorption: “−”) the reactor, \( \dot{m}_W \) is the flow rate of the circulating water, \( \dot{Q}_m \) is heat flux for the change in temperature of reactor shell and metal hydride bed (J s\(^{-1}\)) \( \dot{Q}_{\text{react}} \) is energy produced/consumed in chemical gas-solid reaction (J s\(^{-1}\)), \( \dot{Q}_{\text{H}_2} \) is energy transferred in and out of the reactor with the \( \text{H}_2 \) gas (J s\(^{-1}\)) and \( \dot{Q}_W \) is energy transferred in and out of the reactor with the heating and cooling of water (J s\(^{-1}\)).

To reach the state of thermal equilibrium, one of the main barriers for effective heat transfer is the particle/particle interface heat conduction. This heat conduction can be quantitatively compared using the effective thermal conductivity (\( K_{\text{eff}} \)) in the form of W m\(^{-1}\) K\(^{-1}\), which has been tabulated in Table 6 for materials involved in hydrogen storage. For achieving fast absorption/desorption rates, high thermal conductivity of the material in the bed is necessary. However, in practical scenarios a high thermal conductivity across the hydride bed alone is not sufficient because the thermal conductivity of the individual “elements”, i.e., the hydrogen gas, its pressure, the material of the tank, and heat sinks, etc.; can all affect the heat flux (Figure 9; Wakao and Vortmeyer, 1971).

To illustrate this heat transfer concept, the relationship between effective thermal conductivity and pressure can be used, as it has been reported to follow a typical S-shaped curve (Wakao and Vortmeyer, 1971; Suda et al., 1980, 1983; Nagel et al., 1986; Hahne and Kallweit, 1998; Wu et al., 2009; Kan et al., 2015; Mazzucco and Rokni, 2015). The impact of individual “elements” on this S-shaped curve can be well-understood using the example of a tank that has a metal hydride such as MmNi\(_{4.5}\)Al\(_{0.5}\) alloy embedded in a copper-wire matrix (Nagel et al., 1986) as represented on Figure 9A. At a low hydrogen pressure (< 0.02 MPa), a low effective thermal conductivity of \( K_{\text{eff}} \sim 0.3–0.4 \) W m\(^{-1}\) K\(^{-1}\) is observed (Figure 9A–i; Wakao and Vortmeyer, 1971). At intermediate pressures of 0.02–3 MPa, the effective thermal conductivity of typical MH evolves into an S-shaped curve. To isolate the heat generated under the influence of gas pressure built-up, helium gas can be used because of its inertness toward the hydride forming metal and a thermal conductivity close to that of hydrogen (\( K_{\text{He}} = 0.188 \) W m\(^{-1}\) K\(^{-1}\)) is used.

### Table 6: Thermal conductivity values of materials related to hydrogen storage.

| Materials          | Thermal conductivity (W m\(^{-1}\) K\(^{-1}\)) | References            |
|--------------------|-----------------------------------------------|------------------------|
| **Gas**            |                                               |                        |
| Air                | 0.026                                         | ToolBox, 2003          |
| Argon              | 0.016                                         |                        |
| Helium             | 0.142                                         |                        |
| Hydrogen           | 0.188                                         |                        |
| **Metals**         |                                               |                        |
| Al                 | 247                                           | Lias et al., 2016      |
| Al foam            | 11                                            | Mellouli et al., 2009  |
| Cu                 | 398                                           | Lias et al., 2016      |
| Fe                 | 80                                            | Lias et al., 2016      |
| Graphite           | 130                                           | Azeem and Zain-ul-Abdein, 2012 |
| **Alloys**         |                                               |                        |
| Brass              | 121                                           | Lias et al., 2016      |
| 316 Stainless steel| 16                                            | Lias et al., 2016      |
| Brass              | 121                                           | Lias et al., 2009      |
| LaNi\(_5\)         | 2.4                                           | Mellouli et al., 2009  |
| LaNi\(_{4.5}\)Al\(_{0.5}\) – compacted | 13                                           | Haller, 1988          |
| MmNi\(_{4.5}\)Al\(_{0.5}\) + Al foam | 4                                            | Suda, 1985            |
| Ti/Mn\(_{1.5}\)    | 0.25                                          | Suda et al., 1980      |
| TiFe+ 17 wt% Al    | 13                                            | Groll, 1993           |
| TiFe+ Mg matrix    | 11                                            | Groll, 1993           |

The data on the effective thermal conductivity of metal hydride alloys are often reported as a function of pressure and temperature (Wakao and Vortmeyer, 1971; Suda et al., 1980, 1983; Nagel et al., 1986; Hahne and Kallweit, 1998; Wu et al., 2009; Kan et al., 2015; Mazzucco and Rokni, 2015). The impact of individual “elements” on this S-shaped curve can be well-understood using the example of a tank that has a metal hydride such as MmNi\(_{4.5}\)Al\(_{0.5}\) alloy embedded in a copper-wire matrix (Nagel et al., 1986) as represented on Figure 9A. At a low hydrogen pressure (< 0.02 MPa), a low effective thermal conductivity of \( K_{\text{eff}} \sim 0.3–0.4 \) W m\(^{-1}\) K\(^{-1}\) is observed (Figure 9A–i; Wakao and Vortmeyer, 1971). At intermediate pressures of 0.02–3 MPa, the effective thermal conductivity of typical MH evolves into an S-shaped curve. To isolate the heat generated under the influence of gas pressure built-up, helium gas can be used because of its inertness toward the hydride forming metal and a thermal conductivity close to that of hydrogen (\( K_{\text{He}} = 0.188 \) W m\(^{-1}\) K\(^{-1}\)) is used.
thermal conductivity under hydrogen and helium atmosphere, respectively). By separating the heat from the gas-pressure built up and that related to the entire system, the heat generated by the hydride formation only can be deduced (Figure 9A-i). Although a major influence on the $K_{\text{eff}}$ is observed from H$_2$ gas absorption/desorption in metals (>1.2 W m$^{-1}$K$^{-1}$) (Figure 9A-i), the ability to improve $K_{\text{eff}}$ by optimizing this parameter is limited by $\Delta H^0$, because the later must remain within $-10$ to $-60$ kJ mol$^{-1}$ H$_2$ for the RT hydrides to be reversible (Sandrock, 1999; Bérubé et al., 2007). This suggests that the additional parameters including the gas pressure, the type of metal alloy and the thermal additives used, are the only additional means to control heat management upon hydrogen uptake and release and to improve $K_{\text{eff}}$. Examples of S-shaped effective thermal conductivity curves of various other MH with/without additives are also reported (Figure 9B).

In current investigations, efforts have been driven toward using additives with high thermal conductivity to improve the heat transfer and compensate for the low contact between the hydride particles and their poor thermal conductivity. For example, a typical thermal conductivity factor of $K_{\text{eff}} \approx 0.1$ W m$^{-1}$K$^{-1}$ is observed for RT s hydrides like Ca$_{0.4}$Mm$_{0.6}$Ni$_5$ (Kim et al., 1998) where additives to improve the thermal conductivity of the hydride bed include corrugated copper wires (thermal conductivity of 389 W m$^{-1}$K$^{-1}$) (Nagel et al., 1986), copper-encapsulated metal hydride compact discs (cooling output of approx. 0.8 kW kg$^{-1}$ for Ca$_{0.4}$Mm$_{0.6}$Ni$_5$) (Kim et al., 1998), the addition of expanded graphite (Kim et al., 2001) or insertion of aluminum foam (Lévesque et al., 2000). Other design solutions include that installation of heat exchangers around or across the hydride bed (Lévesque et al., 2000).
Tank Design

 Besides the thermal conductivity of the metal hydride bed as discussed above, the performance of the metal hydride system also depends upon the tank design including heat exchangers configurations, geometrical distribution of the metal hydride in the tank, and tank material and dimensions (Shafiee and McCay, 2016). Although multiple design variations of hydride tanks have been proposed, the basic geometrical configuration of tanks remains the same, i.e., a typical cylindrical structure (Shafiee and McCay, 2016). An example of such a tank structure is shown in Figure 10A using LaNi$_5$ as the storage material (Jemni et al., 1999). To visualize the heat transfer across this metal hydride bed, Wang et al. (2009) performed 3-D modeling and presented a cross-section of the temperature contours at times from 1 to 2000 s (Figure 10B). Upon hydrogen absorption, initially, the temperature of the metal hydride bed evolves uniformly but then varies greatly across the hydride bed due to its poor

![Figure 10A](image1.png) ![Figure 10B](image2.png) ![Figure 10C](image3.png)

**FIGURE 10** | Cross-section of the (A) tank holding LaNi$_5$ alloy (Jemni et al., 1999), (B) its related temperature contour upon hydrogen absorption (Wang et al., 2009) and (C) types of modified metal hydride tank designs to increase the heat transfer radially from the center of the tank (Afzal et al., 2017).
thermal conductivity. The incorporation of metal foams, tubular heat exchangers can help to some extent reduce the temperature heterogeneity across the hydrogen bed, but this is at the expense of the practical hydrogen volumetric and gravimetric storage capacity (Afzal et al., 2017).

To highlight the effects of modifications of the tank design on the heat transfer process, a simplified equation that is governed by how well the heat is conducted through the tank can be used (Afzal et al., 2017):

\[
\dot{Q} = K_{\text{eff}} A \frac{\Delta T}{\Delta x}
\]

(9)

where, \(\dot{Q}\) is the rate of heat transfer, \(K_{\text{eff}}\) is the effective thermal conductivity of the material, \(\Delta x\) is the distance for the heat to propagate through the medium and \(A\) is the surface area in contact.

Using eq. 9, the modifications on the tank design can be directly correlated to the factors that govern the heat transfer process. For example, metal foams and expanded natural graphite enhance the \(K_{\text{eff}}\) parameter, multi-tubular tank reduces the distance \(\Delta x\) for the heat to conduct through and heat transfer fluid tubes/jacket and fins increase the surface area for the heat to transfer (Afzal et al., 2017).

A safety concern that needs to be acknowledged is the possibility of generating stresses on the walls due to swelling of the metal hydride during hydrogen absorption when filling densities are high. It has been reported that localized stress has been generated at the bottom of the vessel when alloy packing fraction of 50 vol% which continues to increase with each cycle even after plastic deformation (Nasako et al., 1998). To mitigate this risk, solutions such as installing the cylindrical tank horizontally instead of vertically to exhibit less strain during hydrogenation, optimizing hydrogen content and packing fraction should be devised (Qin et al., 2008).

A safety concern that also needs to be addressed for the tank design is hydrogen embrittlement. Embrittlement typically occurs due to the hydrogen molecules readily dissociating into atomic hydrogen at metal surfaces, and permeate through the tank wall, to form solid-solutions in the metal lattice and this facilitates local crack formation and the fracture of the tank wall (Birnbaum, 1987, 2003; Gangloff, 2003; Walker, 2008). Austenitic stainless steel and metals such as Cu, Au, Ni, and Al that have FCC structures tend to have low hydrogen permeability compared to BCC metals such as low-alloy and carbon steels (Walker, 2008). The rate of hydrogen permeation is expected to increase at higher surface area and elevated temperatures as shown by Figure 11 for various alloys and metals. A comprehensive study on high temperature permeability have also been recently reported (Sheppard et al., 2019). Typical susceptibility to hydrogen embrittlement of common metals/ alloys as per ISO/TR 15916 standard is tabulated in Table 7 (ISO, 2004). Besides the tank body, these materials can also be used to manufacture the valves and various components to ensure compatibility throughout the system (ISO, 2012).

Alternative Hybrid High-Pressure System

Using MH-filled vessel gives the benefit of high volumetric hydrogen density (>90 H₂- kg⁻³). However, with conventional RT hydrides, the gravimetric hydrogen density remains low. For example to store 5 kg of H₂, 167 kg of an alloy (3 wt% H₂) would be required and this would lead to an overall system of at least 200 kg once material is integrated to a tank with a heat exchanger (2.5 wt% H₂ at system level) (Takeichi et al., 2003). In an attempt to overcome this, the concept of “hybrid hydrogen storage vessel” combining a light-weight pressure vessel with a hydrogen pressure of 10–30 MPa and a hydrogen storage alloy with a high equilibrium hydrogen pressure has been proposed (Figure 12; Takeichi et al., 2003). For example, by integrating TiFe with a high-pressure system, a high gravimetric capacity of 5.4 wt% at the system level has been reported (Takeichi et al., 2003). In comparison, the low-pressure conventional metal hydride system using the same TiFe alloy would achieve a storage capacity of ∼1–2 wt% H₂ at the system level. Also, this hybrid approach provides flexibility in selecting MH with high desorption plateau pressure such as TiCr₁.₅Mn₀.₁Fe₀.₄ (∼10 MPa) and thus possibly reduce the
dependence on temperature to ensure that the pressure plateau stays above atmospheric pressure while releasing hydrogen from the hydride (Chen et al., 2013). Other examples of MH reported in literature for hybrid high pressure vessel are Ti\textsubscript{1−x}V\textsubscript{x}Mn, where \(x = 0.3, 0.5, \) and 0.6 (Shibuya et al., 2008), Ti\textsubscript{1+x}Cr\textsubscript{1−x}Mn\textsubscript{0.3}Fe\textsubscript{0.7} where \(x = 0.002 \) and 0.04 (Chen et al., 2013), TiCr\textsubscript{57.5}V\textsubscript{5} (Takeichi et al., 2003) and TiFe (Takeichi et al., 2003). In addition, the selection of hydrides can be further extended to amorphous alloys like Ti\textsubscript{1−x}Ni\textsubscript{x}, Zr\textsubscript{1−x}Ni\textsubscript{x} and Y\textsubscript{1−x}Fe\textsubscript{x} (where \(0.4 \leq x \leq 0.55\)) that do not have plateau pressures (Broom, 2011) and multiple crystalline phase alloys that can be mixed to form a multi-step plateau pressure providing control over pressure level for hydrogen supply.

Further investigations are needed along the design challenges associated with the concept of hybrid hydrogen storage vessels. For example, a trade-off exists between increasing the amount of metal hydride for enabling higher volumetric energy density and decreasing this amount for higher mass energy density. Stationary applications would typically prioritize volumetric energy density over mass energy density to reduce the cost associated with a square meter of land use (Choi et al., 2010). Therefore, achieving higher volumetric energy density, would favor hybrid vessels completely filled with the metal alloy. However, hybrid vessels that contain at least 10–50% of the metal alloy would require a well-designed heat exchanger and large flow of heat exchange mediums since the storage kinetics would be limited by the rate of the thermal evolution from the hydrogenation of the alloy (Takeichi et al., 2003). It is currently difficult to determine if the complexity in the heat exchange system increases or decreases in comparison to the low-pressure metal hydride tank. This is because of the trade-off between the selection of heat-exchange materials capable of withstanding high operating pressures of 10–30 MPa and the need of reducing the balance of components due to low amount of metal alloy present in the hybrid vessel.

![Figure 12](image-url)

**Figure 12** | Hybrid hydrogen storage vessel: (A) Schematic representation of novel hybrid hydrogen vessel were (i) valve, (ii) tube for hydrogen, (iii) carbon fiber and epoxy resin, (iv) thin aluminum liner and (v) hydrogen storage material such as TiFe and TiCr\textsubscript{57.5}V\textsubscript{5} (Takeichi et al., 2003); (B) Table showing estimated target values of hydrogen storage materials for hybrid high-pressure vessel (Mori et al., 2008; Shibuya et al., 2008).

### AN ALTERNATIVE APPLICATION OF HYDRIDES IN STATIONARY APPLICATIONS

Metal Hydrides have a distinct advantage of being considered carriers for both heat and hydrogen. In thermal storage application, the heat of the reaction liberated during the exothermic reaction of the hydride formation can serve as useful heat (Sheppard et al., 2016). Thereby hydrogen storage materials can be used as thermal storage solutions: (1) in a closed system in which \(H_2\) is preserved and is re-used during the heat storage cycles, or (2) in open systems in which \(H_2\) is released from a high-temperature hydride and is used for gas-to-heat/power application (\(H_2\) combustion) (Felderhoff and Bogdanović, 2009).

A thermal storage system based on a closed system is illustrated in Figure 13A. For this system being used in conjunction with renewable energy sources, it is assumed that the heat required is initially generated from a concentrated solar power plant (Corgnale et al., 2014; d’Entremont et al., 2017). In this case, (i) during daytime hydrogen is released from a high-temperature hydride receiving heat from the concentrated solar plant into a secondary storage vessel; (ii) at night time, useful heat is then generated from the exothermic absorption of hydrogen in the high-temperature hydride. TiH\textsubscript{2}, Zr based MH, MgH\textsubscript{2} and Mg-based MH could be suitable for thermal storage purposes because they store hydrogen at suitable high temperatures for solar thermal applications, i.e., 300–1000°C and have a high enthalpy of formation (Figure 13B; Pelay et al., 2017; Yartys et al., 2019; Poupin et al., 2020). Another example of a metal hydride that can perform as thermal battery is calcium hydride (CaH\textsubscript{2}). This is because of its high heat of formation of 4,312 kJ kg\(^{-1}\) at 25°C, low operating pressures (0.1–0.5 MPa) and a high heat storage capacity of 4,494 kJ kg\(^{-1}\) at 950°C (Manickam et al., 2019; Balakrishnan et al., 2020; Sofianos et al., 2020). However, the challenge is to reduce the decomposition temperature of CaH\textsubscript{2}.

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**Table 1**

| Hydrogen properties | Units | Target |
|---------------------|-------|--------|
| Hydrogen storage capacity | wt.% | >3 |
| Reaction enthalpy (\(\Delta H\)) | kJ/mol | >20 |
| Desorption equilibrium pressure at -30°C | MPa | >1 |
| Absorption equilibrium pressure at 120°C | MPa | <35 |
| Degradation at 1000 cycles | % | <10 |
Heat absorption
Heat release
Heat recovered from low temperature hydride
Heat input e.g. Stirling engine waste heat, ambient heat

(i) Desorption
(ii) Absorption

FIGURE 13 | (A) Schematic representation of using high-temperature hydrides in a closed system for thermal storage purposes under two scenarios: (i) desorption and (ii) absorption process where H₂ is being released and absorbed from high-temperature hydride, respectively (Felderhoff and Bogdanović, 2009); (B) Evaluation of various metal hydrides with different fuel cell systems and their potential for being used as a thermal storage hydride. The desorption temperature values for metal hydrides are measured at 1 MPa plateau pressure. Q_{loss} is associated with heat loss from fuel-cell systems, while -\Delta H^\Theta represents the enthalpy of formation of the presented hydrides (Lototskyy et al., 2017; Pelay et al., 2017). For thermal storage applications, the high-temperature hydrides such as MgH₂ or TiH₂ can be linked to low-temperature hydrides such as TiMn₁.₅Hₓ and LaNi₅Hₓ (\Delta H^\Theta \approx 1/3 of high-temperature hydride) or a standard H₂ pressure vessel that can be used as temporary storage of hydrogen (Felderhoff and Bogdanović, 2009).
as its operating temperature is >1,000°C and the cost associated with expensive containment vessels since both Ca and CaH₂ are highly corrosive (Curtis and Chiotti, 1963; Wang et al., 2012). Therefore, to destabilize CaH₂, additives such as Al and Al₂O₃ have also been explored that form a multi-step reactions for CaH₂ decomposition (Balakrishnan et al., 2020).

Similar to thermal storage, another application for these high-temperature hydrides is to use them in combination with high operating temperatures fuel cell systems such as solid-oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC). This combination allows the utilization of high-temperature hydrides by recovering the heat loss (Q_\text{loss}) from fuel-cell to facilitate the release of hydrogen from these hydrides. For example, ZrV₂Hₓ high temperature hydride can be coupled with SOFC fuel cell and Mg₂CoH₆ can be coupled with both SOFC and MCFC as represented in Figure 13B (Felderhoff and Bogdanović, 2009). Although low-temperature hydrides such as TiMn₅₋ₓ, LaNi₅₋ₓ, VHₓ, TiCoHₓ, NaAlH₄, and LaNi₅AlHₓ are all suitable for low-temperature proton exchange membrane (LT PEM), alkaline fuel cell (AFC), high-temperature proton exchange membrane (HT PEM) and phosphoric acid fuel cell (PAFC), however, the beauty of designing the stationary systems is the amount of flexibility that can introduced into the system such that low-temperature hydrides can also be used for SOFC and MCFC conditions. For example, when the operating temperature of the fuel cell is higher than the required desorption temperature for metal hydride then the excess waste heat from fuel cell can be used for thermal applications (Pasini et al., 2013; Lototskyy et al., 2017).

CONCLUSION

With growing awareness of climate change and deployment of new intermittent renewable energy sources, hydrogen storage can be at the forefront of energy storage solutions. However, to successfully commercialize hydrogen storage solutions, it is vital to have the proper selection of MH that meets the requirements of stationary applications. Although generally, the selection criteria fall toward a specific category of intermetallic hydrides, however, the wide variety of MH with their various properties makes the selection process highly challenging. In addition, different intermetallic hydrides are prone to limitations and have unique ways of overcoming those limitations.

In recent years, new intermetallic hydrides with various compositions are being investigated and studied. This allows broadening the spectrum of metal hydride selection for hydrogen storage. New synthesis approaches have further enabled us to explore even past MH with a new perspective on their characteristic properties. The synergy of Mg and intermetallics, hybrid high-pressure vessels, reactive-milling and mixture of different crystal structures (Laves with BCC) have shown improvements in overcoming past limitations. However, further work needs to be carried out in optimizing these synergistic effects with a focus toward finding a pattern that can determine the optimal composition for metal hydride suitable for stationary applications. Additionally, optimal system design needs to be explored to create a thermal integration of fuel cell and intermetallic hydride. Such designs can then be extended to high-temperature hydrides for thermal storage purposes.

The main challenges toward meeting the targets of stationary applications is the lack of understanding of which method or process is favorable for improving the properties of hydrogen storage material. With this paper, we have managed to address this issue up to a certain extent. However, certain areas still have to be explored to understand how the processes (e.g., annealing, ball-milling and severe plastic deformation) negatively affect the properties of MH.

AUTHOR CONTRIBUTIONS

Both authors listed have made a substantial, direct, and intellectual contribution to the work, and approved it for publication.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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