Boron–nitrogen based hydrides and reactive composites for hydrogen storage

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Hydrogen forms chemical compounds with most other elements and forms a variety of different chemical bonds. This fascinating chemistry of hydrogen has continuously provided new materials and composites with new prospects for rational design and the tailoring of properties. This review highlights a range of new boron and nitrogen based hydrides and illustrates how hydrogen release and uptake properties can be improved.

Introduction

Water is the major naturally occurring liquid compound on earth covering ca. 70% of the earth’s surface. Electrolysis powered by renewable energy sources, for example, wind and solar energy enables the splitting of water to H₂ and O₂. The stored energy can be released as electricity and heat by reacting H₂ and O₂ to form water in a fuel cell. The overall process is a closed sustainable material cycle, where hydrogen is working as an energy carrier [1]. A remaining challenge is to store the significant amounts of hydrogen [2–11].

Hydrogen bonds are vital for biological systems and life, the unique properties of water, and so on. The dihydrogen bond is defined as the interaction between a metal hydride bond (hydridic hydrogen) and an OH or NH group or other proton donor (protic hydrogen). Unlike the classical hydrogen bond, the dihydrogen bond can react in the solid state via elimination of hydrogen by exchanging the weak H⁺⋯·⁻H interactions for strong covalent bonds in H₂, and thus may open new routes to the rational design of structures and hydrogen release reaction mechanisms [12].

A rarer interaction is the hydrogen–hydrogen bond, which occurs between two bonded hydrogen atoms with similar partial charges, which may be significantly stronger than van der Waals interactions and may play an important role for the physical properties of solid molecular borohydrides, for example, Zr(BH₄)₄ [13]. The hydrogen molecule can also act as a ligand in some complexes of the heavier d-block metals, for example, W or Re, and the distance between the hydrogen atoms can be utilized to distinguish between a M(η₃-H₂) complex with H–H bond length in the range 0.74 to ~1.38 Å and polyhydrodido complexes with H–H distances > 1.6 Å. The limiting value 0.74 Å is the internuclear distance in the hydrogen molecule [14].

The ligands NH₃ and BH₄⁻ are three dimensional, while NH₂⁻ and NH₂⁺ are two- and one-dimensional, respectively. The bond length in BH₄⁻ is approx. 1.22–1.24 Å, while the bond length is slightly shorter and decreasing from neutral NH₃ (1.01 Å) toward NH₂⁻ and NH₂⁺.

The hydrogen molecule, H₂, has the lowest number of electrons (2) of all molecules and therefore has the weakest physisorption
interactions. Hydrogen adsorption is often observed to follow Langmuir isotherms (i.e. monolayer adsorption), and the amount of hydrogen adsorbed under saturation conditions is generally proportional to the specific surface area determined by the BET method for the porous adsorbent (known as Chaine’s rule) [15–17]. A significant advantage is that the physisorption process has fast adsorption/desorption kinetics.

Ionic, metallic and covalent bonds are also formed by hydrogen, which has been discussed in another review in this issue of Materials Today [18]. Altogether, this illustrates that hydrogen forms a variety of different types of chemical bonds and interactions with matter and other elements and reacts with almost all other elements in the periodic table [19]. This suggests that there is still room for significant discoveries of a variety of novel hydrogen-containing materials. Furthermore, hydrogen can be released in a chemical reaction between two or more hydrides denoted reactive hydride composites (RHC) [8,11]. Dihydride bonding and the RHC concept provide new schemes for the design and synthesis of new materials with novel properties and for tailoring known materials properties.

Reactive hydride composites

A promising approach for tailoring thermodynamic properties is to allow two or more hydrogen-containing materials to react during the release of hydrogen. Such hydride mixtures are denoted Reactive Hydride Composites (RHC) [20]. In 2002, Chen et al. discovered reversible hydrogen release and uptake of lithium amide-hydride, LiNH₂–LiH, according to reaction scheme (1) [21].

LiNH₂(s) + 2LiH(s) \rightarrow Li₃NH(s) + H₂(g) + Li₃N(s) + 2H₂(g)  
\textbf{(1)}

The first step involves an amide–imide reaction, which may involve hydrogen elimination via dihydrogen-bonded hydrogen, but has also been suggested to involve ammonia [22–24] according to reaction scheme (2).

LiNH₂(s) + H₂(g) \rightarrow LiH(s) + NH₃(g)  
\textbf{(2)}

This reaction reveals a rare example where hydrogen is converted, 8.1 wt%, and heat is absorbed, ΔH = 50 ± 9 kJ/mol [25–27]. The reaction appears to be driven by larger entropy of the ammonia molecule than the hydrogen.

In reaction scheme (1), only the amide–imide reaction is reversible at moderate conditions with a hydrogen storage capacity of p(RH₂) = 6.5 wt% and an enthalpy change of ΔH_{dec} = 66 kJ/mol H₂ [28]. Several other reversible nitrogen-based systems have been investigated recently and are promising for future mobile applications, for example, Mg(NH₂)₂–2LiH with a low calculated decomposition temperature, T_{dec} < 90 °C (at p(H₂) = 1 bar) as a result of a low enthalpy change for the reaction, ΔH_{dec} = 38.9 kJ/mol H₂ [29–31].

Metal borohydrides and a metal amide can also form RHC systems as shown for LiBH₄–2LiNH₂ in reaction scheme (3) [32].

\begin{align*}
\text{LiBH}_4(s) + 2\text{LiNH}_2(s) & \rightarrow \text{Li}_3\text{BN}_2\text{H}_6(s) \\
& \rightarrow \text{Li}_3\text{BN}_2(s) + 4\text{H}_2(g) 
\end{align*}
\textbf{(3)}

In contrast, the analog lithium alanate amide system, LiAlH₄–2LiNH₂, releases 2 equiv. H₂ already during mechanochemical treatment forming an amorphous mixture with the overall composition Li₂AlN₂H₆; see reaction scheme (4a) [33,34]. Lithium aluminum nitride, Li₃AlN₃, absorbs more than 5 wt% H₂ forming 2LiH, LiNH₂ and AlN, reaction (4b), which is another new RHC system.

\begin{align*}
\text{LiAlH}_4(s) + 2\text{LiNH}_2(s) & \rightarrow [\text{Li}_2\text{AlN}_2\text{H}_4](s) + 2\text{H}_2(g) \\
& \rightarrow \text{Li}_3\text{AlN}_2(s) + 4\text{H}_2(g) 
\end{align*}
\textbf{(4a)}

\begin{align*}
2\text{LiH}(s) + \text{LiNH}_2(s) + \text{AlN}(s) & \leftrightarrow \text{Li}_3\text{AlN}_2(s) + 2\text{H}_2(g) 
\end{align*}
\textbf{(4b)}

The most successful reactive hydride composite was discovered independently by the research groups of Vajo, HRL Laboratories, California, USA and Dornheim, Klassen, Bormann and co-workers at HZG, Hamburg, Germany, namely LiBH₄–MgH₂ [35,36]. The great advantage is that the endothermic dehydorgenation of the two hydrides in the composite 2LiBH₄–MgH₂ is followed by the exothermic formation of MgB₂, see reaction (5). The total reaction enthalpy is thereby lowered to a calculated value of, ΔH_{dec} ~ 46 kJ/ (mol H₂) corresponding to a calculated decomposition temperature of T ~ 169 °C (at p(H₂) = 1 bar) [35,37,38]. The hydrogen absorption is facilitated from the MgB₂–LiH composite and occurs at p(H₂) = 50 bar and T < 300 °C. These conditions are substantially more favorable than those of LiBH₄ and are considered a breakthrough in utilizing borohydrides for reversible hydrogen storage. The full reversibility of the LiBH₄–MgH₂ system is only obtained when the decomposition occurs in a hydrogen back pressure of p(H₂) ~ 1–5 bar, which facilitates the formation of MgB₂ possibly owing to suppression of the individual decomposition of LiBH₄ [38–41]. In fact, hydrogen release and uptake is a two-step reaction as shown in reaction scheme (5).

\begin{align*}
\text{2LiBH}_4(s) + \text{MgH}_2(s) & \rightarrow 2\text{LiBH}_4(s) + \text{Mg}(s) + \text{H}_2(g) \\
& \leftrightarrow 2\text{LiH}(s) + \text{MgB}_2(s) + 4\text{H}_2(g) 
\end{align*}
\textbf{(5)}

A similar reaction occurs for a magnesium-rich system, 0.3LiBH₄–MgH₂, during decomposition in p(H₂) > 1 bar, that is, formation of MgB₂, whereas α- and β-alloys of Li₁₋ₓMgₓ are formed under a dynamic vacuum [42–44]. A number of other promising reactive hydride composite systems have also been described, for example, NaBH₄–MgH₂ and Ca(BH₄)₂–MgH₂ [36,45–50]. Additionally, some multicomponent systems have been developed such as LiBH₄–MgH₂–LaH₃ and Ca(BH₄)₂–LiBH₄–MgH₂. They benefit from high cyclic stability and high hydrogen capacity [51,52].

Dihydrogen-bonding – a new approach for hydrogen elimination

The strength and directionality of dihydrogen bonds, H⁺–H, appear to be comparable to conventional hydrogen bonds. The three intermolecular O–H⁺–H₂–B dihydrogen bonds in the compound NaBH₄·2H₂O are in the range 1.77–1.95 Å and shorter
than H–H distances within the BH4− anion, which are ca. 2.0 Å [53]. Indeed, it suggests that the dihydrogen bonds may facilitate hydrogen elimination during thermolysis at moderate temperatures. Metal borohydrides are often hygroscopic and in some cases new crystalline compounds are formed by the absorption of water. NaBH4·2H2O decomposes upon heating at ~40 °C to NaBH4 and 2H2O, which at T > 40 °C slowly react to release hydrogen. Thus, the hydrate NaBH4·2H2O does not directly release hydrogen, but decomposes into anhydrous NaBH4 and water [53]. Similarly, lithium borohydride exposed to air releases hydrogen at ~65 °C possibly due to a reaction between LiBH4 and H2O [54].

Metal borohydride ammoniates, M–BH4−·NH3
Ammonia, NH3, is catalytically split to N2 and H2 and is a candidate for on-board hydrogen storage as a result of its high hydrogen content (17.3 wt%) and the ability to store 30% more energy per volume than liquid hydrogen [55]. However, due to the toxicity of NH3 there are substantial safety issues that hamper widespread utilization. Ammonia reacts with metal borohydrides by coordination to the metal and by formation of dihydrogen bonds to BH4−. Metal borohydride ammoniates, M(BH4)2·nNH3, were discovered in the 1950s and have recently attracted significant attention as potential hydrogen storage materials, mainly for three reasons. First, metal borohydride ammoniates often have high hydrogen capacities and significantly lower dehydrogenation temperatures compared to the metal borohydride owing to the dihydrogen elimination of hydrogen. Destabilization is observed for borohydrides with low electronegativity. For example, Co-catalyzed Li[NH3]1/3·BH4 (i.e. 2/3Li(NH3)2BH4 and 1/3Li(NH3)2BH4 with equivalent protic and hydridic hydrogen atoms), releases ca. 17.8 wt% of H2 in a closed system in the temperature range 135–250 °C, in contrast to LiBH4 which release H2 at T > ~380 °C, C °C, see Fig. 1 [56]. In fact, this is a solid state-gas reaction between LiBH4 and NH3. Secondly, unstable metal borohydrides with a high electronegativity are stabilized by NH3 as demonstrated for several metal borohydrides, such as Zn(BH4)2·nNH3 and Al(BH4)3·nNH3 [57,58]. Ammonia always coordinates directly to the metal and may prevent formation of neutral volatile molecular borohydrides or reduction of the metal. Al(BH4)3 is among the borohydrides with highest capacity (16.9 wt%), but is unstable and volatile (Tbp = 44 °C). However, Al(BH4)3·6NH3 is stable and releases 11.8 wt% of H2 (purity 95%) with Tmax at 168 °C [59]. Thirdly, the composition of the released gas depends on the ratio between NH3 and BH4 coordinated to the metal, excess of NH3 provides increased tendency to release ammonia, that is, ammonia release from M(BH4)2nNH3 for n/m > 1 [60]. For instance, NH3 is released from Mg(BH4)2·6NH3, while mainly H2 is released from Mg(BH4)2·2NH3, see Fig. 2 [61]. Metals with low electronegativity tend to release NH3 upon heating in open systems (p(NH3) ~ 0), but H2 in closed systems [56,62]. Metals with higher electronegativity coordinate more strongly to NH3 giving rise to a collapse of the structure and release of H2 by dihydrogen elimination in the temperature range ~100 to ~200 °C. This may prevent the release of diborane from the more unstable metal borohydrides. A correlation between decomposition temperature and electronegativity of the metal coordinating to NH3 and BH4 is observed in Fig. 1 represented by a dotted line.

In addition to the monometallic borohydride ammoniates, a few bimetallic borohydride ammoniates have been synthesized [60,63–65]. The first example, Li2Al(BH4)5·6NH3, has a remarkable structure consisting of ordered [Al(NH3)4]3+ ammine complexes and [Li2(BH4)3]3− complex anions and reveal attractive decomposition properties [60]. Ammonia is detrimental for low temperature fuel cells, and the NH3/H2 ratio (n/m) requires tailoring to avoid ammonia release. Metal borohydrides readily react with ammonia to obtain M(BH4)2·nNH3. A series of calcium borohydride ammoniates, Ca(BH4)2·nNH3 (n = 1, 2, 4, 6), can be obtained by a sequential heating procedure [62,66]. Some metal borohydride ammoniates with low n/m ratio have successfully been prepared by metathesis reactions between metal chloride ammoniates and lithium borohydride [67]. The amount of NH3 is adjusted by partial release of NH3 from the metal chloride prior to the synthesis. The mechanoc-chemical approach facilitates formation of Zn(BH4)2·2NH3, while Zn(BH4)2·4NH3 is obtained by solvent-based methods [57]. This method introduces significant amounts of LiCl in the final product. Thus, development of new synthesis routes providing halide free materials with specific n/m ratios is important.

Metal borohydride amides, M–BH4−·NH2
An alternative approach to combine partially positive H atoms to hydric hydrogen in metal borohydrides is by using metal amides, M(NH3)n. Numerous combinations between alkali and alkaline earth metal amides and borohydrides have been investigated, for example, Mg(BH4)2·LiNH2 [68], Ca(BH4)2·Mg(NH3)2 [69], and LiBH4·Mg(NH3)2 [70]. As discussed above, LiBH4·2LiNH2 is an example of a reactive hydride composite with dihydrogen bonding [32]. Changing the reactant ratio LiBH4·LiNH2 to (1:1) or (1:3) gives rise to compounds with different chemical compositions, Li2(BH4)·NH3 or Li2(BH4)·(NH3)2, which are also good lithium ion conductors [71]. The detailed crystal structures are known for
Ammonia borane and derivatives

Ammonia borane, $\text{NH}_3\text{BH}_3$ (AB) has attracted significant attention owing to its extreme hydrogen capacities of $\rho_{\text{HN}} = 19.6$ wt% H$_2$, $\rho_{\text{B}} = 146$ g H$_2$/L, and air stability [76]. Solid crystalline ammonia borane has an intermolecular dihydrogen bond network and is not hygroscopic unlike borohydrides. This compound, $\text{NH}_3\text{BH}_3$, releases one equivalent of hydrogen in each of the three decomposition steps forming polyaminoborane, [H$_2$BH$_3$]$_n$ (90–120 °C), polymiminoborane, [NHBH$_3$]$_n$ (120–200 °C) and finally boron nitride, BN (>500 °C) [76]. However, the hydrogen release is accompanied by toxic by-products, such as ammonia ($\text{NH}_3$), diborane ($\text{B}_2\text{H}_6$) and borazine ($\text{N}_3\text{B}_3\text{H}_5$). Furthermore, the decomposition is exothermic ($\Delta H_{\text{dec}} = -21$ kJ/mol H$_2$), hence non-reversible [77]. However, significantly improved properties of $\text{NH}_3\text{BH}_3$ were obtained by infiltration in ordered mesoporous silica facilitating enhanced kinetics (faster hydrogen release) at lower temperatures with reduced borazine emission and improved thermodynamics, $\Delta H_{\text{dec}} = -1$ kJ/mol H$_2$ [78]. Additionally, the work by Autrey and co-workers [78] initiated the focus on nanoconfine as a tool to improve kinetics and possibly thermodynamics of hydrogen storage materials [79]. More recently, nano-sized Co and Ni additives in ammonia borane were observed to improve the kinetics and suppress borazine emission and foaming [80].

An even more hydrogen-rich compound can be prepared: ammonium borohydride, $\text{NH}_4\text{BH}_4$. It has the highest hydrogen content of solid-state materials reported to date ($\rho_{\text{HN}} = 24.5$ wt% H$_2$, $\rho_{\text{B}} = 151$ g H$_2$/L) and releases 3 equivalents of hydrogen ($\sim 18$ wt% H$_2$) in three distinct exothermic steps at $T < 160$ °C [81]. However, $\text{NH}_4\text{BH}_4$ slowly decomposes at RT with a half-life of $\sim 6$ h to a diammoniate of diborane ($\text{NH}_3\text{BH}_2\text{BH}_4$) (DADB) and hydrogen. For long-term storage $\text{NH}_4\text{BH}_4$ must be kept at $T < -40$ °C. Recently, nanocoated $\text{NH}_4\text{BH}_4$ in mesoporous silica was investigated and appears to be destabilized and more rapidly decomposes to DADB [82].

The complicated synthesis methods have hampered the detailed investigation of ($\text{NH}_3$)$_2\text{BH}_2$($\text{BH}_4$). However, recently a mechanochemical reaction between $\text{NH}_4\text{BH}_4$ and $\text{NH}_3\text{BH}_3$ was discovered [83], see scheme (6).

$$\text{NH}_4\text{BH}_4(s) + \text{NH}_3\text{BH}_3(s) \rightarrow [(\text{NH}_3)_2\text{BH}_2][\text{BH}_4](s) + \text{H}_2(g)$$  

(6)

DADB decomposes in reaction steps similar to AB, but with a slightly lower onset temperature, faster kinetics and no significant induction period prior to hydrogen release, possibly due to DADB known to be an intermediate in the decomposition of AB [84].

Metal amidoboranes, M($\text{NH}_3\text{BH}_3$)$_n$, are synthesized by reacting a metal hydride with ammonia borane using either mechanochemistry or solvent-based methods [85], see reaction scheme (7).

$$\text{MH}_n(s) + n\text{NH}_3\text{BH}_3(s) \rightarrow M(\text{NH}_2\text{BH}_3)_n(s) + n\text{H}_2(g)$$  

(7)
Since 2007, a series of metal amidoboranes, M(NH₂BH₃)ₓ (M = Li, Na, K, Ca, Sr), have been synthesized according to reaction scheme (7) and structurally investigated [86–89]. In contrast, Y(NH₂BH₃)₁₃ is synthesized by a metathesis reaction between MNH₂BH₃ and YX₃ (M = Li, Na; X = Cl, F) [90]. The magnesium analog, Mg(NH₂BH₃)₂, was previously considered unstable, but was recently synthesized [91]. Metathesis reaction between FeCl₃ and LiNH₂BH₃ in THF was unsuccessful, but LiCl and polymeric [Fe(HN == BH)]₁₇, was formed together with the release of 1.5 equiv. H₂ in THF at RT [92]. In general, metal amidoboranes have high hydrogen content, good kinetics and low decomposition temperatures. LiNH₂BH₃ decomposes in the temperature range from 75 to 95 °C and releases 10.9 wt% H₂ according to scheme (8) [86]. Formation of metal amidoboranes is considered an approach to prevent release of borazine from ammonia borane [93].

\[ \text{LiNH}_2\text{BH}_3(s) \rightarrow \text{LiNBH}(s) + 2\text{H}_2(g) \]  

(8)

Metal amidoborate ammoniates, M(NH₂BH₃)ₓ-xNH₃ are known for M = Mg, Ca [94,95]. These compounds tend to release NH₃ below 100 °C in an open system (endothermic reaction) and H₂ in a closed system (exo-therm). Recently, hydrogen release was observed from an endothermic reaction from composites of Mg(NH₂BH₃)₂-2NH₃ and NaH/KH [96].

In 2010, the first metal borohydride-ammonia borane complexes, M-BH₄-NH₂BH₃ were reported, that is, Li₂(BH₄)₂NH₂BH₃ and Ca(BH₄)₂(NH₂BH₃) [97]. Since then, LiBH₄(NH₂BH₃) [98], and Mg(BH₄)₂(NH₂BH₃) [99,100] have also been reported, and they are all prepared by mecanochemical treatment of AB and M(BH₄)ₓ (M = Li, Mg, Ca). In contrast, MgBH₄-NH₂BH₃ (M = Na, K, Cs, Rb) do not form new compounds during mecanochemical treatment [99,101]. This class of materials have high hydrogen capacities and low decomposition temperatures, for example, Mg(BH₄)₂(NH₂BH₃) (p₀ = 17.4 wt% H₂, p₁ = 137 g H₂/L) melts at ~48 °C and has an onset temperature for hydrogen release at 75 °C [99]. However, the thermal decomposition of these compounds still involves the release of diborane and borazine similar to NH₂BH₃ reflecting a weak interaction between the borohydride groups and ammonia borane. This is explained by the crystal structures of M(BH₄)ₓ(NH₂BH₃)ₓ where AB keeps its molecular form [97]. The crystal structure of Mg(BH₄)₂(NH₂BH₃) is shown in Fig. 3. Both borohydride groups and AB act as terminal ligands, and molecular complexes are linked in the crystal structure via dihydrogen bonds of N-H⋯H-B (<2 Å).

Hydrazine and hydrazine borane

Hydrazine, N₂H₄ (12.5 wt% H₂) decomposes via two competing reactions forming N₂, H₂ and NH₃. Recently a new class of hydrogen storage materials, borohydride hydrazinates, was successfully synthesized, for example, LiBH₄-N₂H₂NH₂ and LiBH₄-2NH₂NH₂ [102]. Approximately 13.0 wt% H₂ is released from LiBH₄-N₂H₂NH₂ 2NH₂ at 140 °C in the presence of Fe–B catalysts. However, this again leads to the formation of the stable compounds Li₃BN₂ and BN according to reaction scheme (9).

\[ 3(\text{LiBH}_4\text{N}_2\text{H}_4)(s) \rightarrow \text{Li}_3\text{BN}_2(s) + 2\text{BN}(s) + \text{N}_2(g) + 12\text{H}_2(s) \]  

(9)

Furthermore, the decomposition product of AB, polyiminoborane reacts with hydrazine in THF solution to form hydrazine borane (N₂H₂BH₃, HB). HB (15.4 wt% H₂) melts at 61 °C at which point the decomposition initiates yielding NH₂NH₂, (NH₂BH₂), H₂ and NH₃. Interestingly, mecanochemical treatment of LiH–HB (1:1) and (1:3) provided the first metal hydrazinoborane, Li[N₂H₂BH₄] and its hydrazine borane adduct Li[N₂H₄]BH₃-2N₂H₄BH₃ [103]. The metal hydrazinoboranes exhibit dramatically improved hydrogenation properties compared to hydrazine borane (N₂H₂BH₃) with nearly complete hydrogenation in the temperature range 50–225 °C releasing high purity hydrogen. However, the decomposition for both compounds is exothermic, hence non-reversible.

Reversibility of B–N based hydrides

Generally, the B–N compounds discussed in this review paper show high hydrogen storage capacities both gravimetrically and volumetrically and often release hydrogen at low temperatures see Table 1. However, they all suffer from limited reversibility due to the formation of stable boron nitrides in the decomposed residue. Therefore, further research in kinetics and thermodynamics...
related to hydrogen uptake is needed and further investigation of partly decomposed B-N-H materials may be fruitful. Hydrogen uptake in fully decomposed Mg(BH₄)₂ is possible, but requires extreme conditions: 500 °C and p(H₂) = 950 bar [106,107]. However, partial dehydrogenation of Mg(BH₄)₂ at lower temperatures (250 °C) forms Mg(B₃H₆)₂, which is more readily rehydrogenated (250 °C, p(H₂) = 120 bar, 48 h). A similar approach may be successful for B-N-H based compounds. Recently, the regeneration of ammonia borane is reported to take place from polyimino-noborane by reacting with hydrazine in liquid ammonia at 40 °C within 24 h [108]. Fig. 4 illustrates the ideal cycle for reversible hydrogen storage using NH₃BH₃. Importantly, this cycle is closed and the generation of AB from hydrazine takes place in one step and does not involve any noble metal catalysts. This discovery is among the most important breakthroughs for possible utilization of ammonia borane for hydrogen storage and at the same time reveals new classes of materials based on ammonia borane and hydrazine.

Conclusion
This review illustrates the extreme diversity in the fascinating chemistry of hydrogen, regarding the variety of chemical bonds and compounds that can be created. The kinetic and thermodynamic properties and hydrogen storage densities can be tailored, which reveal new perspectives for the development of solid-state hydrogen storage materials. Dihydrogen bonding provides hydrogen elimination at moderate temperatures but reformation of this type of bond is difficult. A similar drawback is observed for ammoniates and amides of metal borohydrides, which otherwise provide extreme hydrogen densities and low decomposition temperatures. Fortunately, the recent discovery of ammonia borane regeneration using hydrazine reveals that further research in partial dehydrogenation may provide new reversible reaction routes for hydrogen release and uptake at moderate conditions. An overwhelming variety of novel boron and nitrogen based materials have been discovered over the past few years, which provide new approaches for the rational design of materials with tailored properties and new hope for the discovery of novel types of hydrogen storage materials. Further research within boron and nitrogen based hydrides may significantly support the implementation of hydrogen as a future energy carrier, for applications including mobile devices, in a sustainable future for humanity.

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References

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>p_m (wt%)</th>
<th>p_V (g H₂/L)</th>
<th>T_onset (°C)</th>
<th>Impurities</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>LiBH₄</td>
<td>18.5</td>
<td>122.5</td>
<td>380</td>
<td>Not observed</td>
<td>[104]</td>
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<tr>
<td>α-Mg(BH₄)₂</td>
<td>14.9</td>
<td>117</td>
<td>250</td>
<td>Not observed</td>
<td>[105]</td>
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<tr>
<td>Mg(BH₄)₂ · 2NH₃</td>
<td>16.0</td>
<td>130</td>
<td>150</td>
<td>NH₃</td>
<td>[61]</td>
</tr>
<tr>
<td>Li3Al(BH₄)₅ 6NH₃</td>
<td>17.6</td>
<td>151</td>
<td>75</td>
<td>NH₃ (&gt;99% H₂)</td>
<td>[60]</td>
</tr>
<tr>
<td>Al(BH₄)₃ · 6NH₃</td>
<td>17.4</td>
<td>150</td>
<td>130</td>
<td>NH₃ (95% H₂)</td>
<td>[59]</td>
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<tr>
<td>Zn(BH₄)₂ · 2NH₃</td>
<td>10.8</td>
<td>135</td>
<td>90</td>
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<td>[57]</td>
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<tr>
<td>NH₃BH₃</td>
<td>24.5</td>
<td>151</td>
<td>85</td>
<td>B₂H₆, B₃N₃H₆, NH₃</td>
<td>[81]</td>
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<tr>
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<td>108</td>
<td>B₂H₆, B₃N₃H₆, NH₃</td>
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<tr>
<td>LiNH₃BH₃</td>
<td>10.9</td>
<td>92</td>
<td>85</td>
<td>NH₃</td>
<td>[86]</td>
</tr>
<tr>
<td>Mg(BH₄)₂(NH₃BH₃)</td>
<td>17.4</td>
<td>137</td>
<td>75</td>
<td>B₂H₆, B₃N₃H₆, NH₃</td>
<td>[99]</td>
</tr>
<tr>
<td>Li₂(BH₄)₂NH₃BH₃</td>
<td>19.0</td>
<td>138</td>
<td>105</td>
<td>B₂H₆, B₃N₃H₆, NH₃</td>
<td>[97]</td>
</tr>
</tbody>
</table>

TABLE 1

Selected solid boron- and nitrogen-based hydrides with high gravimetric (p_m) and volumetric (p_V) hydrogen densities and often with low onset temperatures for hydrogen release (T_onset). Unfortunately, the released hydrogen gas may contain varying amounts of impurities.