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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 H\textsubscript{2} and O\textsubscript{2}. The stored energy can be released as electricity and heat by reacting H\textsubscript{2} and O\textsubscript{2} 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\textsuperscript{+}···H interactions for strong covalent bonds in H\textsubscript{2}, 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(BH\textsubscript{4})\textsubscript{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(H\textsubscript{2}) complex with H–H bond length in the range 0.74 to \textasciitilde 1.38 Å and polyhydroido 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 NH\textsubscript{3} and BH\textsubscript{4}– are three dimensional, while NH\textsubscript{2}– and NH\textsubscript{2}\textsuperscript{2–} are two- and one-dimensional, respectively. The bond length in BH\textsubscript{4}– is approx. 1.22–1.24 Å, while the bond length is slightly shorter and decreasing from neutral NH\textsubscript{3} (1.01 Å) toward NH\textsubscript{2}– and NH\textsubscript{2}\textsuperscript{2–}.

The hydrogen molecule, H\textsubscript{2}, 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 Chahine’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]. Dihydrogen 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].

\[
\text{LiNH}_2(s) + 2\text{LiH}(s) \rightarrow \text{Li}_3\text{NH}(s) \\
+ \text{LiH}(s) + \text{H}_2(g) \rightarrow \text{Li}_3\text{N}(s) + 2\text{H}_2(g) 
\]

(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).

\[
\text{LiNH}_2(s) + \text{H}_2(g) \rightarrow \text{LiH}(s) + \text{NH}_3(g) 
\]

(2)

This reaction reveals a rare example where hydrogen is converted, 8.1 wt%, and heat is absorbed, \(\Delta H = 50 \pm 9\) 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 \(p_{\text{H}_2} = 6.5\) wt% and an enthalpy change of \(\Delta H_{\text{dec}} = 66\) 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, \(T_{\text{dec}} < 90\) °C (at \(p(\text{H}_2) = 1\) bar) as a result of a low enthalpy change for the reaction, \(\Delta H_{\text{dec}} = 38.9\) 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]. Initially, a new crystalline solid with composition \(\text{Li}_3\text{BN}_2\text{H}_8\) forms by mechanochemical treatment, which is an intermediate compound prior to the formation of a very stable decomposition product, \(\text{Li}_3\text{B}_2\text{N}_2\), illustrated in reaction scheme (3). The onset temperature for hydrogen release decreases from \(\sim 380\) to 250 °C for LiBH4 in the composite LiBH4–2LiNH2, and thermal decomposition releases more than 10 wt% H2 in the temperature range 250–350 °C, but, unfortunately, the system is irreversible.

\[
\text{LiBH}_4(s) + 2\text{LiNH}_2(s) \rightarrow \text{Li}_3\text{BN}_2\text{H}_8(s) \\
\rightarrow \text{Li}_3\text{B}_2\text{N}_2(s) + 4\text{H}_2(g) 
\]

(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 Li3AlN2H4, see reaction scheme (4a) [33,34]. Lithium aluminum nitride, Li3AlN2, absorbs more than 5 wt% H2 forming 2LiH, LiNH2 and AlN, reaction (4b), which is another new RHC system.

\[
\text{LiAlH}_4(s) + 2\text{LiNH}_2(s) \rightarrow [\text{Li}_3\text{AlN}_2\text{H}_4](s) + 2\text{H}_2(g) \\
\rightarrow \text{Li}_3\text{AlN}_2(g) + 4\text{H}_2(g) 
\]

(4a)

\[
2\text{LiH}(s) + \text{LiNH}_2(s) + \text{AlN}(s) \rightarrow \text{Li}_3\text{AlN}_2(s) + 2\text{H}_2(g) 
\]

(4b)

The most successful reactive hydride composite was discovered independently by the research groups of Vajo, HRL Laboratories, California, USA and Dornheim, Klassn, Bormann and co-workers at HZG, Hamburg, Germany, namely LiBH4–MgH2 [35,36]. The great advantage is that the endothermic dehydrogenation 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, \(\Delta H_{\text{dec}} \approx 46\) kJ/ (mol H2) corresponding to a calculated decomposition temperature of \(T \approx 169\) °C (at \(p(\text{H}_2) = 1\) bar) [35,37,38]. The hydrogen absorption is facilitated from the MgB2–LiH composite and occurs at \(p(\text{H}_2) = 50\) 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 \(p(\text{H}_2) = 1–5\) 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).

\[
2\text{LiBH}_4(s) + \text{MgH}_2(s) \rightarrow 2\text{LiBH}_4(s) + \text{Mg}(s) + \text{H}_2(g) \\
\rightarrow 2\text{LiH}(s) + \text{MgB}_2(s) + 4\text{H}_2(g) 
\]

(5)

A similar reaction occurs for a magnesium-rich system, 0.3LiBH4–MgH2, during decomposition in \(p(\text{H}_2) > 1\) bar, that is, formation of MgB2, whereas \(\alpha-\) and \(\beta-\) alloys of Li1–\(\alpha\), Mg, 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, \(\text{H}^\alpha\cdots\text{H}^\beta\), appear to be comparable to conventional hydrogen bonds. The three intermolecular \(\text{O}^\alpha\cdots\text{H}^\beta\cdots\text{O}^\gamma\) dihydrogen bonds in the compound NaBH4·2H2O are in the range 1.77–1.95 Å and shorter.
than H - H distances within the BH\textsuperscript{4} 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. NaBH\textsubscript{4}-2H\textsubscript{2}O decomposes upon heating at ~40 °C to NaBH\textsubscript{4} and 2H\textsubscript{2}O, which at T > 40 °C slowly react to release hydrogen. Thus, the hydrate NaBH\textsubscript{4}-2H\textsubscript{2}O does not directly release hydrogen, but decomposes into anhydrous NaBH\textsubscript{4} and water [53]. Similarly, lithium borohydride exposed to air releases hydrogen at ~65 °C possibly due to a reaction between LiBH\textsubscript{4} and H\textsubscript{2}O [54].

**Metal borohydride amoniates, M-BH\textsubscript{4}-NH\textsubscript{3}**

Ammonia, NH\textsubscript{3}, is catalytically split to N\textsubscript{2} and H\textsubscript{2} 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 NH\textsubscript{3} there are substantial safety issues that hamper widespread utilization. Ammonia reacts with metal borohydrides to form coordination with the metal and by formation of dihydrogen bonds to BH\textsubscript{4}\textsuperscript{-}. *Metal borohydride amoniates,* M(BH\textsubscript{4})\textsubscript{m}nNH\textsubscript{3}, were discovered in the 1950s and have recently attracted significant attention as potential hydrogen storage materials, mainly for three reasons. First, metal borohydride amoniates 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(NH\textsubscript{3})\textsubscript{2}BH\textsubscript{4} (i.e. 2/3Li(NH\textsubscript{3})\textsubscript{3}BH\textsubscript{4} and 1/3Li(NH\textsubscript{3})\textsubscript{4}BH\textsubscript{4} with equivalent proton and hydridic hydrogen atoms), releases ca. 17.8 wt% of H\textsubscript{2} in a closed system in the temperature range 135–250 °C, in contrast to LiBH\textsubscript{4} which release H\textsubscript{2} at T > ~380 °C, °C, see Fig. 1 [56]. In fact, this is a solid state-gas reaction between LiBH\textsubscript{4} and NH\textsubscript{3}. Secondly, unstable metal borohydrides with a high electronegativity are stabilized by NH\textsubscript{3} as demonstrated for several metal borohydrides, such as Zn(BH\textsubscript{4})\textsubscript{2}-nNH\textsubscript{3} and Al(BH\textsubscript{4})\textsubscript{2}-nNH\textsubscript{3} [57,58]. Ammonia always coordinates directly to the metal and may prevent formation of neutral volatile molecular borohydrides or reduction of the metal. Al(BH\textsubscript{4})\textsubscript{2} is among the borohydrides with highest capacity (16.9 wt%), but is unstable and volatile (T\text{bp} ~ 44 °C). However, Al(BH\textsubscript{4})\textsubscript{2}-6NH\textsubscript{3} is stable and releases 11.8 wt% of H\textsubscript{2} (purity 95%) with T\text{max} at 168 °C [59]. Thirdly, the composition of the released gas depends on the ratio between NH\textsubscript{3} and BH\textsubscript{4} coordinated to the metal, excess of NH\textsubscript{3} provides increased tendency to release ammonia, that is, ammonia release from M(BH\textsubscript{4})\textsubscript{m}nNH\textsubscript{3} for n/m > 1 [60]. For instance, NH\textsubscript{3} is released from Mg(BH\textsubscript{4})\textsubscript{2}-6NH\textsubscript{3}, while mainly H\textsubscript{2} is released from Mg(BH\textsubscript{4})\textsubscript{2}-2NH\textsubscript{3}, see Fig. 2 [61]. Metals with low electronegativity tend to release NH\textsubscript{3} upon heating in open systems (p(NH\textsubscript{3}) ~ 0), but H\textsubscript{2} in closed systems [56,62]. Metals with higher electronegativity coordinate more strongly to NH\textsubscript{3} giving rise to a collapse of the structure and release of H\textsubscript{2} 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 NH\textsubscript{3} and BH\textsubscript{4} is observed in Fig. 1 represented by a dotted line.

In addition to the monometallic borohydride amoniates, a few bimetallic borohydride amoniates have been synthesized [60,63–65]. The first example, Li\textsubscript{2}Al(BH\textsubscript{4})\textsubscript{3}-6NH\textsubscript{3}, has a remarkable structure consisting of ordered [Al(NH\textsubscript{3})\textsubscript{4}]\textsuperscript{4+} ammine complexes and [Li\textsubscript{2}(BH\textsubscript{4})\textsubscript{3}]\textsuperscript{3–} complex anions and reveal attractive decomposition properties [60].

Ammonia is detrimental for low temperature fuel cells, and the NH\textsubscript{3}/BH\textsubscript{4} ratio (n/m) requires tailoring to avoid ammonia release. Metal borohydrides readily react with ammonia to obtain M(BH\textsubscript{4})\textsubscript{m}nNH\textsubscript{3}. A series of calcium borohydride amoniates, Ca(BH\textsubscript{4})\textsubscript{2}-nNH\textsubscript{3} (n = 1, 2, 4, 6), can be obtained by a sequential heating procedure [62,66]. Some metal borohydride amoniates with low n/m ratio have successfully been prepared by metathesis reactions between metal chloride amoniates and lithium borohydride [67]. The amount of NH\textsubscript{3} is adjusted by partial release of NH\textsubscript{3} from the metal chloride prior to the synthesis. The mechanochemical approach facilitates formation of Zn(BH\textsubscript{4})\textsubscript{2}-2NH\textsubscript{3}, while Zn(BH\textsubscript{4})\textsubscript{2}-4NH\textsubscript{3} 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-BH\textsubscript{4}-NH\textsubscript{2}**

An alternative approach to combine partially positive H atoms to hydric hydrogen in metal borohydrides is by using metal amides, M(NH\textsubscript{2})\textsubscript{m}. Numerous combinations between alkali and alkaline earth metal amides and borohydrides have been investigated, for example, Mg(BH\textsubscript{4})\textsubscript{2}-2LiNH\textsubscript{2} [68], Ca(BH\textsubscript{4})\textsubscript{2}-Mg(NH\textsubscript{2})\textsubscript{2} [69], and LiBH\textsubscript{4}-Mg(NH\textsubscript{2})\textsubscript{2} [70]. As discussed above, LiBH\textsubscript{4}-2LiNH\textsubscript{2} is an example of a reactive hydride composite with dihydrogen bonding [32]. Changing the reactant ratio LiBH\textsubscript{4}-LiNH\textsubscript{2} to (1:1) or (1:3) gives rise to compounds with different chemical compositions, Li\textsubscript{2}(BH\textsubscript{4})(NH\textsubscript{2})\textsubscript{3} or Li\textsubscript{2}(BH\textsubscript{4})(NH\textsubscript{2})\textsubscript{5}, which are also good lithium ion conductors [71]. The detailed crystal structures are known for...
Li₄(BH₄)(NH₂), and Li₂(BH₄)(NH₂) revealing that the borohydride and amide groups remain [72–74].

To the best of our knowledge, the LiBH₄–LiNH₂ system is unique compared to the other metal borohydride amide systems in the sense that new quaternary structures are readily formed by mechanochemical treatment. In all other systems a physical mixture is obtained. The physical mixtures typically react during thermal treatment and decompose at lower temperatures compared to the individual components, but without forming borohydride-amide complexes. However, recently Mg(BH₄)(NH₂) was prepared by combined mechanochemical and thermal treatment of Mg(BH₄)₂ and Mg(NH₂)₂ [75].

**Ammonia borane and derivatives**

*Ammonia borane*, NH₃BH₃ (AB) has attracted significant attention owing to its extreme hydrogen capacities of ρ_m = 19.6 wt% H₂, ρ_v = 146 g H₂/L, and air stability [76]. Solid crystalline ammonia borane has an intermolecular dihydrogen bond network and is not hygroscopic unlike borohydrides. This compound, NH₃BH₃ releases one equivalent of hydrogen in each of the three decomposition steps forming polyaminoborane, [NH₂BH₂]ₙ (90–120 °C), polymimoborane, [NHBH₃]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 (NH₃), diborane (B₂H₆) and borazine (N₂B₂H₆). Furthermore, the decomposition is exothermic (ΔH_dec = −21 kJ/mol H₂), hence non-reversible [77]. However, significantly improved properties of NH₃BH₃ were obtained by infiltration in ordered mesoporous silica facilitating enhanced kinetics (faster hydrogen release) at lower temperatures with reduced borazine emission and improved thermodynamics, ΔH_dec = −1 kJ/mol H₂ [78]. Additionally, the work by Autrey and co-workers [78] initiated the focus on nanoconfinement 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*, NH₆BH₄. It has the highest hydrogen content of solid-state materials reported to date (ρ_m = 24.5 wt% H₂, ρ_v = 151 g H₂/L) and releases 3 equivalents of hydrogen (~18 wt% H₂) in three distinct exothermic steps at T < 160 °C [81]. However, NH₆BH₄ slowly decomposes at RT with a half-life of ~6 h to a diammoniate of diborane (NH₃)₂BH₂(BH₄) (DADB) and hydrogen. For long-term storage NH₆BH₄ must be kept at T < −40 °C. Recently, nanoconfined NH₆BH₄ 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 (NH₃)₂BH₂(BH₄). However, recently a mechanochemical reaction between NH₄BH₄ and NH₃BH₃ was discovered [83], see scheme (6).

\[
\text{NH₄BH₄(s)} + \text{NH₃BH₃(s)} \rightarrow [(\text{NH₃})₂BH₂][\text{BH₄}](s) + \text{H}_2(g) \tag{6}
\]

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(NH₂BH₃)ₙ, are synthesized by reacting a metal hydride with ammonia borane using either mechanochemistry or solvent-based methods [85], see reaction scheme (7).

\[
\text{MH}_x(s) + n\text{NH₃BH₃}(s) \rightarrow M(\text{NH₂BH₃})_x(s) + n\text{H}_2(g) \tag{7}
\]
Since 2007, a series of metal amidoboranes, M(NH2BH3)n (M = Li, Na, K, Ca, Sr), have been synthesized according to reaction scheme (7) and structurally investigated [86–89]. In contrast, Y(NH2BH3)3 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 LiN3BH3 in THF was unsuccessful, but LiCl and polymeric [Fe(HN-BH3)]n 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. LiN3BH3 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].

\[
\text{LiN}_3\text{BH}_3(s) \rightarrow \text{LiNH}_2\text{BH}(s) + 2\text{H}_2(g) \quad (8)
\]

Metal amidoborate ammoniates, M(NH2BH3)3–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 (exoergic). 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–NH3BH2 were reported, that is, Li2(BH4)2NH3BH2 and Ca(BH4)2(NH3BH3)2 [97]. Since then, LiBH4(NH3BH3) [98], and Mg(BH4)2(NH3BH3)2 [99,100] have also been reported, and they are all prepared by mechanochemical treatment of AB and M(BH4)n (M = Li, Mg, Ca). In contrast, MBH4–NH3BH3 (M = Na, K, Cs, Rb) do not form new compounds during mechanochemical treatment [99,101]. This class of materials has high hydrogen capacities and low decomposition temperatures, for example, Mg(BH4)2(NH3BH3)2 (nBH = 17.4 wt% H2, ρH = 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 borane similar to NH3BH3 reflecting a weak interaction between the borohydride groups and ammonia borane. This is explained by the crystal structures of M(BH4)2(NH3BH3)2, where AB keeps its molecular form [97]. The crystal structure of Mg(BH4)2(NH3BH3)2 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•NH3NH2 and LiBH4•2NH2NH2 [102]. Approximately 13.0 wt% H2 is released from LiBH4•2NH2NH2 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).

\[
3(\text{LiBH}_4\cdot\text{N}_2\text{H}_4)(s) \rightarrow \text{Li}_3\text{BN}_2(s) + 2\text{BN}(s) + \text{N}_2(g) + 12\text{H}_2(s) \quad (9)
\]

Furthermore, the decomposition product of AB, polyiminoborane reacts with hydrazine in THF solution to form hydrazine borane (N2H4BH3, HB) (15.4 wt% H2) melts at 61 °C at which point the decomposition initiates yielding NH2NH2, (NHBH2)2, H2 and NH3. Interestingly, mechanochemical treatment of LiH–HB (1:1) and (1:3) provided the first metal hydrazinoborane, LiN2H3BH4, and its hydrazine borane adduct LiN2H2•BH2•2N2H4•BH3 [103]. The metal hydrazinoboranes exhibit dramatically improved hydrogenation properties compared to hydrazine borane (N2H4BH3) 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(B₄H₁₀), 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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