

Technical University of Denmark



Boron-nitrogen based hydrides and reactive composites for hydrogen storage

Jepsen, Lars H.; Ley, Morten B.; Lee, Young-Su; Cho, Young Whan; Dornheim, Martin; Jensen, Jens Oluf; Filinchuk, Yaroslav; Jørgensen, Jens Erik; Besenbacher, Flemming; Jensen, Torben René

Published in:
Materials Today

Link to article, DOI:
[10.1016/j.mattod.2014.02.015](https://doi.org/10.1016/j.mattod.2014.02.015)

Publication date:
2014

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Jepsen, L. H., Ley, M. B., Lee, Y-S., Cho, Y. W., Dornheim, M., Jensen, J. O., ... Jensen, T. R. (2014). Boron-nitrogen based hydrides and reactive composites for hydrogen storage. *Materials Today*, 17(3), 129-135. DOI: 10.1016/j.mattod.2014.02.015

DTU Library

Technical Information Center of Denmark

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.



Boron–nitrogen based hydrides and reactive composites for hydrogen storage

Lars H. Jepsen¹, Morten B. Ley¹, Young-Su Lee², Young Whan Cho²,
Martin Dornheim³, Jens Oluf Jensen⁴, Yaroslav Filinchuk⁵,
Jens Erik Jørgensen⁶, Flemming Besenbacher⁷ and Torben R. Jensen^{1,*}

¹Center for Materials Crystallography, Interdisciplinary Nanoscience Center and Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark

²High Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

³Helmholtz-Zentrum Geesthacht, Department of Nanotechnology, Max-Planck-Straße 1, 21502 Geesthacht, Germany

⁴Department of Energy Conversion and Storage, Technical University of Denmark, Kemitorvet 207, DK-2800 Kgs. Lyngby, Denmark

⁵Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Place L. Pasteur 1, B-1348 Louvain-la-Neuve, Belgium

⁶Department of Chemistry, University of Aarhus, 8000 Aarhus C, Denmark

⁷Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK-8000 Aarhus C, Denmark

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^{δ+}...^{δ-}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(η₂-H₂) complex with H–H bond length in the range 0.74 to ~1.38 Å and polyhydrido 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 NH^{2−} 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 NH^{2−}.

The hydrogen molecule, H₂, has the lowest number of electrons (2) of all molecules and therefore has the weakest physisorption

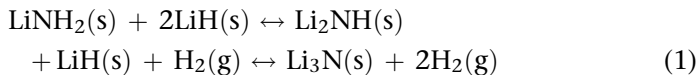
*Corresponding author: Jensen, T.R. (trj@chem.au.dk)

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.

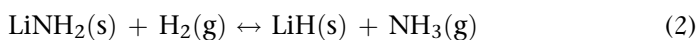
Ionic, metallic and covalent bonds are also formed by hydrogen, which has been discussed in another review in this issue of *Materials Today* [18]. Altogether, this illustrates that hydrogen forms a variety of different types of chemical bonds and interactions with matter and other elements and reacts 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, $\text{LiNH}_2\text{-LiH}$, according to reaction scheme (1) [21].



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).

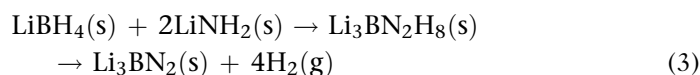


This reaction reveals a rare example where hydrogen is converted, 8.1 wt%, and heat is absorbed, $\Delta H = 50 \pm 9$ kJ/mol [25–27]. The reaction appears to be driven by larger entropy of the ammonia molecule than the hydrogen.

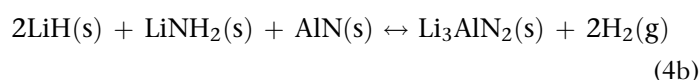
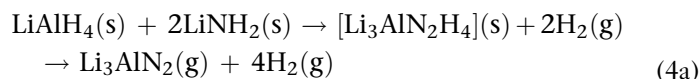
In reaction scheme (1), only the amide–imide reaction is reversible at moderate conditions with a hydrogen storage capacity of $\rho_m = 6.5$ wt% and an enthalpy change of $\Delta H_{\text{dec}} = 66$ kJ/mol H_2 [28]. Several other reversible nitrogen-based systems have been investigated recently and are promising for future mobile applications, for example, $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ 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 H_2 [29–31].

Metal borohydrides and a metal amide can also form RHC systems as shown for $\text{LiBH}_4\text{-2LiNH}_2$ 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, Li_3BN_2 , illustrated in reaction scheme (3). The onset temperature for hydrogen release decreases from ~ 380 to 250 °C for LiBH_4 in the composite $\text{LiBH}_4\text{-2LiNH}_2$, and thermal

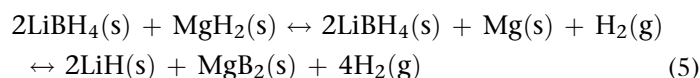
decomposition releases more than 10 wt% H_2 in the temperature range $250\text{--}350$ °C, but, unfortunately, the system is irreversible.



In contrast, the analog lithium alanate amide system, $\text{LiAlH}_4\text{-2LiNH}_2$, releases 2 equiv. H_2 already during mechanochemical treatment forming an amorphous mixture with the overall composition $\text{Li}_3\text{AlN}_2\text{H}_4$, see reaction scheme (4a) [33,34]. Lithium aluminum nitride, Li_3AlN_2 , absorbs more than 5 wt% H_2 forming 2LiH , LiNH_2 and AlN , reaction (4b), which is another new RHC system.



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 $\text{LiBH}_4\text{-MgH}_2$ [35,36]. The great advantage is that the endothermic dehydrogenation of the two hydrides in the composite $2\text{LiBH}_4\text{-MgH}_2$ is followed by the exothermic formation of MgB_2 , see reaction (5). The total reaction enthalpy is thereby lowered to a calculated value of, $\Delta H_{\text{dec}} \sim 46$ kJ/(mol H_2) corresponding to a calculated decomposition temperature of $T \sim 169$ °C (at $p(\text{H}_2) = 1$ bar) [35,37,38]. The hydrogen absorption is facilitated from the $\text{MgB}_2\text{-LiH}$ composite and occurs at $p(\text{H}_2) = 50$ bar and $T < 300$ °C. These conditions are substantially more favorable than those of LiBH_4 and are considered a breakthrough in utilizing borohydrides for reversible hydrogen storage. The full reversibility of the $\text{LiBH}_4\text{-MgH}_2$ system is only obtained when the decomposition occurs in a hydrogen back pressure of $p(\text{H}_2) \sim 1\text{--}5$ bar, which facilitates the formation of MgB_2 possibly owing to suppression of the individual decomposition of LiBH_4 [38–41]. In fact, hydrogen release and uptake is a two-step reaction as shown in reaction scheme (5).



A similar reaction occurs for a magnesium-rich system, $0.3\text{LiBH}_4\text{-MgH}_2$, during decomposition in $p(\text{H}_2) > 1$ bar, that is, formation of MgB_2 , whereas α - and β -alloys of $\text{Li}_{1-x}\text{Mg}_x$ are formed under a dynamic vacuum [42–44]. A number of other promising reactive hydride composites have also been described, for example, $\text{NaBH}_4\text{-MgH}_2$ and $\text{Ca}(\text{BH}_4)_2\text{-MgH}_2$ [36,45–50]. Additionally, some multicomponent systems have been developed such as $\text{LiBH}_4\text{-MgH}_2\text{-LaH}_3$ and $\text{Ca}(\text{BH}_4)_2\text{-LiBH}_4\text{-MgH}_2$. 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, $\text{H}^{\delta+} \cdots \delta\text{H}$, appear to be comparable to conventional hydrogen bonds. The three intermolecular $\text{O-H}^{\delta+} \cdots \delta\text{H-B}$ dihydrogen bonds in the compound $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ are in the range $1.77\text{--}1.95$ Å and shorter

than H...H distances within the BH_4^- anion, which are ca. 2.0 \AA [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. $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ decomposes upon heating at $\sim 40^\circ\text{C}$ to NaBH_4 and $2\text{H}_2\text{O}$, which at $T > 40^\circ\text{C}$ slowly react to release hydrogen. Thus, the hydrate $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ does not directly release hydrogen, but decomposes into anhydrous NaBH_4 and water [53]. Similarly, lithium borohydride exposed to air releases hydrogen at $\sim 65^\circ\text{C}$ possibly due to a reaction between LiBH_4 and H_2O [54].

Metal borohydride ammoniates, $\text{M}(\text{BH}_4)_m \cdot n\text{NH}_3$

Ammonia, NH_3 , is catalytically split to N_2 and H_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_3 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 BH_4^- . Metal borohydride ammoniates, $\text{M}(\text{BH}_4)_m \cdot n\text{NH}_3$, 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 $\text{Li}(\text{NH}_3)_{4/3}\text{BH}_4$ (i.e. $2/3\text{Li}(\text{NH}_3)\text{BH}_4$ and $1/3\text{Li}(\text{NH}_3)_2\text{BH}_4$ with equivalent protic and hydridic hydrogen atoms), releases ca. 17.8 wt% of H_2 in a closed system in the temperature range $135\text{--}250^\circ\text{C}$, in contrast to LiBH_4 which release H_2 at $T > \sim 380^\circ\text{C}$, $^\circ\text{C}$, see Fig. 1 [56]. In fact, this is a solid state-gas reaction between

LiBH_4 and NH_3 . Secondly, unstable metal borohydrides with a high electronegativity are stabilized by NH_3 as demonstrated for several metal borohydrides, such as $\text{Zn}(\text{BH}_4)_2 \cdot n\text{NH}_3$ and $\text{Al}(\text{BH}_4)_3 \cdot n\text{NH}_3$ [57,58]. Ammonia always coordinates directly to the metal and may prevent formation of neutral volatile molecular borohydrides or reduction of the metal. $\text{Al}(\text{BH}_4)_3$ is among the borohydrides with highest capacity (16.9 wt%), but is unstable and volatile ($T_{\text{bp}} \sim 44^\circ\text{C}$). However, $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ is stable and releases 11.8 wt% of H_2 (purity 95%) with T_{max} at 168°C [59]. Thirdly, the composition of the released gas depends on the ratio between NH_3 and BH_4 coordinated to the metal, excess of NH_3 provides increased tendency to release ammonia, that is, ammonia release from $\text{M}(\text{BH}_4)_m \cdot n\text{NH}_3$ for $n/m > 1$ [60]. For instance, NH_3 is released from $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$, while mainly H_2 is released from $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$, see Fig. 2 [61]. Metals with low electronegativity tend to release NH_3 upon heating in open systems ($p(\text{NH}_3) \sim 0$), but H_2 in closed systems [56,62]. Metals with higher electronegativity coordinate more strongly to NH_3 giving rise to a collapse of the structure and release of H_2 by dihydrogen elimination in the temperature range ~ 100 to $\sim 200^\circ\text{C}$. 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_3 and BH_4 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, $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$, has a remarkable structure consisting of ordered $[\text{Al}(\text{NH}_3)_6]^{3+}$ ammine complexes and $[\text{Li}_2(\text{BH}_4)_5]^{3-}$ complex anions and reveal attractive decomposition properties [60].

Ammonia is detrimental for low temperature fuel cells, and the NH_3/BH_4 ratio (n/m) requires tailoring to avoid ammonia release. Metal borohydrides readily react with ammonia to obtain $\text{M}(\text{BH}_4)_m \cdot n\text{NH}_3$. A series of calcium borohydride ammoniates, $\text{Ca}(\text{BH}_4)_2 \cdot n\text{NH}_3$ ($n = 1, 2, 4, 6$), 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 NH_3 is adjusted by partial release of NH_3 from the metal chloride prior to the synthesis. The mechanochemical approach facilitates formation of $\text{Zn}(\text{BH}_4)_2 \cdot 2\text{NH}_3$, while $\text{Zn}(\text{BH}_4)_2 \cdot 4\text{NH}_3$ 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, $\text{M}(\text{BH}_4)_m \cdot \text{NH}_2$

An alternative approach to combine partially positive H atoms to hydridic hydrogen in metal borohydrides is by using metal amides, $\text{M}(\text{NH}_2)_n$. Numerous combinations between alkali and alkaline earth metal amides and borohydrides have been investigated, for example, $\text{Mg}(\text{BH}_4)_2\text{--LiNH}_2$ [68], $\text{Ca}(\text{BH}_4)_2\text{--Mg}(\text{NH}_2)_2$ [69], and $\text{LiBH}_4\text{--Mg}(\text{NH}_2)_2$ [70]. As discussed above, $\text{LiBH}_4\text{--}2\text{LiNH}_2$ is an example of a reactive hydride composite with dihydrogen bonding [32]. Changing the reactant ratio $\text{LiBH}_4\text{--LiNH}_2$ to (1:1) or (1:3) gives rise to compounds with different chemical compositions, $\text{Li}_2(\text{BH}_4)(\text{NH}_2)$ or $\text{Li}_4(\text{BH}_4)(\text{NH}_2)_3$, which are also good lithium ion conductors [71]. The detailed crystal structures are known for

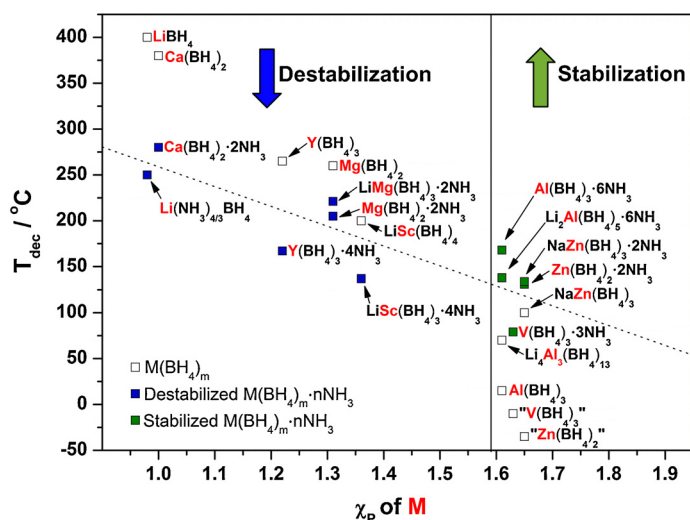


FIGURE 1

Experimentally observed decomposition temperatures, T_{dec} , for selected metal borohydrides and metal borohydride ammoniates plotted as a function of the electronegativity, χ_p , of the metal. Metal borohydrides with low electronegativity are destabilized by ammoniate formation while those with higher electronegativity are stabilized. The dashed line indicates a correlation between decomposition temperatures and electronegativity for metal borohydrides ammoniates and a new approach for rational design of materials properties.

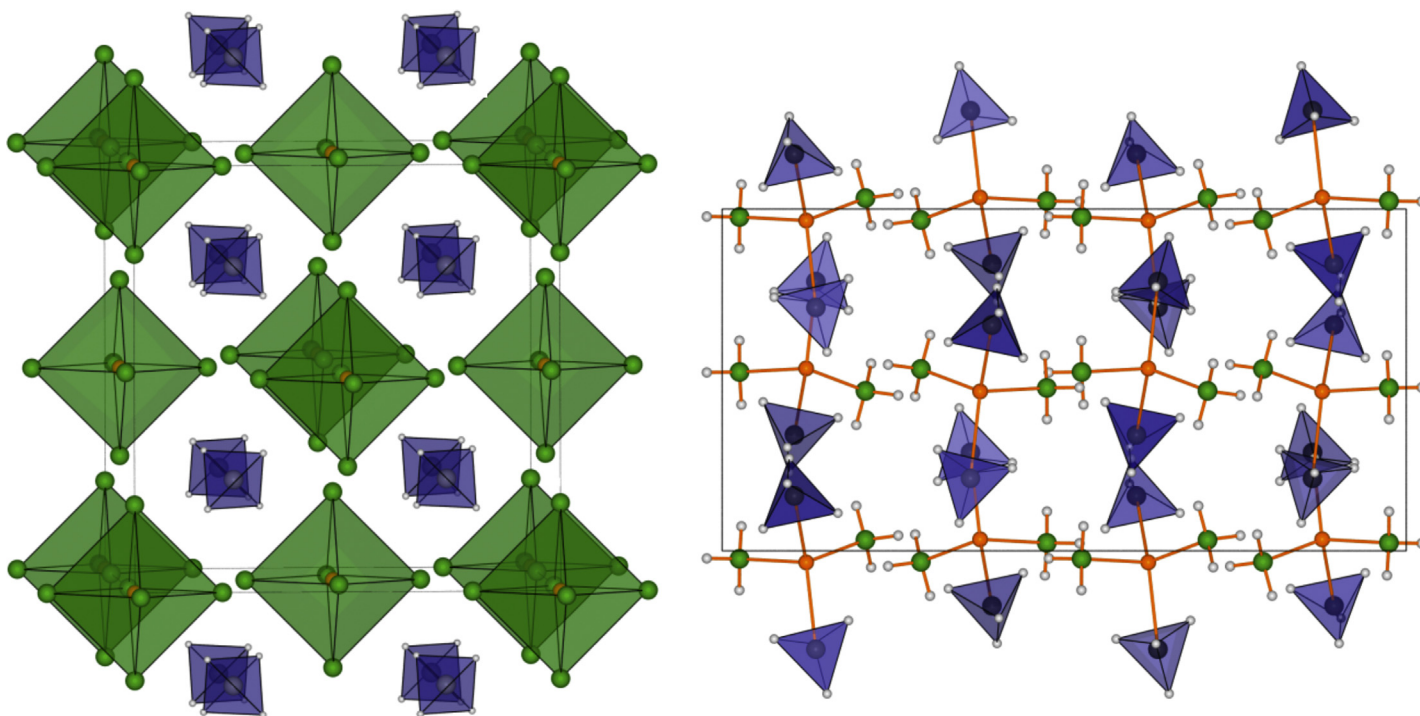


FIGURE 2

The crystal structures of $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$ (top) and $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$. NH_3 (N green, H light gray) coordinates to magnesium (orange) in the crystal structures, while BH_4 (blue tetrahedra) coordinates either to the metal or acts as a counter ion in the solid state [61]. For clarity, hydrogen atoms in the ammonia molecules are not shown in $\text{Mg}(\text{BH}_4)_2 \cdot 6\text{NH}_3$.

$\text{Li}_4(\text{BH}_4)(\text{NH}_2)_3$ and $\text{Li}_2(\text{BH}_4)(\text{NH}_2)$ revealing that the borohydride and amide groups remain [72–74].

To the best of our knowledge, the LiBH_4 – LiNH_2 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 $\text{Mg}(\text{BH}_4)(\text{NH}_2)$ was prepared by combined mechanochemical and thermal treatment of $\text{Mg}(\text{BH}_4)_2$ – $\text{Mg}(\text{NH}_2)_2$ [75].

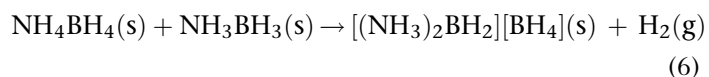
Ammonia borane and derivatives

Ammonia borane, NH_3BH_3 (AB) has attracted significant attention owing to its extreme hydrogen capacities of $\rho_m = 19.6 \text{ wt}\% \text{ H}_2$, $\rho_v = 146 \text{ g H}_2/\text{L}$, and air stability [76]. Solid crystalline ammonia borane has an intermolecular dihydrogen bond network and is not hygroscopic unlike borohydrides. This compound, NH_3BH_3 releases one equivalent of hydrogen in each of the three decomposition steps forming polyaminoborane, $[\text{NH}_2\text{BH}_2]_n$ (90–120 °C), polyimino-borane, $[\text{NHBH}]_n$ (120–200 °C) and finally boron nitride, BN (>500 °C) [76]. However, the hydrogen release is accompanied by toxic by-products, such as ammonia (NH_3), diborane (B_2H_6) and borazine ($\text{N}_3\text{B}_3\text{H}_3$). Furthermore, the decomposition is exothermic ($\Delta H_{\text{dec}} = -21 \text{ kJ/mol H}_2$), hence non-reversible [77]. However, significantly improved properties of NH_3BH_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, $\Delta H_{\text{dec}} = -1 \text{ kJ/mol H}_2$ [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].

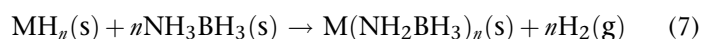
An even more hydrogen-rich compound can be prepared: *ammonium borohydride*, NH_4BH_4 . It has the highest hydrogen content of solid-state materials reported to date ($\rho_m = 24.5 \text{ wt}\% \text{ H}_2$, $\rho_v = 151 \text{ g H}_2/\text{L}$) and releases 3 equivalents of hydrogen ($\sim 18 \text{ wt}\% \text{ H}_2$) in three distinct exothermic steps at $T < 160 \text{ °C}$ [81]. However, NH_4BH_4 slowly decomposes at RT with a half-life of $\sim 6 \text{ h}$ to a diammoniate of diborane ($\text{NH}_3)_2\text{BH}_2(\text{BH}_4)$ (DADB) and hydrogen. For long-term storage NH_4BH_4 must be kept at $T < -40 \text{ °C}$. Recently, nanoconfined NH_4BH_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 NH_4BH_4 and NH_3BH_3 was discovered [83], see scheme (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, $\text{M}(\text{NH}_2\text{BH}_3)_n$, are synthesized by reacting a metal hydride with ammonia borane using either mechanochemistry or solvent-based methods [85], see reaction scheme (7).



Since 2007, a series of metal amidoboranes, $M(\text{NH}_2\text{BH}_3)_n$ ($M = \text{Li, Na, K, Ca, Sr}$), have been synthesized according to reaction scheme (7) and structurally investigated [86–89]. In contrast, $\text{Y}(\text{NH}_2\text{BH}_3)_3$ is synthesized by a metathesis reaction between MNH_2BH_3 and YX_3 ($M = \text{Li, Na; X = Cl, F}$) [90]. The magnesium analog, $\text{Mg}(\text{NH}_2\text{BH}_3)_2$, was previously considered unstable, but was recently synthesized [91]. Metathesis reaction between FeCl_3 and LiNH_2BH_3 in THF was unsuccessful, but LiCl and polymeric $[\text{Fe}(\text{HN}=\text{BH})_n]$ was formed together with the release of 1.5 equiv. H_2 in THF at RT [92]. In general, metal amidoboranes have high hydrogen content, good kinetics and low decomposition temperatures. LiNH_2BH_3 decomposes in the temperature range from 75 to 95 °C and releases 10.9 wt% H_2 according to scheme (8) [86]. Formation of metal amidoboranes is considered an approach to prevent release of borazine from ammonia borane [93].

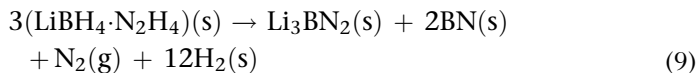


Metal amidoborane ammoniates, $M(\text{NH}_2\text{BH}_3)_n \cdot x\text{NH}_3$ are known for $M = \text{Mg, Ca}$ [94,95]. These compounds tend to release NH_3 below 100 °C in an open system (endothermic reaction) and H_2 in a closed system (exothermic). Recently, hydrogen release was observed from an endothermic reaction from composites of $\text{Mg}(\text{NH}_2\text{BH}_3)_2 \cdot 2\text{NH}_3$ and NaH/KH [96].

In 2010, the first *metal borohydride–ammonia borane complexes*, $M\text{--BH}_4\text{--NH}_3\text{BH}_3$ were reported, that is, $\text{Li}_2(\text{BH}_4)_2\text{NH}_3\text{BH}_3$ and $\text{Ca}(\text{BH}_4)_2(\text{NH}_3\text{BH}_3)_2$ [97]. Since then, $\text{LiBH}_4(\text{NH}_3\text{BH}_3)$ [98], and $\text{Mg}(\text{BH}_4)_2(\text{NH}_3\text{BH}_3)_2$ [99,100] have also been reported, and they are all prepared by mechanochemical treatment of AB and $M(\text{BH}_4)_n$ ($M = \text{Li, Mg, Ca}$). In contrast, $\text{MBH}_4\text{--NH}_3\text{BH}_3$ ($M = \text{Na, K, Cs, Rb}$) do not form new compounds during mechanochemical treatment [99,101]. This class of materials have high hydrogen capacities and low decomposition temperatures, for example, $\text{Mg}(\text{BH}_4)_2(\text{NH}_3\text{BH}_3)_2$ ($\rho_m = 17.4$ wt% H_2 , $\rho_v = 137$ g H_2/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 NH_3BH_3 reflecting a weak interaction between the borohydride groups and ammonia borane. This is explained by the crystal structures of $M(\text{BH}_4)_n(\text{NH}_3\text{BH}_3)_x$, where AB keeps its molecular form [97]. The crystal structure of $\text{Mg}(\text{BH}_4)_2(\text{NH}_3\text{BH}_3)_2$ 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 $\text{N}\text{--H}^{\delta+} \cdots \text{B}\text{--H}^{\delta-}$ (<2 Å).

Hydrazine and hydrazine borane

Hydrazine, N_2H_4 (12.5 wt% H_2) decomposes via two competing reactions forming N_2 , H_2 and NH_3 . Recently a new class of hydrogen storage materials, borohydride hydrazinates, was successfully synthesized, for example, $\text{LiBH}_4 \cdot \text{NH}_2\text{NH}_2$ and $\text{LiBH}_4 \cdot 2\text{NH}_2\text{NH}_2$ [102]. Approximately 13.0 wt% H_2 is released from $\text{LiBH}_4 \cdot \text{NH}_2\text{NH}_2 \cdot 2\text{NH}_2$ at 140 °C in the presence of Fe–B catalysts. However, this again leads to the formation of the stable compounds Li_3BN_2 and BN according to reaction scheme (9).



Furthermore, the decomposition product of AB, polyiminoborane reacts with hydrazine in THF solution to form hydrazine

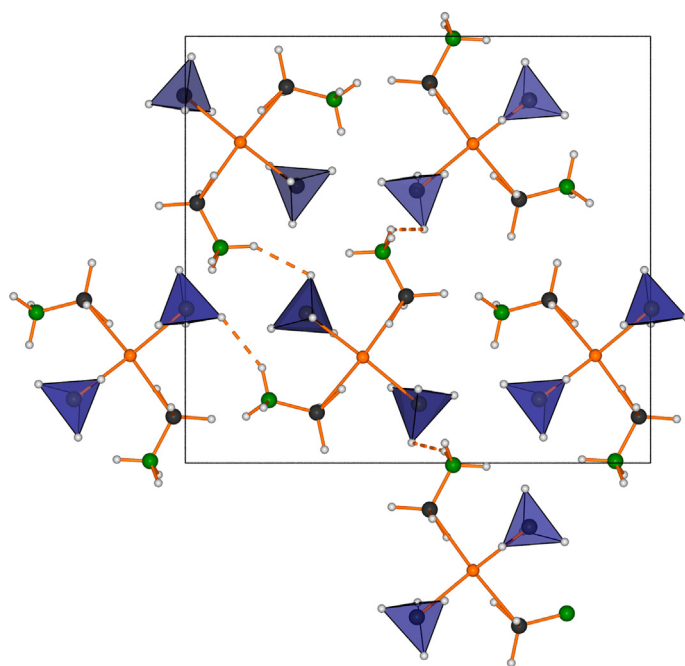


FIGURE 3

Crystal structure of $\text{Mg}(\text{BH}_4)_2(\text{NH}_3\text{BH}_3)_2$. Molecular complexes of $[\text{Mg}(\text{BH}_4)_2(\text{NH}_3\text{BH}_3)_2]$ are connected by dihydrogen bonds (dotted lines). Mg, N, B and H are represented by orange, green, blue and light gray spheres and the $[\text{BH}_4]$ complexes as blue tetrahedra [99].

borane ($\text{N}_2\text{H}_4\text{BH}_3$, HB). HB (15.4 wt% H_2) melts at 61 °C at which point the decomposition initiates yielding NH_2NH_2 , $(\text{NHBH}_2)_2$, H_2 and NH_3 . Interestingly, mechanochemical treatment of $\text{LiH}\text{--HB}$ (1:1) and (1:3) provided the first *metal hydrazinoborane*, $\text{LiN}_2\text{H}_3\text{BH}_3$, and its hydrazine borane adduct $\text{LiN}_2\text{H}_3\text{BH}_3 \cdot 2\text{N}_2\text{H}_4\text{BH}_3$ [103]. The metal hydrazinoboranes exhibit dramatically improved dehydrogenation properties compared to hydrazine borane ($\text{N}_2\text{H}_4\text{BH}_3$) with nearly complete dehydrogenation 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

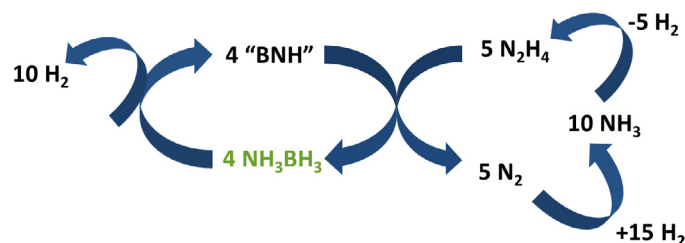


FIGURE 4

Reaction mechanism for ammonia borane, NH_3BH_3 , regeneration from polyiminoborane, 'BNH' using hydrazine, N_2H_4 (modified from Ref. [108]).

TABLE 1

Selected solid boron- and nitrogen-based hydrides with high gravimetric (ρ_m) and volumetric (ρ_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.

Compound	ρ_m (wt%)	ρ_v (g H ₂ /L)	T_{onset} (°C)	Impurities	Ref.
LiBH ₄	18.5	122.5	380	Not observed	[104]
α -Mg(BH ₄) ₂	14.9	117	250	Not observed	[105]
Mg(BH ₄) ₂ ·2NH ₃	16.0	130	150	NH ₃	[61]
Li ₂ Al(BH ₄) ₅ ·6NH ₃	17.6	151	75	NH ₃ (>99% H ₂)	[60]
Al(BH ₄) ₃ ·6NH ₃	17.4	150	130	NH ₃ (95% H ₂)	[59]
Zn(BH ₄) ₂ ·2NH ₃	10.8	135	90	Not observed	[57]
NH ₄ BH ₄	24.5	151	85	B ₂ H ₆ , B ₃ N ₃ H ₆ , NH ₃	[81]
NH ₃ BH ₃	19.4	144	108	B ₂ H ₆ , B ₃ N ₃ H ₆ , NH ₃	[76]
LiNH ₂ BH ₃	10.9	92	85	NH ₃	[86]
Mg(BH ₄) ₂ (NH ₃ BH ₃) ₂	17.4	137	75	B ₂ H ₆ , B ₃ N ₃ H ₆ , NH ₃	[99]
Li ₂ (BH ₄) ₂ NH ₃ BH ₃	19.0	138	105	B ₂ H ₆ , B ₃ N ₃ H ₆ , NH ₃	[97]

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 $p(\text{H}_2) = 950$ bar [106,107]. However, partial dehydrogenation of Mg(BH₄)₂ at lower temperatures (250 °C) forms Mg(B₃H₈)₂, which is more readily rehydrogenated (250 °C, $p(\text{H}_2) = 120$ 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-borane 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.

Acknowledgements

The work was supported by the Danish Council for Strategic Research via the research project *HyFillFast*, the Danish National Research Foundation, Center for Materials Crystallography (DNRF93), and by European Community FP7/2007–2013, FCH JU under grant agreement no. 303428 – Bor4Store and by the COST Action MP1103 ‘Nanostructured materials for solid-state hydrogen storage’. We are grateful to the Carlsberg Foundation.

References

- [1] D.J.C. MacKay, *Sustainable Energy – Without the Hot Air*, UIT, Cambridge, 2009.
- [2] J.A. Ritter, et al. *Mater. Today* 6 (9) (2003) 18.
- [3] A. Züttel, *Mater. Today* 6 (9) (2003) 24.
- [4] A. Züttel, A. Borgschulte, L. Schlapbach, *Hydrogen as a Future Energy Carrier*, Wiley-VCH Verlag GmbH & Co., Weinheim, 2008.
- [5] G. Walker, *Solid-state Hydrogen Storage: Materials and Chemistry*, Woodhead Publishing, 2008.
- [6] L. Schlapbach, A. Züttel, *Nature* 414 (6861) (2001) 353.
- [7] W.I.F. David, *Faraday Discuss.* 151 (2011) 399.
- [8] M. Hirscher, *Handbook of Hydrogen Storage*, Wiley-VCH Verlag GmbH & Co., Germany, Weinheim, 2010.
- [9] U. Eberle, et al. *Angew. Chem. Int. Ed.* 48 (36) (2009) 6608.
- [10] S.I. Orimo, et al. *Chem. Rev.* 107 (10) (2007) 4111.
- [11] L.H. Rude, et al. *Phys. Status Solidi* 208 (2011) 1754.
- [12] J. Lu, et al. *Inorg. Chem.* 45 (21) (2006) 8749.
- [13] L.H. Rude, et al. *J. Phys. Chem. C* 116 (38) (2012) 20239.
- [14] D.R. Lide, *CRC Handbook of Chemistry and Physics*, 88th ed., CRC Press, 2007.
- [15] M.-A. Richard, et al. *Angew. Chem. Int. Ed.* 55 (11) (2009) 2985.
- [16] M. Hirscher, B. Panella, *Scr. Mater.* 56 (10) (2007) 809.
- [17] B. Panella, M. Hirscher, *Adv. Mater.* 17 (5) (2005) 538.
- [18] M.B. Ley, et al. *Mater. Today* 17 (3) (2014) 121.
- [19] W. Grochala, P.P. Edwards, *Chem. Rev.* 104 (3) (2004) 1283.
- [20] M. Dornheim, et al. *Adv. Eng. Mater.* 8 (5) (2006) 377.
- [21] P. Chen, et al. *Nature* 420 (6913) (2002) 302.
- [22] W.I.F. David, et al. *J. Am. Chem. Soc.* 129 (6) (2007) 1594.
- [23] T. Ichikawa, et al. *J. Phys. Chem. B* 108 (23) (2004) 7887.
- [24] Y.H. Hu, E. Ruckenstein, *J. Phys. Chem. A* 107 (46) (2003) 9737.
- [25] Y. Kojima, et al. *J. Mater. Res.* 24 (07) (2009) 2185.
- [26] S. Hino, et al. *J. Appl. Phys.* 105 (2) (2009) 023527.

- [27] H. Yamamoto, et al. *Int. J. Hydrogen Energy* 34 (24) (2009) 9760.
- [28] Y. Kojima, Y. Kawai, *J. Alloys Compd.* 395 (1/2) (2005) 236.
- [29] K.C. Kim, et al. *Phys. Chem. Chem. Phys.* 13 (15) (2011) 7218.
- [30] Z. Xiong, et al. *Adv. Mater.* 16 (17) (2004) 1522.
- [31] W.F. Luo, *J. Alloys Compd.* 385 (1–2) (2004) 316.
- [32] F.E. Pinkerton, et al. *J. Phys. Chem. B* 109 (1) (2005) 6.
- [33] Xiong, et al. *Adv. Funct. Mater.* 17 (7) (2007) 1137.
- [34] J. Huot, et al. *Prog. Mater. Sci.* 58 (1) (2013) 30.
- [35] J.J. Vajo, et al. *J. Phys. Chem. B* 109 (9) (2005) 3719.
- [36] G. Barkhordarian, et al. *J. Alloys Compd.* 440 (1/2) (2007) L18.
- [37] Y.W. Cho, et al. *Calphad* 30 (1) (2006) 65.
- [38] U. Bösenberg, et al. *Acta Mater.* 55 (11) (2007) 3951.
- [39] U. Bösenberg, et al. *Acta Mater.* 58 (2010) 3381.
- [40] U. Bösenberg, et al. *J. Phys. Chem. C* 114 (35) (2010) 15212.
- [41] J.H. Shim, et al. *J. Phys. Chem. Lett.* 1 (1) (2009) 59.
- [42] T.E.C. Price, et al. *J. Am. Chem. Soc.* 133 (34) (2011) 13534.
- [43] O. Friedrichs, et al. *Phys. Chem. Chem. Phys.* 11 (10) (2009) 1515.
- [44] X.B. Yu, et al. *Chem. Commun.* 37 (2006) 3906.
- [45] G. Barkhordarian, et al. *J. Phys. Chem. C* 112 (7) (2008) 2743.
- [46] T.K. Nielsen, et al. *ACS Nano* 4 (7) (2010) 3903.
- [47] R. Gosalawit-Utke, et al. *J. Phys. Chem. C* 114 (22) (2010) 10291.
- [48] R. Gosalawit-Utke, et al. *Int. J. Hydrogen Energy* 38 (8) (2013) 3275.
- [49] K.S. Alcantara, et al. *J. Phys. Chem. C* 116 (12) (2012) 7207.
- [50] C. Pistidda, et al. *J. Phys. Chem. C* 114 (49) (2010) 21816.
- [51] M. Gao, et al. *J. Mater. Chem. A* 1 (39) (2013) 12285.
- [52] Y. Zhou, et al. *J. Phys. Chem. C* 116 (1) (2012) 1588.
- [53] Y. Filinchuk, H. Hagemann, *Eur. J. Inorg. Chem.* 20 (2008) 3127.
- [54] L. Mosegaard, et al. *J. Alloys Compd.* 446–447 (2007) 301.
- [55] P.J. Feibelman, et al. *Phys. Today* 58 (6) (2005) 13.
- [56] X. Zheng, et al. *Energy Environ. Sci.* 4 (9) (2011) 3593.
- [57] Q. Gu, et al. *Energy Environ. Sci.* 5 (6) (2012) 7590.
- [58] Y. Guo, et al. *Angew. Chem. Int. Ed.* 50 (5) (2011) 1087.
- [59] Y. Guo, et al. *Chem. Commun.* 48 (37) (2012) 4408.
- [60] Y. Guo, et al. *J. Am. Chem. Soc.* 133 (13) (2011) 4690.
- [61] G. Soloveichik, et al. *Inorg. Chem.* 47 (10) (2008) 4290.
- [62] H. Chu, et al. *Chem. Mater.* 22 (21) (2010) 6021.
- [63] G. Xia, et al. *J. Mater. Chem.* 22 (15) (2012) 7300.
- [64] W. Sun, et al. *Chem. Eur. J.* 18 (22) (2012) 6825.
- [65] F. Yuan, et al. *Int. J. Hydrogen Energy* 38 (13) (2013) 5322.
- [66] Z. Tang, et al. *J. Mater. Chem.* 22 (12) (2012) 5312.
- [67] F. Yuan, et al. *Chem. Mater.* 24 (17) (2012) 3370.
- [68] X.B. Yu, et al. *J. Phys. Chem. C* 114 (10) (2010) 4733.
- [69] H. Chu, et al. *Dalton Trans.* 39 (44) (2010) 10585.
- [70] X.Y. Chen, et al. *J. Phys. Chem. C* 114 (41) (2010) 17947.
- [71] M. Matsuo, et al. *J. Am. Chem. Soc.* 131 (45) (2009) 16389.
- [72] Y.E. Filinchuk, et al. *Inorg. Chem.* 45 (4) (2006) 1433.
- [73] P.A. Chater, et al. *Chem. Commun.* 45 (2007) 4770.
- [74] H. Wu, et al. *Chem. Mater.* 20 (4) (2008) 1245.
- [75] T. Noritake, et al. *Int. J. Hydrogen Energy* 38 (16) (2013) 6730.
- [76] A. Staubitz, et al. *Chem. Rev.* 110 (7) (2010) 4079.
- [77] G. Wolf, et al. *Thermochim. Acta* 343 (1/2) (2000) 19.
- [78] A. Gutowska, et al. *Angew. Chem. Int. Ed.* 44 (23) (2005) 3578.
- [79] T.K. Nielsen, et al. *Nanoscale* 3 (2011) 2086.
- [80] T. He, et al. *Chem. Mater.* 21 (11) (2009) 2315.
- [81] A. Karkamkar, et al. *Chem. Mater.* 21 (19) (2009) 4356.
- [82] T.K. Nielsen, et al. *Dalton Trans.* 43 (2013) 680.
- [83] M. Bowden, et al. *Chem. Commun.* 46 (45) (2010) 8564.
- [84] Z. Fang, et al. *Phys. Chem. Chem. Phys.* 13 (16) (2011) 7508.
- [85] Y.S. Chua, et al. *Chem. Commun.* 47 (2011) 5116–5129.
- [86] Z. Xiong, et al. *Nat. Mater.* 7 (2) (2008) 138.
- [87] H.V.K. Diyabalanage, et al. *J. Am. Chem. Soc.* 132 (34) (2010) 11836.
- [88] H.V.K. Diyabalanage, et al. *Angew. Chem. Int. Ed.* 119 (47) (2007) 9153.
- [89] Q. Zhang, et al. *J. Phys. Chem. C* 114 (3) (2010) 1709.
- [90] R.V. Genova, et al. *J. Alloys Compd.* 499 (2) (2010) 144.
- [91] J. Luo, et al. *Energy Environ. Sci.* 6 (3) (2013) 1018.
- [92] T. He, et al. *J. Mater. Chem.* 22 (15) (2012) 7478.
- [93] H. Wu, et al. *J. Am. Chem. Soc.* 130 (44) (2008) 14834.
- [94] Y.S. Chua, et al. *Chem. Commun.* 46 (31) (2010) 5752.
- [95] Y.S. Chua, et al. *Chem. Mater.* 21 (20) (2009) 4899.
- [96] Y.S. Chua, et al. *Chem. Mater.* 24 (18) (2012) 3574.
- [97] H. Wu, et al. *J. Mater. Chem.* 20 (31) (2010) 6550.
- [98] J. Luo, et al. *Int. J. Hydrogen Energy* 37 (14) (2012) 10750.
- [99] L.H. Jepsen et al., 2013 (submitted for publication).
- [100] X. Chen, et al. *Dalton Trans.* 42 (40) (2013) 14365.
- [101] L.H. Jepsen, et al. *J. Alloys Compd.* 580 (2013) S287–S291.
- [102] T. He, et al. *Energy Environ. Sci.* 5 (2) (2012) 5686.
- [103] H. Wu, et al. *Energy Environ. Sci.* 5 (6) (2012) 7531.
- [104] J.P. Soulie, et al. *J. Alloys Compd.* 346 (1/2) (2002) 200.
- [105] Y. Filinchuk, et al. *Chem. Mater.* 21 (5) (2009) 925.
- [106] M. Chong, et al. *Chem. Commun.* 47 (4) (2011) 1330.
- [107] C. Pistidda, et al. *J. Alloys Compd.* 508 (1) (2010) 212.
- [108] A.D. Sutton, et al. *Science* 331 (6023) (2011) 1426.