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Review

Complex Metal Hydrides for Hydrogen, Thermal and Electrochemical Energy Storage

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Abstract: Hydrogen has a very diverse chemistry and reacts with most other elements to form compounds, which have fascinating structures, compositions and properties. Complex metal hydrides are a rapidly expanding class of materials, approaching multi-functionality, in particular within the energy storage field. This review illustrates that complex metal hydrides may store hydrogen in the solid state, act as novel battery materials, both as electrolytes and electrode materials, or store solar heat in a more efficient manner as compared to traditional heat storage materials. Furthermore, it is highlighted how complex metal hydrides may act in an integrated setup with a fuel cell. This review focuses on the unique properties of light element complex metal hydrides mainly based on boron, nitrogen and aluminum, e.g., metal borohydrides and metal alanates. Our hope is that this review can provide new inspiration to solve the great challenge of our time: efficient conversion and large-scale storage of renewable energy.

Keywords: complex metal hydrides; thermal energy storage; hydrogen storage; solid-state electrolytes; electrodes; fuel cell

1. Introduction

The ultimate challenge of our time is the development of an environmentally friendly energy system based on sustainable renewable energy to replace our fossil fuel dependency. Fossil fuels are burnt and energy release is accompanied by release of carbon dioxide (CO₂), nitrogen oxides (NOₓ), particles etc. and may locally lead to extreme air pollution and smog while climate changes are observed globally. Hence, the great challenge of our time is efficient conversion and large-scale storage of renewable energy for days, weeks, and maybe months [1]. However, renewable energy sources generally vary significantly over time and place [2]. Thus, the realization of this scenario calls for a range of novel ideas, technologies, and a paradigm shift in design and development of novel energy materials with new functionalities. Incremental improvement of known materials never changes the
world, but just one new material may, since novel materials often form the basis for technological paradigm shifts. The chemistry of hydrogen is very diverse and a wide range of novel hydrides have been discovered during the past decade with a rich and fascinating structural chemistry and a range of useful properties, e.g., energy storage, which is the topic of this review.

Renewable energy occurs mainly as heat from the sun or electricity from sun or wind. Electricity can be used directly, stored in a battery, or used to split water to hydrogen and oxygen, see Figure 1.

![Figure 1](image-url) **Figure 1.** Illustration of a sustainable global energy system based on energy storage in either batteries, as heat storage, using hydrogen as a carrier (left) or a carbon neutral cycle (right). Modified figure from [1].

Hydrogen (H\(_2\)), is the lightest element of all and also has some unique properties among known substances, e.g., the highest gravimetric energy density, the fastest diffusion speed in air, and a low density both as a gas and liquid. The latter makes hydrogen challenging to store in a dense manner. Figure 1 illustrates that maybe in the future, carbon dioxide from the atmosphere is reacted with hydrogen to create ‘carbon neutral’ hydrocarbons or carbohydrates. Oxidation of such hydrocarbons/carbohydrates will not increase the carbon dioxide level in the atmosphere. Sustainability means that all material cycles are closed, including our energy system. Therefore, all materials that we use must be reused as illustrated in Figure 1.

This review reveals metal hydrides as a diverse class of materials with a range of compositions, structures and properties towards multi-functionality. The focus is on light elemental hydrides, consisting mainly of boron, nitrogen or aluminum, which may be used for storage of hydrogen, solar heat or as novel battery materials. It is hoped that this review will provide new inspiration to create new materials and technologies for efficient conversion and large-scale storage of renewable energy.

2. Complex Metal Hydrides for High-Density Hydrogen Storage

Complex metal hydrides (CMHs) formed by light elements, such as boron, nitrogen, or aluminum often have extreme hydrogen densities but also poor thermodynamic and kinetic properties and limited reversibility [1–4]. Initially, the discovery of reversibility in titanium-catalyzed NaAlH\(_4\) initiated a paradigm shift in hydrogen storage research towards complex anions [5]. Hence, research was extended to include metal borohydrides, e.g., LiBH\(_4\) and nitrogen-based complex hydrides, e.g., LiNH\(_2\) [6–8]. The complex hydride anions consist mainly of covalent bonds with well-defined directionality, whereas ionic bonding dominates in the solid state between the complex anions and counter cations, e.g., in LiBH\(_4\), NaBH\(_4\), and NaAlH\(_4\). Solid state CMHs have high volumetric and gravimetric hydrogen densities (see Table 1), which makes them interesting as hydrogen storage materials. However, the poor thermodynamic and kinetic properties only allow hydrogen release and
uptake at elevated temperatures and pressures, which makes them unsuitable for portable applications. The hydrogen release pathway from complex hydrides is complicated compared to metallic and ionic hydrides, and thus remains not fully understood.

Amide-hydride composite systems, e.g., LiNH₂-LiH, has been investigated as possible candidates for hydrogen storage [7]. The LiNH₂-LiH composite has a high calculated hydrogen content of ρ_m = 10.5 wt % H₂ and releases hydrogen according to reaction scheme (1).

LiNH₂(s) + 2LiH(s) ↔ Li₂NH(s) + LiH(s) + H₂(g) ↔ Li₃N(s) + 2H₂(g)  

(1)

The decomposition reaction initiates at T = 180 °C, which is lower than those of the individual reactants, i.e., 300 °C for LiNH₂ and 600 °C for LiH [7]. Thus, similar composite systems have been considered [9–13], e.g., Mg(NH₂)₂-2LiH (5.6 wt % H₂) with suitable thermodynamic properties (ΔH_des = 39 kJ mol⁻¹ H₂, ΔS_des = 112 J K⁻¹ mol⁻¹ H₂), i.e., dehydrogenation may occur below 90 °C at p(H₂) = 1 bar [14]. However, experimental results reveal that T > 180 °C is required to achieve hydrogen release [9]. Addition of CaH₂ (8 mol %) catalyzes the reaction and decreases the activation energy, i.e., the decomposition begins at 78 °C [15]. Generally, the dehydrogenation of amide-hydride systems suffer from sluggish kinetics that might be caused by interface reactions, nucleation/nuclei growth, and/or diffusion processes. Mechanical milling was found to be effective in increasing the dehydrogenation kinetics, due to the reduced grain size and increased homogeneous distribution of amide and hydride particles [16,17]. An effective catalyst may significantly improve the kinetics. Recently, K₂[Zn(NH₄)₂] was synthesized by mechanochemical milling and the composite K₂[Zn(NH₄)₂]-8LiH showed release of 4.2 wt % H₂ below 400 °C [18–20]. Remarkably, the composite may be fully hydrogenated in 30 s at 230 °C and p(H₂) = 50 bar [18–20]. The LiAl(NH₂)₄-4LiH desorbs 5.0 wt % H₂ at 130 °C [21]. However, the instability of LiAl(NH₂)₄, one of the desorption products, prevents rehydrogenation [21]. Metal amides and metal hydroxides may also form solid solutions, such as in the NaNH₂-NaOH system [22].

| Table 1. Properties of selected light element complex metal hydrides [23,24]. | M = molar mass; ρ = volumetric mass density; ρ_m = gravimetric hydrogen density; ρ_V = volumetric hydrogen density; ΔH_dec = decomposition enthalpy; T(1 bar) = equilibrium temperature at p(H₂) = 1 bar; T_dec = decomposition temperature. |
|---|---|---|---|---|---|---|
| M (g/mol) | ρ (g/mL) | ρ_m (wt % H₂) | ρ_V (g H₂/L) | ΔH_dec (kJ/mol) | T(1 bar) (°C) | T_dec (°C) |
| LiBH₄ | 21.78 | 0.66 | 18.4 | 122.5 | 74 | 370 | -400 |
| NaBH₄ | 37.83 | 1.07 | 10.8 | 115.6 | 108 | 534 | -500 |
| LiAlH₄ | 37.95 | 0.92 | 10.6 | 97.5 | -10 | - | - |
| Li₂AlH₄ | 53.85 | 1.02 | 11.2 | 114.2 | 25 | -81 | -200 |
| NaAlH₄ | 54.00 | 1.28 | 7.3 | 93.4 | 33.1 | 18 | -230 |
| Na₃AlH₄ | 102.00 | 1.45 | 5.9 | 85.6 | 49.0 | 103 | -275 |
| LiNH₂ | 22.96 | 1.18 | 8.8 | 103.6 | 67 | - | -300 |

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2.1. Complex Aluminum Hydrides

2.1.1. Aluminum Hydride

Aluminum hydride (AlH₃, alane), is a promising hydrogen-storage material based on the gravimetric and volumetric hydrogen density of ρ_m = 10.1 wt % H₂ and ρ_V = 149 g H₂/L, respectively. Additionally, alane has a low hydrogen desorption temperature and fast desorption kinetics, whilst aluminum is abundant [32]. Alane is thermodynamically unstable at room temperature due to a positive Gibbs free energy of formation, ΔG_f = 46.5 kJ/mol, however, the crystalline α-AlH₃ is kinetically stable at room temperature [33–35]. Alane was first synthesized in its pure form in
1947 [36]. Since then, a variety of six polymorphs of alane has been discovered (α, α′, β, γ, δ and ε) [37]. The obtained polymorph is entirely dependent on the chosen synthesis route [38]. The structures of α-, α′-, β-, and γ-AlH₃ consist of corner-sharing AlH₆ octahedra whereas γ-AlH₃ also possesses edge-sharing AlH₆ octahedra [37,39–43].

Alane can be produced directly from the elements by hydrogenation of aluminum. However, this synthesis method is impractical as it requires a hydrogen pressure above 25 kbar at room temperature [44]. Another synthesis method is by mechanochemical treatment at liquid nitrogen temperature (cryomilling, T = −196 °C) where a thermodynamically spontaneous metathesis reaction, ΔG° = −191 kJ/mol, between AlCl₃ and LiAlH₄ occurs (see reaction scheme (2)), producing several polymorphs of alane (α, α′, β, and γ-AlH₃) [40,45,46].

$$\text{AlCl}_3(s) + 3\text{LiAlH}_4(s) \rightarrow 3\text{LiCl}(s) + 4\text{AlH}_3(s)$$

(2)

Furthermore, ball milling of AlCl₃ and LiAlH₄ at room temperature under hydrogen pressure (p(H₂) > 210 bar) only leads to formation of α-AlH₃ [47]. A solid state reaction is facilitated by thermal treatment at T ~75 °C followed by solvent extraction of LiCl [48]. The monomeric alane can also be stabilized as a solvate R·AlH₃ (R = Et₂O, amines or tetrahydrofuran (THF)) by reaction in donating solvents such as ethers or amines [49,50]. Subsequently, the solvent can be removed from the AlH₃ adduct by heating in vacuum. Alane readily reacts with metal hydrides to form other complex hydrides [51], e.g., NaAlH₄, which will be discussed in the next section.

2.1.2. Metal Alanates

The potential of complex aluminum hydrides was seriously established with the discovery of titanium-catalyzed NaAlH₄ by Bogdanović in 1997 [5]. The system shows a reversible capacity approximately twice of any of the conventional metal hydrides [52]. The complex aluminum hydrides are based on the tetrahydridoaluminate(1−) or hexahydridoaluminate(3−) complex anion, AlH₄⁻ or AlH₆³⁻, respectively, which is commonly denoted alanates.

In the 1960s it was discovered that a range of alkali metal alanates can be prepared through direct hydrogenation of the alkali metal hydride (MH, M = Li, Na, K, Cs) and aluminum either in the solid state or in a solvent-mediated reaction [53,54]. The reaction is commonly described as a two-step reaction [55,56], see reaction schemes (3) and (4)

$$3\text{MH}(s) + \text{Al}(s) + 3/2\text{H}_2(g) \leftrightarrow M_3\text{AlH}_6(s)$$

(3)

$$M_3\text{AlH}_6(s) + 2\text{Al}(s) + 3\text{H}_2(g) \leftrightarrow 3\text{MAI}_4(s)$$

(4)

However, the detailed reaction mechanism for different metal alanates is debatable and other intermediates may be involved [55,57].

LiAlH₄ (pₜₐᵣᵦ = 10.5 wt % H₂) was synthesized in the late 1940s and is widely used as a reducing agent in organic chemistry [58], but it attained increased attention as a hydrogen storage material with the discovery of the titanium-catalyzed NaAlH₄. Thermolysis of LiAlH₄ is initiated by the melting of LiAlH₄, Tₘₜₑₜₐᵦ(LiAlH₄) = 125 °C [23], which subsequently decomposes into solid Li₃AlH₄ and Al accompanied by an exothermic release of hydrogen gas in the temperature range 150–220 °C [59,60]. The exothermic decomposition in this first step hinders the full reversibility of the system. The second decomposition step occurs around 190–260 °C as an endotherm [61,62]. Ball milling metal alanates tends to lower the decomposition temperature as particle size is reduced and defects are introduced. However, LiAlH₄ often decomposes during milling with additives, e.g., TiCl₃, VCl₃, and Fe [63–66]. Furthermore, addition of TiCl₃ only reduces the decomposition temperature but does not enable rehydrogenation [67]. A way to overcome the energy barrier preventing rehydrogenation of LiAlH₄ is to use a solvent-mediated synthesis route, hence LiH and Al stirred in, e.g., THF or Me₂O and apply hydrogen pressure as low as p(H₂) > 10 bar [68,69].
Sodium alanate, NaAlH$_4$ ($\rho_m = 7.4$ wt % H$_2$) is the most investigated metal alanate with moderate rehydrogenation conditions of titanium-catalyzed NaAlH$_4$ (at $T = 170$ °C, $p$(H$_2$) = 150 bar) [5]. However, the useful capacity is low (5.6 wt % H$_2$) and not ideal for consideration in mobile applications. Thus, a tremendous effort has been carried out in research to tailor the system, e.g., by addition of dopants or nanoconfinement [70–77]. Furthermore, NaAlH$_4$ has also been widely used as a precursor in metathesis reactions to synthesize new metal alanate compounds, e.g., Mg(AlH$_4$)$_2$, Ca(AlH$_4$)$_2$, Sr(AlH$_4$)$_2$, and Eu(AlH$_4$)$_2$ [78–80].

Potassium alanate, KAlH$_4$ ($\rho_m = 5.7$ wt % H$_2$), has a less understood mechanism of decomposition as compared to LiAlH$_4$ and NaAlH$_4$. The formation of an intermediate has been observed experimentally and a crystal structure and composition of K$_3$AlH$_6$ has been suggested by density functional theory (DFT) calculations [37,81–83]. In contrast, experimental observations suggest a K$_y$AlH$_x$ compound with $1 \leq y \leq 3$ and $4 \leq x \leq 6$ [57]. The main advantage of KAIH$_4$ over LiAlH$_4$ and NaAlH$_4$ is the reversible hydrogen sorption at low pressure (<10 bar) and moderate temperature (250–300 °C) without the need of additives [84].

In general the alkali metal alanates are less stable than the alkali metal borohydrides with decomposition temperatures of 60 to 300 °C as compared to $T > 350$ °C, respectively [2,67]. Hence, they may more easily become a practical hydrogen storage material, but generally with lower gravimetric hydrogen storage capacity.

2.2. Metal Borohydrides

In 2003, lithium borohydride, LiBH$_4$, was proposed as a hydrogen storage material. Since then, a wide range of novel metal borohydrides has been discovered, due to the great coordination flexibility of the complex BH$_4^-$ anion, which can act as a counter ion in the solid state, or coordinate to a metal via corner sharing ($\eta^1$), edge sharing ($\eta^2$), or face sharing ($\eta^3$) [3,85]. Metal borohydride structures appear to be related to structures of metal oxides, e.g., polymorphs of Ca(BH$_4$)$_2$ are isostructural to polymorphs of TiO$_2$ [85].

2.2.1. Monometallic Borohydrides

Lithium is one of the lightest elements and LiBH$_4$ has a high gravimetric and volumetric hydrogen density of $\rho_m = 18.4$ wt % H$_2$ and $\rho_V = 122.5$ g H$_2$/L, respectively [6,8,86,87]. The structure of LiBH$_4$ is orthorhombic (Pnma), o-LiBH$_4$, at room temperature whereas a first-order polymorphic transition into a hexagonal (P6$_3/mc$) structure, denoted h-LiBH$_4$, occurs at $T \sim 108$ °C [8,86,88]. Both polymorphs contain relatively rigid, regular, and undistorted BH$_4^-$ tetrahedra [89]. Furthermore, LiBH$_4$ melts at $T \sim 275$ °C and eventually decomposes at $T > 350$ °C into LiH and elemental B where the enthalpy change amounts to $\Delta H_{dec} = 74$ kJ/mol H$_2$ [25]. The other alkali metal borohydrides MBH$_4$, $M = \text{Na, K, Rb and Cs}$ have higher thermal stability and all crystallize in the Rock salt structure. Sodium borohydride is also stable in basic aqueous solutions, which has been used as a hydrogen storage media [90]. Alkali metal borohydrides are known to have the highest thermal stability, which hampers the possible application as hydrogen storage materials.

Only recently, the full series of alkaline earth metal borohydrides was completed with the discovery of Ba(BH$_4$)$_2$, Sr(BH$_4$)$_2$, and their chloride derivatives [91–93]. The alkaline earth metal borohydrides show decreasing degree of covalent and directional bonding in the series, Mg > Ca > Sr > Ba. Magnesium borohydride is known in seven different polymorphs and, remarkably, one of these, $\gamma$-Mg(BH$_4$)$_2$, has permanent porosity and 30 % of open space in the structure [94–103]. The heavier alkali earth metal borohydrides form three to four polymorphs [3].

A few transition metal borohydrides have also been described and those that are stable at room temperature have electron configurations $d^0$, $d^5$ or $d^{10}$ [2], i.e., containing the metal ions, Sc$^{3+}$, Y$^{3+}$, Zr$^{4+}$, Mn$^{2+}$, Zn$^{2+}$ or Cd$^{2+}$. A few less stable transition metal borohydrides are also described, e.g., Ti(BH$_4$)$_3$ ($d^1$) which sublimes at $T \sim 0$ °C, or Fe(BH$_4$)$_2$ which is stable in solution (at $T \sim -30$ °C) and can be stabilized as [Fe(NH$_3$)$_6$](BH$_4$)$_2$ [104,105].
Some monometallic borohydrides form molecular solids and sublime at low temperatures, e.g., Al(BH$_4$)$_3$ and Zr(BH$_4$)$_4$, where the latter is the most stable, $T_{\text{sub}} = 29$ °C and may be prepared by vapour deposition [106].

### 2.2.2. Bimetallic Borohydrides

Lithium potassium borohydride, LiK(BH$_4$)$_2$, was the first discovered bimetallic borohydride [107,108]. Later, a range of lithium, rubidium, and caesium borohydrides were described while also a solid solution of Na$_{1-x}$K$_x$BH$_4$ was discovered [85,109]. These compounds have structures similar to their parent monometallic borohydrides.

Bimetallic borohydrides, where the metals have increasing difference in Pauling electronegativity, have structures constructed of larger metal complexes with the most electronegative metal as the central ion and the less electronegative metal with dominantly ionic coordination. Thus, lithium scandium borohydride, LiSc(BH$_4$)$_4$, consists of [Sc(BH$_4$)$_4$]$^-\text{ complexes and Li}^+\text{ ions. Additionally, a relationship between the Pauling electronegativity of the metal cation and the thermal stability of the metal borohydride has been established as higher electronegativity results in lower decomposition temperature, see Figure 2 [2,110,111].

![Figure 2](image)

**Figure 2.** Thermal decomposition temperature of metal borohydrides as a function of the central metals electronegativity.

Sodium zinc borohydrides are known in two compositions, NaZn(BH$_4$)$_3$ and NaZn$_2$(BH$_4$)$_5$, which contain the complex ions [Zn(BH$_4$)$_3$]$^-\text{ and [Zn}_2\text{(BH}_4\text{)}_5\text{]}^-\text{, respectively. The latter can also be described as two identical interpenetrated three-dimensional frameworks [112–114]. Strong and directional Zn-BH$_4$ bonding by edge sharing (η$^2$) is observed, which defines the structural architecture. The compound LiCe(BH$_4$)$_3$Cl, has a very unique structure consisting of tetranuclear anionic clusters [Ce$_4$Cl$_4$(BH$_4$)$_{12}$]$^{1-\text{ with a distorted cubane Ce}_4\text{Cl}_4\text{ core [3,115].

Perovskite structures have long been known for metal hydrides, e.g., CsCaH$_3$ and NaMgH$_3$ containing the anion H$^-$ [117–121]. However, only recently the first perovskite-type metal borohydride, KMn(BH$_4$)$_3$, was reported, though followed up by extensive research reporting multiple new perovskite-type metal borohydrides containing the complex anion BH$_4^-$, see also Figure 3 [116,122–124]. Structurally, the metal borohydride perovskites differ from regular oxide and halide A$	ext{BX}_3$ perovskites as their polymorphic transitions are not always intuitively towards higher symmetry with increasing temperature. H-H repulsion between the BH$_4^-$ ligands may in some cases result in lower symmetry [123,125].
Some monometallic borohydrides form molecular solids and sublime at low temperatures, e.g., LiK(BH4)2, which was the first discovered bimetallic borohydride [85,109]. These compounds have structures similar to those of double perovskites Li2M(BH4)2 [111]. The first trimetallic borohydrides, Li3MZn5(BH4)15, M = Mg and Mn, presented in 2013 [126], were prepared by partial cation substitution in LiZn2(BH4)15 using the chemical knowledge that the ions, Li+, Mg2+, Mn2+, and Zn2+ share some chemical properties and may substitute for each other in the solid state. The two compounds, Li3MZn5(BH4)15, M = Mg and Mn, are isostructural with cation disorder in the hexagonal (P63/mcm) structure related to bimetallic LiZn2(BH4)5 [126]. The five trimetallic compounds AlLiM(BH4)4 (A = K or Rb; M = Mg or Mn) and K3Li2Mg2(BH4)3 have negatively charged Li-Mg/Mn layered structures [127]. These trimetallic compounds have interesting structural relationships to aluminosilicates, e.g., KAlSi3O8 (feldspar), and may open new research directions, e.g., preparation of zeolite-like metal borohydrides. Similarly, zeolites contain three-dimensional negatively charged Al-Si-O networks [127]. Double perovskites Li2M(BH4)4 have been observed for large alkali metals A = Rb, Cs and M = Y, Ce, Gd while the smaller alkali metal A = K stabilizes the garnet-type structure Li3K3M2(BH4)12 for M = La, Ce [128,129].

2.2.4. Metal Borohydrides Modified by Neutral Molecules

Metal borohydrides have been modified with neutral molecules in order to improve hydrogen release and uptake properties [3]. Nitrogen-based molecules have attracted significant attention, e.g., ammonia, NH3, hydrazine, N2H4, and ammonia borane, NH3BH3, in order to introduce dihydrogen bonding via partly positively charged hydrogen atoms, e.g., B–H⋯⋅⋅⋅H–N in the solid state. Dihydrogen bonding is explored for tailoring thermal stability and decomposition. Trends in composition, structure, and properties for a range of new ammine metal borohydrides, M(BH4)n·nNH3, have been investigated recently. The interest in ammine metal borohydrides has increased tremendously during the past ~5 years [3,4]. The number of BH4− anions (m) in the compounds is fixed and determined by the oxidation state of the metal, whereas the number of NH3 ligands (n) may range from 1 to 8, e.g., Ca(BH4)2·NH3 and Zr(BH4)4·8NH3 [130,131]. In all cases the ammonia molecule, NH3, coordinates via the lone pair on N to the metal, and the BH4− anions coordinate in a more flexible way (η0−η7). The most extensive series of crystalline ammine metal borohydride is formed by Y(BH4)3·nNH3 (n = 1, 2, 4, 5, 6 and 7), which illustrates the great structural flexibility ranging from cation complexes (n = 6 and 7), molecular neutral complexes (n = 4 and 5), one-dimensional chain like (n = 2), and two-dimensional layered structure (n = 1) [132].

Ammine metal borohydrides have been considered promising hydrogen storage materials, e.g., Al(BH4)3·6NH3, Li2Al(BH4)5·6NH3, and Zn(BH4)2·2NH3 release 9 to 12 wt % H2 in the temperature range 115 to 170 °C with traces of NH3 [133–135].

Interestingly, ammonia has a destabilizing effect for metal borohydrides with low metal electronegativity (χp < ~1.6) and a stabilizing effect for those with χp > ~1.6. Thus the latter are often more thermally stable than their respective metal borohydride [104,130]. The stabilization may be due to complex formation and a shielding effect of the metal cation, which would otherwise be reduced to the metallic state, e.g., Zn(BH4)2·4NH3 and Zn(BH4)2·2NH3 [135].
Previously, a low \( \text{NH}_3/\text{BH}_4^- \) ratio \((n/m \sim 1)\) and strong dihydrogen bonds were assumed to provide \( \text{H}_2 \) rich (and \( \text{NH}_3 \) poor) gas release during thermolysis. However, recent experimental results disagree with this hypothesis \([130,132,136]\). The composition of the released gas appears to depend on the thermal stability of the ammine metal borohydride, i.e., if it is similar to or higher than the thermal stability of the corresponding metal borohydride, then \( \text{H}_2 \) is released. In contrast, mainly \( \text{NH}_3 \) is released if the thermal stability of the ammine metal borohydride is significantly lower than the corresponding metal borohydride. For instance, the compounds, \( \text{M}(\text{BH}_4)_m \cdot n\text{NH}_3 \), \( \text{M} = \text{Al}, \text{Zn}, \text{Zr}, \text{and} \ V \), release \( \text{H}_2 \) (and maybe some \( \text{NH}_3 \)), e.g., \( \text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3 \) releases \( \text{H}_2 \) and a small amount of \( \text{NH}_3 \) at \( T \sim 165 \, \text{°C} \) \([131,133,135,137]\).

Ammonia borane metal borohydride compounds have also been investigated, \( \text{M}(\text{BH}_4)_m \cdot n\text{NH}_3 \cdot \text{BH}_3 \cdot \text{NH}_3 \), \( \text{M} = \text{Li}, \text{Mg}, \text{Ca}, \text{or} \text{Al} \) \([138–142]\). They tend to separate during thermal treatment and \( \text{NH}_3 \) \( \text{BH}_3 \) decomposes at \( T > 200 \, \text{°C} \) and the release of the toxic gasses is not suppressed, as observed for metal amidoboranes, \( \text{M}(\text{NH}_2\text{BH}_3)_m \) \([143]\). An interesting amidoborane is the complex \( \text{Na}[\text{Al}(\text{NH}_2\text{BH}_3)_4] \) which was found to reversibly absorb 1.7 mole of \( \text{H}_2 \), although between two amorphous decomposition states \([144]\). Replacement of the \( \text{Na}^+ \) ion with a \( \text{K}^+ \) ion results in similar thermal decomposition temperatures. However, the reversibility seem to be disabled by this cation substitution \([145]\).

3. Complex Metal Hydrides for Electrochemical Applications

Ni-metal hydride (Ni-MH) batteries have been used commercially in portable electrical devices since the early 1990’s. The cathode consists of \( \text{Ni(OH)}_2 \), while the anode is a \( \text{MH} + \text{Ni(OH)}_2 \) and the electrolyte is an alkaline solution \([146]\). The overall reaction is:

\[
\text{MH} + \text{NiOOH} \leftrightarrow \text{M} + \text{Ni(OH)}_2 \quad M: \text{Hydrogen storage alloy} \tag{5}
\]

The LaNi\(_5\)-based AB\(_5\) type alloy was modified and commercially used as negative electrodes for Ni-metal hydride batteries \([147]\). Even though the energy densities of these batteries are smaller than those of Li-ion batteries, they still play an important role in the market, especially for hybrid and fuel cell vehicles. Furthermore, several metal hydrides have been proposed as conversion type electrodes and others as electrolytes for complete solid state batteries. Different properties of metal hydrides have also been highlighted elsewhere \([148]\).

3.1. Metal Hydrides as Electrode Materials

In 2008 use of metal hydrides as conversion type anodes in Li-ion batteries was proposed for the first time by Oumellal et al. \([149]\). In this concept, hydrides store lithium through the following general conversion reaction:

\[
\text{MH}_n + n\text{Li} \rightarrow n\text{LiH} + \text{M} \quad M: \text{Metal or intermetallic hydride} \tag{6}
\]

The first investigation in 2008 focused on \( \text{MgH}_2 \) as the anode material, but the study also showed successful conversion reactions for \( \text{TiH}_2, \text{NaH}, \text{LaNi}_{14.25}\text{Mn}_{0.75}\text{H}_5 \) and \( \text{Mg}_2\text{NiH}_3.7 \). The high theoretical capacities of the hydrides (e.g., 2038 mAh/g for \( \text{MgH}_2 \), i.e., more than five times that of graphite) naturally caused significant interest for this new class of anodes. Furthermore, the investigation revealed that magnesium hydride exhibits smaller cell polarization (\( \Delta V \) between charge and discharge) than any of the other previously investigated conversion type electrodes (e.g., electrodes based on nitrides, sulfides and oxides) \([149]\). Unfortunately, hydride materials show limitations in their initial capacity (relative to the theoretical values) and large capacity loss upon cycling, which is subscribed to poor electronic conductivity and the large volume change occurring in the electrode during cycling, which may lead to poor contact. The capacity of \( \text{MgH}_2 \) can be improved by limiting the amount of inserted lithium \([149]\), through careful formulation (e.g., choice of binder) and choice of electrolyte. Hereby, a capacity retention for \( \text{MgH}_2 \) of 542 mAh/g over 40 cycles has been achieved \([150]\).
Subsequently, several studies have investigated Li-ion storage in MgH\textsubscript{2} \cite{151-158}, TiH\textsubscript{2} \cite{159,160}, AlH\textsubscript{3} \cite{151,161}, M-LiH (M = Mg, Ti) \cite{162} and TiH\textsubscript{2}-MgH\textsubscript{2} \cite{163} composites as well as a series of Mg-based complex hydrides such as Mg\textsubscript{2}FeH\textsubscript{6}, Mg\textsubscript{2}CoH\textsubscript{5} and Mg\textsubscript{2}NiH\textsubscript{4} \cite{164}. For detailed descriptions of these results we refer to other reviews \cite{165,166}.

Li-ion storage through conversion reactions in lithium and sodium alanate, LiAlH\textsubscript{4} and NaAlH\textsubscript{4}, were investigated for the first time in 2015 \cite{161,167,168}. The theoretical capacity for these materials is \(~2000\) mAh/g when considering reaction with 3 Li equivalents and full reduction to LiH and metallic aluminium. Silvestri et al.\cite{168} obtained an initial discharge capacity of 1180 mAh/g for LiAlH\textsubscript{4}, corresponding to storage of 1.67 Li equivalent, at discharge potentials dominated by extended plateaus at 0.78, 0.26 and 0.16 V versus Li. The conversion reaction has been shown by powder X-ray diffraction to occur through the following steps:

\begin{eqnarray}
2\text{LiAlH}_4 + 3\text{Li}^+ + 3e^- & \rightarrow & \text{Li}_3\text{AlH}_6 + \text{Al} + 2\text{LiH} \quad (7) \\
\text{Li}_3\text{AlH}_6 + 3\text{Li}^+ + 3e^- & \rightarrow & \text{Al} + 6\text{LiH} \quad (8)
\end{eqnarray}

The formation of Al results in formation of the LiAl alloy according to the following reaction, which is predicted to occur below 0.29 V \cite{168}.

\begin{equation}
\text{Li}^+ + e^- + \text{Al} \rightarrow \text{LiAl} \quad (9)
\end{equation}

The reversible capacity in the first charge is less than 1/3 of the capacity in the first discharge with the alloying/de-alloying reaction being responsible for the majority of the reversible capacity.

For NaAlH\textsubscript{4} anodes initial capacities of 1700–1800 mAh/g can be achieved according to Reale et al.\cite{167} with the majority of the Li storage reaction taking place at potentials <0.45 V. High energy ball milling with conductive carbon (Super P) for 15 h improves the reversible capacity in the first cycle from less than 30% to almost 70%. The discharge mechanism is still not completely agreed upon. In general, multiple reaction steps are reported and the bi-alkali hexa-alanate, LiNa\textsubscript{2}AlH\textsubscript{6} is a common intermediate \cite{161,167}.

\begin{eqnarray}
\text{NaAlH}_4 + 3/2\text{Li}^+ + 3/2 e^- & \rightarrow & 1/2\text{LiNa}_2\text{AlH}_6 + 1/2\text{Al} + \text{LiH} \quad (10) \\
\text{LiNa}_2\text{AlH}_6 + 5\text{Li}^+ + 5 e^- & \rightarrow & 2\text{Na} + \text{Al} + 6\text{LiH} \quad (11)
\end{eqnarray}

However, Reale et al.\cite{167} also observed formation of the sodium hexa-alanate, Na\textsubscript{3}AlH\textsubscript{6} (Equation (12)), which is suggested to be a competitive process affected by kinetic limitations. Formation of Na\textsubscript{3}AlH\textsubscript{6} during discharge was also confirmed in a separate study through \textsuperscript{23}Na and \textsuperscript{27}Al solid state NMR \cite{169}.

\begin{equation}
3\text{NaAlH}_4 + 6\text{Li} + 6 e^- \rightarrow \text{Na}_3\text{AlH}_6 + 6\text{LiH} + 2\text{Al} \quad (12)
\end{equation}

Reale et al. also used the hexa-alanates Na\textsubscript{3}AlH\textsubscript{6} and LiNa\textsubscript{2}AlH\textsubscript{6} directly as anodes, which were found to behave similarly to the alanates.

Recently, attempts were made to improve the reversibility of NaAlH\textsubscript{4} by nanoconfinement in mesoporous carbon scaffolds \cite{170,171}. Nanoconfinement seems to alter the conversion mechanism by enhancing the conversion from NaAlH\textsubscript{4} to Na\textsubscript{3}AlH\textsubscript{6}. Also it appears to increase the capacity retention of the system, however the results suggests that the majority of the long term capacity stems from the carbon scaffolds \cite{171}.

Metal borohydrides have very high theoretical capacities, e.g., 4992 mAh/g for LiBH\textsubscript{4} and thus have great potential as future anode materials. However, only a few studies of borohydride-based anodes exists \cite{172,173}. Theoretical calculations predict that Li-conversion reactions are thermodynamically feasible for a long list of metal borohydrides both through a one-step mechanism with direct formation of the metal, elemental boron and lithium hydride, or through
a two-step reaction with formation of a metal hydride as an intermediate. In the same investigation, five mono-metallic borohydrides, $M(BH_4)_n$ ($M = \text{Li, Na, K, Mg and Ca}$) were tested as anodes in Li-ion batteries. Ca$(BH_4)_2$ appears to be electrochemically inactive, and for LiBH$_4$ and KBH$_4$ capacities below 75 mAh/g were achieved in the first discharge. Mg$(BH_4)_2$ and NaBH$_4$ exhibited initial capacities of ~540 and 250 mAh/g, which is well below their theoretical capacities of 3971 and 2834 mAh/g, respectively. Furthermore, the reversible capacity in the second discharge is less than 50%. Thus, it appears that metal borohydride based systems require further improvements in order to yield results comparable to those obtained for the metal alanates.

3.2. Complex Metal Hydrides as Electrolytes

Metal borohydrides have recently been employed as a new class of solid-state electrolytes for batteries [174,175] and the main advantages of light-weight CMHs are: (i) low material density compared to similar oxides and chalcogenides (can be two to three times lower); (ii) thinner solid state electrolytes, hence (i) and (ii) provide higher battery energy density; (iii) safer batteries because flammable organic ionic liquids and polymeric electrolytes are avoided; and (iv) easier assembly of all-solid-state batteries [176].

Research on metal borohydrides and derivatives, oxides and chalcogenides as solid state electrolytes have been mainly focused on mono-valent alkali metals, Li$^+$ and Na$^+$. Indeed, multivalent cations, e.g., Mg$^{2+}$, Ca$^{2+}$, and Al$^{3+}$, may further increase the energy density of solid state batteries. However, development of fast ion conductors for these cations is challenging due to much larger charge density as compared to mono-valent cations. Therefore, very large, low charge density anions, such as closo-boranes, $B_{12}H_{12}^{2-}$, or closo-carboranes, $CB_{11}H_{12}^{-}$, may prove useful for design of new electrolytes.

The high-temperature polymorph $h$-LiBH$_4$ was among the first metal hydrides to be discovered as fast ion conductors with Li$^+$ conductivity of the order of $10^{-3}$ S cm$^{-1}$ at $T > 115$ °C [177]. Attempts to stabilize the high-temperature polymorph at room temperature were successful by halide-substitution of the borohydride group, i.e., $h$-Li$(BH_4)_{1-x}I_x$ [178–180]. Reversible Mg stripping/plating has been demonstrated using Mg$(BH_4)_2$ as an electrolyte in THF and dimethoxyethane solutions [181]. However, the conductivity of solid state Mg$(BH_4)_2$ is very low (<$10^{-12}$ S cm$^{-1}$ at 30 °C) [182] but may be enhanced in double anion compounds, e.g., Mg$(BH_4)(NH_2)$ has a Mg$^{2+}$ conductivity of $1 \times 10^{-6}$ S cm$^{-1}$ at $T = 150$ °C [183]. Recently, the addition of ethylene diamine, NH$_2$(CH$_2$)$_2$NH$_2$ (en), to Mg$(BH_4)_2$ resulted in the formation of cis-Mg(en)$(BH_4)_2$ which shows ion conductivity between $5 \times 10^{-8}$ and $6 \times 10^{-5}$ S cm$^{-1}$ in the temperature range 30 to 70 °C, respectively [182]. So far, the most promising compounds are Na$_2$B$_9$H$_{19}$ and Na$_3$B$_{12}$H$_{22}$, which show superionic conductivity in the high-temperature polymorphs (phase transition at 87 and 207 °C, respectively) with Na ion conductivity of ~0.01 and 0.1 S cm$^{-1}$, respectively [184,185].

Intermolecular anion substitution in metal borohydrides has been explored as a valuable technique for tailoring physical and chemical properties [3]. The heavier halides have provided a wide range of metal borohydride halides with either fully ordered, e.g., KZn$(BH_4)_2$Cl or Sr$(BH_4)_2$Cl [92,186], partly ordered, e.g., NaY$(BH_4)_{2-x}Cl_{2-x}$ [187,188], or disordered structures, e.g., K$_2$Zn$(BH_4)_3Cl_{1-x}$ [189]. The smaller fluoride ion can substitute for the hydride ion, i.e., intramolecular anion substitution, F$^- \rightarrow$ H$^+$, in the BH$_4^-$ complex and the composite NaBH$_4$-NaBF$_4$ provided the first fluoride-substituted borohydride, NaBH$_2$F$_{1.9}$, observed in the temperature range of 200–215 °C [190,191].

Recently, a new class of Li ion conductors was discovered, Li$^+$ at La, Ce, Pr, Nd, Sm, Gd, with an interesting new structure type [115,192–194]. The structure reveals disordered Li$^+$ ions that occupy only 2/3 of the 12d Wyckoff sites, but a fully ordered anion lattice. The Li$^+$ ion conductivity for LiCe$(BH_4)_2$Cl was measured to be $1.03 \times 10^{-4}$ Scm$^{-1}$, at 20 °C [115]. Additionally, solid-state $^3$H, $^{11}$B, and $^{7}$Li NMR measurements of spin-lattice relaxation rates of LiLa$(BH_4)_2$Cl reveal two types of dynamics on the same frequency scale, i.e., Li$^+$ diffusion and reorientational motion of BH$_4^-$ groups. Therefore the Li-ion diffusion and the dynamics of BH$_4^-$ complexes appear to be
correlated, which suggests a paddle wheel mechanism is responsible for fast ionic mobility [195, 196]. Anion substitution in this class of materials is also possible, i.e., LiLa(BH$_4$)$_3$X, X = Cl, Br, I, which may open new possibilities for improvement of ion conductivity by tailoring the structural aperture for cation diffusion in the solid materials [197, 198].

New types of double anion hydride-oxides, i.e., containing BH$_4^-$ and BO$_3^{3-}$, have also been discovered recently [199, 200], which may suggest formation of new types of hydrides containing, also SO$_4^{2-}$, PO$_4^{3-}$, or PS$_4^{3-}$, which may be compatible with known electrode materials.

A new class of silver closo-boranes was discovered recently, Ag$_2$B$_2$H$_{12}$ and Ag$_2$B$_{10}$H$_{16}$, with high ion conductivities. Anion substitution with iodine stabilizes a high temperature polymorph with ion conductivity up to 3.2 mS cm$^{-1}$ at room temperature [201]. Partly or fully halogenated closo-boranes may in future be useful to create new materials with higher conductivities [202, 203].

Substitution of a boron atom with a carbon atom in closo-boranes leads to the formation of closo-carboranes, e.g., CB$_{11}$H$_{12}^-$ with even lower charge density. Particularly, LiCB$_{11}$H$_{12}$ and NaCB$_{11}$H$_{12}$ have lower polymorphic transition temperatures (127 and 107 °C, respectively) compared to the analogues Li$_2$B$_2$H$_{12}$ and Na$_2$B$_2$H$_{12}$ (342 and 256 °C, respectively) while showing some of the most promising Li and Na ion conductivities of $>$ 0.1 S cm$^{-1}$ yet observed [204].

4. Complex Metal Hydrides for Thermal Energy Storage

There are thousands of metals, metal alloys and compounds that can reversibly react with gaseous hydrogen [205] at temperatures as low as $-100$ °C (TiCr$_{12}$H$_{3.5}$ [206]) and as high as 1100 °C (LaH$_x$ [207]). The absorption of hydrogen is an exothermic process that releases heat while the desorption of hydrogen is an endothermic process that absorbs heat and the direction of the reaction can be controlled by changing either the hydride temperature or hydrogen pressure. This property of metal hydrides means that they can be exploited for a wide range of closed-loop energy storage and energy transformation applications including as; H$_2$ compressors; hydride heat engines, actuators and temperature sensors; thermochemical heat storage; heat pumping and thermally driven refrigeration. In fact, many of the relevant engineering principles were developed and proven during the 1970s and 1980s based on the high-cost, low capacity intermetallic hydrides known at the time. Extensive reviews on the progress of metal hydrides for these applications have been published [208–211]. However, a consistent road block to the commercialisation of metal hydrides for these applications has been the relatively low H$_2$ capacity and high cost of traditional intermetallic hydrides based on transition metals [210].

With the commercialization of concentrating solar power plants (CSPs) incorporating molten nitrate salts heat storage and, in conjunction with the U.S. Department of Energy SunShot Initiative to drive down the cost of solar electricity [212], there has been a renewed focus on the potential of low-cost, high-temperature metal hydrides to be the second generation of CSP heat storage materials that can operate at temperatures above 600 °C [213–217]. This is because the thermochemical heat storage capacity of metal hydrides can exceed the sensible heat storage capacity of molten salts by a factor of $>$ 10 [216]. In fact, the theoretical thermochemical heat storage capacity of some metal hydrides, such as LiH and CaH$_2$, are only exceeded by methane reforming reactions [214, 218]. Specific details about the energy cycle for using metal hydrides as high temperature heat storage materials for CSP can be found elsewhere [67, 214, 219–222]. Besides the intermetallic hydrides first considered for heat storage in the 1970s and 1980s, most of the research on metal hydrides for high temperature heat storage (T $>$ 400 °C) has focused on a few particular sub-sets. These include: simple binary/ternary hydrides and their partially fluorinated analogues [216], such as MgH$_2$ [222–227], NaH/NaH$_{1-x}$F$_x$ [215, 218], NaMgH$_3$/NaMgH$_2$F [229, 230], and TiH$_x$ [213]; destabilized binary hydrides, such as LiH-Al [231], xLiH-Si [232, 233], and CaH$_2$-Al [234] and; complex transition metal hydrides, such as Mg$_2$NiH$_4$ [235, 236], Mg$_2$FeH$_6$ [236, 237], Mg$_2$CoH$_3$, and Mg$_2$CoH$_{11}$ [236]. The high thermodynamic stability in conjunction with their high hydrogen capacity make CMHs intriguing candidates as thermochemical heat storage materials for CSP and for industrial waste heat recovery.
and utilization. Despite this, CMHs have rarely been considered for heat storage applications with examples in the literature limited to: the Li$_2$NH/Li$_4$NH system [238]; Na$_3$AlH$_6$, Na$_2$LiAlH$_6$ and K$_2$NaAlH$_6$ [215] and; 6LiBH$_4$ + CaH$_2$ [239].

For this review, we have used the thermodynamic data reported in the literature for the H$_2$ absorption/desorption from CMHs to calculate properties relevant for heat storage, Figure 4a,b and Table 2. Figure 4a shows the theoretical gravimetric and volumetric heat storage capacities of 15 CMH systems compared to other well-known: (1) thermochemical heat storage materials (TCMs) based on metal hydrides, carbonates, hydroxides and oxides; (2) phase change materials (PCMs) and; (3) sensible heat storage materials (SHMs). Another important factor in determining the suitability of a metal hydride for a particular application is the H$_2$ equilibrium pressure which increases exponentially with temperature. Figure 4b shows the temperature dependent H$_2$ equilibrium pressure for the CMH systems, with NaH, MgH$_2$, Mg$_2$NiH$_4$, Mg$_2$FeH$_6$ and TiH$_{1.0–1.6}$H included as comparisons. The H$_2$ equilibrium pressures have been plotted up to a value of 150 bar except for where thermodynamic data is not available, i.e., above the melting point of NaBH$_4$.

Figure 4. (a) Theoretical volumetric heat storage capacities versus gravimetric heat storage capacities for complex hydrides with a number of other heat storage materials included for comparison; (b) Hydrogen absorption equilibrium pressures of complex hydrides versus temperature. Data for some well-known heat storage metal hydrides are included as a comparison. Open symbols refer to data for complex hydrides. TCM = thermochemical heat storage material, PCM = phase change heat storage material, SHM = sensible heat storage material.

Figure 4a shows that the theoretical gravimetric and volumetric heat storage capacities of LiBH$_4$ (4936 kJ/kg and 3296 kJ/L at 727 °C [240]), NaBH$_4$ (5176 kJ/kg and 5559 kJ/L at 507.5 °C [241]) and KBH$_4$ (4248 kJ/kg and 4986 kJ/L at 615.5 °C [241]) are some of the highest known for a gas-solid thermochemical reaction. Only LiH (8389 kJ/kg and 6543 kJ/L at 938 °C [241]) and CaH$_2$ (3857 kJ/kg and 7374 kJ/L at 1018 °C [241]) have theoretical gravimetric and/or volumetric heat storage capacities that are higher. However, the theoretical operating temperatures for LiBH$_4$, NaBH$_4$ and KBH$_4$ are well within the target window of 600–800 °C for next generation CSP [212], whereas LiH and CaH$_2$
Table 2. Properties of complex metal hydrides compared to selected heat storage materials. * Volumetric heat storage capacity (in kJ/L) calculated based on the room-temperature crystalline density of materials unless otherwise noted. # The operating temperature ranges correspond to H2 equilibrium pressures that range between 1 bar and 150 bar unless otherwise noted.

<table>
<thead>
<tr>
<th>Hydride Materials</th>
<th>Theoretical H2 Capacity (wt.%)</th>
<th>ΔHf (kJ/mol, H2)</th>
<th>kJ/g</th>
<th>°C</th>
<th>Operating Temperature Range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBH4 ↔ Na + H2 + 2/3 H2O</td>
<td>3.7</td>
<td>284.4 ± 35.2 [24]</td>
<td>681.8</td>
<td>680.3</td>
<td>25–202</td>
</tr>
<tr>
<td>LiAlH4 ↔ Li + Al + 3/2 H2</td>
<td>2.86</td>
<td>47.6 ± 46.1 [42]</td>
<td>678.0</td>
<td>935.0</td>
<td>100–290</td>
</tr>
<tr>
<td>LiAlH4 ↔ 2LiH + Al + 3/2 H2</td>
<td>3.52</td>
<td>54.9 ± 5.4 [364]</td>
<td>595.0</td>
<td>1374</td>
<td>135–325</td>
</tr>
<tr>
<td>NaBH4 ↔ 2BH3 + NaH + Al + 3/2 H2</td>
<td>2.25</td>
<td>94.8 ± 90.4 [24]</td>
<td>1093.5</td>
<td>1831.8</td>
<td>280–450</td>
</tr>
<tr>
<td>KAlH4 + Li2CO3 ↔ Li2Al + 3/2 H2</td>
<td>2.09</td>
<td>37.6 ± 37.6 [5]</td>
<td>501.2</td>
<td>729.2</td>
<td>111–396</td>
</tr>
<tr>
<td>KAlH4 + Na → NaH + Al + 3/2 H2</td>
<td>2.19</td>
<td>42.5 ± 42.5 [5]</td>
<td>726.4</td>
<td>1111.8</td>
<td>334–574</td>
</tr>
<tr>
<td>Mg(H2)2 ↔ Mg + H2</td>
<td>5.58</td>
<td>58.9 ± 5.4 [24]</td>
<td>2093.3</td>
<td>2166.5</td>
<td>75–250</td>
</tr>
<tr>
<td>LiNH2 + LiH ↔ Li2 + H2</td>
<td>6.52</td>
<td>64.5 ± 5.2 [324]</td>
<td>912.6</td>
<td>2086.1</td>
<td>270–375</td>
</tr>
<tr>
<td>Mg + H2O ↔ MgO + H</td>
<td>2.07</td>
<td>6.4 ± 6.4 [72]</td>
<td>1077.8</td>
<td>1257.3</td>
<td>750–850</td>
</tr>
<tr>
<td>LiBH4 + LiH + B + 3/2 H2</td>
<td>13.88</td>
<td>57.3 ± 57.2 [20]</td>
<td>9457.9</td>
<td>2634.9</td>
<td>460–600</td>
</tr>
<tr>
<td>LiBH4 + Na + B + 3/2 H2</td>
<td>13.94</td>
<td>71.3 ± 71.3 [24]</td>
<td>4906.8</td>
<td>3196.5</td>
<td>390–432</td>
</tr>
<tr>
<td>NaBH4 + Na → Na2 + 3/2 H2</td>
<td>10.66</td>
<td>87.0 ± 87.0 [24]</td>
<td>5176.0</td>
<td>5559.1</td>
<td>302.5</td>
</tr>
<tr>
<td>KLiH + B ↔ B3H3</td>
<td>7.47</td>
<td>114.6 ± 114.6 [24]</td>
<td>4293.1</td>
<td>4985.9</td>
<td>615–515</td>
</tr>
<tr>
<td>2LiBH4 + MgH2 ↔ 3LiH + 3H2</td>
<td>11.54</td>
<td>48.3 ± 48.3 [5]</td>
<td>2566.6</td>
<td>2590.0</td>
<td>205–467</td>
</tr>
<tr>
<td>NaBH4 + Na → Na2 + 3/2 H2</td>
<td>11.54</td>
<td>118.6 ± 118.6 [24]</td>
<td>2433.5</td>
<td>2535.7</td>
<td>427–438</td>
</tr>
<tr>
<td>MgBH4 + Mg + H2O</td>
<td>7.66</td>
<td>74.4 ± 74.4 [214]</td>
<td>2013.2</td>
<td>3944.2</td>
<td>262–354</td>
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<tr>
<td>LiBH4 + MgH2 ↔ 2LiH + 2/3 H2</td>
<td>3.62</td>
<td>64.4 ± 64.4 [25]</td>
<td>1197.9</td>
<td>3142.7</td>
<td>253–523</td>
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<tr>
<td>MgBH4 + Na → Na2 + 3/2 H2</td>
<td>5.47</td>
<td>77.4 ± 77.4 [515]</td>
<td>2101.1</td>
<td>5797.0</td>
<td>300–566</td>
</tr>
<tr>
<td>TiH4 + H2O ↔ 2H3 + 2H2</td>
<td>1.22</td>
<td>2.69 ± 2.69 [5]</td>
<td>1033.2</td>
<td>3727.0</td>
<td>645–921</td>
</tr>
</tbody>
</table>

Other Thermochemical Materials (TCM) | ΔHf (kJ/mol, H2O Gas) | kJ/g | °C | Temperature Range (°C) |
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCN2 ↔ CaH2 + 3/2 H2O</td>
<td>1730 ± 1736 [219]</td>
<td>1744</td>
<td>2550.0</td>
<td></td>
</tr>
<tr>
<td>CaH2 + 3/2 H2O ↔ CaCN2</td>
<td>1024 ± 3024 [219]</td>
<td>1404</td>
<td>3950–3900</td>
<td></td>
</tr>
<tr>
<td>2Ca(H2)2 ↔ CaH2 + 2H2O</td>
<td>2050 ± 2050 [219]</td>
<td>844</td>
<td>1324</td>
<td></td>
</tr>
<tr>
<td>2NaH + 3/2 H2O ↔ Na2H + H2</td>
<td>777 ± 777 [219]</td>
<td>469</td>
<td>2316.1</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Phase Change Materials (TCM)</th>
<th>ΔHf</th>
<th>kJ/mg</th>
<th>°C</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>l → s (LiH)</td>
<td>27.0 ± 27.0 [210]</td>
<td>1041</td>
<td>2747.2</td>
<td>849</td>
</tr>
<tr>
<td>l → s (LiH)</td>
<td>20.9 ± 20.9 [42]</td>
<td>463</td>
<td>968.8</td>
<td>603</td>
</tr>
<tr>
<td>NaAlH4</td>
<td>48.2 ± 48.2 [210]</td>
<td>402</td>
<td>1033.4</td>
<td>801</td>
</tr>
</tbody>
</table>

"n.a. = data not available. * The lower temperature limit is based on the thermodynamics of the system. In practice, however, temperatures above ~100 °C are required for reasonable kinetics. ** NaAlH4 is molten above 183 °C [243]. † Upper temperature potentially limited by melting point of NaH, ~638 °C [241], and KH, ~619 °C [241], decomposition products. There are some indications that NaH and KH may also form a eutectic melt at a temperature as low as 280 °C [246]. ‡ There are some discrepancies in the reported thermodynamics for KAIH4. The enthalpy of formation of KAIH4, ΔHf = −175.4 kJ/mol, was taken as the average of the values reported in [241,251] while the entropy of KAIH4, S° = 120.9 J/mol K, was taken as the average of the values reported in [241,252]. § At ~574 °C, decomposition directly to liquid sodium metal rather than solid NaH becomes thermodynamically preferred according to the reaction KAIH4 + NaCl + KCl + Na(s) + H2(g). The H2 equilibrium pressure at this temperature is ~332 bar. ¶ Limited to melting point of LiH < 375 °C [253]. ‖ Calculated up to the α-CaH2 to β-CaH2 phase transition at 780 °C [241]. At this temperature, the H2 equilibrium pressure for the reaction CaH2 + Al + H2O ↔ CaO + Al + 2H2(g) is ~100 bar. The H2 equilibrium pressure for the 6LiBH4(l) + CaH2 ↔ 6LiH(1) + CaB6 + 10H2(g) system is ~132.4 bar. © The melting point of LiH is ~688 °C. The enthalpy and entropy of melting are ΔHm = 21.8 kJ/mol and ΔSm = 22.6 J/mol K, respectively [241]. † The melting point of NaBH4 is 507.5 °C, which is taken as the average of reference values [254,255]. This temperature corresponds to an H2 equilibrium pressure of ~0.26 bar [211]. The thermodynamics of molten NaBH4 have not been experimentally determined. ¶ Thermodynamic data source for: (1) LiBH4 is reference [240]; (2) Mg is reference [241]; (3) MgH2 is reference [256] and; (4) MgB2 is reference [257]. ‡ At 467 °C, the H2 equilibrium pressure is ~57.8 bar for the reaction between 2LiBH4 and MgH2. Above this temperature the direct decomposition of MgH2 becomes thermodynamically preferred which is then followed by the reaction of metallic Mg with LiBH4(l). †† Data is for solid NaH up to its melting point ~638 °C [307,241]. The H2 equilibrium pressure at this temperature is ~106.5 bar. ‡‡ The operating temperature range is limited to ~400 °C due to Mg sintering and capacity loss above this temperature [258]. ‡§ Enthalpy and entropy for the reaction TiH1.5 – TiH0.3H2(g) calculated using data extracted for 527 °C ≤ T ≤ 707 °C from Figure 2 on p 241 of [207]. ‡ The operating temperature range corresponds to a CO2(g) partial pressure of between 0 and 10 bar [218]. ‖ The operating temperature range corresponds to a CO2(g) partial pressure of between 0 and 1 bar [218]. ″ Weighted average of the values for NaN3O6(1) (1.83 kJ/kg K), and KNO3(1) (1.22 kJ/kg K), respectively [259]. ‡ Due to the substantial volume change upon melting, the volumetric heat storage capacity at 400 °C, ρ = 1.84 g/cm3 [261]. It has also been included for 60 wt % NaN3O6/40 wt % KNO3.
Complex Metal Hydrides and Fuel Cell Applications

An emerging research direction is that of CMHs as H₂ storage materials for stationary fuel cells (FCs) for clean power generation in seasonal storage, remote area and off-grid applications [261–264]. Unlike the closed-loop applications discussed in Section 4, this application utilizes an electrolyser to produce H₂, which is stored (e.g., in a metal hydride) until the consumption of hydrogen by the fuel cell is required for electricity production. Interest in the use of classic intermetallic hydrides for this role began in the 1990s [261,262] and an in-depth review of the principles and progress on the use of metal hydrides in fuel cell applications has recently been published [264]. Some of the advantages of energy storage based on a photo voltaic (PV)-electrolyser-H₂ storage-fuel cell configuration over a PV-Li ion battery system include:

Self-discharge: All batteries steadily lose charge over time and the self-discharge rate of Li-ion is highly dependent on temperature and the state-of-charge (SOC). The higher the temperature/SOC, the higher self-discharge rate [265]. The self-discharge rate of Li-ion batteries is usually 3–5% a month [265]. However, ageing of the battery may influence the self-discharge rate significantly [266]. In comparison, metal hydrides do not undergo “self-discharge” and can store their “charge” indefinitely.

Safety: Li-ion batteries suffer from lithium dendrite formation which may lead to short-circuit of the battery. Additionally, the organic electrolyte is hazardous in the presence of an oxidizing agent, which may result in runaway reactions and the battery catching fire or exploding [267]. The classic intermetallic hydrides first studied at near-ambient temperatures in combination with FCs have intrinsic safety due to their modest H₂ pressures and operating temperatures combined with the endothermic nature of the H₂ release process [264]. A more complicated scenario is presented by CMHs due to the fact that they are, in general, strong reducing agents, and many have the potential to be flammable or pyrophoric upon contact with air or water. However, in practical applications CMHs are typically used in the form of dense compacts and research on these has shown that they only undergo a mild temperature increase on exposure to air, and that direct immersion in water results in a mild temperature increase combined with slow release of H₂ [268,269]. A comprehensive determination of the safety of CMHs would require performing reactivity testing at their practical operating temperatures.

Deep discharge: Unlike rechargeable batteries [270], metal hydride systems do not, in general, suffer capacity loss from being fully discharged [263].

Longevity: A battery’s cycle life is defined as the number of cycles until the capacity reaches 80% of its initial reversible value [271]. Commonly, Li-ion batteries have a cycle life between 1000 and 4500 cycles, i.e., a lifetime between 7 and 20 years [272]. Li-ion batteries with a 95% retention after 30,000 cycles have been discovered, however, at the expense of energy density [273], which is a severe drawback. In comparison, LaNi₅ showed no capacity loss over 3300 cycles when using a H₂ purity above 99.9999% [274]. Furthermore, TiFe₀.₈Ni₀.₂ showed only a 16% capacity loss after 65,000 cycles: equivalent to a ~178 year product lifetime based on a daily cycling regime [275]. The biggest issue so far for the CMHs is the reversibility and cyclic stability and much less long term cycling has been performed.

System size: As the energy density of CMHs is much higher than for Li-ion batteries, the system size of a stationary energy storage system will be much denser [263]. Additionally, the mass of an extensive Li-ion battery capable of storing large amounts of energy is considerable [276].

An additional benefit of thermally integrating CMHs with moderate- and high-temperature FCs is that, by consuming a significant fraction of the waste heat generated, the CMHs could actually improve the thermal control of high-temperature FC stacks [264].

One of the original driving forces for reducing the operating temperature of high capacity CMHs was that they could be used in mobile applications/passenger vehicles, where the waste heat (~80 °C) of Low Temperature Proton Exchange Membrane Fuel Cells (LT-PEMFCs) could
be used to release $\text{H}_2$ for FC consumption. However, $\text{H}_2$ storage in complex hydrides with high thermodynamic stability is less of an issue for stationary applications as a number of different types of fuel cells are available that operate in different temperature ranges (AFC = Alkaline Fuel Cell, HT-PEMFC = High-Temperature Proton Exchange Membrane Fuel Cell, PAFC = Phosphoric Acid Fuel Cell, MCFC = Molten Carbonate Fuel Cell, SOFC = Solid Oxide Fuel Cell). Consequently, using complex hydride systems such as NaAlH$_4$ [277–282] and Mg(NH$_2$)$_2$ + 2LiH [283] in conjunction with HT-PEMFCs is now being investigated. The integration of SOFCs with MgH$_2$ [284–288], a metal hydride that historically suffered from high thermodynamic stability and poor kinetics, highlights the potential of CMHs for this application.

The different types of FCs are characterized by different operating temperatures as well as different efficiencies. The efficiency of the FC determines the amount of waste heat generated, $Q_{\text{loss}}$, which can be used to release $\text{H}_2$ from the metal hydride provided it exceeds the enthalpy of desorption, $\Delta H_{\text{des}}$. The potential for thermal integration of a CMH with a particular type of FC can be assessed by considering their respective operating temperatures and the amount of waste heat available in comparison to that required to release $\text{H}_2$ from the CMH. Figure 5 presents this comparison for the CMH systems and NaH, MgH$_2$, Mg$_2$NiH$_4$, Mg$_2$FeH$_6$ and TiH$_{1.0–1.6}$. It also includes the general range that applies to intermetallic hydrides, as a comparison, since most fuel cell integration research has been performed with these types of hydrides. Not all metal hydrides are suitable as $\text{H}_2$ storage materials when paired with FCs. As an example, TiH$_{1.0–1.6}$ would not be appropriate for use with any of the fuel cells, regardless of type, as the thermal energy required for $\text{H}_2$ release, exceeds the waste heat available from the fuel cell.

**Figure 5.** Potential of various metal hydrides, based on their $\text{H}_2$ enthalpy of desorption ($\Delta H_{\text{des}}$), and the associated heat loss ($Q_{\text{loss}}$) of different types of fuel cells. The operating temperature range of the metal hydrides corresponds to $\text{H}_2$ absorption equilibrium pressures of between 1 and 150 bar unless otherwise noted in Table 2. The step changes that occur for the NaH and LiBH$_4$ curves are a result of a phase change for either one of the reactants or products. This figure is based on that from reference [264].

The choice of CMH for $\text{H}_2$ storage when paired with a particular FC will be dependent on the application under consideration. Some of the potential deciding factors include: CMH cost; cost and
complexity of thermal integration between the CMH and FC; CMH footprint/volume; CMH operating temperature range; \( H_2 \) equilibrium pressure of the CMH; \( H_2 \) sorption kinetics of the CMH as a function of temperature and; the amount of FC waste heat available. The supply of \( H_2 \) from CMHs with operating temperatures below ~250 °C requires only modest energy input where simple heat transfer solutions with low-efficiency, but low-cost, can be implemented. In principle, metal hydrides that operate at either low- or high-temperature are suitable for use with high-temperature fuel cells (MCFCs and SOFCs).

Figure 5 shows that, in general, the classic intermetallic hydrides are suitable for use with low- and moderate-temperature FCs (i.e., ~250 °C and below), including LT- and HT-PEMFCs, AFCs and PAFCs. In contrast, of all the CMH systems, only NaAlH\(_4\) and the Mg(NH\(_2\))\(_2\) + 2LiH system can theoretically operate at low enough temperatures for use with a LT-PEMFC. However, in practice, these systems only display sufficient \( H_2 \) sorption kinetics above ~100 °C, which excludes their practical use with LT-PEMFCs. The CMH systems based on Na\(_3\)AlH\(_6\), Na\(_2\)LiAlH\(_6\) and KAlH\(_4\) + LiCl can also, in theory, operate with the low- and moderate-temperature FCs other than LT-PEMFCs. Of these systems, uncatalyzed KAlH\(_4\)-LiCl also has kinetic limitations with the maximum rate of \( H_2 \) release only achieved at ~230 °C [247]. Figure 5 also shows that all of the CMHs can potentially be used for \( H_2 \) storage when paired with MCFCs and SOFCs. The choice of CMH would then be determined by the best match of the FC operating conditions, CMH properties and the application requirements.

To summarize, the high thermal stability of CMHs makes them attractive as heat storage materials as the energy density may be tenfold higher than current state-of-the-art materials. Secondly, CMHs in combination with a fuel cell for stationary energy storage, have several advantages compared to commercially available Li-ion batteries, e.g., no self-discharge, higher safety and energy density.

5. Conclusions

The chemistry of complex metal hydrides is extremely diverse, and has provided a wide range of novel materials in the past decade. Especially metal borohydrides with gravimetric hydrogen density of >10 mass %, have received increasing interest as solid state hydrogen storage materials. Furthermore, these materials have extremely rich chemistry based on structural flexibility and a wide range of elemental compositions.

The potential of complex metal hydrides for use in a range of new applications have also been highlighted in this review, see Figure 6. Examples are: as electrodes or electrolytes in solid state batteries, e.g., the high-temperature polymorph of Na\(_2\)B\(_12\)H\(_{12}\) which has a high ionic conductivity; thermal energy storage, e.g., at 507.5 °C NaBH\(_4\) has theoretical gravimetric and volumetric heat storage capacities of 5176 kJ/kg and 5559 kJ/L, respectively; and fuel cell applications. Indeed, many other properties, e.g., optical and magnetic properties are also promising and have been discovered in the metal borohydrides CsEu(BH\(_4\))\(_3\) and K\(_2\)Gd(BH\(_4\))\(_5\) as fluorescent and magnetocaloric properties, respectively [123,289]. Furthermore, the metal closo-boranes, Ag\(_2\)B\(_{10}\)H\(_{10}\) and Ag\(_2\)B\(_{12}\)H\(_{12}\), display photosensitivity analogous to silver halides and forms silver nanofilaments upon electron beam exposure [201].

Hopefully, new metal borohydrides will be possible to design with desired chemical composition, atomic coordination, and exciting properties, based on the extensive knowledge about novel compounds, e.g., new combinations of light elements and boron, nitrogen or aluminum in complexes with hydrogen may lead to new interesting possibilities in applications.
**Figure 6.** State-of-the-art applications for complex metal hydrides [1,123,290–292].

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