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# Complex hydrides for hydrogen storage – new perspectives

Morten B. Ley<sup>1</sup>, Lars H. Jepsen<sup>1</sup>, Young-Su Lee<sup>2</sup>, Young Whan Cho<sup>2</sup>, José M. Bellosta von Colbe<sup>3</sup>, Martin Dornheim<sup>3</sup>, Masoud Rokni<sup>4</sup>, Jens Oluf Jensen<sup>5</sup>, Mikael Sloth<sup>6</sup>, Yaroslav Filinchuk<sup>7</sup>, Jens Erik Jørgensen<sup>8</sup>, Flemming Besenbacher<sup>9</sup> and Torben R. Jensen<sup>1,\*</sup>

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

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

<sup>3</sup> Helmholtz-Zentrum Geesthacht, Department of Nanotechnology, Max-Planck-Straße 1, 21502 Geesthacht, Germany

<sup>4</sup> Department of Mechanical Engineering, The Technical University of Denmark, Nils Koppels Allé 403, 2800 Kgs. Lyngby, Denmark

<sup>5</sup> Department of Energy Conversion and Storage, Technical University of Denmark, Kemitorvet 207, DK-2800 Kgs. Lyngby, Denmark

<sup>6</sup> H2 Logic A/S, Industriparken 34 B, DK-7400 Herning, Denmark

<sup>7</sup> Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Place L. Pasteur 1, B-1348 Louvain-la-Neuve, Belgium

<sup>8</sup> Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

<sup>9</sup> Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, Aarhus University, Ny Munkegade 120, DK-8000 Aarhus C, Denmark

Since the 1970s, hydrogen has been considered as a possible energy carrier for the storage of renewable energy. The main focus has been on addressing the ultimate challenge: developing an environmentally friendly successor for gasoline. This very ambitious goal has not yet been fully reached, as discussed in this review, but a range of new lightweight hydrogen-containing materials has been discovered with fascinating properties. State-of-the-art and future perspectives for hydrogen-containing solids will be discussed, with a focus on metal borohydrides, which reveal significant structural flexibility and may have a range of new interesting properties combined with very high hydrogen densities.

## Introduction

The first *wake-up call* drawing attention toward our fossil fuel dependencies and the vulnerability of our present energy system came in 1973 with the oil crisis. And a second came after the turn of the millennium with increased focus on climatic changes due to increasing levels of carbon dioxide in the atmosphere. Since the start of industrialization the global energy demand has increased exponentially and is expected to increase by ~75% in the period 2000–2030, partly due to the expanding world population, which might reach 8 billion people within the same time frame. Despite the extreme human energy consumption there is plenty of renewable energy available to us. The sun is the primary renewable energy source for the earth and the energy influx is 8000 times larger than the total human energy consumption. This energy is

created by the fusion of 600 million tons of *hydrogen* per second forming helium in the sun. A major inconvenience is that renewable energy sources such as sunlight and wind fluctuate strongly over time and geography, and the most difficult challenge appears to be the development of efficient and reliable long-term storage, over days, weeks and months [1]. Perhaps, someday, humans will convert some of this renewable energy back to *hydrogen*, which is considered a promising future *energy carrier* [2,3]. Electricity, which is the other main energy carrier of today (beside hydrocarbons), cannot presently be stored efficiently in large amounts, so production and consumption must be maintained in a very delicate balance [4,5].

The idea of creating a *hydrogen society* was initially proposed by a Danish scientist, Poul La Cour (1846–1908), who utilized hydrogen for the storage of wind energy as early as 1895 and produced up to 1000 L H<sub>2</sub>/h, which was stored in a gas tank [6]. In this scenario,

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

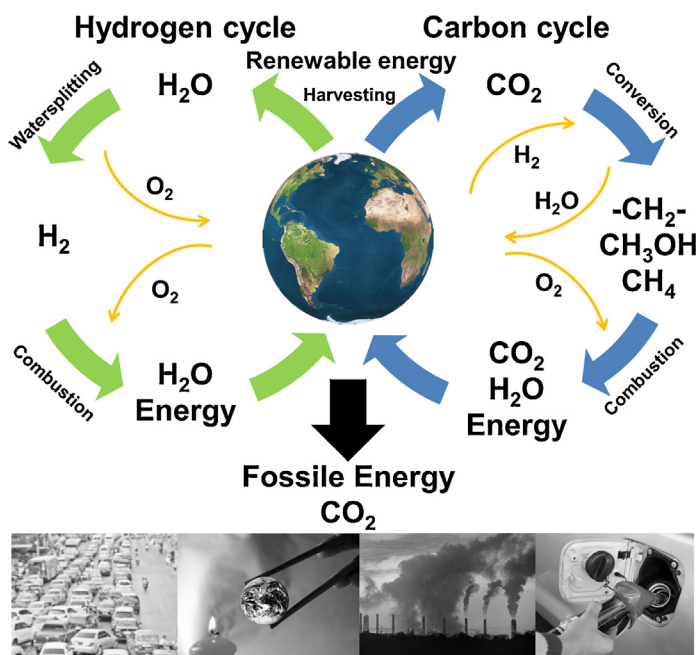


FIGURE 1

Water can be 'split' into oxygen and hydrogen (green arrows) either electrochemically from 'renewable' electricity or in future maybe by direct photocatalytic water splitting [10,11]. Most of the energy used in this process can be released again when hydrogen reacts with oxygen providing 120.0 MJ/kg  $H_2$  (lower heating value) either in a fuel cell or an internal combustion engine. A carbon-based energy carrier system is also illustrated (blue arrows) but hydrocarbons are currently energy-consuming and difficult to produce from biomass or  $CO_2$  from the atmosphere and hydrogen from renewable sources [12]. However, this may be possible in the future. Notice, a sustainable future can only be created with closed materials cycles for all chemicals and materials that we use. Today, most materials are unfortunately 'single-use' and not re-cycled. Likewise,  $CO_2$  produced from fossil fuels is discarded into the atmosphere symbolized by personal vehicles and industrial emission ultimately leading to global warming (black arrow, picture row) [13].

hydrogen is produced using renewable wind energy, which can then be conveniently transported as a gas, stored and utilized as an *energy carrier*. This is illustrated in Fig. 1. In fact, 'city gas' containing about 50% hydrogen, was used for ca. 100 years from mid-1800 to mid-1900 and was transported in cast iron pipe lines [7]. The first 240 km steel pipe lines for pure hydrogen was established in 1938 in the Rhine-Ruhr district in Europe and is still in operation. Today, there are about 1600 km pipelines for distribution of hydrogen in Europe and ca. 900 km in North America, which was also an argument for suggesting hydrogen as an energy carrier in the late 1960s [8,9] (Text box 1).

In the industrialized world a large fraction of the total energy consumption is used for transportation, e.g.  $\sim 2/3$  in the USA and  $\sim 1/4$  in the EU [15,16]. The U.S. Department of Energy (DOE) has invested significant effort in the research and development of hydrogen storage for mobile applications and published important documents and targets mainly based on present day vehicles as well as demands from the automobile industry [16–19]. Furthermore, fossil fuels are indirectly subsidized by neglecting the impacts on human health, the cost of increased healthcare from noxious emissions and the segregation of greenhouse gasses from the atmosphere to avoid climate change, which hamper and often bias direct economical comparisons with renewable, sustainable

## TEXT BOX 1

Hydrogen is the most abundant element and accounts for  $\sim 90\%$  of all atoms in the universe and  $\sim 15\%$  on the surface of earth and occurs in compounds like water, natural gas and biomass, but rarely as a free element. Hydrogen forms kinetically stable mixtures with oxygen similar to natural gas and is a nonpoisonous, odorless, colorless and tasteless gas [14]. Hydrogen, the lightest element of all ( $Z = 1$ ), has the largest gravimetric energy density of all chemical substances, a factor  $\sim 3$  higher than gasoline. Unfortunately, hydrogen has a very low density both as a gas and as a liquid, i.e. 0.0899 g/L in gaseous state (at 20 °C and 1 bar, which is 7% of the density of atmospheric air) and 70.8 g/L as a liquid at  $-253$  °C (7% of the density of water) [15,16]. Therefore, the volumetric energy density of hydrogen is very low, which is a fundamental drawback for the utilization of hydrogen as a gas or liquid, in particular for mobile applications.

energy systems [20]. A multitude of criteria must be satisfied, simultaneously; the storage must be lightweight and compact, still with significant capacity to allow long-range use but also safe, inexpensive and should allow rapid refueling. The latter appears as one of the most difficult challenges, since heat is released during hydrogen absorption in a solid.

Despite significant research effort and advances within solid-state hydrogen storage, a material that fulfills all the demands simultaneously and can act as the successor for gasoline in mobile applications has not yet been discovered [21–25]. Nevertheless, a variety of novel materials with fascinating structures and properties have been discovered, which will be illustrated in this review and in another paper in this issue of *Materials Today*.

Today, the leading car manufacturers focus on on-board compressed hydrogen gas storage (700 bar) mainly due to fast refueling ( $< 3$  min) and it being a mature technology. This also opens a new research field to be explored: solid-state hydrogen storage at  $p(H_2) = 300\text{--}700$  bar. The combination of high-pressure tanks and metal or complex hydrides working in a suitable temperature-pressure range could help fulfill the targets for volumetric storage density. This is the focus of a research initiative funded by the Danish Council for Strategic Research via the project HyFillFast [26].

### Solid-state hydrogen storage – how it began

The interstitial metal hydrides (MH) formed by the heavier *d*- and *f*-block metals and some alloys have received significant attention due to reversible hydrogen storage at moderate conditions. Unfortunately, the gravimetric hydrogen storage density is low, typically 1–2 wt%  $H_2$ , but the heat release upon hydrogen uptake is moderate,  $\Delta H_T \sim -30$  kJ/mol  $H_2$ , allowing relatively fast hydrogen uptake with cooling [21,22]. Moreover, from a chemical point of view the reaction is simple without any intermediate compounds, but with significant volume changes ( $\sim 20\%$ ). Clearly, mobile material handling applications, such as fork lifts, based on hydrogen stored in transition metal alloys and converted to electricity and heated by a fuel cell (FC) can compete on performance with similar lead acid battery technologies, e.g. no gradual loss of lifting power and much faster ( $> 20\times$ ) re-charging of the alloy with hydrogen. The replacement of 'empty' MH tanks at hydrogen refueling stations has also been suggested, which may

allow the heat released during refueling to be used for water electrolysis. The advantage may be faster recharging with a minor loss of cycling capacity compared to a lithium battery of similar mass. In colder places the H<sub>2</sub>-FC technology both provides heat and electricity, which may contribute to a similar driving range in both summer and winter [27]. Thus, MH may provide the highest 'round trip' energy efficiency compared to compressed or liquefied hydrogen [28].

Some metals and alloys, e.g. Pd and Pd<sub>0.8</sub>Ag<sub>0.2</sub>, absorb large amounts of hydrogen and simultaneously retain a high degree of ductility, hydrogen diffusion rate and practically negligible permeability of all other gases, including helium [29]. Thus, highly selective filters for production of ultra-pure hydrogen and for removing hydrogen from mixtures, such as natural gas and hydrogen transported in the natural gas grid may be produced. Other thin film MH reveal novel properties as sensors and 'smart windows', which change transparency as a function of hydrogen content [30].

### Magnesium-based hydrogen storage materials

Virtually limitless amounts of magnesium are available, i.e. 0.13 wt% in sea water and 2.7 wt% in the earth crust of this cheap and light metal ( $\rho = 1.74 \text{ g/cm}^3$ ). Magnesium hydride, MgH<sub>2</sub>, has both high gravimetric and volumetric hydrogen contents,  $\rho_m(\text{MgH}_2) = 7.6 \text{ wt\% H}_2$  and  $\rho_v(\text{MgH}_2) = 109 \text{ g H}_2/\text{L}$ , and a rutile structure, which suggests partly covalent bonding [14]. Unfortunately, magnesium hydride has a high exothermic formation enthalpy, i.e. unfavorable thermodynamics for mobile applications,  $\Delta H \sim -75 \text{ kJ/mol}$  and  $\Delta S \sim -135 \text{ kJ/mol}$  [38]. Several different approaches have been explored in order to improve the thermodynamics and kinetics for hydrogen release and uptake in magnesium hydride, e.g. nanoconfinement [39,40], nanostructuring by ball milling [41], utilization of catalytic additives [42] or alloying with different metals [43,44]. MgH<sub>2</sub> nanoparticles (~7 nm) embedded in a LiCl matrix and MgH<sub>2</sub> in a carbon aerogel (pore size ~7 and 22 nm) reveal improvement of the thermodynamic and kinetic properties, respectively [38,40]. Most additives appear to react in different ways, which usually improves the kinetics and may also influence the thermodynamics. The metals, Al, Cu and Pd, form alloys [45–47] and Ni and Fe form complex hydrides, i.e. Mg<sub>2</sub>NiH<sub>4</sub> or Mg<sub>2</sub>FeH<sub>6</sub> [48–50]. Halides, e.g. ScCl<sub>3</sub>, and oxides, e.g. Nb<sub>2</sub>O<sub>5</sub>, may be reduced to MH or metals, but also inert MgCl<sub>2</sub> or the very stable magnesium oxide MgO is formed, which significantly reduces the hydrogen storage capacity [51,52]. In contrast, magnesium in combination with a heat storage material (phase-change material) provides a safe and efficient method for stationary large-scale hydrogen storage (up to 700 kg), long lifetime (>5000 absorption/desorption cycles), without degradation of the hydrogen uptake capacity (>6.6 wt%) [53–55].

The high stability and high formation enthalpy of magnesium hydride and similar compounds can be utilized for heat storage in solar thermal power technology. By changing the applied hydrogen pressure or temperature an M/MH system may either absorb hydrogen and release heat, or release hydrogen and absorb heat. Thus, the large heat exchange involved in hydrogen release and uptake can be utilized to store solar energy and make it available also at night time [32,56].

### Complex hydrides

Clearly, the light elements and more covalent hydrides, BH<sub>3</sub>, AlH<sub>3</sub> and NH<sub>3</sub> have high energy densities, but are very difficult to handle safely and they decompose to very stable elements, B, Al and N<sub>2</sub>, which are very challenging to re-fuel with hydrogen on board a vehicle. All three compounds readily react with ionic hydrides, e.g. alkali MH, forming LiBH<sub>4</sub>, NaAlH<sub>4</sub> and LiNH<sub>2</sub> [57–59]. This class of material contains stable solids, which are more convenient to handle and consist of an electropositive counter ion and a coordination complex where hydrogen is covalently bonded, i.e. [BH<sub>4</sub>]<sup>−</sup>, [AlH<sub>4</sub>]<sup>−</sup> and [NH<sub>2</sub>]<sup>−</sup>. A significant paradigm shift occurred in the mid-nineties where Bogdanović observed hydrogen release and uptake for titanium-catalyzed sodium tetrahydridoalane, NaAlH<sub>4</sub> (often denoted sodium alanate), at moderate conditions [60]. Reversible nitrogen-based complex hydrides, e.g. based on LiNH<sub>2</sub>–Li<sub>2</sub>NH–LiH, were discovered by P. Chen in 2002 [61] while A. Züttel and K. Yvon and co-workers were among the first to investigate metal tetrahydrido-borates, e.g. LiBH<sub>4</sub> in 2003 [62,63]. This class of materials, known as *metal borohydrides*, is the focus of the remaining part of this review paper and new methods for tailoring structure and properties are discussed.

### Metal borohydrides

The initial interest in studies of metal borohydrides as possible hydrogen storage materials originates from their extreme hydrogen content and the fact that a correlation exists between the experimentally observed decomposition temperature and the electronegativity of the metal, which coordinates most strongly to the BH<sub>4</sub><sup>−</sup> groups [64,65]. This highlights the key role of the complex anions in the structural stability of bimetallic borohydrides [66]. The bonding in the complex anions, such as [Sc(BH<sub>4</sub>)<sub>4</sub>]<sup>−</sup> or [Zn<sub>2</sub>(BH<sub>4</sub>)<sub>5</sub>]<sup>−</sup> in MSc(BH<sub>4</sub>)<sub>4</sub> and MZn<sub>2</sub>(BH<sub>4</sub>)<sub>5</sub>, M = Li or Na, is mainly covalent with well-defined directionality, whereas dominantly ionic bonding exists in the solid state between the complex anions and counter cations [67–69]. The structures of mono-metallic borohydrides range from ionic to framework structures, e.g. Mg(BH<sub>4</sub>)<sub>2</sub> and Ca(BH<sub>4</sub>)<sub>2</sub>, [70,71] and molecular structures, e.g. Al(BH<sub>4</sub>)<sub>3</sub> and Zr(BH<sub>4</sub>)<sub>4</sub>, [72] illustrating increasing degrees of directionality and covalence in the bonding. Interestingly, all metal borohydrides appear to be structurally related to oxides, possibly due the fact that the ions BH<sub>4</sub><sup>−</sup> and O<sup>2−</sup> are isoelectronic [73]. Structural investigations reveal that polymorphs of Ca(BH<sub>4</sub>)<sub>2</sub> are related to polymorphs of TiO<sub>2</sub> and Mg(BH<sub>4</sub>)<sub>2</sub> to SiO<sub>2</sub> structures [73,74]. It is also interesting to note that only *d*-block metal borohydrides based on metals with *d*<sup>0</sup>, *d*<sup>5</sup> or *d*<sup>10</sup> electron configurations have been successfully obtained so far [66]. This provides a hint that not only the electronegativity but also the electron configurations of the metal may play a significant role in the stability of the borohydride. The above-mentioned trends provide guidelines for the rational design of novel materials and the number of known compositions, structures and derivatives of metal borohydrides has expanded much over the past few years. Clearly, the structural chemistry is fascinatingly diverse, in some cases resembling covalently bonded metal organic frameworks, MOF, and with new possibilities for tailoring physical properties (Figs. 2 and 3).

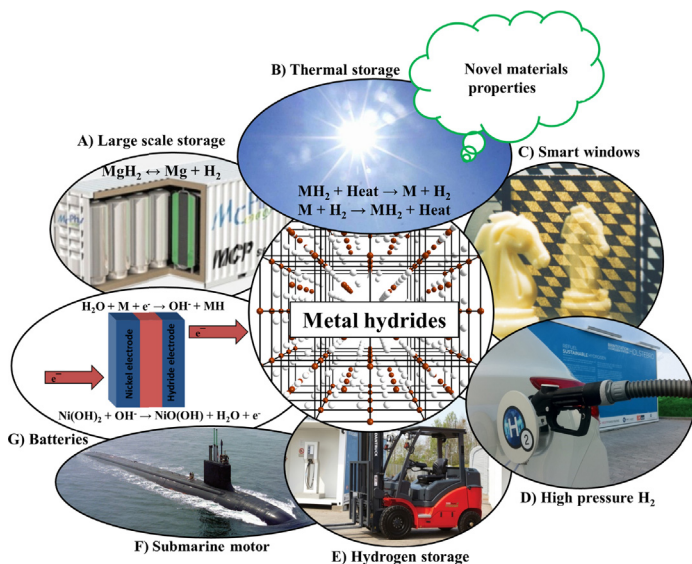


FIGURE 2

Illustration of the state-of-the-art within applications of hydrogen technology. (a) Magnesium hydride combined with heat storage in phase-change materials is commercialized for large-scale solid-state hydrogen storage [31]. (b) The large heat exchange during hydrogen release and uptake in some metal hydrides can be utilized for solar thermal energy storage [32]. (c) Metal hydrides for novel sensors or smart windows have also been discovered, e.g. based on the metallic and reflecting yttrium dihydride,  $\text{YH}_2$ , which may absorb hydrogen and convert to a semiconducting and transparent trihydride,  $\text{YH}_3$  [30,33]. (d) High-pressure hydrogen gas provides fast refueling and in combination with a fuel cell and a Li-battery also high energy efficiency, which is ideal for a small vehicle [34]. (e) Traditional metal hydrides are used for solid-state hydrogen storage and this technology is very competitive with similar lead battery vehicles on performance, e.g. for material handling. (f) Solid-state hydrogen storage in metal hydrides and fuel cell technology is also implemented in modern submarines, which allows long stay under water and less noisy operation [35,36]. (g) Metal hydride batteries are today commercially available [37].

## Reversible hydrogen storage

The exact mechanism for hydrogen release and uptake for metal borohydrides is not fully understood and a drawback appears to be the very complex boron-hydrogen chemistry. An increased tendency for formation of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  is observed during decomposition of  $\text{LiBH}_4$  at  $p(\text{H}_2) > 10$  bar, whereas amorphous boron is also obtained at  $p(\text{H}_2) < 10$  bar [75,76]. Experimental data also show that the *closo*-boranes, such as  $\text{Li}_2\text{B}_{10}\text{H}_{10}$  and  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  can form in a reaction between  $\text{LiBH}_4$  and  $\text{B}_2\text{H}_6$ , and that  $\text{LiBH}_4$  can be prepared in a reaction between  $\text{LiH}$  and  $\text{B}_2\text{H}_6$  [77,78]. Thus, 'BH<sub>3</sub>' or diborane,  $\text{B}_2\text{H}_6$  may be an intermediate for hydrogen release and uptake. A high pressure of inert gas may also facilitate hydrogen release possibly related to the physical state, which may involve a melt, as well as sometimes eutectic melting and foaming during hydrogen release [79–81]. For other metal borohydrides decomposition under hydrogen pressure tends to facilitate the formation of a metal boride, which was clearly observed for the system  $\text{LiBH}_4$ - $\text{MgH}_2$  forming  $\text{MgB}_2$  at  $T > 400$  °C and  $p(\text{H}_2) = 2$ –5 bar [82,83]. Magnesium borohydride contains large amounts of hydrogen (14.8 wt%) and has a major hydrogen release of  $\sim 10$  wt% at  $300 < T < 400$  °C [84]. The rehydrogenation is possible but requires extreme conditions of  $T \sim 400$ –500 °C and  $p(\text{H}_2) \sim 800$ –950 bar

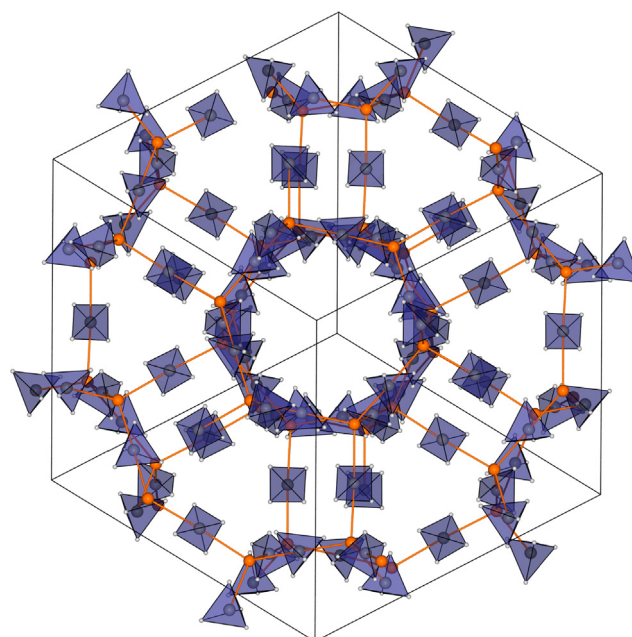


FIGURE 3

Crystal structure of nanoporous cubic  $\gamma$ - $\text{Mg}(\text{BH}_4)_2$  [74]. Mg atoms are illustrated as orange spheres and  $\text{BH}_4^-$  as dark blue tetrahedra. The pore diameter is about 8.8 Å and there is  $\sim 33\%$  'empty space' in the structure.

[85,86]. On the other hand, partial decomposition of  $\text{Mg}(\text{BH}_4)_2$  at lower temperatures (200 °C) appears to produce another borohydride,  $\text{Mg}(\text{B}_3\text{H}_8)_2$ , which is more readily rehydrogenated ( $T = 250$  °C,  $p(\text{H}_2) = 120$  bar and  $t = 48$  h) [87].

## The first nanoporous hydride $\gamma$ - $\text{Mg}(\text{BH}_4)_2$

The extreme structural flexibility observed for metal borohydrides can be illustrated by numerous structurally different polymorphs of  $\text{Mg}(\text{BH}_4)_2$ , e.g.  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ - and  $\epsilon$ - $\text{Mg}(\text{BH}_4)_2$  [70,74,88,89]. Magnesium borohydride,  $\text{Mg}(\text{BH}_4)_2$ , is a potential solid-state hydrogen storage material with a very high gravimetric hydrogen content of 14.9 wt%  $\text{H}_2$  (Table 1). A new cubic nanoporous polymorph  $\gamma$ - $\text{Mg}(\text{BH}_4)_2$  has 33% empty space in the structure and reveals a remarkable volume collapse of 44% upon compression and transforms to a new high-pressure polymorph,  $\delta$ - $\text{Mg}(\text{BH}_4)_2$  [74,89].  $\delta$ - $\text{Mg}(\text{BH}_4)_2$  has the second-highest volumetric hydrogen density,  $\rho_v = 147$  g  $\text{H}_2$ /L, among all known hydrides, only slightly below  $\rho_v(\text{Mg}_2\text{FeH}_6) = 150$  g  $\text{H}_2$ /L [74]. Notice, this is more than twice the density of liquid hydrogen,  $\rho(\text{H}_2) = 71$  g/L and there

TABLE 1

Specific densities ( $\rho$ ) of  $\text{LiBH}_4$  and  $\text{Mg}(\text{BH}_4)_2$  polymorphs and their gravimetric ( $\rho_m$ ) and volumetric ( $\rho_v$ ) hydrogen contents ( $\rho_v = \rho_m \times \rho$ ).

| Compound  | Space group             | $\rho$ (g/cm <sup>3</sup> ) | $\rho_m$ (wt%) | $\rho_v$ (g H <sub>2</sub> /L) | Ref. |
|---|-------------------------|-----------------------------|----------------|--------------------------------|------|
| $\text{LiBH}_4$   | <i>Pnma</i>             | 0.668                       | 18.5           | 121                            | [63] |
| $\alpha$ - $\text{Mg}(\text{BH}_4)_2$                     | <i>P6<sub>1</sub>22</i> | 0.783                       | 14.9           | 117                            | [90] |
| $\beta$ - $\text{Mg}(\text{BH}_4)_2$                      | <i>Fddd</i>             | 0.761                       | 14.9           | 113                            | [91] |
| $\gamma$ - $\text{Mg}(\text{BH}_4)_2$                     | <i>I4-3a</i>            | 0.550                       | 14.9           | 82                             | [74] |
| $\gamma$ - $\text{Mg}(\text{BH}_4)_2 \cdot 0.8\text{H}_2$ | <i>I4-3a</i>            | 0.565                       | 17.4           | 98                             | [74] |
| $\delta$ - $\text{Mg}(\text{BH}_4)_2$                     | <i>P4<sub>2</sub>nm</i> | 0.987                       | 14.9           | 147                            | [74] |

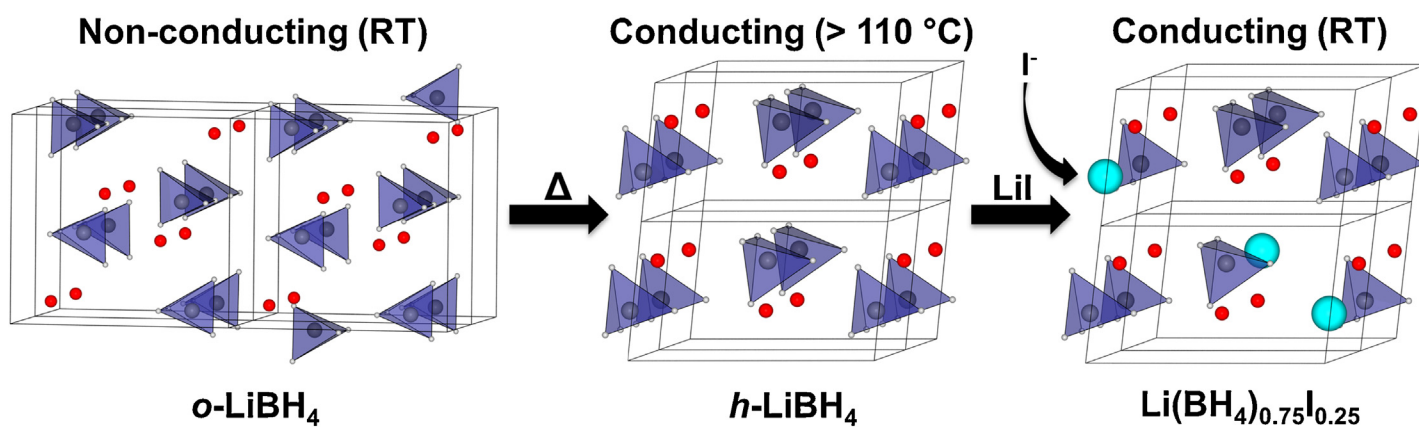


FIGURE 4

Complex borohydrides have recently shown potential as fast lithium ion conductors. Substitution of the larger bromide and iodide ions in lithium borohydride stabilizes the hexagonal polymorph, *h*-LiBH<sub>4</sub> at room temperature and significantly improves the lithium ion conductivity (Lithium red, iodide blue and BH<sub>4</sub> dark blue) [97,98,102,103].

remains a huge potential for discovering novel solids with extreme hydrogen densities.

The polymorph  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> has a 3D net of interpenetrated channels with pore size up to  $\sim 8.8$  Å and is the first MH which reversibly adsorbs smaller molecules such as hydrogen, nitrogen and CH<sub>2</sub>Cl<sub>2</sub>. Recent in situ diffraction studies suggest a composition of  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub>·0.8H<sub>2</sub> at  $p(\text{H}_2) = 105$  bar ( $T \sim -143$  °C), which corresponds to  $\rho_m = 17.4$  wt% H<sub>2</sub> [74]. The desorption isobars extracted from diffraction data indicate that the isosteric heats of adsorption of hydrogen in  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> are  $Q_{st}(\text{H}_2) > 7$  kJ/mol at a loading of 15 mg H<sub>2</sub>/g ( $\sim 6$  kJ/mol average value), which is among the highest values measured for MOFs and other porous solids [74].

A standard fuel cell based family car may need 5 kg hydrogen to reach a driving range of 500 km, which is about 60 m<sup>3</sup> of gas (at ambient temperature and atmospheric pressure), but only a volume of 34 L and a mass of 34 kg if it is stored in the new magnesium borohydride,  $\delta$ -Mg(BH<sub>4</sub>)<sub>2</sub>.

### Anion substitution in metal borohydrides

The first example of anion substitution in metal borohydride materials was reported in 2006 for a mixture of LiBH<sub>4</sub>-LiCl [92]. The heavier halide anions change size according to the sequence I<sup>-</sup> (2.20 Å) > BH<sub>4</sub><sup>-</sup> (2.05 Å) > Br<sup>-</sup> (1.96 Å) > Cl<sup>-</sup> (1.81 Å) [93], providing an efficient tool to tune the unit cell volume, the internal lattice pressure and possibly physical properties of borohydrides [94].

Some trends in the structural chemistry appear to describe anion substitution of metal borohydrides with the heavier halides, (i) the solid containing the smaller anion tends to dissolve into the compound containing the larger anion, and the structure of the latter tends to be preserved in the obtained solid solution. This trend can be interpreted as an increase in the lattice energy due to the clearly observed decrease in the unit cell volume. Secondly, (ii), some polymorphs of metal borohydrides are more prone to anion substitution than others, typically at elevated temperatures, e.g. *h*-LiBH<sub>4</sub> or  $\beta$ -Mg(BH<sub>4</sub>)<sub>2</sub> (Fig. 4) [95,96]. Experimental evidence suggests that anion substitution is facilitated by dynamics of the BH<sub>4</sub> unit, which appears to make it more spherical and similar to

halides. Thirdly, (iii), if compounds are isostructural then anion substitution may occur in both compounds, which may lead to two solid solutions observed for LiBH<sub>4</sub>-LiBr, LiBH<sub>4</sub>-LiI and NaBH<sub>4</sub>-NaCl systems. Notice that  $\beta$ -LiBr,  $\beta$ -LiI and *h*-LiBH<sub>4</sub> and also NaBH<sub>4</sub> and NaCl are isostructural. In general, anion substitution with the heavier halides tends to stabilize the hydride, i.e. hydrogen release at increased temperatures, but facilitates hydrogen uptake [97–101].

### Multi-functional metal borohydrides

A new series of isostructural mixed-cation mixed-anion borohydride chlorides based on rare-earths elements, LiM(BH<sub>4</sub>)<sub>3</sub>Cl, M = La, Gd, or Ce, was recently discovered [104–106]. The structure contains isolated tetranuclear anionic clusters [M<sub>4</sub>Cl<sub>4</sub>(BH<sub>4</sub>)<sub>12</sub>]<sup>4-</sup> with a distorted cubane Ce<sub>4</sub>Cl<sub>4</sub> core charge-balanced by Li<sup>+</sup> cations (Fig. 5). The Li<sup>+</sup> ions are disordered and occupy 2/3 of the available sites. DFT calculations indicate that LiCe(BH<sub>4</sub>)<sub>3</sub>Cl is stabilized by larger entropy rather than smaller energy and agrees well with the very high lithium ion conductivity measured for the LiM(BH<sub>4</sub>)<sub>3</sub>Cl samples (Table 2) [104,106]. Interestingly, solid-state NMR of LiLa(BH<sub>4</sub>)<sub>3</sub>Cl reveals that the diffusive

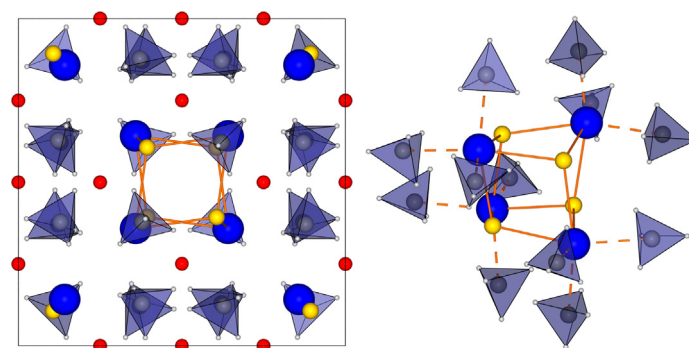


FIGURE 5

The structure of LiCe(BH<sub>4</sub>)<sub>3</sub>Cl (left) contains isolated tetranuclear anionic clusters of [Ce<sub>4</sub>Cl<sub>4</sub>(BH<sub>4</sub>)<sub>12</sub>]<sup>4-</sup> (right) with a distorted cubane Ce<sub>4</sub>Cl<sub>4</sub> core charge-balanced by Li<sup>+</sup> cations (red spheres). Ce atoms (blue) coordinate three chloride ions (yellow) and three borohydride groups (dark blue) via the  $\eta^3$ -BH<sub>3</sub> faces [104].

TABLE 2

**The new compounds LiM(BH<sub>4</sub>)<sub>3</sub>Cl (M = La, Ce or Gd) simultaneously carry moderate amounts of hydrogen released at relatively low temperatures and are fast Li-ion conductors.**

| Compound   | $\rho$<br>(wt%) | $T_{\text{dec}}$<br>(°C) | Li-ion<br>( $\times 10^{-4}$ S cm <sup>-1</sup> ) | $T_{\text{ionic}}$<br>(°C) | Ref.     |
|--|-----------------|--------------------------|---|----------------------------|----------|
| LiLa(BH <sub>4</sub> ) <sub>3</sub> Cl                 | 5.36            | 260                      | 2.3   | 25                         | [106]    |
| LiCe(BH <sub>4</sub> ) <sub>3</sub> Cl                 | 5.33            | 260                      | 1.03  | 25                         | [104]    |
| LiGd(BH <sub>4</sub> ) <sub>3</sub> Cl                 | 4.95            | 260                      | 3.6   | 25                         | [106]    |
| LiBH <sub>4</sub>                                      | 18.6            | 400                      | 10  | >110                       | [98,114] |
| Li(BH <sub>4</sub> ) <sub>0.75</sub> I <sub>0.25</sub> | 6.07            | 400                      | 0.1   | 25                         | [98,103] |

Li ion jumps and a certain type of BH<sub>4</sub> reorientation occur at the same time scale and may be correlated [107]. In a number of other borohydride systems, e.g. *h*-LiBH<sub>4</sub> and LiBH<sub>4</sub>-LiI, the fast Li ion diffusion is accompanied by the very fast BH<sub>4</sub> reorientations, suggesting a “paddle wheel” conductivity mechanism [108–110].

Unfortunately, solid-state batteries assembled using LiBH<sub>4</sub>-based solid-state electrolytes often suffer from fast capacity loss after just one cycle [111]. A new type of magnesium battery with a liquid electrolyte of Mg(BH<sub>4</sub>)<sub>2</sub> dissolved in dimethyl ether was recently proposed but also suffers from capacity loss [112]. Magnesium batteries have high volumetric energy capacity compared to their lithium counterparts as well as improved safety, and theoretical work suggests that the high-temperature polymorph of Mg(BH<sub>4</sub>)<sub>2</sub> may be a new solid-state electrolyte [113].

A number of rare-earth metal borohydrides have been discovered over the past few years, which shows a clear trend in structure type as a function of metal ion radius for the metal that coordinates to BH<sub>4</sub><sup>-</sup> i.e. Li<sup>+</sup> (0.76 Å) ~ Sc<sup>3+</sup> (0.75 Å) < Yb<sup>3+</sup> (0.87) < Y<sup>3+</sup> (0.90 Å) < Gd<sup>3+</sup> (0.94 Å) < Ce<sup>3+</sup> (1.02 Å) < La<sup>3+</sup> (1.01 Å). Apparently, anionic structures are preferred for the smallest ions, e.g. LiSc(BH<sub>4</sub>)<sub>4</sub> and LiYb(BH<sub>4</sub>)<sub>3</sub>Cl containing [Sc(BH<sub>4</sub>)<sub>4</sub>]<sup>-</sup> and [Yb(BH<sub>4</sub>)<sub>3</sub>Cl]<sup>-</sup>, [68,115] and framework structures for the medium sized rare-earth metals, e.g. Y(BH<sub>4</sub>)<sub>3</sub> and Gd(BH<sub>4</sub>)<sub>3</sub> [106,116]. The larger lanthanides appear to facilitate the formation of more complex structures containing isolated tetranuclear anionic clusters [Ce<sub>4</sub>Cl<sub>4</sub>(BH<sub>4</sub>)<sub>12</sub>]<sup>4-</sup> as for LiCe(BH<sub>4</sub>)<sub>3</sub>Cl (Fig. 5) [104,106]. However, a rich diversity exists as Yb<sup>3+</sup> also forms Yb(BH<sub>4</sub>)<sub>3</sub> isostructural to Y(BH<sub>4</sub>)<sub>3</sub> and when heated Gd<sup>3+</sup> forms LiGd(BH<sub>4</sub>)<sub>3</sub> Cl [106,115,117].

This recent research reveals that the chemically very similar rare earths metals have fascinating and diverse borohydride structural chemistry. Furthermore, the partly filled *f*-orbitals may provide new routes for rational design of materials with tailored magnetic and optical properties illustrated by the discovery of highly luminescent divalent lanthanide borohydrides, Ln(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>2</sub> (Ln = Eu or Yb) [118].

## Conclusion

A wide range of *novel metal borohydrides* has been discovered during the past few years and our knowledge on this class of materials has increased tremendously. This review describes new trends in their crystal structures, thermal behavior and properties. New research directions within rational design, synthesis and characterization of hydrides have been developed. However, there is still limited knowledge on the materials composition after the release of hydrogen and the mechanism for hydrogen absorption. Several

other obstacles also need to be addressed, e.g. how to avoid the release of diborane, segregation of amorphous boron or formation of the more stable *closo*-boranes. Surprisingly, novel materials such as the nanoporous  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> have completely unexpected properties and both store hydrogen adsorbed to the inner surface and also chemically bonded to boron. Other new materials show tendencies toward multifunctionality, i.e. hydrogen storage properties combined with e.g. ion conductivity, magnetic or optical properties. The multitude of hydrides and their diversity in structure and properties provide new hope for solid-state hydrogen storage, also for mobile applications. New focus in off-board regeneration of MH and combined use of solid-state storage and high-pressure hydrogen gas systems has provided new promising research directions that may prove fruitful in the near future.

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