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Review

Recent Progress in Metal Borohydrides for Hydrogen Storage

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Abstract: The prerequisite for widespread use of hydrogen as an energy carrier is the development of new materials that can safely store it at high gravimetric and volumetric densities. Metal borohydrides $M(BH_4)_n$ (n is the valence of metal M), in particular, have high hydrogen density, and are therefore regarded as one such potential hydrogen storage material. For fuel cell vehicles, the goal for on-board storage systems is to achieve reversible store at high density but moderate temperature and hydrogen pressure. To this end, a large amount of effort has been devoted to improvements in their thermodynamic and kinetic aspects. This review provides an overview of recent research activity on various $M(BH_4)_n$, with a focus on the fundamental dehydrogenation and rehydrogenation properties and on providing guidance for material design in terms of tailoring thermodynamics and promoting kinetics for hydrogen storage.

Keywords: hydrogen; hydride; borohydride; hydrogen storage

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1. Introduction

Development of advanced hydrogen storage materials for onboard hydrogen storage systems is regarded as a key prerequisite for widespread adoption of fuel cell vehicles. For commercial vehicle

applications, hydrogen storage materials must possess all the following capabilities: high gravimetric hydrogen density, adequate hydrogenation-dehydrogenation temperature/rate, cycling stability, and low cost [1].

Metal borohydrides $M(BH_4)_n$ (n indicates the valence of M) have high gravimetric hydrogen densities and thus have attracted great interest for use in hydrogen storage [2]. The gravimetric hydrogen densities and physical properties of various $M(BH_4)_n$ [3] are shown in Figure 1 and Table 1, respectively.

Figure 1. Elements M formed $M(BH_4)_n$, their gravimetric hydorgne densities in the unit of mass%. Asterisks indicate compounds stabilizaed at room temperature by coordiantion with ligands. Brackets indicate compounds reported to be unstable at room temperature but may be isolated at low temperature [3]. Reproduced with permission from reference 3.

1	2											13	14
Li 18.5	Be 20.8												
Na 10.7	Mg 14.9	3	4	5	6	7	8	9	10	11	12	[Al] 16.9	
K 7.5	Ca 11.6	Sc 13.5	Ti III 13.1 IV 15.0	V 12.7	Cr 9.9	[Mn] 9.5	[Fe] 9.4	[Co] 9.1	[Ni] 9.1	[Cu]* 5.1	Zn 4.4	[Ga] 10.6	Ge 12.2
Rb 4.0	Sr 6.9	Y 9.1	Zr 10.7	Nb 8.8						[Ag]* 3.3	[Cd] 2.9	[In] 7.6	[Sn] 9.1
Cs 2.7	Ba 4.8	Ln	Hf 6.8							[Au] 1.9	Hg 1.8	Tl 4.9	
		Ac											

Ln	La 6.6	Ce 6.6		Nd 6.4		Sm 6.2	Eu 6.2	Gd 6.0	Tb 5.9	Dy 5.8	Ho 5.8	Er 5.7	Tm 5.7	Yb 5.6	Lu 5.5
Ac		Th 5.5	Pa 5.6	U III 4.3 IV 5.4	Np 5.4	Pu 5.4									

Table 1. Density of $M(BH_4)_n$ and hydrogen density in $M(BH_4)_n$ [3]. Reproduced with permission from reference 3.

$M(BH_4)_n$	CAS No.	Density (g/mol)	Density (g/cm^3)	Hydrogen Density (mass%)	Hydrogen Density (kg/m^3)
$LiBH_4$	16949-15-8	21.78	0.66	18.5	122.1
$NaBH_4$	16940-66-2	37.83	1.07	10.7	114.5
KBH_4	13762-51-1	53.94	1.17	7.5	87.8
$RbBH_4$	20346-99-0	100.31	1.92	4.0	76.8
$CsBH_4$	-	147.75	2.42	2.7	65.3
$Be(BH_4)_2$	17440-85-6	38.70	0.702	20.8	146.0
$Mg(BH_4)_2$	16903-37-0	53.99	0.989	14.9	147.4
$Ca(BH_4)_2$	17068-95-0	69.76	(1.07)	11.6	(124.1)
$Mn(BH_4)_2$	-	84.62	(1.24)	9.5	(117.8)
$Al(BH_4)_3$	16962-07-5	71.51	0.79	16.9	133.5
$Zr(BH_4)_4$	12370-59-1	150.6	1.179	10.7	126.2
$Hf(BH_4)_4$	53608-70-1	237.6	1.65	6.8	112.2

Densities in brackets shows the value calculated from the crystal structure.

First-principles calculations of the electronic structures of $M(BH_4)_n$ show that they are nonmetallic and have relatively large energy gaps of 1.8−6.8 eV. A boron atom forms covalent bonds with four surrounding H atoms to form $[BH_4]^-$ anions, the charge of which is compensated by metal cations M^{n+}. The electronic structures indicate that charge transfer from the metal cations M^{n+} to the $[BH_4]^-$ anions is a key feature determining the thermodynamic stability of $M(BH_4)_n$ [4–8].

Some $M(BH_4)_n$ have been used as "one-way" hydrogen sources that release the hydrogen on contact with water (via hydrolysis) [9–11]. Because the hydrolysis reaction is highly irreversible, such materials are certainly not candidates for reversible hydrogen storage. In this review, we focus on the recent progress in the dehydrogenation and rehydrogenation reactions of $M(BH_4)_n$ at controlled temperature and hydrogen pressure. Some several excellent reviews on $M(BH_4)_n$ are also available [2,12–18].

2. Fundamentals of Hydrogen Storage Properties

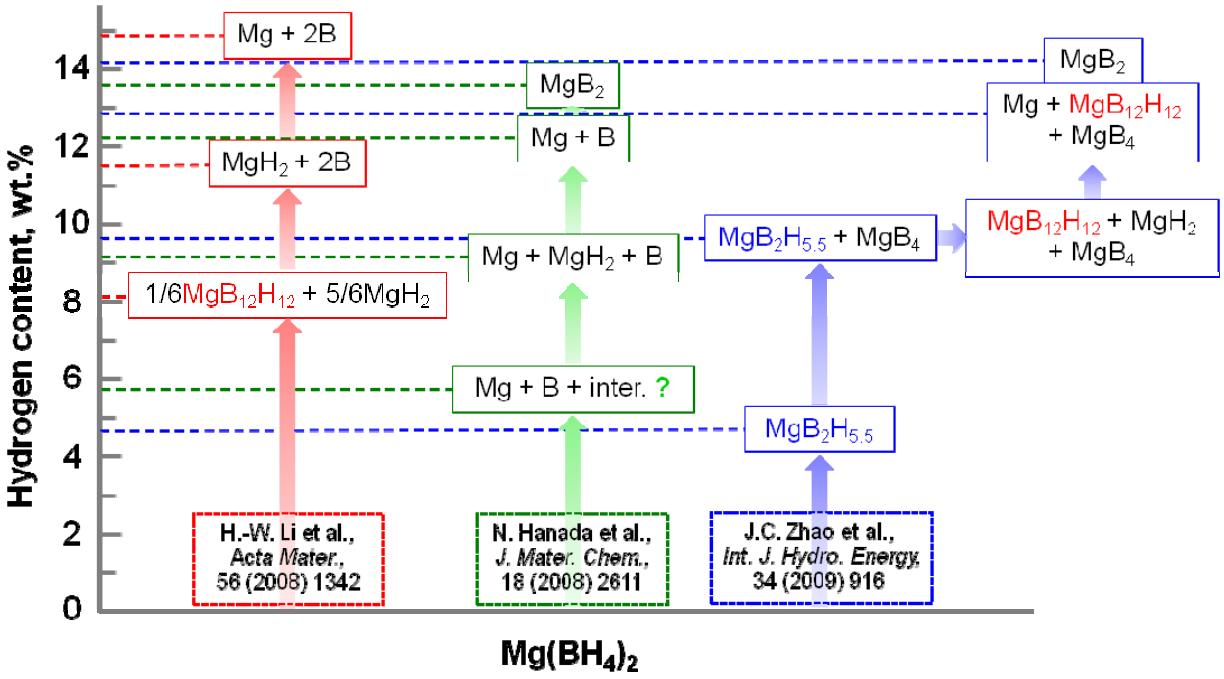
The study of $M(BH_4)_n$ as a candidate hydrogen storage material started with $LiBH_4$ [19]. It releases 13.8 mass% of hydrogen by decomposition into LiH and B [19–25]. The dehydrogenation process at a low heating rate (0.5 K/min) exhibits three distinct desorption peaks, which indicates that it involves several intermediate steps [25]. This was recently explained by the formation of $Li_2B_{12}H_{12}$ as an intermediate compound, evidenced by Raman and solid-state CP/MAS NMR analyses, as well as theoretical prediction [26–29]. $Li_2B_{12}H_{12}$ has a cubic crystal structure with *Pa*3 symmetry [30]. A mechanistic explanation of the formation of $Li_2B_{12}H_{12}$ indicates that the diborane or higher borane species formed during the decomposition of $LiBH_4$ would react with the remaining $LiBH_4$ to afford $Li_2B_{12}H_{12}$ and possibly even $Li_2B_{10}H_{10}$ [31]. To understand the mechanism of dehydrogenation better, intensive investigations on the dynamics have been performed, including on the rotational and vibration motions of BH_4 tetrahedra; the atomic motions of H, Li, and B; H–D exchange in BH_4 units, *etc*. [32–50]. The enthalpy ΔH and entropy ΔS of dehydrogenation were found to be 74 kJ mol^{-1} H_2 and 115 J K^{-1} mol^{-1} H_2, respectively, based on the pressure-concentration-temperature (PCT) isotherm measurement [51].

Dehydrogenation of $LiBH_4$ is reversible, because the end products lithium hydride (LiH) and boron absorb hydrogen at 873 K in a hydrogen pressure of 35 MPa for 12 h [23] or at 1000 K under a hydrogen pressure of 15 MPa for over 10 h [25] to form $LiBH_4$. The high rehydrogenation temperature of above 873 K might be due to the sluggish kinetics of rehydrogenation, which requires recombination of the dehydrogenated LiH and B, that is, breaking of the rigid boron lattice, and the subsequent diffusion of Li and B atoms toward each other would be mainly responsible for the sluggish kinetics. The sluggish kinetics can be enhanced by preparing a homogenous dispersion of Li and B atoms on an atomic level. For example, forming a binary LiB_x compound (e.g., Li_7B_6, LiB_3, and LiB, *etc*.) has been proved to significantly improve the reaction kinetics of $LiBH_4$ formation over that of the Li/B mixture [51–53]. In addition, the formation of $LiBH_4$ might be related to diborane B_2H_6 [53–55].

$Mg(BH_4)_2$ releases approximately 14.9 mass% of hydrogen when heated up to 870 K [56–66]. The dehydrogenation process is found to also proceed through multiple steps together with the formation of intermediate compounds [62,63,65], as summarized in Figure 2. Thus far, one of the intermediate

compounds has been theoretically predicted and experimentally confirmed as being $MgB_{12}H_{12}$ [28,29,62,65–70] similar to that in the case of $LiBH_4$ [26]. The lowest energy configuration of $MgB_{12}H_{12}$ was predicted as being monoclinic in the space group *C2/m* (No. 12) [29]. Anhydrous $MgB_{12}H_{12}$ cannot be obtained from simple thermal decomposition of $Mg(H_2O)_6B_{12}H_{12}{\cdot}6H_2O$ [71]. The apparent enthalpy and entropy for the conversion of $Mg(BH_4)_2$ to MgH_2 were estimated from PCT measurement to be 39 kJ mol^{-1} H_2 and 91 J K^{-1} mol^{-1} H_2 [56], respectively. In a later work, different values were reported: $\Delta H = 57$ kJ mol^{-1} H_2 and $\Delta S = 128$ J K^{-1} mol^{-1} H_2 [62]. These differences might originate from differences in the measurement conditions. For example, a shorter equivalent judgment time will lead to a higher plateau due to the sluggish kinetics.

Figure 2. The dehydrogenation processes of $Mg(BH_4)_2$ based on the respective reports. Question mark indicates the possibility of the formation of an intermediate compound during the dehydrogenation.



Rehydrogenation of $Mg(BH_4)_2$ occurs at 543 K in a hydrogen pressure of 40 MPa for 48 h. Approximately 6.1 mass% of hydrogen is rehydrogenated through the formation of $MgB_{12}H_{12}$ [62,66]. The formation of $MgB_{12}H_{12}$, rather than $Mg(BH_4)_2$, after rehydrogenation may be explained from the viewpoint of the crystal (cluster) structure. The formation of $Mg(BH_4)_2$ is more thermodynamically favorable than that of $MgB_{12}H_{12}$ from the dehydrogenated products (MgH_2 and boron) at 573 K. However, for the formation of $Mg(BH_4)_2$, the B–B bonds in the icosahedral cluster of B should be broken and the B atoms should spatially migrate to form $[BH_4]^-$. The barrier against breaking of the B–B bonds and migration of the B atoms is probably too high to overcome under the present rehydrogenation conditions [66]. However, it is almost the same boron icosahedral clusters in between B and $MgB_{12}H_{12}$ that facilitate the formation of $[B_{12}H_{12}]^{2-}$. In other words, the formation of $Mg(BH_4)_2$ requires higher temperature and pressure to overcome the aforementioned barriers. This was proven in a recent study: partial formation of $Mg(BH_4)_2$ was confirmed in rehydrogenation experiments carried out at 663 K in a hydrogen pressure of 90 MPa for 3 days [72]. In addition, $Mg(BH_4)_2$ can be prepared

by hydrogenation of MgB_2 at 673 K under a hydrogen pressure of 90 MPa for a few days [73]. This hydrogenation reaction can be greatly promoted by using nanostructures with grain boundary defects introduced by mechanical milling [73–75]. Recently, $Mg(BH_4)_2$ was found to be formed by hydrogenation of $Mg(B_3H_8)_2$ at 523 K under a hydrogen pressure of 12 MPa [76].

$Ca(BH_4)_2$ was theoretically predicted to release 9.6 mass% of hydrogen according to the following reaction [77]:

$$Ca(BH_4)_2 = 2/3\ CaH_2 + 1/3\ CaB_6 + 10/3\ H_2 \quad (1)$$

Experimentally, approximately 9.0 mass% of hydrogen was released when $Ca(BH_4)_2$ was heated to 800 K [78–80]. This value shows good agreement with that predicted by Equation 1. The presence of two endothermic peaks corresponding to dehydrogenation suggests the formation of intermediate compounds, which is confirmed by the powder X-ray diffraction (XRD) analyses of the dehydrogenated products that were heated to approximately 663 K [78] and after the plateau in the PCT profile measured at 593 K [79]. The intermediate compound is suggested to be a CaB_2H_x compound having a $HgCl_2$-type structure with *Pnma* symmetry according to the high-resolution synchrotron radiation powder XRD measurement [81]. By contrast, the proposed CaB_2H_x was predicted to be both structurally unstable and too high in energy to be a dehydrogenation intermediate based on the plane wave density functional theory calculations [82]. The formation of $CaB_{12}H_{12}$ as an intermediate compound is suggested by the experiment and first-principle calculations [29,69,70,83]. A pure $CaB_{12}H_{12}$ compound has been synthesized and the crystal structure has been determined to be monoclinic with *C*2/*c* symmetry [84]. Identification of the intermediate compound is expected to increase our understanding of the dehydrogenation process of $Ca(BH_4)_2$. The enthalpy and entropy change for the first step of dehydrogenation are estimated to be ΔH = 87 kJ mol^{-1} H_2 and ΔS = 158 J K^{-1} mol^{-1} H_2 [80], respectively.

Regarding the rehydrogenation properties of pure $Ca(BH_4)_2$, no tangible data are available. $Ca(BH_4)_2$ has been predicted theoretically to have limited viability as a reversible storage material for on-board storage due to the formation of a stable intermediate compound of $CaB_{12}H_{12}$ [83]. It was found that the ball-milled mixtures of $CaB_{12}H_{12}$ and CaH_2 do not produce $Ca(BH_4)_2$ during the rehydrogenation test at 670 K in a hydrogen pressure of 100 MPa [84]. With additives, approximately 57% of the $Ca(BH_4)_2$ is obtained by rehydrogenation at 623 K in a hydrogen pressure of 10 MPa [85–87].

$Y(BH_4)_3$ releases approximately 7.8 mass% of hydrogen when heated to 773 K [88–93]. This value is almost equal to the theoretical dehydrogenation content (7.5 mass%) according to the assumed reaction:

$$Y(BH_4)_3 = YH_2 + 3\ B + 5\ H_2 \quad (2)$$

The whole reaction process of $Y(BH_4)_3$ on heating to 773 K is summarized as follows: (1) phase transformation, (2) melting, (3) decomposition of $Y(BH_4)_3$ into an intermediate compound and YH_3, (4) decomposition of the intermediate compound, and (5) decomposition of YH_3 into YH_2 [89]. Approximately 1.1–1.3 mass% of hydrogen was rehydrogenated at 573 K in a hydrogen pressure of 35 MPa for 24 h [89]. Similar to that of $Y(BH_4)_3$, a multistep dehydrogenation process were also confirmed in $Ce(BH_4)_3$ [94]. In addition, there are several other $M(BH_4)_n$ (e.g., M = Zn, Al, Ti, Mn and

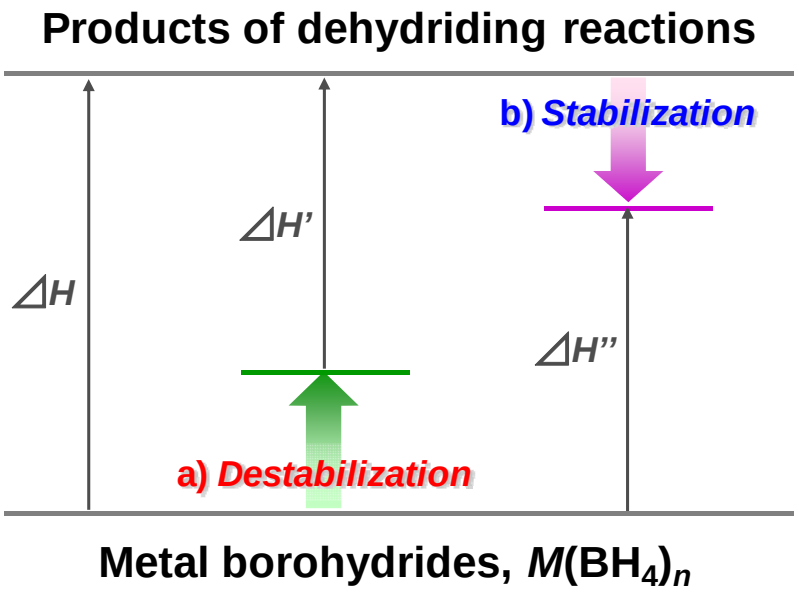
Zr) [95–103]. Most of these were found to be irreversible due to their low melting temperatures and the release of diborane with hydrogen.

3. Improvement of Hydrogen Storage Properties

3.1. Tailoring Thermodynamics

In principle, the Gibbs free energy for a certain reaction determines the reaction temperature. Taking into account that the entropy change ΔS mainly comes from the gaseous hydrogen (*i.e.*, a constant S^0_{H2} = 130 J · K^{-1} mol^{-1} H_2), enthalpy change ΔH becomes the specific indicator to evaluate thermodynamic stability. For metal borohydrides, ΔH is calculated from the difference in the heat of formation between the product and starting materials. Therefore, two main approaches to tailor the thermodynamic stabilities from both sides—the starting materials and products—are expected: (a) destabilization of $M(BH_4)_n$ and (b) stabilization of dehydrogenation products, as shown in Figure 3.

Figure 3. Schematic illustration of two main approaches to tailor the thermodynamic stabilities of metal borohydrides $M(BH_4)_n$: (a) destabilization of $M(BH_4)_n$ and (b) stabilization of dehydrogenation products.



One approach to reducing the enthalpy change ΔH_{deh} is the destabilization of $M(BH_4)_n$, as illustrated in Figure 3. The thermodynamic stabilities for the series of metal borohydrides $M(BH_4)_n$ (M = Li, Na, K, Mg, Ca, Sc, Zr, Hf, Cu, Zn, and Al; n = 1–4) have been systematically investigated using first-principles calculations [104]. A good correlation between the predicted heat of formation ΔH_{form} of $M(BH_4)_n$ and the Pauling electronegativity χ_P of M is found, which suggests that the χ_P is a useful indicator to estimate the thermodynamic stability of $M(BH_4)_n$.

The enthalpy change ΔH_{deh} of the dehydrogenation of $M(BH_4)_n$ correlates not only with the stability of $M(BH_4)_n$, but also with the stability of the products. The dehydrogenation reactions were assumed as the following equation:

$$M(BH_4)_n = MH_m + n\,B + (4n - m)/2\,H_2 \quad (3)$$

In the case of no MH_m formation, direct decomposition into elements was assumed. Then, the ΔH_{deh} of the dehydrogenation was estimated using the reported values of ΔH_{prod} and predicted ΔH_{form}:

$$\Delta H_{deh} = \Delta H_{prod} - \Delta H_{form} \quad (4)$$

A good correlation between ΔH_{deh} and χ_P was also obtained according to the theoretical prediction. Furthermore, it is expected that $M(BH_4)_n$ with $\chi_P \geq 1.5$ are thermodynamically unstable [3]. The dehydrogenation properties were experimentally investigated using thermal desorption analysis during the heating process for milling samples [104–106]. A good correlation between T_d (defined as the temperature of the first peak) and χ_P was confirmed experimentally, and was similar to that predicted by the first-principles calculations. Therefore, both the theoretical prediction and the experimental results consistently indicate that T_d can be roughly estimated by considering χ_P as an indicator.

Inspired by this finding, an approach of producing multi cation borohydrides $MM'(BH_4)_n$, in which M and M' have different electronegativities has been proposed to precisely tailor the thermodynamic stability [107]. Several typical samples has been synthesized, including $LiZr(BH_4)_5$, $Li_2Zr(BH_4)_6$, $LiK(BH_4)_2$, $LiSc(BH_4)_4$, $KSc(BH_4)_4$, and so on [107–117]. Note that some samples were reported to form a large $[M'(BH_4)_n]^{m-}$ complex anion units such as $[Sc(BH_4)_4]^-$ [109,117], rather than the bimetallic borohydrides. Most of the $MM'(BH_4)_n$ exhibit moderate thermodynamic stabilities between $M(BH_4)_n$ and $M'(BH_4)_n$. The appropriate combination of cations might be an effective method for adjusting the thermodynamic stability of metal borohydrides, similar to the conventional "alloying" method for hydrogen storage alloys. The detailed dehydrogenation-rehydrogenation properties of the recently synthesized $MM'(BH_4)_n$ are given in Table 2.

Table 2. Hydrogen storage properties of bimetallic borohydrides, $MM'(BH_4)_n$.

Borohydrides	Hydrogen (mass%)			Conditions: temp (K) [pressure (MPa)]		Reference
	Ideal	Obs (First Dehyd)	Obs (Rehyd)	First Dehyd	Rehyd	
$ZrLi(BH_4)_5$	11.7			595–873		[107]
$ZrLi_2(BH_4)_6$	12.5			650–873		[107]
$LiK(BH_4)_2$	10.6			653–		[108]
$LiSc(BH_4)_4$	14.5	4.38–6.4 ^{m}		415–673	673 [7]	[109,111]
$LiZn_2(BH_4)_5$ *	9.5			238–473		[112]
$NaZn_2(BH_4)_5$ *	8.8			241–		[112]
$NaSc(BH_4)_4$	12.7	0.97 ^{m}		440–750		[113]
$Na_2Mn(BH_4)_4$	10.1	2.9		393		[114]
$KSc(BH_4)_4$	11.2	4.4 ^{p}		470–580		[117]
$LiBH_4/Mg(BH_4)_2$	16.0	12.5	2.5	513–773	673 [10]	[115]
$xLiBH_4 + (1-x)Ca(BH_4)_2$ $(0 < x < 1)$	9.6–18.5	10 (x = 0.4, 0.6)	4 (x = 0.4)	473–773	673 [9]	[116]

* represents that the release of B_2H_6 in the decomposition process; ^{m} indicates the value referred to the mixture of metal borohydride with side products, while ^{p} indicates the value referred to the pure metal borohydride.

The other approach to reducing enthalpy change ΔH_{deh} is the stabilization of dehydrogenated products by the combination of $M(BH_4)_n$ with elements, metal hydrides, complex hydrides, and so on. A typical example for this approach is the 2 $LiBH_4$ + MgX system [118]. Pure $LiBH_4$ releases approximately 13.8 mass% of hydrogen according to the following reaction:

$$LiBH_4 = LiH + B + 3/2\ H_2 \quad (5)$$

The enthalpy and entropy for Equation 5 have been predicted to be 66.6 kJ mol^{-1} H_2 and 97.4 J K^{-1} mol^{-1} [119], respectively, which means T_d (in 0.1 MPa H_2) is approximately 683 K. This temperature is too high for practical applications, although the combination with Mg-based compounds clearly results in a large reduction of ΔH_{deh}. Dehydrogenation of the $LiBH_4/MgH_2$ system proceeds as follows:

$$2\ LiBH_4 + MgH_2 = 2\ LiH + MgB_2 + 4\ H_2 \quad (6)$$

In this case, due to the formation of MgB_2, ΔH_{deh} was reduced to 45.8 kJ mol^{-1} H_2 and T_d (in 0.1 MPa H_2) decreased to approximately 441 K [120]. At the same time, a significant destabilization of $LiBH_4$ due to combination with the $LiNH_2$ system was reported [121], as indicated by the much higher dehydrogenation pressure of the combined materials than that of $LiBH_4$ alone. Due to these significant destabilization effects, a large number of combination materials have been developed. The recent progress on these combination systems [120–185] is summarized in Table 3.

This approach not only reduces the enthalpy of the dehydrogenation, which decreases T_d, but also kinetically enhances the rehydrogenation reaction. That is, in contrast to the formation of pure $LiBH_4$ (from right to left in Equation 5) discussed in Section 2, $LiBH_4$ and MgH_2 form simultaneously (from right to left in Equation 6) under fairly moderate conditions: 5 MPa hydrogen pressure in the temperature range 523–573 K [136]. The difference between these two reactions is attributed to the different crystal structures and boron bonding of pure boron and MgB_2, as shown in Figure 4. That is, in pure boron, the common building blocks are icosahedral units that consist of 12 boron atoms, and each atom is connected to five other atoms via covalent bonds. By contrast, in MgB_2, each boron atom is connected to a maximum of three other boron atoms. The recent activities of the above-mentioned metal boride systems [136,186–192] are summarized in Table 4.

Figure 4. Schematic illustrations of (a) B_{12} icosahedral unit in boron and (b) layer structure of MgB_2.

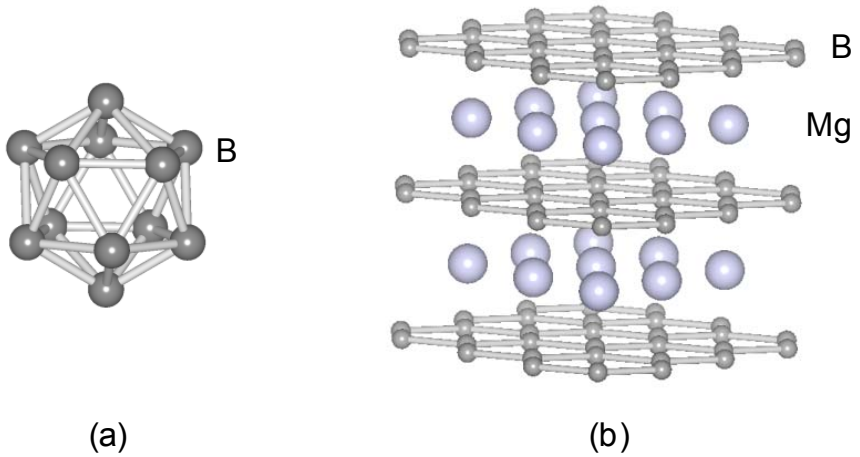


Table 3. Hydrogen storage properties of the combination systems of $M(BH_4)_n$ with metal hydrides, complex hydrides, metals, *etc*.

Reaction	Hydrogen (mass%)			Conditions: temp (K) [pressure (MPa)]		Theor/Exp ΔH_{dehyd} (kJ mol^{-1} H_2)	Reference
	Ideal	Obs (First Dehyd)	Obs (Rehyd)	First Dehyd	Rehyd		
$LiBH_4$ + 1/2 MgH_2 = LiH + 1/2 MgB_2 + 2 H_2	11.5	8.0–10.6	8.0–10	543–723	503–723 [10]	T 50.4–66.8/ E 40.5	[29,120,124, 134–136,142,145,156, 168,172,186]
$LiBH_4$ + 2 $LiNH_2$ = Li_3BN_2 + 4 H_2	11.9	7.8–12	0.1	622–673	573 [5]	E 23	[121,123,124, 127–130,132,149, 160,166]
$LiBH_4$ + 1/2 Al = LiH + 1/2 AlB_2 + 3/2 H_2	8.6	6.8–7.2	5–7.6	553–823	573–773 [10–15.5]	T 18.8–57.9	[134,135,137,163–165]
$LiBH_4$ + 1/2 $LiAlH_4$ = 3/2 LiH + 1/2 AlB_2 + 9/4 H_2	11.1	6–10	4.8–5.1	327–773	623–873 [4–7]		[157]
$LiBH_4$ + 1/2 Mg = LiH + 1/2 MgB_2 + 3/2 H_2	8.9	5.6		648–773		T 46.4	[134,135]
$LiBH_4$ + 1/6 CaH_2 = LiH + 1/6 CaB_6 + 10/6 H_2	11.7	5.1–11.1	9–11.1	423–773	673 [10]	T 45.4–66.5	[19,135,137,142,144, 168]
$LiBH_4$ + 1/2 ScH_2 = LiH + 1/2 ScB_2 + 2 H_2	8.9	4.5		553–723		T 34.1	[134,135,142,143]
$LiBH_4$ + 1/6 CeH_2 = LiH + 1/6 CeB_6 + 10/6 H_2	7.4	6.1–6.2	6.0	443–723	623 [10]	T 44.1	[144,168,177]
$LiBH_4$ + 1/4 YH_3 = LiH + ¼ YB_4 + 15/8 H_2	8.4	7.2		623			[168]
$LiBH_4$ + 1/4 MgH_2 + 1/4 Al = LiH + 1/4 $MgAlB_4$ + 7/4 H_2	10.0	9.4	6	533–673	673 [4]	E 57	[159]
$Ca(BH_4)_2$ + MgH_2 = CaH_2 + MgB_2 + 4 H_2	8.4	7.1		623–723		T 47	[135]

Table 3. *Cont.*

$Ca(BH_4)_2 + MgH_2 = 2/3\ CaH_2 + 1/3\ CaB_6 + Mg + 13/3\ H_2$	9.1	8.1	5.5	593–773	623 [9]	T 45	[187]
$Mg(BH_4)_2 + LiNH_2$ = Li-Mg + BN-related + 5 H_2	13.1	11.4		433–873			[174]
$NaBH_4 + 1/2\ MgH_2 = Na + 1/2\ MgB_2 + 5/2\ H_2$	9.9	9	6	330–723	723 [5]	T 62	[183,186]
$NaBH_4 + 2\ NaNH_2 = Na_3BN_2 + 4\ H_2$ *	7.0			500–773			[173]
x $LiBH_4$ + *y* $(LiNH_2)_2$ + *z* (MgH_2) = $Li_3BN_2 + Mg_3N_2 + LiH + H_2$					453 [15]		[140,141,155]
x:*y*:*z* = 2:1:1	13.0	8.5	2.9	413–743			
2:0.5:1	13.6	8.6	3.7	413–743			
2:1:2	11.8	6.6	3.1	428–743			
1:1:1	11.3	5.6	2.7	428–743			
3:1:1.5	13.4	9.1		413–743			

* represents that the release of NH_3 in the decomposition process: T and E represent the theoretic and experimental values, respectively.

Table 4. Hydrogen storage properties of metal borides and metal hydrides systems.

Reaction	Hydrogen (mass%)			Conditions: temp (K) [pressure (MPa)]		Reference
	Ideal	Obs (First Hyd)	Obs (Dehyd)	First Hyd	Dehyd	
$LiH + 1/2\ MgB_2 + 2\ H_2 = LiBH_4 + 1/2\ MgH_2$	11.5	3.2–11	3.0–8.0	538–673 [9–35]	538–723 [0–0.6]	[120,145, 182,186,187]
$LiF + 1/2\ MgB_2 + H_2 = LiBH_{4-y}F_y + 1/2\ MgF_2 + LiH_{1-x}F_x$		6.6	6.4	663 [6]	693 [0.5]	[189]
$Li_7Sn_2 + 7/2\ MgB_2 + 14\ H_2 = 7\ LiBH_4 + 7/4\ Mg_2Sn + 1/4\ Sn$	5.9	2.5–3		573–673 [20–30]		[186]
$CaH_2 + MgB_2 + 4H_2 = Ca(BH_4)_2 + MgH_2$	8.4	4.7–7		573–673 [20–35]		[186,187]
$NaH + 1/2\ MgB_2 + 2\ H_2 = NaBH_4 + 1/2\ MgH_2$	7.9	6.2–6.7		573–673 [20–35]		[186]
$1/3\ CaB_6 + 2/3\ CaH_2 + 10/3\ H_2 = Ca(BH_4)_2$	9.6	4.8		623 [10]	543–573	[186]
$2/3\ CaH_2 + 1/3\ CaB_6 + 1/2\ Mg + 23/6\ H_2 = Ca(BH_4)_2 + 1/2\ MgH_2$	9.3		4.9–5.9	623–673 [9]		[192]
$MgNi_{2.5}B_2 + 2\ LiH + 4\ MgH_2 + 4H_2 = 2\ LiBH_4 + 5/2\ Mg_2NiH_4$	2.5	1.0	1.0	623 [16]	613 [0.4]	[167]
$MgB_2 + 4\ H_2 = Mg(BH_4)_2$	14.9		11.0	673 [95]		[73,74]

3.2. Promoting Kinetics

$M(BH_4)_n$ dehydrogenates via stepwise reactions accompanied by the formation of intermediate compounds. Although the rate-controlling step has not been determined, the complicated dehydrogenation feature makes the promotion of kinetics rather challenging. There are two approaches that have been extensively studied to reduce the reaction barrier: (a) appropriate additives with catalytic abilities and (b) the nanoconfinement approach.

Complex hydrides including alanates, amides, and borohydrides are commonly known to exhibit sluggish kinetics. Since Bogdanovic *et al.* found that the addition of Ti-based compounds significantly promoted the dehydrogenation-rehydrogenation reactions of $NaAlH_4$ [193], the development of complex hydrides for hydrogen storage has significantly increased. Stimulated by this finding, a large number of additives from oxides, halides, metals, and carbon-based materials to $M(BH_4)_n$ have been examined [19,20,58,87,101,130,144,150,161,168,170,171,191,194–210]; the corresponding dehydrogenation and rehydrogenation properties are summarized in Table 5. For instance, the most effective additive for $LiBH_4$ was found to be the mixture of 0.2 $MgCl_2$ + 0.1 $TiCl_3$, in which approximately 5 mass% of hydrogen was released from 333 K and 4.5 mass% of hydrogen was rehydrogenated at 873 K in 7 MPa H_2 [195]. The addition of $TiCl_3$ was also proved to be effective for $Mg(BH_4)_2$, the starting dehydrogenation temperature of which was reduced to 361 K [58]. Titanium isopropoxide was reported to be an effective additive for the combination system of 2 $LiBH_4$ + MgH_2 [136]. According to the X-ray absorption spectroscopy analysis, titanium isopropoxide was demonstrated to form a disordered TiO_2 anatase during ball milling with 2 $LiBH_4$ + MgH_2. After several dehydrogenation-rehydrogenation cycles, Ti species were demonstrated to change to Ti_2O_3 and TiB_2 [181]. Similar phenomena were reported for most additives, and the oxidation states of the initial additives vary with cycling experiments, though the catalytic mechanism is still uncertain.

The dehydrogenation-rehydrogenation reactions of $M(BH_4)_n$ are accompanied by the diffusion of constituent elements such as *M*, B, and H. The relatively high reaction temperature further prolongs the diffusion distance and enlarges the crystallite size of *M* and B, thus further degrading the hydrogen storage properties. Fabricating and maintaining the nanosized metal borohydrides is expected to be an effective way to overcome the aforementioned barriers. One known approach is to incorporate hydrogen storage materials into nanoporous materials. It was first applied in the NH_3BH_3 system [211] and good improvement was obtained: The dehydrogenation temperature was largely decreased and the amount of borazine gas (an impurity) was significantly reduced. Recently, this approach was introduced for $M(BH_4)_n$ materials, and some recent achievements [160,212–222] are summarized in Table 6.

By the incorporation into nanoporous carbon scaffolds with a 13-nm pore size, the dehydrogenation rates of $LiBH_4$ were found to be up to 50 times faster than those in the bulk materials measured at 573 K [212]. In addition, the capacity loss over three cycles was reduced from 72% for bulk $LiBH_4$ to ~40% for nanoconfined $LiBH_4$. Further, a recent report confirmed the synergetic effects of nanoconfinement and Ni addition on the dehydrogenation and rehydrogenation properties of $LiBH_4$. The nanoconfinement of the mixture of $LiBH_4$ and Ni addition in a nanoporous carbon scaffold shows a higher rehydrogenation rate and larger rehydrogenation amount than those of the samples without Ni addition at 593 K in a hydrogen pressure of 4 MPa [220]. This suggests that the combination of nanoconfinement and additives would be a valid way to improve the hydrogen storage properties of $M(BH_4)_n$.

Table 5. Hydrogen storage properties of $M(BH_4)_n$ with additives (oxides, halides, carbon, *etc*.).

$M(BH_4)_n$	Additives		Hydrogen (mass%)		Conditions: temp (K) [pressure (MPa)]		Toxic Byproduct	Reference
	Type	Amount	Obs (First Dehyd)	Obs (Rehyd)	First Dehyd	Rehyd		
$LiBH_4$	SiO_2	10–25 mass%	9–10 [m]		423–873			[19,20,204]
	TiO_2	25–80 mass%	4–9 [m]	3.5–8.3 [m]	373–873	873 [7–10]		[197,209]
	ZrO_2	25 mass%	8–9 [m]		448–873			[197]
	V_2O_3	25 mass%	8–9 [m]	8 [m]	448–873	873 [10]		[197]
	SnO_2	25 mass%	8–9 [m]		448–873			[197]
	Nb_2O_5	50–80 mass%	4–6 [m]		373–873			[209]
	Fe_2O_3	50–66.7 mass%	5.7–9 [m]		373–873			[209]
	V_2O_5	50–66.7 mass%	5.7–9 [m]		373–873			[209]
	$TiCl_3$	10–88 mass%	2.8–9.2 [m]	3.4 [m]	373–873	773 [7]	B_2H_6	[197,208]
	$CoCl_2$	5–100 mol%	10.5–18.3 [p]		503–873		B_2H_6	[213]
	TiH_2	10–50 mol%	6–15 [m]	2.5–4.5 [m]	573–873	773 [7]		[208]
	TiF_3	10–50 mol%	6.4–14 [m]	0.2–4.0 [m]	373–773	623–773 [7–10]	B_2H_6	[208,211]
	ZnF_2	10–50 mol%	3.7–7 [m]	1–4 [m]	393–773	773 [7]	B_2H_6	[208]
	mixture of $MgCl_2/TiCl_3$	30 mol%	5 [m]	4.5 [m]	333–873	873 [7]		[198]
	Mg	10–20 mol%	9 [m]		333–873			[198]
	Al	20 mol%	7.8 [m]	3.5 [m]	353–873	873 [10]		[198]
	Sc	33 mol%	2.9 [m]		673–773			[134]
	Ti	33 mol%	2.5 [m]		673–773			[134]
	V	33 mol%	4.4 [m]		673–773			[134]
	Cr	33 mol%	4.4 [m]		673–773			[134]
$LiBH_4$	MgH_2	80 mass%	8.8–9.2 [m]	8.5 [m]	627–853	673 [10]		[126,172]
	graphite	30 mass%	9.9 [p]	2.6 [p]	663–773	673 [10]		[212]
	activated carbon	30 mass%	11.2 [p]	4.6 [p]	623–773	673 [10]		[212]
	single-walled carbon nanotubes	30 mass%	11.4 -12.3 [p]	3.7 [p]	553–773	673 [10]		[205,212]
	single-walled carbon nanotubes	9.1–50 mass%	5–11.8 [p]	3.7–6.1 [p]	723 (iso)	673 [10]		[207]

Table 5. *Cont.*

	mesoporous carbon	50 mass%	7 [m]	6 [m]	605–873	623 [3]		[200]
	mixture of TiF_3/SiO_2	50 mass%	8.3 [m]	4 [m]	343–823	773 [4.5]		[204]
	Pt/C	10–50 mass%	9.2–15.7 [m]	6.1 [m]	553–973	873 [3]		[206]
$LiBH_4$ + $1/2MgH_2$	Ti-iso	5–10 mol%	6.5–8.4 [m]	6.0 [m]	673 (iso)	623 [5]		[170,136]
	Zr-iso	10 mol%	5.5 [m]		673 (iso)			[150]
	$ZrCl_4$	10 mol%	7.5 [m]		673 (iso)			[150]
	SiO_2	5 mol%	9.3 [m]		673 (iso)			[136]
	VCl_3	5 mol%	9.1 [m]		673 (iso)			[136]
	graphite	10 mass%	9.5 [p]		723 (iso)			[168]
	carbon nanofibers	10 mass%	10.0 [p]		723 (iso)			[168]
	activated carbon	10 mass%	10.0 [p]		723 (iso)			[168]
	single-walled carbon nanotubes	10 mass%	10.0 [p]	6.7 [p]	~573–773	673 [7.5]		[168]
	muti-walled carbon nanotubes	10 mass%	10.0 [p]		723 (iso)			[168]
	TiF_3	5 mol%	9.7 [p]		573 (iso)			[72]
$Li_3BN_2H_8$	Pt/Vulcan carbon	1–10 mass%	9–13 [m]	1.4 [m]	388–673	423 [8.4]	NH_3	[130]
	Pd	5–10 mass%	11.8–13 [m]		473–673			[130]
	$PdCl_2$	8.3 mass%	10.4 [m]		473–673			[130]
	$CoCl_2$	5 mass%	8–10 [m]		388–493			[149]
$Li_4BN_3H_{10}$	$NiCl_2$	11 mass%	7.6 [p]		433–673		NH_3	[161]
$Ca(BH_4)_2$ + MgH_2	Ti-iso	1 mass%	7.1 [m]		523–723			[190]
$Ca(BH_4)_2$	NbF_5	2 mol%	8.3 [m]	4.6–5.0 [m]	~593–823	623 [9]		[87]
	$NbCl_5$	2 mol%	4.1–5.0 [m]	3.1–4.5 [m]	~593–823	623 [9]		[87]
	TiF_3	2 mol%	4.1–5.0 [m]	2.5–4.2 [m]	~593–823	623 [9]		[87]
	$TiCl_3$	2 mol%	4.1–5.0 [m]	3.5–4.4 [m]	~593–823	623 [9]		[87]
$Mg(BH_4)_2$	$TiCl_3$	25 mass%	13.7 [p]		361–800			[58]
	TiO_2	25 mass%	13.7 [p]		483–800			[58]

[m] indicates the value referred to the mixture of metal borohydride with side products, while [p] indicates the value referred to the pure metal borohydride.

Table 6. Hydrogen storage properties of $M(BH_4)_n$ confined by nanoporous materials.

Reaction	Type of Nano Scaffold (size (nm))	Loading Ratio (mass%)	Hydrogen (mass%)		Conditions: temp (K) [pressure (MPa)]		Reference
			Obs (First Dehyd)	Obs (Rehyd)	First Dehyd	Rehyd	
$LiBH_4 = LiH + B + 3/2\ H_2$	Nanoporous Carbon (13–25)	25–50	4.6–6.4 ^{m}		503–873	673 [10]	[212]
	Activated carbon (1.75–3.2)	28.4	11.2 ^{p}	6.6 ^{p}	493–773	573 [5]	[213]
	Mesoporous carbon (4)	33	3.4 ^{m}		473–773		[214]
	Nanoporous Carbon (2)		8.8 ^{p}		493–673		[219]
$Li_3BN_2H_8 = Li_3BN_2 + 4\ H_2$ *	Nanoporous carbon scaffolds (16 ± 3)	33	11.1 ^{p}	3.8 ^{p}	523–673	573 [5]	[160]
	activated carbon AX-21 (2)	33	10.7 ^{p}	4.0 ^{p}	438–673	573 [5]	[160]
$Mg(BH_4)_2 = MgB_2 + 4\ H_2$	Activated carbon (<2)	44 ± 3	6.0 ^{m}		443–773		[216]
$LiBH_4$ + 3.75 mass%Ni	Nanoporous carbon (2–3)	25	14 ^{p}	10 ^{p}	473–673	593 [4]	[220]
$LiBH_4 + 1/2\ MgH_2 = LiH + 1/2\ MgB_2 + 2\ H_2$	Nanoporous carbon aerogel (~21)		4.7 ^{m}	4 ^{m}	533–743	643–663 [5–10]	[221]

* represents that the release of NH_3 in the decomposition process; ^{m} indicates the value referred to the mixture of metal borohydride with side products, while ^{p} indicates the value referred to the pure metal borohydride.

4. Conclusions

Metal borohydrides $M(BH_4)_n$ with an extremely high hydrogen density, have been regarded as potential candidates for on-board hydrogen storage. The high reaction temperature and sluggish kinetics, however, decrease their potential for practical applications. In order to overcome these barriers, a number of efforts have been devoted to improving the hydrogen storage properties in both thermodynamic and kinetic areas. The thermodynamic stability of $M(BH_4)_n$ can be predicted and tailored by considering the electronegativity of *M*. The multistep reaction pathway together with the formation of an intermediate compound such as $M(B_{12}H_{12})_{n/2}$, might account for the high reaction temperature and slow kinetics. The suppression of the formation of $M(B_{12}H_{12})_{n/2}$ can be realized by the combination of $M(BH_4)_n$ with other hydrides or metals. This approach changes the reaction pathway, and therefore, improves the hydrogen storage properties in both thermodynamic and kinetic areas. Regarding the improvement of reaction kinetics, both additives and nanoconfinement have been proved to be vital.

None of the current materials can fulfill the requirements of on-board hydrogen storage for fuel cell vehicles; therefore, continued efforts are required to develop novel materials. According to theoretical predications, many $M(BH_4)_n$ have the potential to release hydrogen at a moderate temperature, and the sluggish kinetics are considered to be mainly responsible for the high reaction temperature. Effective strategies to achieve fast reaction kinetics will be an important research direction to achieve practical success with metal borohydrides.

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