Review

Boron Hydrogen Compounds: Hydrogen Storage and Battery Applications

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Abstract: About 25 years ago, Bogdanovic and Schwickardi (B. Bogdanovic, M. Schwickardi: J. Alloys Compd. 1–9, 253 (1997) discovered the catalyzed release of hydrogen from NaAlH4. This discovery stimulated a vast research effort on light hydrides as hydrogen storage materials, in particular boron hydrogen compounds. Mg(BH4)2, with a hydrogen content of 14.9 wt %, has been extensively studied, and recent results shed new light on intermediate species formed during dehydrogenation. The chemistry of B3H8−, which is an important intermediate between BH4− and B12H122−, is presented in detail. The discovery of high ionic conductivity in the high-temperature phases of LiBH4 and Na2B12H12 opened a new research direction. The high chemical and electrochemical stability of closo-hydroborates has stimulated new research for their applications in batteries. Very recently, an all-solid-state 4 V Na battery prototype using a Na4(CB11H12)2(B12H12) solid electrolyte has been demonstrated. In this review, we present the current knowledge of possible reaction pathways involved in the successive hydrogen release reactions from BH4− to B12H122−, and a discussion of relevant necessary properties for high-ionic-conduction materials.

Keywords: boron hydrides; hydrogen storage; solid ionic conductors

1. Introduction

Boron hydrogen compounds have been intensively studied for almost a century since the pioneering studies of A. Stock [1]. Boron hydrogen compounds are also energetic materials and were considered as rocket or jet fuels [2]; however, the toxicity of boranes has prevented their extended use. Currently, nontoxic compounds such as ammonia-borane are also studied as hypergolic propellants [3,4]. Recently, many different applications of boron hydrogen compounds have emerged [5]. In particular, compounds derived from closo-hydroborates such as B12H122− have found many new applications, including new all-solid-state batteries, medical applications, and as catalysts [6–11]. Since the discovery of catalyzed hydrogen release in NaAlH4 by Bogdanovic and Schwickardi [12], light boron and aluminum hydrides were intensively studied and reviewed as potential hydrogen storage materials [13–22]. The dehydrogenation reactions of metal borohydrides ultimately lead to hydrogen, metal and boron, or metal borides. In this reaction process, intermediate species are formed, particularly compounds with closo-hydroborate anion B12H122− [23,24]. B12H122− is particularly stable and can thus also act as a detrimental thermodynamic sink for further dehydrogenation reactions. The properties of closo-hydroborates and related anions were addressed in several recent publications [6,25–28]. New research on the thermal properties of closo-hydroborate salts revealed a high-temperature phase transition in Na2B12H12 leading to a superionic phase [29]. Thus, the controlled dehydrogenation of a borohydride salt can be used to safely prepare new closo- and nido- hydroborate salts for potential battery applications [30] without using toxic boranes such as B10H14, which were used for the synthesis of this large boron species [31].

In this review, we first describe experimental results on hydrogen storage in Mg(BH4)2, which has a large hydrogen content of 14.9 wt %. Hydrogen storage in other borohydrides, such as LiBH4, was recently reviewed [32]. Recent results on potential dehydrogenation...
intermediates for Mg(BH$_4$)$_2$ provide new insights on the potential reaction intermediates and are reported here. In this context, we then present recent results based on DFT calculations to explore possible reaction paths for successive dehydrogenation reactions starting from BH$_4^-$.

These paths are described in more detail in the following section, which discusses the formation and reactions of B$_3$H$_8^{2-}$, as this ion is considered to be one of the reaction intermediates during the dehydrogenation of borohydride compounds. The high-temperature dehydrogenation of B$_3$H$_8^{-}$ leads to the formation of closo-hydroborate anions B$_{10}$H$_{10}^{2-}$ and B$_{12}$H$_{12}^{2-}$, which form excellent solid ionic conductors for new all-solid-state batteries [30]. The properties of these ionic conductors are presented in the last section.

2. Magnesium Borohydride

Among the many compounds considered for hydrogen storage, Mg(BH$_4$)$_2$ is particularly interesting and has been studied by many authors. The earlier studies on Mg(BH$_4$)$_2$ were reviewed in detail in 2016 [22]. Mg(BH$_4$)$_2$ has a hydrogen content of 14.9 mass % [22,33]. This compound can be prepared in different crystalline modifications, and high-pressure-phase transitions were also observed [33]. Porous γ-Mg(BH$_4$)$_2$ can also adsorb 0.8 H$_2$ at low temperatures and 100 bar to achieve a total hydrogen mass content of 17.4% [33]. High-pressure phase δ-Mg(BH$_4$)$_2$ has a very high volumetric hydrogen content of 147 g H$_2$/L. Mg(BH$_4$)$_2$ can also form amorphous solids. Overall dehydrogenation reaction

$$\text{Mg(BH}_4\text{)}_2 \rightarrow \text{MgB}_2 + 4 \text{H}_2$$

is, in fact, a multistep reaction (see Figure 1) with various reaction intermediates, such as Mg(B$_3$H$_8$)$_2$, MgH$_2$, and MgB$_{12}$H$_{12}$, which were proposed both experimentally and theoretically [22,34–36]. MgB$_2$ is the decomposition product obtained after heating to 500 °C [37]. Boron-rich MgB$_7$ films are obtained by heating volatile Mg(B$_3$H$_8$)$_2$ solvates with dimethyl ether and diethyl ether [38].

![Figure 1. Illustration of Mg(BH$_4$)$_2$ dehydrogenation reactions (blue arrows) and rehydrogenation reactions (red arrows) reported in the literature [22,34–44]. Upon further heating, these intermediate species, which are associated with (amorphous) MgH$_2$, form MgB$_2$.](image)

MgB$_2$ can be rehydrogenated, although under drastic conditions (950 bar H$_2$ at 400 °C) [40]. The rehydrogenation of MgB$_2$ can be accelerated with THF, MgH$_2$, and Mg [41]. Mechanically milled mixtures of MgB$_2$, THF, and 40 mol % Mg could thus ab-
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sorb 6 wt % of H$_2$ at 300 °C under 700 bar of H$_2$, which is less drastic than that without THF. Recently, rehydrogenation at room temperature with mechanical activation by ball milling was reported [42]. These rehydrogenation reactions of MgB$_2$ demonstrate the principle that hydrogen storage in Mg(BH$_4$)$_2$ is indeed reversible. A recent combined experimental and theoretical study concluded that the initial stages of rehydrogenation are associated with the formation of σ bonds of hydrogen with boron on the reactive edges of the MgB$_2$ solid [43]. The rehydrogenation of intermediate compounds was also studied. MgB$_2$THF can be rehydrogenated under milder conditions than those of dry MgB$_2$H$_8$ (50 bar H$_2$ and 200 °C for 5 h vs. 120 bar H$_2$ and 250 °C for 48 h) [44]. MgH$_2$ is formed in intermediate reaction steps, such as

$$6 \text{Mg}(\text{BH}_4)_2 \rightarrow \text{MgB}_12\text{H}_{12} + 5 \text{MgH}_2 + 13 \text{H}_2$$

Magnesium hydride dissociates into Mg and H$_2$ at high temperatures and low H$_2$ pressures. The different reaction products observed under various conditions (see Figure 1) show that the reaction kinetics can be influenced by various parameters, which also include the initial crystalline modification of Mg(BH$_4$)$_2$.

The overall enthalpy of reaction for the dehydrogenation of Mg(BH$_4$)$_2$ (ΔH$^\circ = -208$ kJ/mol) to form MgB$_2$ (ΔH$^\circ = -91.96$ kJ/mol) and hydrogen can be calculated [45–47] to be equal to $+116$ kJ/mol, i.e., less than 30 kJ/mol per hydrogen molecule released, which is, in principle, in the correct range for a hydrogen storage material [13]. The first step of a dehydrogenation reaction of BH$_4^-$ is likely to be the breaking of a B–H bond. Isotope exchange reactions of Mg(BH$_4$)$_2$ with D$_2$ allow for producing a complete exchange to form Mg(BD$_4$)$_2$, and the corresponding activation energy was estimated to be about 51 kJ/mol [48]. For Ca(BH$_4$)$_2$, the corresponding activation energy was found to be 82 and 98.5 kJ/mol for the reverse reaction, confirming that breaking a bond with hydrogen or deuterium is the rate-limiting step [49]. Theoretical calculations of potential defects in Mg(BH$_4$)$_2$ suggest that, in the initial phase of the dehydrogenation, a H$^-$ ion is formed that can diffuse in the lattice [50]. On the other hand, gas diffusion in the solid is also a contribution to exchange kinetics, as was shown by isotope exchange reactions with the highly porous modification of γ-Mg(BH$_4$)$_2$ with a high surface area compared to a ball-milled sample with a strongly reduced surface area [51].

The reaction kinetics of hydrogen release in Mg(BH$_4$)$_2$ can be significantly enhanced by various additives, such as TiCl$_3$ [52] or NbF$_5$ and TiO$_2$ [53]. Lewis bases in the form of solvates of Mg(BH$_4$)$_2$ can also accelerate the hydrogen release [54]. As shown in Figure 1, the THF solvate releases H$_2$ gas below 200 °C to form Mg(B$_{10}$H$_{10}$). The formation of B$_2$H$_6^-$ and B$_{12}$H$_{22}^2 $− was also observed, but with THF and dimethyl ether, B$_{12}$H$_{22}^2 $− remained a minor reaction product. The physical properties of Mg(BH$_4$)$_2$-3THF were recently investigated in detail [55]. In this compound, Mg$^{2+}$ is coordinated to 2 BH$_4^-$ ions and 3 THF molecules. The orientational mobilities of the BH$_4^-$ ions are not particularly sensitive to the presence of THF. The authors concluded that “the presence of THF also disrupts the stability of the crystalline phase leading to enhanced kinetics for the dehydrogenations”.

Recently, Tran et al. [56] reported that the presence of different glymes with Mg(BH$_4$)$_2$ results in various ratios of MgB$_{10}$H$_{10}$ and MgB$_{12}$H$_{12}$ upon thermolysis at 160–200 °C, and allows for selectively obtaining MgB$_{10}$H$_{10}$ with one equivalent of monoglyme. Mixtures of Mg(BH$_4$)$_2$ with (CH$_3$)$_2$NBH$_4$ (5:1 molar) reveal reversible melting around 180–195 °C [57] with enhanced stability compared to melts of pure Mg(BH$_4$)$_2$ and (CH$_3$)$_2$NBH$_4$. [Ph$_4$P]$_2$[Mg(BH$_4$)$_4$] gradually loses mass over 225–230 °C, but heating to 500 °C does not lead to the mass loss expected for the formation of MgB$_2$. A similar behavior was observed for [Me$_4$N]$_2$[Mg(BH$_4$)$_4$] [58]. These findings suggest that derivatives of Mg(BH$_4$)$_2$ with organic cations are rather stabilized.

Solvant-free Mg(B$_3$H$_8$)$_2$ can be prepared by ball milling MgB$_2$ with NaB$_3$H$_9$ [38,59]. Kim et al. [38] reported the formation of boron-rich MgB$_7$ films upon heating under vacuum above 425 °C due to some evaporation of Mg under these conditions. Thermogravimetry (TG) experiments [59] revealed a 30 wt % mass loss setting in above ca 80 °C corresponding to the evolution of B$_2$H$_6$, B$_3$H$_9$ and H$_2$. The residual solid after heating to 200 °C was a
mixture of mainly Mg(BH$_4$)$_2$, Mg(B$_{10}$H$_{10}$), and Mg(B$_{12}$H$_{12}$), and the combined evolution of H$_2$, B$_2$H$_4$, and B$_2$H$_6$ was confirmed by mass spectrometry [60]. The addition of activated (ball-milled) MgH$_2$ to Mg(B$_3$H$_6$)$_2$ results in a strong reduction in borane evolution and up to 88% conversion back to Mg(BH$_4$)$_2$ at 100 °C. The presence of activated MgH$_2$ thus substantially decreases the formation of (closo-hydro)borates and provides the necessary hydrogen for the conversion of B$_3$H$_8^-$ back into BH$_4^-$.

These experiments suggest that, while Lewis acids may favor the dehydrogenation reactions of Mg(BH$_4$)$_2$, they do not necessarily catalyze the rehydrogenation reactions, as transition metal halides do not appear to affect the rehydrogenation of MgB$_2$ [40,61]. THF and other Lewis bases appear to accelerate both the dehydrogenation and rehydrogenation reactions of Mg(BH$_4$)$_2$, and encourage more studies to even further improve the kinetics.

3. DFT Calculations

The results presented above for Mg(BH$_4$)$_2$ suggest the formation of various intermediate species such as B$_2$H$_6^{2-}$, B$_3$H$_8^-$, B$_4$H$_{10}^{2-}$, B$_5$H$_{12}^{2-}$ and the closo-borates B$_n$H$_{2n}^{2-}$ ($n = 8–12$). For hydrogen storage applications, the only gaseous species resulting from dehydrogenation reactions should be hydrogen; thus, neutral boranes are a priori not involved in the reaction mechanisms. Many other anionic boron hydrides have been reported in the literature and could be involved in one reaction step or another. In 1999, some reactions between neutral and anionic boron hydrides related to the formation of B$_3$H$_8^-$, B$_5$ anions, and some other species were reviewed [62].

In order to assess the driving forces for different reactions, thermodynamic information can be very useful, but experimental data are very scarce. For alkali borohydrides, thermodynamical data are available [47], but only few other experimental data are available. Using the experimental values of the formation enthalpy of Mg(BH$_4$)$_2$ [45] and La(BH$_4$)$_3$ [63], the formation enthalpy of other M(BH$_4$)$_2$ and M(BH$_4$)$_3$ compounds were estimated, assuming that the lattice enthalpy of bromides and borohydrides with the same metal ion were identical within about 15 kJ/mol [46]. The experimental formation enthalpy of NH$_4$B$_3$H$_6$ ($-530 \pm 33$ kJ/mol) [64], (NH$_4$)$_2$B$_{10}$H$_{10}$ ($-359.2 \pm 10$ kJ/mol) [65], and of guanidinium and other nitrogen-based closo-borates was reported [66]. Recently, new heat capacity measurements for Na, K, Rb, Cs, Mg, Ca borohydrides were reported [67]. The knowledge of all thermodynamic properties in principle allows for quantitatively describing the phase diagram of a system, which was performed using available data for the Mg–B–H system [68].

In the absence of experimental data, theoretical data are obtained. It is quite challenging to obtain accurate results of formation enthalpies using DFT. Nguyen et al. [69] calculated for the formation enthalpy of (NH$_4$)$_2$B$_{10}$H$_{10}$ with the G3 method the value of $-184$ kJ/mol, which is quite different from the experimental value of $-359.2$ kJ/mol. For $\alpha$-Mg(BH$_4$)$_2$, formation enthalpy values ranging from $-67$ to $-277$ kJ/mol were reported in the literature [68], while the experimental value was $-208$ kJ/mol [45]. Zhang et al. [23] computed relative formation energies of potential solid intermediates formed during the dehydrogenation of Mg(BH$_4$)$_2$, in combination with a Monte Carlo-based structure prediction method. They predicted a potential Mg$_2$(B$_3$H$_6$)$_2$ intermediate with a B$_3$H$_8^{3-}$ ion, while Mg(B$_3$H$_8$)$_2$ was found to be very high in relative energy and thereby unlikely to be formed.

The principal difficulty for estimating the formation enthalpy of crystalline solids is the evaluation of lattice energy, as different approaches (volume-based, Kaputinski equation etc.) lead to different values. Further, lattice energies can only be computed for crystalline materials, preferentially on the basis of experimental structure data, but experiments showed that a significant fraction of the reaction intermediates remain amorphous, complicating things even further.

DFT calculations in the gas phase are quite reliable, and allow for obtaining good structural data and vibrational frequencies, in particular when anharmonicity is included. Several studies report the formation enthalpy of borohydride ions in the gas phase [69–72].
Anharmonic DFT calculations allow for obtaining improved agreement with experimental vibrational spectra, from which heat capacity data were calculated [73]. Figure 2 compares experimental [74] and DFT calculated [69–72] formation enthalpy data for neutral and anionic boron hydrogen species. Figure 2 shows that the calculated formation enthalpy for a given species (e.g., $B_3H_8^-$) can differ by about 100 kJ/mol for different sources. These values are derived, for instance, from isodesmic reactions with known formation heat [69], thus generating a potential propagation of errors if the initial formation enthalpy values are different. We outline all reported values to highlight the limitations of the accuracy of these data.

![Figure 2](image-url)

**Figure 2.** Experimental (bold) and theoretical formation enthalpy values for neutral (red) monoanionic (black) and dianionic (blue) species. *Closa* species, circles; *nido*, #; *arachno*, crossed squares. Data from [69–72,74–76]. For *closa* ions $B_nH_{2n}^{2-}$, data (blue circles) from 2 different studies [69,72] reveal systematic differences. All monoanionic species (in black) have negative formation enthalpies, while all neutral boranes (in red) have positive formation enthalpy.

Figure 2 shows that the experimental formation enthalpies of neutral species are all positive [74], with values ranging from 36 kJ/mol (for $B_2H_6$) to 210 kJ/mol for ($B_2H_4$). Gas phase reaction

$$2 \text{B}_2\text{H}_6 \rightarrow \text{B}_4\text{H}_{10} + \text{H}_2$$

has an enthalpy change of $66.1 - 2 \times 36.4 = -6.7$ kJ/mol, and shows that increasing the number of boron atoms in the cluster can be thermodynamically favorable for neutral species. Other reactions towards larger hydroboranes may become favorable at higher temperatures from the liberation of hydrogen. The first theoretical studies of enthalpy changes for reactions of neutral boranes were reported by M.L. McKee in 1990 [70], who showed that a sequence of BH$_3$ additions followed by H$_2$ elimination from $B_2H_6$ to $B_4H_{10}$ is overall exothermic, but with two less stable reaction intermediates ($B_3H_9$ and $B_4H_8$) that can act as barrier steps for the kinetics. Figure 2 shows that anionic species with 9–12 boron atoms are the most stable, which indicates that there is a thermodynamic driving force towards these anions. The most stable species in this figure is the *closa* $B_{12}H_{12}^{2-}$ ion, and its stability is related to its 3-dimensional aromaticity [6]. The formation enthalpy of $B_{12}H_{12}^{2-}$ in the gas phase was estimated to be between $-325.5$ and $-428.6$ kJ/mol according to different theoretical studies [72,75,76]. One key intermediate in the overall dehydrogenation reactions of $BH_4^-$ appears to be ion $B_3H_8^-$, which is discussed in the next section.
4. Formation and Reactions of $\text{B}_3\text{H}_8^-$

As mentioned above, the formation of $\text{Mg(B}_3\text{H}_8)_2$ was observed during the decomposition of $\text{Mg(BH}_4)_2$ under dynamic vacuum [54,77], and $\text{Y(B}_3\text{H}_8)_3$ was obtained after heating $\text{Y(BH}_4)_3$ under hydrogen pressure of 1–10 bar [78]. There are several reports in the literature on the synthesis of $\text{B}_3\text{H}_8^-$ that highlight that various routes can lead to this ion. Starting from diborane under strongly reducing conditions, dianion $\text{B}_2\text{H}_6^{2-}$ was reported to form [62,79]

$$2\text{B}_2\text{H}_6 + 2\text{C}_8\text{H}_{10}^- \rightarrow [\text{BH}_3^{2-}] + \text{BH}_3 + 2\text{C}_8\text{H}_{10}^→ [\text{B}_2\text{H}_6^{2-}] + 2\text{C}_8\text{H}_{10}^-$$

$\text{BH}_3^{2-}$ and $\text{B}_2\text{H}_6^{2-}$ intermediates were identified by NMR. The reaction of $\text{B}_2\text{H}_6^{2-}$ with additional diborane yields $\text{B}_3\text{H}_8^−$ + $\text{BH}_4^−$, and no further intermediate was observed:

$$\text{B}_2\text{H}_6 + \text{B}_2\text{H}_6^{2-} \rightarrow \text{B}_3\text{H}_8^- + \text{BH}_4^-$$

Another reaction observed was the reaction of potassium metal with THF$\cdot$BH$_3$ [80].

$$2\text{K} + 4 \text{THF\cdotBH}_3 \rightarrow 2\text{K}^+ + \text{B}_3\text{H}_8^- + \text{BH}_4^-$$

Beall and Gaines [62] argue that also in this case, $\text{B}_2\text{H}_6^{2-}$ is the reaction intermediate, which can then react with THF$\cdot$BH$_3$ to form either $\text{B}_3\text{H}_8^-$ + $\text{BH}_4^-$ with the addition of the fourth THF$\cdot$BH$_3$ $\text{B}_3\text{H}_8^-$, or first with THF$\cdot$BH$_3$ the ion $\text{B}_3\text{H}_8^{2-}$, which then reacts with THF$\cdot$BH$_3$ to yield $\text{B}_3\text{H}_8^-$ + $\text{BH}_4^-$. $\text{B}_3\text{H}_8^-$ can also be formed from the reaction of $\text{BH}_4^-$ with diborane [81]:

$$\text{BH}_4^- + \text{B}_2\text{H}_6 \rightarrow \text{B}_3\text{H}_8^- + \text{H}_2$$

$$\text{BH}_4^- + \text{B}_2\text{H}_6 \rightarrow \text{B}_3\text{H}_8^- + \text{H}_2$$

$$\text{BH}_4^- + \text{B}_2\text{H}_6 \rightarrow \text{B}_3\text{H}_8^- + \text{H}_2$$

$$\text{BH}_4^- + \text{B}_2\text{H}_6 \rightarrow \text{B}_3\text{H}_8^- + \text{H}_2$$

This reaction can proceed either via $\text{B}_2\text{H}_7^-$ (hydride transfer) and $\text{B}_3\text{H}_10^-$ (BH$_3$ addition) followed by H$_2$ detachment or via $\text{B}_2\text{H}_7^-$, which first loses H$_2$ to form $\text{B}_2\text{H}_5^-$, which then adds BH$_3$. The efficient synthesis of alkali metal octahydrotriborates ($\text{M} = \text{Na, K, Rb, Cs}$) from the reaction of MBH$_4$ with 2 equivalents of dimethyl sulfide borane was reported [82]. The formation of ion $\text{B}_2\text{H}_7^-$ was observed by NMR for the reaction of LiBH$_4$ with THF$\cdot$BH$_3$ in THF [83], and during the solvothermal reaction of $\text{BH}_4^-$ with $\text{CH}_2\text{Cl}_2$ at 70 ºC [84]. The reaction of BD$_3^−$ requires higher temperatures (90 ºC) [84], which suggests that the rate-determining reaction step is associated with the breaking of a boron–hydrogen (deuterium) bond, which could be the formation of a reactive Lewis adduct of BH$_3$ from $\text{BH}_4^-$, which then reacts with other BH$_4^-$ to form $\text{B}_2\text{H}_7^-$ etc., as outlined above.

Once formed, $\text{B}_3\text{H}_8^-$ can further react to yield $\text{B}_9$ to $\text{B}_{12}$ hydroborate anions. Using the DFT calculation formation enthalpies of $\text{B}_9\text{H}_{14}^-$, $\text{B}_3\text{H}_8^-$ and $\text{BH}_4^-$ [71], for the gas phase reactions, one obtains

$$4\text{B}_3\text{H}_8^- \rightarrow \text{B}_9\text{H}_{14}^- + 3\text{BH}_4^- + 3\text{H}_2$$

$$4\text{B}_3\text{H}_8^- \rightarrow \text{B}_{10}\text{H}_{10}^{2-} + 2\text{BH}_4^- + 9\text{H}_2$$

4-exothermic reaction enthalpy values of $-413$ and $-49.8$ kJ/mol, respectively, and a strong entropy increase that even further favors the reaction at higher temperatures. These spontaneous overall reaction enthalpies also explain why potential reaction intermediates with 6 to 8 boron atoms are practically not observed. The simultaneous production of $\text{BH}_3^-$ in these reactions adds a thermodynamic driving force (as the formation enthalpy of $\text{BH}_3^-$ is negative) for these reactions.

In the presence of hydrides, Grinderslev et al. [85] observed the following decomposition reaction at 150 and 200 ºC of KB$_3$H$_8$ under 380 bar of H$_2$:

$$\text{KB}_3\text{H}_8 + 2\text{KH} \rightarrow \text{KB}_4 + \text{K}_2\text{B}_{12}\text{H}_{12} + \text{K}_2\text{B}_{10}\text{H}_{10} + \text{K}_2\text{B}_9\text{H}_9$$
As shown above, heating solvent-free Mg(B₃H₈)₂ + 4 MgH₂ either with or without H₂ gas results in up to 88% back conversion to Mg[BH₄]₂ with some MgB₁₂H₁₁₂ [60]. These results show that B₃H₈⁻ can react in many different ways to either form larger boron hydride clusters or regenerate BH₄⁻. This can be exploited, for instance, to achieve the direct synthesis of B₁₀H₁₀₂⁻ and B₁₂H₁₂₂⁻ to prepare solid ionic conductors such as Na₄(B₁₀H₁₀)(B₁₂H₁₂), as demonstrated by Gigante et al. [86]. This synthesis starts with the conversion of NaBH₄ into (Et₄N)BH₄, which reacts solvothermally with CH₂Cl₂ to form (Et₄N)BH₄. (Et₄N)B₃H₈ is then heated in toluene at 185 °C to form a mixture of (Et₄N)B₁₀H₁₀ and (Et₄N)B₁₂H₁₂, which can then either be separated by fractional crystallization or directly converted with sodium tetraphenylborate into ionic conductor Na₄(B₁₀H₁₀)(B₁₂H₁₂).

5. Closoborates and Related Species as Solid Ionic Conductors

Solid ionic conductors for lithium or sodium batteries allow for avoiding the use of a flammable organic electrolyte and are thus expected to considerably improve the safety of batteries. A good solid electrolyte must fulfill several empirical criteria, according to [87]:

- “open structure” with a low coordination number of the mobile ion;
- The presence of structural phase transitions at low pressure. In the case of AgI, the ambient pressure wurtzite structure (space group P6₃mc) transforms at 3 kbar and 315 K into a NaCl structure (space group Fm-3m), thus going from a rather covalent network with coordination number 4 to a rather ionic structure with coordination number 6. The associated charge fluctuations between ions can potentially be coupled to vibrational motions and thus dynamically favor ionic conduction.

For practical applications, the conductivity of the material should be higher than 1 mS/cm. Further, the material should have high chemical and thermal stability, and a high electrochemical stability window. Additionally, it must be electronically insulating to avoid battery self-discharge or shortage. Further, the electrolyte should be deformable in order to accommodate the volume changes of anode and cathode materials upon lithium or sodium insertion and removal. This can thus limit the formation of fractures that reduce the performance of the battery. Lastly, the material should not be toxic and be cheap enough for the considered applications.

The discovery of superionic conductivity in the high-temperature phases of LiBH₄ [88] and Na₂B₁₂H₁₂ [29] has stimulated new research for similar compounds with high ionic conductivity at lower temperatures. These compounds include closo-hydroborates, nido-hydroborates (B₁₁H₁₄⁻), and closo-hydrocarborates (CB₉H₁₀⁻, CB₁₁H₁₁⁻). Ions B₁₀H₁₀²⁻ and B₁₂H₁₂₂⁻ are not very toxic. Mutterties et al. [89] reported LD₅₀ values for Na₂B₁₀H₁₀ and Na₂B₁₂H₁₂ administered orally to rats to be around or higher than 7.5 g/kg of body weight for both compounds.

The crystal chemistry of inorganic hydroborates except BH₄⁻ was recently presented in detail [90], while the crystal chemistry of salts with BH₄⁻ was addressed in an earlier review [18]: “All nonmolecular hydroborate crystal structures can be derived by simple deformation of the close-packed anionic lattices, i.e., cubic close packing (ccp) and hexagonal close packing (hcp), or bodycentered cubic (bcc), by filling tetrahedral or octahedral sites” [90]. This observation can be illustrated considering group–subgroup relationships of encountered crystal structures, as illustrated in Figure 3 for some relevant compounds [90–102]. Crystal packing is governed by large anions, leaving in some space groups empty cationic sites, which, of course, favor ionic conduction. For instance, β-Na₂B₁₂H₁₂ crystallizes in the Pm-3n space group with a statistical population of 6 sites occupied by 4 Na⁺ ions.

Perturbations of the anionic sublattice further allow for stabilizing the conductive phase at lower temperatures. This was first demonstrated for solid solutions of LiBH₄ with LiBr and LiI [103]. Phase stability and ionic conductivity in mixed LiBH₄–LiX (X = Cl, Br) was recently studied in detail [104]. Perturbations of the structure by ball milling or partial substitution was demonstrated for Na₂B₁₂H₁₂ with a partial introduction of iodine ions in the closo-hydroborate [105]. In a further step, solid solutions of closo-hydroborate and
closo-carbahydroborates, and solid solutions of nido-hydroborates with closo-hydroborates were studied [106–112]. Representative examples of mixed borate ionic conductors are shown in Table 1.

| Compound | Temperature | Conductivity | Reference |
|----------|-------------|--------------|-----------|
| 0.7 Li(CB₁₀H₁₀)–0.3 Li(CB₁₁H₁₂) | 298 K | 6.7 mS/cm | [106] |
| Li₂(B₁₁H₁₂)(CB₁₁H₁₂) | 298 K | 0.11 mS/cm | [107] |
| Li₂(B₁₁H₁₂)(CB₁₁H₁₂) | 298 K | 1.1 mS/cm | [107] |
| Na₃(CB₁₁H₁₂)(B₁₂H₁₂) | 298 K | 2 mS/cm | [108] |
| Na₄(CB₁₁H₁₂)(B₁₂H₁₂) | 298 K | 2 mS/cm | [108] |
| Na₄(B₁₀H₁₀)(B₁₂H₁₂) | 298 K | 0.9 mS/cm | [109] |
| Na₂(B₁₀H₁₀)–3 Na₂(B₁₂H₁₂) | 298 K | 0.34 mS/cm | [110] |
| Naₓ₀₂ₓ(B₁₁H₁₄)ₓ(B₁₂H₁₂)₀₉ | 298 K | 3–4 mS/cm | [111] |

The mechanism of ionic conduction in these compounds is related to the dynamical properties of the borohydride or carbohydride ions. These properties can be addressed using NMR [113] and neutron techniques [114], in conjunction with temperature-dependent conductivity and X-ray diffraction, and are supported by theoretical calculations [76,77,88]. A detailed study of ionic conductor Na₄(B₁₂H₁₂)(B₁₀H₁₀) [115] with all these techniques revealed 3 different regimes with increasing temperature. Below ~50 °C, conductivity remains very low. Above this temperature, an apparent activation energy of 0.6 eV was found, related to significant couplings of anionic and cationic motions. Above 70 °C, activation energy decreases to 0.37 eV, as thermal energy leads to noncorrelated ionic motions.

One important aspect of solid ionic conductors is their electrochemical stability, which is a critical limit for a reversible battery application. Asakura et al. [116] developed a linear sweep voltammetry method to reliably measure the electrochemical stability of borohydride-based solid electrolytes. The measured oxidative stability of LiBH₄ of 2.0 V
vs. Li\textsuperscript{+}/Li was significantly smaller than that in initial reports claiming a stability of up to 5 V [117]. For Na\textsubscript{4}(B\textsubscript{12}H\textsubscript{12})(B\textsubscript{10}H\textsubscript{10}), two oxidation onsets at 3.02 and 3.22 V vs. Na\textsuperscript{+}/Na were tentatively assigned to the onset of decomposition of the less stable [B\textsubscript{10}H\textsubscript{10}]\textsuperscript{2−} and more stable [B\textsubscript{12}H\textsubscript{12}]\textsuperscript{2−} ions, respectively [116]. Closo-carborane ions are even more stable, as for Na\textsubscript{4}(CB\textsubscript{11}H\textsubscript{12})\textsubscript{2}(B\textsubscript{12}H\textsubscript{12}), where a large anodic current was observed above 4 V vs. Na\textsuperscript{+}/Na, together with a small onset at 2.93 V. For Li\textsubscript{2}(CB\textsubscript{9}H\textsubscript{10})(CB\textsubscript{11}H\textsubscript{12}), the onset of decomposition was observed at 2.86 V vs. Li\textsuperscript{+}/Li [116]. Nido-borates are electrochemically less stable. The oxidative stability limit for Na\textsubscript{5}(B\textsubscript{11}H\textsubscript{14})(B\textsubscript{12}H\textsubscript{12})\textsubscript{2} was 2.6 V vs. Na\textsuperscript{+}/Na, and for Li\textsubscript{2}B\textsubscript{11}H\textsubscript{14}, 2.6 V vs. Li\textsuperscript{+}/Li [107].

These developments have also led to several all-solid-state battery prototypes based on these mixed borate ionic conductors. Duchêne et al. [118] presented a 3 V sodium battery using Na\textsubscript{4}(B\textsubscript{12}H\textsubscript{12})(B\textsubscript{10}H\textsubscript{10}), and Murgia et al. [119] showed Na stripping/plating over >500 h in a Na cell with Na\textsubscript{4}(CB\textsubscript{11}H\textsubscript{12})\textsubscript{2}(B\textsubscript{12}H\textsubscript{12}). Recently, Asakura et al. [120] demonstrated a 4 V sodium battery with the same solid-state conductor, Na\textsubscript{4}(CB\textsubscript{11}H\textsubscript{12})\textsubscript{2}(B\textsubscript{12}H\textsubscript{12}). These results show that closo-hydroborates and their derivatives are very promising materials for chemically and electrochemically stable all-solid-state ionic conductors.

6. Conclusions

In the last 20 years, many studies on borohydride species have considerably increased our knowledge on the properties of these materials. For hydrogen storage applications, the kinetics and reversibility of the dehydrogenation reactions remain a major challenge for practical applications. The chemistry of borohydrides from BH\textsubscript{4}− to B\textsubscript{12}H\textsubscript{12}\textsuperscript{2−} in the gas phase and in solution has been theoretically and experimentally addressed; however, in solids, these studies are very challenging, as structural data of potential reaction intermediates such as Mg(B\textsubscript{3}H\textsubscript{8})\textsubscript{2} are elusive, and not all intermediates can be observed. If the reaction intermediates are amorphous, X-ray diffraction cannot be used, and theoretical approaches can lead to many different potential structures. The presence of additional hydrides or of Lewis bases such as THF, as shown for the reactions of KB\textsubscript{3}H\textsubscript{8} and Mg(B\textsubscript{3}H\textsubscript{8})\textsubscript{2}, strongly modifies the reaction products upon heating. We are thus still very far from a full microscopic understanding of these hydrogenation–dehydrogenation reactions and in the search for optimal catalysts for these processes.

For hydrogen storage, B\textsubscript{3}H\textsubscript{8}− is an interesting species that can be rehydrogenated back to BH\textsubscript{4}−. Even though only 25% of the hydrogen is available for this reversible hydrogen storage, the temperatures (less than 200 °C) and kinetics of these reactions approach practical conditions.

The closo-hydroborate ions that are formed and identified as intermediates of dehydrogenation reactions have found new and very promising applications as solid-state ionic conductors, as they present many very favorable properties for this use. The recent demonstration of a 4 V all-solid-state battery using solid sodium electrolyte Na\textsubscript{4}(CB\textsubscript{11}H\textsubscript{12})\textsubscript{2}(B\textsubscript{12}H\textsubscript{12}) [120] highlights this potential. Whether compounds such as Mg(B\textsubscript{10}H\textsubscript{10}), which can be obtained starting from Mg(BH\textsubscript{4})\textsubscript{2}·2THF, are applicable for new Mg-based batteries remains to be demonstrated. In the preparation of these closo-hydroborates and their derivatives, starting from BH\textsubscript{4}− instead of neutral boranes, has the great advantage to reduce the toxicity of the reactants. B\textsubscript{2}H\textsubscript{6}, B\textsubscript{3}H\textsubscript{6} and B\textsubscript{10}H\textsubscript{14} are highly toxic and thereby not really suitable for industrial production processes of closo-hydroborates at a higher scale. Thus, boron–hydrogen compounds have a future for new green energy applications.

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References

1. Stock, A. The Hydrides of Boron and Silicon; Cornell University Press: New York, NY, USA, 1933.

2. Martin, D.R. The Development of Borane Fuels. J. Chem. Educ. 1959, 36, 208–214. [CrossRef]

3. Baier, M.J.; Veeraraghavan Ramachandran, P.; Son, S.F. Characterization of the Hypergolic Ignition Delay of Ammonia Borane. J. Propuls. Power 2019, 35, 182–189. [CrossRef]

4. Zheng, Z.; Zhao, Z.; Wang, B.; Zhang, J. Boron based hypergolic ionic liquids: A review. Green Energy Environ. 2020, 6, 794–822. [CrossRef]

5. Huang, Z.; Wang, S.; Dewhurst, R.D.; Ignat’ev, N.V.; Finze, M.; Braunschweig, H. Boron: Its Role in Energy-Related Processes and Applications. Angew. Chem. Int. Ed. 2020, 59, 8800–8816. [CrossRef]

6. Zhao, X.; Yang, Z.; Chen, H.; Wang, Z.; Zhou, X.; Zhang, H. Progress in three-dimensional aromatic-like closo-dodecaborate. Coord. Chem. Rev. 2021, 444, 214042. [CrossRef]

7. Stauber, J.M.; Schwan, J.; Axtell, J.C.; Jung, D.; McNicholas, B.J.; Oyala, P.H.; Martinolich, A.J.; Winkler, J.R.; See, K.A.; et al. A Super-oxidized Radical Cationic Icosahedral Boron Cluster. J. Am. Chem. Soc. 2020, 142, 12948–12953. [CrossRef]

8. Tu, D.; Yan, H.; Poater, J.; Solà, M. The nido-Cage-··· π Bond: A Non-covalent Interaction between Boron Clusters and Aromatic Rings and Its Applications. Angew. Chemie Int. Ed. 2020, 59, 9018–9025. [CrossRef] [PubMed]

9. Alam, C.; Dávila, B.; García, M.F.; Sánchez, C.; Kovacs, M.; Trias, E.; Barbeito, L.; Gabay, M.; Zeineh, N.; Gavish, M.; et al. Sunitinib-Containing Carbaborane Pharmacophore with the Ability to Inhibit Tyrosine Kinases Receptors FLT3, KIT and PDGFR-β, Exhibits Powerful In Vivo Anti-Glioblastoma Activity. Cancers 2020, 12, 3423. [CrossRef] [PubMed]

10. Ali, F.; S Hosmane, N.; Zhu, Y. Boron Chemistry for Medical Applications. Molecules 2020, 25, 828. [CrossRef]

11. Stockmann, P.; Gozzi, M.; Kuhnert, R.; S, M.B.; Hey-Hawkins, E. New keys for old locks: Carbaborane-containing drugs as platforms for mechanism-based therapies. Chem. Soc. Rev. 2019, 48, 3497–3512. [CrossRef]

12. Bogdanovic, B.; Schwickerath, M. Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials. J. Alloys Compd. 1997, 253–254, 1–9. [CrossRef]

13. Yang, J.; Sridhar, A.; Wolverton, C.; Siegel, D. High capacity hydrogen storage materials: Attributes for automotive applications and techniques for materials discovery. Chem. Soc. Rev. 2010, 39, 656–675. [CrossRef]

14. Bellosta von Colbe, J.; Ares, J.-R.; Barale, J.; Baricco, M.; Buckley, C.; Capurso, G.; Gallandat, N.; Grant, D.M.; Guzik, M.N.; Jacob, I.; et al. Application of hydrides in hydrogen storage and compression: Achievements, outlook and perspectives. Int. J. Hydrog. Energy 2019, 44, 7780–7808. [CrossRef]

15. Schneemann, A.; White, J.L.; Kang, S.; Jeong, S.; Wan, L.F.; Cho, E.S.; Heo, T.W.; Prendergast, D.; Urban, J.J.; Wood, B.C.; et al. Nanostructured Metal Hydrides for Hydrogen Storage. Chem. Rev. 2018, 118, 10775–10839. [CrossRef]

16. Ohno, S.; Banik, A.; Dewald, G.F.; Kraft, M.A.; Krauskopf, T.; Minafra, N.; Till, P.; Weiss, M.; Zeier, W.G. Materials design of ionic conductors for solid state batteries. Prog. Energy 2020, 2, 022001. [CrossRef]

17. Paskevicius, M.; Jepsen, L.H.; Schouwink, P.; Černš, V.; Wolverton, C. Theoretical Prediction of Metastable Intermediates in the Decomposition of Mg[BH₄]₂. J. Phys. Chem. C 2012, 116, 10522–10528. [CrossRef]

18. Černš, R.; Schouwink, P. The crystal chemistry of inorganic metal borohydrides and their relation to metal oxides. Acta Cryst. 2015, B71, 619–640. [CrossRef]

19. Moussa, G.; Moury, R.; Demirci, U.B.; Sener, T.; Miele, P. Boron-based Hydrides for Chemical Hydrogen Storage. Int. J. Energy Res. 2013, 37, 825–842. [CrossRef]

20. Suárez-Alcántara, K.; Tena-García, J.R.; Ricardo Guerrero-Ortiz, R. Alanates, a Comprehensive Review. Materials 2019, 12, 2724. [CrossRef]

21. Dobins, T.A. Overview of the Structure–Dynamics–Function Relationships in Borohydrides for Use as Solid-State Electrolytes in Battery Applications. Molecules 2021, 26, 3239. [CrossRef] [PubMed]

22. Zavorotynska, O.; El-Kharbach, A.; Deleda, S.; Hauback, B.C. Recent progress in magnesium borohydride Mg[BH₄]₂: Fundamentals and applications for energy storage. Int. J. Hydrog. Energy 2016, 41, 14387–14403. [CrossRef]

23. Zhang, Y.; Majzoub, E.; Ozolinš, V.; Wolverton, C. Theoretical Prediction of Metastable Intermediates in the Decomposition of Mg[BH₄]₂. J. Phys. Chem. C 2012, 116, 10522–10528. [CrossRef]

24. Hwang, S.-J.; Bowman, R.C.; Reiter, J.W.; Rijsenbeek, J.; Soloveichik, G.L.; Zhao, J.-C.; Kabbour, H.; Ahn, C.C. NMR confirmation for formation of B₂H₄[O₂H]₂ complexes during hydrogen desorption from metal borohydrides. J. Phys. Chem. C 2008, 112, 3164–3169. [CrossRef]

25. Golub, I.E.; Filipпов, O.A.; Belkova, N.V.; Epstein, L.M.; Shubina, E.S. The Reaction of Hydrogen Halides with Tetrahydroborate Anion and Hexahydro-closo-hexaborane Dianion. Molecules 2021, 26, 3754. [CrossRef]

26. Voinova, V.V.; Selivanov, N.A.; Plyushchenko, I.V.; Vokuev, M.F.; Bykov, A.Y.; Klyukin, I.N.; Novikov, A.S.; Zhidanov, A.P.; Grigorjev, M.S.; Rodin, I.A.; et al. Fused 1,2-Diboraoxazoles Based on closo-Decaborate Anion–Novel Members of Diboroheterocycle Class. Molecules 2021, 26, 248. [CrossRef]

27. Andreichuk, E.P.; Anufriev, S.A.; Suponitsky, K.Y.; Sivaev, I.B. The First Nickelacarborane with closo-nido Structure. Molecules 2020, 25, 6099. [CrossRef]
55. Dimitrievska, M.; Chong, M.; Bowden, M.E.; Wu, H.; Zhou, W.; Nayyar, J.; Ginovska, B.; Gennett, T.; Autrey, T.; Jensen, C.M.; et al. Structural and reorientational dynamics of tetrahydroborate (B\(_4\))\(^{−}\) and tetrahydrofuran (THF) in a Mg(BH\(_4\))\(_2\)-3THF adduct: Neutron-scattering characterization. Phys. Chem. Chem. Phys. 2020, 22, 368–378. [CrossRef]

56. Tran, B.L.; Allen, T.N.; Bowden, M.E.; Autrey, T.; Jensen, C.M. Effects of Glymes on the Distribution of Mg(B\(_{10}\)H\(_{10}\)) and Mg(B\(_{12}\)H\(_{12}\)) from the Thermolysis of Mg(BH\(_4\))\(_2\). Inorg. Chem. 2021, 9, 41. [CrossRef]

57. Bell, R.T.; Strange, N.A.; Leick, N.; Stavila, V.; Bowden, M.E.; Autrey, T.S.; Gennett, T. Mg(BH\(_4\))\(_2\)-Based Hybrid Metal–Organic Borohydride System Exhibiting Enhanced Chemical Stability in Melt. ACS Appl. Energy Mater. 2021, 4, 1704–1713. [CrossRef]

58. Wegner, W.; Jaros, T.; Dobrowolski, M.A.; Dobrzycki, Ł.; Cyrański, M.K.; Grochala, W. Organic derivatives of Mg(BH\(_4\))\(_2\) as precursors towards MgB2 and novel inorganic mixed-cation borohydrides. Dalton Trans. 2016, 45, 14370–14377. [CrossRef]

59. Moury, R.; Gigante, A.; Remhof, A.; Roedern, E.; Hagemann, H. Experimental investigation of Mg(B\(_2\)H\(_{6}\))\(_2\) dimensionality, materials for energy storage applications. Dalton Trans. 2020, 49, 12168–12173. [CrossRef]

60. Gill, N.; Hagemann, H.; Jaroń, T.; Dobrowolski, M.A.; Dobrzycki, Ł.; Cyrański, M.K.; Grochala, W. Organic derivatives of Mg(BH\(_4\))\(_2\) as precursors towards MgB2 and novel inorganic mixed-cation borohydrides. Inorg. Chem. 2021, 50, 3737–3747. [CrossRef]

61. Newhouse, R.J.; Stavila, V.; Hwang, S.-J.; Klebanoff, L.E.; Zhang, J.Z. Reversibility and Improved Hydrogen Release of Magnesium Borohydride. J. Phys. Chem. C 2010, 114, 5224–5232. [CrossRef]

62. Beall, H.; Gaines, D.F. Mechanistic aspects of boron hydride reactions. Inorg. Chem. Acta 1999, 289, 1–10. [CrossRef]

63. Kurbonbekov, A.; Alikhonova, T.K.; Badalov, A.; Murufi, V.K.; Mursaidov, U. Solubility in the lanthanum borohydride -potassium dihydrogen phosphate system at 25 °C and some thermodynamic characteristics of lanthanum borohydride. Dokl. Akad. Nauk Tadzh. SSR 1990, 33, 393–395.

64. Huang, Z.; Chen, X.; Yisgedu, T.; Meyers, E.A.; Shore, S.G.; Zhao, J.-C. Ammonium Octahydropotinate (NH\(_4\)B\(_4\)H\(_8\)): New Synthesis, Structure, and Hydrolytic Hydrogen Release. Inorg. Chem. 2011, 50, 3738–3742. [CrossRef]

65. Good, W.D.; Mansson, M. The Thermochromism of Boron and Some of Its Compounds. The Enthalpies of Formation of Orthoboric Acid, Triethylamineborane, and Diammoniumdecaborane. J. Phys. Chem. 1966, 70, 97–104. [CrossRef]

66. Hanumantha Rao, M.; Muralidharan, K. closo-Dodecaborate (B\(_{12}\))\(^{−}\) salts with nitrogen based cations and their energetic properties. Polyhedron 2016, 115, 105–110.

67. Dematteis, E.M.; Jensen, S.R.; Jensen, T.R.; Baricco, M. Heat capacity and thermodynamic properties of alkali and alkali-earth borohydrides. J. Chem. Thermodyn. 2020, 143, 106055. [CrossRef]

68. Pinatel, E.R.; Albanese, E.; Civalleri, B.; Baricco, M. Thermodynamic modelling of Mg(BH\(_4\))\(_2\). J. Alloys Comp. 2015, 645, 564–568. [CrossRef]

69. Nguyen, M.T.; Matus, M.H.; Dixon, D.A. Heats of Formation of Boron Hydride Anions and Dianions and Their Ammonium Salts [B\(_y\)H\(_{3n+1}\)]\(^{−}\) [NH\(_4\)]\(_y\) with y = 1–2. Inorg. Chem. 2007, 46, 7561–7570. [CrossRef]

70. McKee, M.L. Estimation of Heats of Formation of Boron Hydrides from ab Initio Energies. J. Phys. Chem. 1990, 94, 435–440. [CrossRef]

71. Kelley, S.P.; McCray, P.D.; Flores, L.; Garner, E.B.; Dixon, D.A.; Rogers, R.D. Structural and Theoretical Study of Salts of the [B\(_y\)H\(_{3n+1}\)]\(^{−}\) Ion: Isolation of Multiple Isomers and Implications for Energy Storage. ChemPlusChem 2016, 81, 922–925. [CrossRef]

72. Sethio, D.; Lawson Daku, L.M.; Hagemann, H.; Kraka, E. Quantitative Assessment of B–B–B, B–H, and B–H Bonds: From BH\(_3\) to B\(_2\)H\(_{12}\). - ChemPhysChem 2019, 20, 1967–1977. [CrossRef]

73. Maillard, R.; Sethio, D.; Hagemann, H.; Lawson Daku, L.M. Accurate Computational Thermodynamics Using Anharmonic Theory Function Calculations: The Case Study of B–H Species. ACS Omega 2019, 4, 8786–8794. [CrossRef]

74. Yu, C.L.; Bauer, S.H. Thermochromism of the boranes. J. Phys. Chem. Ref. Data 2010, 98, 807–835. [CrossRef]

75. Lee, T.B.; Mc Kee, M.L. Redox Energetics of Hypercloso Boron Hydrides B\(_n\)H\(_n\) (n = 6–13) and B\(_2\)X\(_{12}\) (X = F, Cl, OH, and CH\(_3\)). Inorg. Chem. 2012, 51, 4205–4214. [CrossRef]

76. Lee, T.B.; Mc Kee, M.L. Dissolution Thermochromism of Alkali Metal Dianion Salts (M\(_2\)X\(_{12}\)) \((M = Li, Na, K^+ with X = CO\(_3\))\(^{2−}\), SO\(_4\))\(^{2−}\), C\(_2\)H\(_4\))\(^{2−}\), and B\(_2\)H\(_{12}\))\(^{2−}\)). Inorg. Chem. 2011, 50, 11412–11422. [CrossRef]

77. Yan, Y.; Remhof, A.; Rentsch, D.; Züttel, A. The role of MgB\(_{12}\)H\(_{12}\) in the hydrogen desorption process of Mg(BH\(_4\))\(_2\). Chem. Commun. 2015, 51, 700–702. [CrossRef]

78. Yan, Y.; Remhof, A.; Rentsch, D.; Lee, Y.S.; Cho, Y.W.; Züttel, A. Is Y\(_2\)(B\(_{12}\)H\(_{12}\))\(_3\) the main intermediate in the decomposition process of Y(BH\(_4\))\(_3\). Chem. Commun. 2013, 49, 5224–5226. [CrossRef]

79. Godfroid, R.A.; Hill, T.G.; Onak, T.P.; Shore, S.G. Formation of [BH\(_3\)]\(^{2−}\) and [B\(_2\)H\(_6\)]\(^{2−}\) From the Homogeneous Reduction of B\(_2\)H\(_6\). J. Am. Chem. Soc. 1994, 116, 12107–12108. [CrossRef]

80. Hill, T.G.; Godfroid, R.A.; White III, J.P.; Shore, S.G. Reduction of borane THF by alkali metal (potassium, rubidium, cesium) and ytterbium mercury amalgams to form salts of octahydropotinate(1−); a simple procedure for the synthesis of tetraborane(10). Inorg. Chem. 1991, 30, 2952–2954. [CrossRef]

81. Gaines, D.F.; Schaeffer, R.; Tebbe, F. Convenient Preparations of Solutions Containing the Triborohydrine Ion. Inorg. Chem. 1963, 2, 526–528. [CrossRef]

82. Chen, X.; Liu, X.-R.; Wang, X.; Chen, X.-M.; Jing, Y.; Wie, D. A Safe and Efficient Synthetic Method of the Alkali Metal Octahydropotinate, Unravelling a General Mechanism of Constructing the Delta B3 Unit of Polyhedral Boranes. Dalton Trans. 2021, 50, 13676–13679. [CrossRef]
83. Chen, X.-M.; Ma, N.; Zhang, Q.-F.; Wang, J.; Feng, X.; Wei, C.; Wang, L.-S.; Zhang, J.; Chen, X. Elucidation of the Formation Mechanisms of the Octahydrotriborate Anion ($\text{B}_3\text{H}_{10}^-$) through the Nucleophilicity of the B–H Bond. *J. Amer. Chem. Soc.* 2018, 140, 6718–6726. [CrossRef]

84. Moury, R.; Gigante, A.; Hagemann, H. An alternative approach to the synthesis of $\text{NaB}_2\text{H}_8$ and $\text{Na}_2\text{B}_2\text{H}_12$ for solid electrolyte applications. *Int. J. Hydrog. Energy* 2017, 42, 22417–22421. [CrossRef]

85. Grindernov, J.B.; Møller, K.T.; Yan, Y.; Chen, X.-M.; Li, Y.; Li, H.-W.; Zhou, W.; Skibsted, J.; Chen, X.; Jensen, T.R. Potassium octahydrotriborate: Diverse polypomorphism in a potential hydrogen storage material and potassium ion conductor. *Dalton Trans.* 2019, 48, 8872–8881. [CrossRef]

86. Gigaide, A.; Duchêné, L.; Moury, R.; Pupier, M.; Remhof, A.; Hagemann, H. Direct solution–based synthesis of the $\text{Na}_2(\text{B}_2\text{H}_12)_{(\text{B}_2\text{H}_10)}$ solid electrolyte. *ChemSusChem* 2019, 12, 4832–4837. [CrossRef]

87. Aniya, M. A chemical approach for the microscopic mechanism of fast ion transport in solids. *Solid State Ion.* 1992, 50, 125–129. [CrossRef]

88. Matsuo, M.; Nakamori, Y.; Orimo, S.; Maekawa, H.; Takamura, H. Lithium superionic conduction in lithium borohydride accompanied by structural transition. *Appl. Phys. Lett.* 2007, 91, 224103. [CrossRef]

89. Muetterties, E.L.; Balthis, J.H.; Chia, Y.T.; Knoth, W.H.; Miller, H.C. Chemistry of Boranes. VIII. Salts and Acids of $\text{B}_3\text{H}_8$ and $\text{B}_2\text{H}_12$. *Inorg. Chem.* 1964, 3, 444–451. [CrossRef]

90. Černý, R.; Brighi, M.; Murgia, F. The Crystal Chemistry of Inorganic Hydroborates. *Chemistry* 2020, 2, 805–826. [CrossRef]

91. Wu, H.; Tang, W.S.; Stavila, V.; Zhou, W.; Rush, J.J.; Udovic, T.J. Structural Behavior of $\text{Li}_2\text{B}_2\text{H}_{10}$. *J. Phys. Chem. C* 2015, 119, 6481–6487. [CrossRef]

92. Her, J.-H.; Yousufuddi, M.; Zhou, W.; Jalisatgi, S.S.; Kulleck, J.G.; Zan, J.A.; Hwang, S.-J.; Bowman, R.C.; Udovic, T.J. Crystal structure of $\text{Li}_2\text{B}_2\text{H}_2$: A possible intermediate species in the decomposition of LiBH$_4$. *Inorg. Chem.* 2008, 47, 9757–9759. [CrossRef]

93. Paskevicius, M.; Pitt, M.P.; Brown, D.H.; Sheppard, D.A.; Chumphongphan, S.; Buckley, C.E. First-order phase transition in the $\text{Li}_2\text{B}_2\text{H}_12$ system. *Phys. Chem. Chem. Phys.* 2013, 15, 15825–15828. [CrossRef] [PubMed]

94. Wu, H.; Tang, W.S.; Zhou, W.; Stavila, V.; Rush, J.J.; Udovic, T.J. The structure of monoclinic $\text{Na}_2\text{B}_2\text{H}_{10}$: A combined diffraction, spectroscopy, and theoretical approach. *Cryst. Eng.Comm. 2015, 17, 3533–3540. [CrossRef]

95. Verdal, N.; Her, J.-H.; Stavila, V.; Soloninin, A.V.; Babanova, O.A.; Skiprov, A.V.; Udovic, T.J.; Rush, J.J. Complex high-temperature phase transitions in $\text{Li}_2\text{B}_2\text{H}_12$ and $\text{Na}_2\text{B}_2\text{H}_12$. *J. Solid State Chem.* 2014, 212, 81–91. [CrossRef]

96. Wunderlich, J.A.; Lipscomb, W.N. Structure of $\text{B}_2\text{H}_12^{-2}$ ion. *J. Amer. Chem. Soc.* 1960, 82, 4427–4428. [CrossRef]

97. Hofmann, K.; Albert, B. Crystal structures of $\text{M}_2[\text{B}_2\text{H}_{10}]$ (M = Na, K, Rb) via real space simulated annealing powder techniques. *Z. Kristall.* 2005, 220, 142–146. [CrossRef]

98. Bukovsky, E.V.; Peryshkov, D.V.; Wu, H.; Zhou, W.; Tang, W.S.; Jones, W.M.; Stavila, V.; Udovic, T.J.; Strauss, S.H. Comparison of the Coordination of $\text{B}_2\text{F}_2^{-2}$, $\text{B}_2\text{Cl}_2^{-2}$, and $\text{B}_2\text{H}_2^{-2}$ to Na+ in the Solid State: Crystal Structures and Thermal Behavior of $\text{Na}_2\text{B}_2\text{F}_12\text{Na}_2(\text{H}_2\text{O})\text{B}_2\text{H}_12$, $\text{Na}_2\text{B}_2\text{Cl}_12$, and $\text{Na}_2(\text{H}_2\text{O})_6\text{B}_2\text{Cl}_12$. *Inorg. Chem.* 2017, 56, 4369–4379. [CrossRef] [PubMed]

99. Guggenberger, L.J. Chemistry of boranes. XXXII. The crystal structure of $\text{B}_2\text{B}_2\text{H}_4$. *Inorg. Chem.* 1968, 7, 2260–2264. [CrossRef]

100. Verdal, N.; Wu, H.; Udovic, T.J.; Stavila, V.; Zhou, W.; Rush, J.J. Evidence of a transition to reorientational disorder in the cubic alkali-metal dodecahydro-closo-dodecaborates $\text{M}_2\text{B}_2\text{H}_12$. *J. Solid State Chem.* 2011, 184, 3110–3116. [CrossRef]

101. Mouri, R.; Lodziana, Z.; Remhof, A.; Duchêné, L.; Roedern, E.; Gigante, A.; Hagemann, H. Pressure-induced phase transitions in $\text{Na}_2\text{B}_2\text{H}_12$: structural investigation on a candidate for solid-state electrolyte. *Acta Cryst. B* 2019, B75, 406–413. [CrossRef]

102. Maekawa, H.; Matsuo, M.; Takamura, H.; Ando, M.; Noda, Y.; Karahashi, T.; Orimo, S. Halide-stabilized LiBH$_4$, a room-temperature lithium fast-ion conductor. *J. Amer. Chem. Soc.* 2009, 894–895. [CrossRef]

103. Gulino, V.; Brighi, M.; Dematteis, E.M.; Murgia, F.; Nervi, C.; Černý, R.; Baricco, M. Phase Stability and Fast Ion Conductivity in the Hexagonal LiBH$_4$-LiBr-LiCl Solid Solution. *Chem. Mater.* 2019, 31, 5133–5144. [CrossRef]

104. Sadikin, Y.; Schouwink, P.; Brighi, M.; Lodziana, Z.; Černý, R. Modified anion packing of $\text{Na}_2\text{B}_2\text{H}_12$ in close to room temperature superionic conductors. *Inorg. Chem.* 2017, 56, 5006–5016. [CrossRef]

105. Kim, S.; Oguchi, H.; Toyama, N.; Sato, T.; Takagi, S.; Otomo, T.; Arunkumar, D.; Kusawa, N.; Kawamura, J.; Orimo, S. A complex hydride lithium superionic conductor for high-energy-density all-solid-state lithium metal batteries. *Nat. Commun.* 2019, 10, 1081. [CrossRef]

106. Payandeh, S.H.; Rentsch, D.; Lodziana, Z.; Asakura, R.; Bigler, L.; Černý, R.; Battaglia, C.; Remhof, A. Nido-Hydroborate-Based Electrolytes for All-Solid-State Lithium Batteries. *Adv. Funct. Mater.* 2021, 31, 2010046. [CrossRef]

107. Brighi, M.; Murgia, F.; Lodziana, Z.; Schouwink, P.; Włoczky, A.; Černý, R. A mixed anion hydroborate/carbon-hydroborate as a room temperature Na ion solid electrolyte. *J. Power Sources* 2019, 404, 7–12. [CrossRef]

108. Duchêné, L.; Kühlner, R.-S.; Rentsch, D.; Remhof, A.; Hagemann, H.; Battaglia, C. A highly stable sodium solid-state electrolyte based on a dodeca/deca-borate equimolar mixture. *Chem. Commun.* 2017, 53, 4195–4198. [CrossRef]

109. Yoshida, K.; Sato, T.; Unemoto, A.; Matsuo, M.; Ikeshoji, T.; Udovic, T.J.; Orimo, S.I. Fast sodium ionic conduction in $\text{Na}_2\text{B}_2\text{H}_{10}$–$\text{Na}_2\text{B}_2\text{H}_12$ pseudo-binary complex hydride and application to a bulk-type all-solid-state battery. *Appl. Phys. Lett.* 2017, 110, 103901. [CrossRef]
111. Payandeh, S.H.; Asakura, R.; Avramidou, P.; Rentsch, D.; Łodziana, Z.; Černý, R.; Remhof, A.; Battaglia, C. Nido-Borate/Closo-borate mixed-anion electrolytes for all-solid-state batteries. Chem. Mater. 2020, 32, 1101–1110. [CrossRef]

112. Brighi, M.; Murgia, F.; Černý, R. Closo-Hydroborate Sodium Salts as an Emerging Class of Room-Temperature Solid Electrolytes. Cell Rep. Phys. Sci. 2020, 1, 100217. [CrossRef]

113. Skripov, A.V.; Soloninin, A.V.; Babanova, O.A.; Skoryunov, R.V. Anion and Cation Dynamics in Polyhydroborate Salts: NMR Studies. Molecules 2020, 25, 2940. [CrossRef]

114. Lohstroh, W.; Heere, M. Structure and Dynamics of Borohydrides Studied by Neutron Scattering Techniques: A Review. J. Phys. Soc. Jpn. 2020, 89, 1–12. [CrossRef]

115. Duchêne, L.; Lunghammer, S.; Burankova, T.; Liao, W.-C.; Embs, J.P.; Coperet, C.; Wilkening, H.M.R.; Remhof, A.; Hagemann, H.; Battaglia, C. Ionic conduction mechanism in the Na$_2$(B$_{12}$H$_{12}$)$_{0.5}$(B$_{10}$H$_{10}$)$_{0.5}$ closo-borate solid-state electrolyte: Interplay of disorder and ion–ion interactions. Chem. Mater. 2019, 31, 3449–3460. [CrossRef]

116. Asakura, R.; Duchêne, L.; Kühnel, R.-S.; Remhof, A.; Hagemann, H.; Battaglia, C. Electrochemical Oxidative Stability of Hydroborate-Based Solid-State Electrolytes. ACS Appl. Energy Mater. 2019, 2, 6924–6930. [CrossRef]

117. Matsuo, M.; Orimo, S. Lithium Fast-Ionic Conduction in Complex Hydrides: Review and Prospects. Adv. Energy Mater. 2011, 1, 161–172. [CrossRef]

118. Duchêne, L.; Kühnel, R.-S.; Stilp, E.; Reyes, E.C.; Remhof, A.; Hagemann, H.; Battaglia, C. A Stable 3 V all-solid-state sodium-ion battery based on a closo-borate electrolyte. Energy Environ. Sci. 2017, 10, 2609–2615. [CrossRef]

119. Murgia, F.; Brighi, M.; Černý, R. Room-temperature-operating Na-ion solid state-battery with complex hydride as electrolyte. Electrochim. Comm. 2019, 106, 106534. [CrossRef]

120. Asakura, R.; Reber, D.; Duchêne, L.; Payandeh, S.; Remhof, A.; Hagemann, H.; Battaglia, C. 4 V room-temperature all-solid-state sodium battery enabled by a passivating cathode/hydroborate solid electrolyte interface. Energy Environ. Sci. 2020, 13, 5048–5058. [CrossRef]