

Review



Properties and Applications of Metal (M) dodecahydro-*closo*-dodecaborates ($M_{n=1,2}B_{12}H_{12}$) and Their Implications for Reversible Hydrogen Storage in the Borohydrides

Aiden Grahame and Kondo-François Aguey-Zinsou *

MERlin Group, School of Chemical Engineering, The University of New South Wales, Sydney 2052, Australia; aidengrahame@gmail.com

* Correspondence: f.aguey@unsw.edu.au; Tel.: +61-293-857-970

Received: 3 September 2018; Accepted: 27 September 2018; Published: 1 October 2018

Abstract: Hydrogen has long been proposed as a versatile energy carrier that could facilitate a sustainable energy future. For an energy economy centred around hydrogen to function, a storage method is required that is optimised for both portable and stationary applications and is compatible with existing hydrogen technologies. Storage by chemisorption in borohydride species emerges as a promising option because of the advantages of solid-state storage and the unmatched hydrogen energy densities that borohydrides attain. One of the most nuanced challenges limiting the feasibility of borohydride hydrogen storage is the irreversibility of their hydrogen storage reactions. This irreversibility has been partially attributed to the formation of stable dodecahydro-*closo*-dodecaborates ($M_{n=1,2}B_{12}H_{12}$) during the desorption of hydrogen. These dodecaborates have an interesting set of properties that are problematic in the context of borohydride decomposition but suggest a variety of useful applications when considered independently. In this review, dodecaborates are explored within the borohydride thermolysis system and beyond to present a holistic discussion of the most important roles of the dodecaborates in modern chemistry.

Keywords: borohydride; dodecaborate; closo-dodecaborate; hydrogen storage; solid-state electrolyte

1. Introduction

The international community is coming to terms with the need for significant changes to the global energy economy, but even the most aggressive renewable energy expansion efforts are limited by the status of the technology. The most difficult quality of petrochemicals to replicate has proven to be their unmatched versatility. Fossil fuels are unique in that they can serve as both a primary source of energy and as a vector for transportation. Given the dynamic nature of energy utilisation in the modern era, an effective energy carrier is key to the overall functionality of an energy economy.

The identification of a single, versatile energy carrier is especially crucial to the feasibility of an energy economy based on renewables. Energy storage solutions are vital to the facilitation of large-scale and remote renewable energy production, as well the use of renewable energy for portable applications. Additionally, the standardisation of all energy systems to use one energy vector enables the integration of a diverse range of energy sources into the supply chain without any modifications to the energy utilisation infrastructure.

Hydrogen emerges as a promising energy carrier for a number of reasons. First, hydrogen is extremely abundant and a major component in what is perhaps the most well-studied chemical: water. Hydrogen's high energy density (120 MJ kg⁻¹ compared to 45 MJ kg⁻¹ for gasoline) and the simplicity

of its combustion reaction are also significant [1,2]. Furthermore, a method of producing electricity from hydrogen has been known for almost two centuries, as the first fuel cells were invented by chemists Christian Friedrich Schonbein and Sir William Robert Grove in the late 1830s [3]. It is these considerations that gave rise to the concept of a "hydrogen economy", wherein all energy is stored, transported and distributed in the form of hydrogen (Figure 1).

This theory was considered as early the 19th century, when the work of the Danish scientist, Poul La Cour concerning the storage of wind energy in gaseous hydrogen gave rise to his idea of a "hydrogen society" wherein hydrogen is used as the dominant energy vector [4]. However, the modern terminology used to describe this concept was only coined at the dawn of the energy crisis of the 1970s, when the global community was first confronted with the instability of an energy economy entirely dependent on petrochemicals. In a paper published in 1972, just over a year before the peak of the 1973 world oil shortage, John O'.M. Bockris and A. John Appleby originated the term "hydrogen economy" to encompass the "energetic, ecological and economic aspects" of an energy system centred around hydrogen [2,5].



Figure 1. Schematic overview of a hydrogen based energy economy.

The lack of a suitable hydrogen storage method is currently the most significant limiting factor to the realisation of a hydrogen economy. Conventional methods include storage as a pressurised gas at 35–70 MPa [6] and cryogenic liquid storage at temperatures in the range of -250 °C [7]. However, these established methods of hydrogen storage have been found to have various prohibitive limitations that preclude widespread hydrogen usage [8–10]. Any viable storage method must be able to reversibly release and absorb hydrogen at reasonable conditions, while attaining high gravimetric capacities and having good hydrogen cycling kinetics.

Chemisorption by a borohydride compound has been identified as a promising mechanism of solid-state hydrogen storage that has the potential to meet all of those outlined requirements. The fundamental appeal of the metal borohydrides is their ability to achieve gravimetric and volumetric capacities that far exceed those possible using liquid or pressurised gas storage [1,11]. However, hydrogen storage using a borohydride carrier is not currently feasible due to the extremely high temperatures required for thermal dehydrogenation. Additionally, the irreversibility of the metal borohydride hydrogen cycling reactions is a serious barrier to their practical application.

Significant research has been dedicated to moving borohydrides closer to industrial system requirements by lowering the hydrogen release temperature and optimising their desorption kinetics to allow for faster hydrogen release [12–17]. However, the irreversibility of the borohydride dehydrogenation process is a question that remains largely un-answered within the field, likely because borohydrides have yet to reach optimal desorption conditions for a single cycle. If borohydrides

are ever to find widespread practical application, the ability to store hydrogen reversibly will be non-negotiable.

The focus of this review is on the factors that contribute to this irreversibility, with particular emphasis on the formation of dodecahydro-*closo*-dodecaborates ($M_{n=1,2}B_{12}H_{12}$) during decomposition. Commonly referred to as the "dodecaborates", these compounds have a distinctive icosahedral molecular structure that has been found to result in a number of remarkable properties, including exceptional thermal stability. To clarify the role of the dodecaborates in the overall dehydrogenation scheme, the mechanisms that govern thermolysis are reviewed for the light alkali and alkaline earth borohydrides. This review also serves to identify possible routes of mitigating the impact of dodecaborates, thereby aiding in the development a borohydride-based hydrogen storage material that meets reversibility targets. An exploration of the chemical properties and proposed applications of dodecaborates is then discussed to inform the behaviour that has been observed within the context of borohydride systems.

2. Metal Borohydrides for Hydrogen Storage

The ability of a hydrogen carrier to reliably complete a dehydrogenation and rehydrogenation cycle is fundamental to its potential as a storage material. Hydrogen release from metal borohydrides can be invoked through hydrolysis or thermolysis. Hydrogen generation from NaBH₄ by hydrolysis has been extensively investigated because of its spontaneous, low temperature reaction with water and the high gravimetric hydrogen storage capacity of the NaBH₄ – H₂O liquid fuel [18]. Hydrogen release from NaBH₄ through hydrolysis proceeds according to the following ideal reaction:

$$NaBH_4 + 2H_2O \longrightarrow NaBO_2 + 4H_2 \tag{1}$$

However, the viability of borohydride dehydrogenation by hydrolysis is fundamentally limited by the irreversibility of the hydrolysis reaction [19–21]. In the NaBH₄ system, the hydrated sodium borate (NaBO₂) by-product can be regenerated to borohydride by annealing with magnesium hydride MgH₂ under high H₂ back-pressure (0.1–7 MPa) [22]. Although this method achieves very high maximum yields (97–98%), it is not optimised for cost or energy efficiency. Furthermore, this method only achieves high yields using dehydrated NaBO₂, rather than the true hydrated complex formed during the solution-phase hydrolysis reaction. Various improvements have been proposed and remain under investigation, but none have satisfied all of the technical and economic requirements for industrial implementation [23–26]. Hence, thermolytic dehydrogenation processes are the focus of most current investigations and this review.

Thermolysis refers to the decomposition of a compound through the application of heat. During thermolysis, the chemisorption of hydrogen is reversed through the cleavage of the chemical bonds that bind it within the lattice of a storage material [7]. The metal borohydrides are comprised of two main components: the metal Mⁿ⁺ cation and the [BH₄]⁻ anion, composed of four hydrogen atoms covalently bonded to a central boron. During themolysis, sufficient energy must be input into the system to break the boron–hydrogen bonds within the borohydride anion and allow hydrogen to reform diatomic gas molecules.

Both the internal bonding of the $[BH_4]^-$ anion and the bonding between the metal cation and the anion have been shown to have a strong dependence upon the properties of the metal species [27]. This dependence includes the desorption temperature of a given metal hydride, as an inverse correlation has been observed between cation Pauling electronegativity and borohydride stability [28,29]. The $[BH_4]^-$ anion is formed by covalently bonding four hydrogen atoms to a central boron, which requires the donation of an additional electron by a cation species. When the donating cation is very electronegative, the charge transfer between the cation and borohydride anion is suppressed and the boron-hydrogen bonds are destabilised [30]. Light alkali and alkaline earth metal cations form gravimetrically optimised borohydrides, but their low electronegativies also contribute to exceptional thermodynamic stability [31]. This stability is a significant barrier to their utilisation as hydrogen carriers because of the resulting increase in energy input required to free the hydrogen atoms from the solid lattice. As summarised in Table 1, all alkali and alkaline earth borohydrides are found to have decomposition temperatures that are not energetically or practically feasible.

Table 1. Key thermodynamic properties for common $M(BH_4)_n$ (M = Li, Na, K, Mg, Ca) compounds [32]. Enthalpy of decomposition (ΔH_{dec}) values are given as ranges to reflect differing results from the variety of experimental and theoretical methods that have been utilised to specify this parameter. Because of the impact of hydrogen back-pressure on the temperature at which hydrogen release begins, the decomposition temperature (T_{dec}) is reported for a hydrogen equilibrium pressure of P = 0.1 MPa to allow for easy comparison between different species.

Borohydride	ΔH_{dec} (kJ mol ⁻¹ H ₂)	T_{dec} at 0.1 MPa H_2 (°C)	Reference
LiBH ₄	56–75	370	[33,34]
NaBH ₄	89.6-108	539	[35,36]
KBH_4	113.9	826	[36]
$Mg(BH_4)_2$	39.3–57	157	[37,38]
$Ca(BH_4)_2$	40.6-87	278	[39,40]

Regenerating the borohydride species from decomposition products after thermal dehydrogenation has also proven challenging. While rehydrogenation has been accomplished for some of the borohydrides, the temperature/pressure conditions are not viable and capacity losses are always registered [41–43]. For example, only 8.3 mass % H₂ of LiBH₄ total 18.5 mass % H₂ capacity is regenerated after treatment at 600 °C under 15.5 MPa of H₂ [44], with an increase to 35 MPa of H₂ at 600 °C required to achieve nearly complete rehydrogenation [45]. All of these obstacles stem from the problematic kinetics, associated mass transfer and thermodynamics of the borohydride thermal dehydrogenation scheme.

2.1. Possible H₂ Desorption Pathways

As a chemisorption process, thermal dehydrogenation is known to proceed via a multi-step mechanism. Each step in the scheme is governed by different kinetics and thermodynamics, and will be impacted differently by the manipulation of reaction conditions such as temperature and pressure, or the use of a particular destabilising agent [46,47]. Furthermore, the properties of the intermediate products formed during these steps will also impact the performance of the overall hydrogen storage system. Given these considerations, it is unsurprising that the thermal dehydrogenation of the borohydrides has been found to be exceedingly complex. Although an appreciable amount of study has been dedicated to describing the specifics of this mechanism, it remains controversial and poorly understood. This is illustrated most clearly through a discussion of the multiple, often conflicting, decomposition schemes that have been proposed for each borohydride species.

2.1.1. Alkali Borohydrides

The dehydrogenation processes of many of the alkali borohydrides have been studied in detail, and dehydriding pathways have been proposed. However, the greatest volume of research exists for the lightest alkali borohydrides of LiBH₄ and NaBH₄ because they are commonly available and have advantageous hydrogen storage properties. Moreover, correlation between the electronegativity of the metal species and the thermodynamic stability of its borohydride results in a preference for the most electronegative alkali metals (Li and Na) that are predicted to dehydrogenate more readily [28,29]. LiBH₄: Because of its high gravimetric hydrogen capacity (18.5 mass %) and thermodynamic instability relative to the other light alkali borohydrides, significant efforts have focused on developing LiBH₄

as a hydrogen storage material. At ambient conditions, LiBH₄ exists as a single polymorph: *o*-LiBH₄, which has an orthorhombic (*Pnma*) structure [48]. While the polymorphism of LiBH₄ was reported as early as the 1970s [49], a complete specification of its crystal structure and phase transitions did not occur until much later (Table 2).

Metal Species	Polymorph	Crystal System	Space Group	Reference
Li	o-LiBH4	Orthorhombic	Pnma	[48]
	h–LiBH4	Hexagonal	Р6 ₃ тс	[48]
	hp1–LiBH4	Orthorhombic	Ama2	[50]
	hp2-LiBH4	Cubic	Fm3m	[50]
Na	α–NaBH4	Cubic	Fm3m	[51]
	β –NaBH ₄	Tetragonal	$P42_1c$ or $P4_2/nmc$	[31,52]
	γ –NaBH $_4$	Orthorhombic	Pnma	[53]
К	α–KBH ₄	Cubic	Fm3m	[51]
	β' –KBH ₄	Tetragonal	$P4_2$ / <i>nmc</i> or $P42_1c$	[54]
	γ –KBH ₄	Orthorhombic	Pnma	[55]

Table 2. Known experimental structures of the common alkali borohydrides MBH₄ (M = Li, Na, K) [32].

One of the most comprehensive studies was carried out using a combination of synchrotron and Raman spectroscopy to specify the crystal structure of *o*-LiBH₄ at ambient conditions and with increasing temperature [48]. The ambient *o*-LiBH₄ was observed to undergo a phase transition at approximately 108 °C, resulting in the formation of hexagonal h–LiBH₄. Further investigation found that this phase transition is endothermic, with an enthalpy of 4.18 kJ mol⁻¹ at 118 °C [56]. High-pressure polymorphs have been described using in-situ measurements up to 20 GPa [50]. The transition of ambient *o*-LiBH₄ at 1.2 GPa results in the formation of a secondary orthrohomic phase with differing space group symmetry. Furthermore, a secondary transition is observed at 10 GPa, indicated by a volume drop of 2.9%. This third phase was found to have a cubic crystal system, with a *Fm3m* arrangement of Li cations and BH₄ anions.

Most generally, LiBH₄ has been observed to decompose according to the following reaction [33]:

$$LiBH_4 \longrightarrow LiH + B + \frac{3}{2}H_2$$
⁽²⁾

One of the first studies that considered LiBH₄ as a potential hydrogen storage material was conducted by Züttel et al. They found that mixing LiBH₄ with SiO₂ powder successfully facilitated the desorption reaction, exhibiting a similar thermal desorption spectra to pure LiBH₄, with the hydrogen release steps shifted to lower temperatures [56]. Later investigation of this system clarified that the observed temperature shift was caused by a reaction between the two components rather than a catalytic influence [57]. However, in the study by Züttel et al., they found that the dehydrogenation profiles of both the pristine LiBH₄ and LiBH₄/SiO₂ mixtures showed the same three hydrogen desorption features, which were analysed to infer the following preliminary mechanism:

$$\text{LiBH}_4 \longrightarrow \text{LiBH}_{4-x} + \frac{1}{2}(x)\text{H}_2 \qquad T = 108\,^{\circ}\text{C}$$
 (3a)

$$\text{LiBH}_{4-x} \longrightarrow \text{``LiBH}_2\text{''} + \frac{1}{2}(1-x)\text{H}_2 \qquad T = 200\,^{\circ}\text{C} \tag{3b}$$

$$\text{``LiBH}_2\text{''} \longrightarrow \text{LiH} + \text{B} + \frac{1}{2}\text{H}_2 \qquad \text{T} = 453\,^{\circ}\text{C} \tag{3c}$$

Notably, the intermediate "LiBH₂" is given in quotes, as the composition was estimated from the amount of desorbed hydrogen measured, and had yet to be confirmed through structural analysis.

While further study was required to clarify specifics, this work provided compelling evidence that the thermolysis reaction was a multi-step process in which intermediates play an important role.

Early first-principles study of the thermal decomposition of LiBH₄ applied DFT-based methodology to predict the stability of potential reaction intermediates [34]. From theoretical analysis, it was determined that the most energetically preferable pathway proceeded through a dodecaborate intermediate, $Li_2B_{12}H_{12}$. A proposed reaction scheme for the overall decomposition of LiBH₄, including the energetically optimised $Li_2B_{12}H_{12}$ phase, is given below [34]:

$$\text{LiBH}_4 \longrightarrow \frac{1}{12}\text{Li}_2\text{B}_{12}\text{H}_{12} + \frac{5}{6}\text{LiH} + \frac{13}{12}\text{H}_2 \longrightarrow \text{LiH} + \text{B}\frac{3}{2}\text{H}_2 \tag{4}$$

This mechanism was also supported by first-principles studies conducted using a combination of the prototype electrostatic ground state (PEGS) search method and a DFT-based linear programming approach [58].

However, experimental research conducted by Friedrichs et al. found that diborane (B_2H_6) plays a more significant role in both the formation and decomposition of LiBH₄ than previously reported [59]. Diborane evolution during borohydride dehydrogenation is considered to be an unfavourable by-product because it compromises the purity of the released hydrogen, represents a safety concern and reduces the storage capacity of the system with each cycle because of the loss of boron to the gas phase. However, Friedrichs et al. proposed that diborane evolution also contributes to the formation of Li₂B₁₂H₁₂ as a reaction by-product (rather than an intermediate), resulting from the in-situ reaction of LiBH₄ and B_2H_6 [59].

$$2\operatorname{LiBH}_4 + 5\operatorname{B}_2\operatorname{H}_6 \longrightarrow \operatorname{Li}_2\operatorname{B}_{12}\operatorname{H}_{12} + 13\operatorname{H}_2 \tag{5}$$

They also suggested an overall reaction mechanism, wherein LiBH₄ decomposition proceeds through a LiH intermediate, accompanied by diborane evolution. Because of the thermal instability of diborane and the high temperatures required for LiBH₄ thermolysis, diborane then spontaneously decomposes to B and H_2 [59].

$$\text{LiBH}_4 \longrightarrow \text{LiH} + \frac{1}{2} B_2 H_6 \tag{6a}$$

$$B_2H_6 \longrightarrow B + \frac{3}{2}H_2 \tag{6b}$$

A later first-principles study came to a similar conclusion, finding that $Li_2B_{12}H_{12}$ would be a reaction product rather than an intermediate due to its highly negative enthalpy of formation [60]. In this work, the enthalpy and Gibbs free energy are reported for a range of possible decomposition pathways of LiBH₄. By modelling the mechanism as a decomposition into a combination of all proposed products, several $Li_2B_{12}H_{12}$ formation mechanisms were identified in agreement with those proposed previously in literature [34]. It was also proposed that diborane evolution can occur concurrently to $Li_2B_{12}H_{12}$ production, as shown in Reactions (7a) and (7b) [60].

$$14 \text{LiBH}_4 \longrightarrow \text{Li}_2 B_{12} H_{12} + 12 \text{Li} + B_2 H_6 + 19 H_2$$
(7a)

$$15 \text{LiBH}_4 \longrightarrow \text{Li}_2 \text{B}_{12} \text{H}_{12} + 12 \text{Li} + \text{LiB} + \text{B}_2 \text{H}_6 + 21 \text{H}_2$$
(7b)

These reactions were found to be energetically favourable as compared to those not including $Li_2B_{12}H_{12}$ formation. When considering the overall decomposition, it was then determined that the pathway with the lowest enthalpy of reaction at T = 0 K and the lowest free energy of reaction per mole of LiBH₄ proceeded via the formation of a ternary phase with the analytical formula LiBH_{2.5} (Reaction (8)) [60].

$$4 \operatorname{LiBH}_4 \longrightarrow \operatorname{LiBH}_{2.5} + 3 \operatorname{H}_2 \tag{8}$$

This echoes the early experimental findings of Züttel et al., who referred to a ternary intermediate "LiBH₂" whose composition was estimated from the amount of desorbed hydrogen [56]. Hence, through the manipulation of the ternary intermediate, some pathways could potentially result in products that can be re-hydrogenated. This may be further tailored through adjustments to the decomposition pressure and temperature.

NaBH₄: Because of the higher stability of NaBH₄ and the resulting increase in hydrogen desorption temperature, much of the preceding research has focused on dehydrogenation by hydrolysis rather than thermolysis [61]. The use of aqueous NaBH₄ as a liquid fuel continues to garner interest, despite the technical challenges of regenerating NaBH₄ from hydrolysis products [62]. Like LiBH₄, NaBH₄ also exists as a single polymorph under ambient conditions: α –NaBH₄, which has a cubic (*Fm3m*) structure [51] (Table 2). However, unlike LiBH₄, NaBH₄ also has a low temperature polymorph, transitioning to β –NaBH₄ (tetragonal *P42*₁*c*) below temperatures of approximately –83 °C [52].

That same tetragonal polymorph is also observed to form in high-pressure conditions, when α -NaBH₄ transitions back to β -NaBH₄ at 6.3 GPa [63]. While β -NaBH4 was initially interpreting as having the $P42_1c$ space group structure, first-principles study proposed an alternate $P4_2/nmc$ symmetry [31]. However, it is not possible to differentiate between these two symmetries based on diffraction data so the $P42_1c$ structure is most commonly accepted. Beyond 6.3 GPa, another transition to an orthorhombic phase is observed at 8.9 GPa. This high-pressure γ -NaBH₄ phase was found to follow *Pnma* symmetry, similar to the structure of BaSO₄ and the ambient polymorph of LiBH₄ [53].

The thermal dehydrogenation of NaBH₄ is extremely energy intensive, with decomposition under 0.1 MPa of H₂ occurring only at temperatures above approximately 534 $^{\circ}$ C [35]. The decomposition directly to the metal elements is cited as the overall reaction because of the extreme conditions required for NaBH₄ desorption.

$$NaBH_4 \longrightarrow Na + B + 2H_2 \tag{9}$$

This reaction mechanism was proposed based on dynamic pressure, composition and temperature (PCT) measurements taken during NaBH₄ desorption under constant hydrogen flow [35]. The resulting pressure-composition isotherms (Figure 2) reveal that hydrogen desorption occurs in a single step, indicated by a single isotherm plateau.



Figure 2. Pressure, composition, and temperature (PCT) isotherms measured for the thermal decomposition of NaBH₄ under a constant hydrogen flow of 2, 1, and 0.5 cm³ (STP) min⁻¹. Reprinted from [35].

From X-ray Diffraction (XRD) analysis of the solid residue remaining after desorption, it was determined that the composite phases were elemental sodium, some boron-rich binary Na–B compound and traces of NaH. While Na was the dominant phase, the traces of NaH present suggested that decomposition proceeds at least partially through NaH. Using these findings to constrain

first-principles modeling, the energetic favourability of the two most commonly reported mechanisms of alkali borohydride decomposition was compared (Reactions (10a) and (10b)).

$$NaBH_4 \longrightarrow Na + B + 2H_2 \qquad \Delta H_{reaction}^{T=0K} = 245.5 \, kJ \, mol^{-1}$$
(10a)

$$2 \operatorname{NaBH}_4 \longrightarrow 2 \operatorname{NaH} + 2 \operatorname{B} + 3 \operatorname{H}_2 \qquad \Delta \operatorname{H}_{reaction}^{T=0K} = 199.9 \,\mathrm{kJ} \,\mathrm{mol}^{-1} \tag{10b}$$

$$2 \operatorname{NaBH}_4 \longrightarrow 2 \operatorname{NaH} + 2 \operatorname{B} + 3 \operatorname{H}_2 \Longrightarrow 2 \operatorname{Na} + 2 \operatorname{B} + 4 \operatorname{H}_2$$
(10c)

While these paths are competitive from a thermodynamic perspective, it can also be noted that the conditions required for complete NaBH₄ dehydrogenation exceed the desorption temperature of NaH into its elements. Therefore, the equilibrium shown in Reaction (10c) favours elemental sodium irrespective of the underlying mechanism.

Further DFT calculations have been used to characterise the underlying mechanism of mass transport and diffusion in NaBH₄ by analysing the properties of its lattice defects [64]. These findings emphasise the ionic character of NaBH₄, proposing a mechanism in which hydrogen diffuses through the lattice structure as the ion unit $[BH_4]^-$ and decomposes to H⁻ ions and BH₃ molecules on the surface. While the H⁻ ions convert NaBH₄ to NaH within the lattice, the BH₃ molecules may escape to the gas phase. This could result in the production of diborane, which in turn might result in in-situ formation of Na₂B₁₂H₁₂ through the reaction of diborane and NaBH₄, in a similar mechanism as proposed for LiBH₄ [65].

Despite these theoretical findings, experimental consensus does not exist to support the evolution of diborane during NaBH₄ decomposition [66]. In contrast, multiple studies have confirmed the presence of Na₂B₁₂H₁₂ in the decomposition products of various NaBH₄ thermolysis systems [67–69]. While this is compelling evidence for the significance of Na₂B₁₂H₁₂ to the thermal decomposition of NaBH₄, no fundamental mechanism for its formation has been proposed and its role in the dehydrogenation reaction remains unclear.

KBH₄: Because of its higher decomposition temperature and lower gravimetric hydrogen capacity, little research has focused on the thermal dehydrogenation of KBH₄ [11]. During early study of the structure and properties of NaBH₄ and KBH₄, it was found that KBH₄ shares the same cubic (*Fm3m*) structure as NaBH₄ at room temperature [51] (Table 2). In addition, following the behaviour of NaBH₄, KBH₄ was found to have a low temperature polymorph. At temperatures below $-203 \degree C$, KBH₄ transitions to a tetragonal crystal system [54]. At this low temperature, the [BH₄]⁻ complexes follow a $P4_2/nmc$ structure that is much more ordered than the *Fm3m* room temperature structure.

A study of KBH₄ under compression found that this tetragonal β –KBH₄ phase is also formed at 3.8 GPa, following a similar $P42_1c$ symmetry [55]. A final high-pressure polymorph γ –KBH₄ (orthorhombic *Pnma*) is observed at pressures > 6.8 GPa. In general, it can be noted that the overall phase transition scheme for KBH₄ is remarkably similar to that of NaBH₄. Likewise, it is assumed that its overall decomposition is similar to NaBH₄, with the reaction products being elemental K and B [47].

$$KBH_4 \longrightarrow K + B + 2H_2 \tag{11}$$

Preliminary first-principles calculations have also predicted the formation of $K_2B_{12}H_{12}$ intermediate compounds, as noted for other borohydrides [70].

2.2. Alkaline Earth Borohydrides

Of the alkaline earth metals, $Mg(BH_4)_2$ and $Ca(BH_4)_2$ have garnered the most attention. In particular, $Mg(BH_4)_2$ is especially well suited to dehydrogenation by thermolysis because of the aforementioned inverse correlation observed between cation Pauling electronegativity and borohydride stability. As the Pauling electronegativity of Mg (1.33) is greater than those of Na, Li, and Ca (0.93, 0.98 and 1.00, respectively), it follows that $Mg(BH_4)_2$ is the most unstable and will decompose most readily (Table 1) [29].

Mg(BH₄)₂: Because of the advantageous thermodynamic properties of Mg(BH₄)₂ and its high theoretical gravimetric hydrogen capacity (14.9 mass %), its dominance over the sphere of borohydride research has been rivalled only by LiBH₄. Evidenced by its large number of polymorphs, Mg(BH₄)₂ is the most extreme example of structural complexity observed within the group of borohydrides considered in this review. Experimentally, Mg(BH₄)₂ has been shown to have as many as five different polymorphs (Table 3). However, theoretical predictions indicate that Mg(BH₄)₂ has many other polymorphs that have yet to be observed [32].

Metal Species	Polymorph	Crystal System	Space Group	Reference
	α –Mg(BH ₄) ₂	Hexagonal	<i>P6</i> ₁ 22	[71]
	β –Mg(BH ₄) ₂	Orthorhombic	Fddd	[72]
Mg	γ –Mg(BH ₄) ₂	Cubic	Ia3d	[73]
	δ –Mg(BH ₄) ₂	Tetragonal	P4 ₂ nm	[73]
	ζ –Mg(BH ₄) ₂	Hexagonal	<i>P3</i> ₁ 12	[73]
	α –Ca(BH ₄) ₂	Orthorhombic	F2dd	[74]
Ca	α' –Ca(BH ₄) ₂	Tetragonal	I42d	[74]
	β –Ca(BH ₄) ₂	Tetragonal	$P4 \text{ or } P4_2/m$	[74]
	γ –Ca(BH ₄) ₂	Orthorhombic	Pbca	[75]

Table 3. Known experimental structures of the common alkaline earth borohydrides M(BH₄)₂ (M = Mg, Ca) [32].

The α -Mg(BH₄)₂ (hexagonal *P*6₁22) phase was specified through the investigation of well crystallised Mg(BH₄)₂ at room temperature [71]. Heat treatment of α -Mg(BH₄)₂ yields a transition to orthorhombic β -Mg(BH₄)₂ (*Fddd*) at 180 °C [72]. However, the most notable Mg(BH₄)₂ polymorph is the γ -Mg(BH₄)₂ phase, specified through the investigation of a novel synthesis method for Mg(BH₄)₂ [73]. The structure of γ -Mg(BH₄)₂ is unique, as it is essentially composed of a 3D matrix of pores similar to those seen in zeolites and other microporous materials. Hence, γ -Mg(BH₄)₂ is the first hydride observed to have large, permanent porosity: with empty volume accounting for approximately 33% of the unit cell.

Investigation of the thermal dehydrogenation of Mg(BH₄)₂ has sparked an active debate and numerous mechanisms have been proposed in literature without the emergence of a consensus opinion. Matsunaga et al. investigated the synthesis and thermal dehydrogenation of Mg(BH₄)₂ through dynamic PCT measurements and XRD analysis of the desorption products [37]. The PCT measurements were carried out under a hydrogen back-pressure greater than 0.1 MPa, at three temperatures (290, 320 and 350 °C). The resulting PCT showed two distinct isotherm plateaus for the desorption at 350 °C, and single plateau at lower temperatures (Figure 3). The presence of a second plateau in the high temperature isotherm indicates that hydrogenated products remain after the first thermal decomposition steps.



Figure 3. Absorption/desorption isotherms for $Mg(BH_4)_2$ as synthesised from LiBH₄ and $MgCl_2$ through heat treatment at 320 °C: (**a**) desorption at 350 °C; (**b**) desorption at 320 °C; and (**c**) desorption at 290 °C. Reprinted from [37].

XRD analysis performed on the residue resulting from each of the three desorption reactions supported the conclusions drawn from the PCT. MgH₂ was observed in the products at low decomposition temperature, while only Mg was observed in the products at 350 °C. Hence, a two-step desorption process was proposed to explain the H₂ release from Mg(BH₄)₂.

$$Mg(BH_4)_2 \longrightarrow MgH_2 + 2B + 3H_2 \qquad T < 350 \,^{\circ}C \qquad (12a)$$

$$MgH_2 \longrightarrow Mg + H_2$$
 T > 350 °C (12b)

However, a later study by Li et al. conducted using mass spectrometry and thermogravimetric analysis indicated that further intermediate steps were probable [38]. A derivative of the thermogravimetric curve was found to show four distinct peaks (Figure 4), suggesting that the dehydrogenation of Mg(BH₄)₂ occurs in four endothermic stages. This was further validated by the presence of at least three overlapped peaks in the mass spectrum measured during thermal dehydrogenation, indicating at least three desorption steps.



Figure 4. TG-DTA and mass spectrum curves of the thermal desorption of Mg(BH₄)₂: (a) the thermogravimetry curve (black), its derivative (red) and the differential thermal analysis (green) curves of Mg(BH₄)₂; and (b) associated mass spectrum of the as-synthesised Mg(BH₄)₂ (blue). Reprinted from [38].

Raman spectroscopic analysis performed to elucidate the intermediates formed during desorption indicated that $MgB_{12}H_{12}$ was likely involved in one or more of the steps. Based on these conclusions, the following three-stage reaction scheme was proposed for the overall dehydrogenation of $Mg(BH_4)_2$ [38]:

$$Mg(BH_4)_2 \longrightarrow \frac{1}{6}MgB_{12}H_{12} + \frac{5}{6}MgH_2 + \frac{13}{6}H_2 \longrightarrow MgH_2 + 2B + 3H_2 \longrightarrow MgB_2 + 4H_2$$
(13)

Another study by Soloveichik et al. also confirmed at least four decomposition steps [76]. However, they proposed that the reaction proceeds through multiple amorphous intermediates, including $MgB_{12}H_{12}$ (Figure 5).



Figure 5. Decomposition pathways of Mg(BH₄)₂, reproduced from Soloveichik et al. (Path C), where D1–D4 indicate hydrogen evolution events measured by temperature programmed desorption (TPD) [76]. Path A [37,77] proposed by Matsunaga et al. and Path B [38] proposed by Li et al. refer to mechanisms described in previous publications. Amorphous phases are denoted by an asterisk, observed hydrogen evolution steps are marked by dashed red lines. Reproduced from [76].

Beyond the four endothermic decomposition steps, an exothermic event was observed at 350 °C (X1 in Figure 5) and this was attributed to the crystallisation of MgH₂. However, the X1 event could also be the result of an exothermic decomposition of the intermediate "MgB₂H_{2.5}" phase to give MgB₁₂H₁₂ and MgH₂. As shown in Path C of Figure 5, the desorption of Mg(BH₄)₂ proceeds through at least three polyborane species, one of which was conclusively identified as MgB₁₂H₁₂, and results in MgB₂ [38] as the final desorption product as opposed to Mg and B [37].

Beyond this mechanism, it can also be noted that the desorption process of Mg(BH₄)₂ has also been found to be extremely pressure dependent [78]. However, the findings of Soloveichik et al. emphasised a fundamental dependence of the reaction pathway on the behaviour of various polyborane intermediates (including MgB₁₂H₁₂) [76]. Not currently considered is the unprecedented level of polymorphism of Mg(BH₄)₂ (Table 3), which introduces another level to an already complicated desorption process [32]. For example, the cubic polymorph γ –Mg(BH₄)₂ was found to desorb via an eight step decomposition mechanism that included two polymorphic transitions and several unidentified ternary Mg-B-H phases [79].

Ca(BH₄)₂: Although Ca(BH₄)₂ has a slightly lower theoretical gravimetric hydrogen capacity (11.6 mass%) than Mg(BH₄)₂, it has still been well studied as a potential hydrogen storage material. The commonly utilised wet chemistry synthesis of Ca(BH₄)₂ in tetrahydrofuran (THF) solvent yields a mixture of two room temperature polymorphs: α -Ca(BH₄)₂ and β -Ca(BH₄)₂ [74] (Table 3). Additionally, a phase transition at around 223 °C is also noted, resulting in a high-temperature tetragonal polymorph, α' -Ca(BH₄)₂.

A fourth polymorph has also been specified, originating from a mechanochemical synthesis procedure using MgB₂ and CaH₂ as the starting materials [75]. This orthorhombic γ –Ca(BH₄)₂ structure was found in room temperature samples of the as-synthesised Ca(BH₄)₂, and after heating to >127 °C. A high-temperature variant of β –Ca(BH₄)₂ with P4₂/m symmetry has also been identified, resulting from a phase transition of α –Ca(BH₄)₂ above 127 °C.

A preliminary first-principles study of the thermal properties of Ca(BH₄)₂ predicted that it would desorb according to the following reaction [80]:

$$Ca(BH_4)_2 \longrightarrow \frac{2}{3}CaH_2 + \frac{1}{3}CaB_6 + \frac{10}{3}H_2$$
(14)

A reaction pathway involving a dodecaborate product has also been theorised (Reaction (15)) and predicted to be more energetically favourable than Reaction (14) [58]. However, the reaction enthalpies calculated at T = 0 K for the proposed mechanisms (35.2 kJ mol⁻¹ H₂ for Reaction (14) and 34.2 kJ mol⁻¹ H₂ for Reaction (15)) only differ by 1 kJ mol⁻¹ H₂, which is not sufficient to conclusively exclude one or the other on the basis of energetic preference.

$$6 \operatorname{Ca}(BH_4)_2 \longrightarrow \operatorname{Ca}B_{12}H_{12} + 5 \operatorname{Ca}H_2 + 13 \operatorname{H}_2 \tag{15}$$

The framework of the desorption mechanism was described experimentally by Kim et al. through a comprehensive investigation of the thermal decomposition of $Ca(BH_4)_2$ [81]. The adduct-free $Ca(BH_4)_2$ used in the experiments was prepared from a $Ca(BH_4)_2 - 2$ THF precursor and all heating procedures were conducted under vacuum. From this characterisation, it was concluded that $Ca(BH_4)_2$ decomposition begins with a polymorphic transformation (at 167 °C) and proceeds via an unknown ternary Ca-B-H intermediate compounds (347–387 °C). However, in the XRD spectra of the final desorption products, the only crystalline component detected was CaH_2 and further characterisation of the amorphous products was not attempted.

Review of the research that has been amassed concerning the thermal dehydrogenation of Ca(BH₄)₂ suggests that the desorption proceeds via more than one different mechanism and is strongly influenced by the reaction conditions. In general, the findings of experimental investigations coalesce around two competing reaction pathways [82]:

$$Ca(BH_4)_2 \longrightarrow amorphous intermediates$$
 (16a)

amorphous intermediates
$$\longrightarrow CaB_2H_x + (4 - \frac{x}{2})H_2$$
 (16b)

$$CaB_2H_x + (4 - \frac{x}{2})H_2 \longrightarrow \frac{1}{3}CaB_6 + \frac{2}{3}CaH_2 + (\frac{x}{2} - \frac{2}{3})H_2$$
 (16c)

and

$$Ca(BH_4)_2 \longrightarrow amorphous intermediates$$
 (17a)

amorphous intermediates
$$\longrightarrow \frac{1}{6} CaB_{12}H_{12} + \frac{5}{6} CaH_2 + \frac{13}{6} H_2$$
 (17b)

A ¹¹B MAS-NMR study of the decomposition process emphasised temperature dependence, concluding that desorption under vacuum conducted within the temperature range of 320–350 °C results in CaB₆ as the major boron phase in the products, whereas higher temperatures from 400–450 °C result in amorphous elemental boron [83]. These findings suggest that Ca(BH₄)₂ may also desorb according to a third mechanism, involving the formation of amorphous boron:

$$Ca(BH_4)_2 \longrightarrow CaH_2 + 2B + 3H_2 \tag{18}$$

13 of 38

The low-temperature mechanism discussed in this study aligns with Reactions (16a)–(16c), as they identified CaB_2H_6 (a CaB_2H_x phase) as the reaction intermediate in the 320–350 °C range and did not detect $CaB_{12}H_{12}$ in the desorption products. Alternatively, the CaB_2H_x intermediate has also been assigned the CaB_2H_2 stoichiometry [84], and other investigations have also reported potential crystal structures [85].

Decomposition to $CaB_{12}H_{12}$ has been supported by multiple theoretical studies using first-principles calculations [58,86]. Notably, significant $CaB_{12}H_{12}$ formation has been observed experimentally in systems desorbed under H₂ back-pressure. An investigation of Ca(BH₄)₂ desorption was conducted under 0.1 MPa of H₂ using in-situ analysis by ¹¹B MAS-NMR and structural analysis of desorbed products by XRD [87]. Under these conditions, uncharacterised amorphous intermediates were found to decompose to both CaB₆ and CaB₁₂H₁₂ starting at approximately 340 °C.

A later investigation considered a wider range of hydrogen back-pressures ($p(H_2) = 0.1, 0.5, 1$ and 1 MPa), finding that formation of the commonly reported CaB₂H_x intermediate was suppressed with increasing back-pressure [88]. Also noted was a decrease in CaB₁₂H₁₂ and CaB₆ formation under high H₂ pressure, accompanied by an increase in amorphous boron (possibly indicating desorption according to Reaction (18)). Despite these observations, the fundamental cause of the temperature and pressure dependence of the Ca(BH₄)₂ desorption mechanism is still uncertain and further clarification is required to effectively control the reaction pathway.

3. Dodecaborates in the Borohydride System

In all of the potential mechanisms that have been discussed, thermolysis proceeds via a multi-step process with multiple reaction intermediates. One interesting commonality shared between the dehydrogenation pathways of many borohydrides is the presence of dodecaborate compounds ($M_{n=1,2}B_{12}H_{12}$) formed either as by-products or intermediates. Dodecaborates have garnered significant attention, as their thermodynamic stability has been cited as a potential cause for difficulties experienced in re-hydrogenating borohydrides. While their importance is acknowledged, the role of dodecaborates in borohydride dehydrogenation remains debated and largely unclear.

3.1. Chemical Structure and Properties

Dodecahydro-*closo*-dodecaborates are a unique borohydride species that exists as the dianion $[B_{12}H_{12}]^{2-}$ and most commonly reacts with metal cations to form salts. The "closo" in their name refers to the closed, icosahedral structure of the molecule (Figure 6). Because of this distinctive structure, the *closo*-dodocaborates can be classified as cage compounds, in the same vein as closed carbon nano-structures such as nanospheres [89]. Many of the most consequential properties of dodecaborates can be attributed to the symmetry and regularity of their molecular structure.



Figure 6. Schematic view of the icosahedral $[B_{12}H_{12}]^{2-}$. Pink spheres denote boron atoms and white spheres denote hydrogen atoms.

Of most consequence to their role in the dehydrogenation of borohydrides is the exceptionally high thermal stability of monometallic dodecaborate salts like those formed during the desorption process. For example, $Cs_2B_{12}H_{12}$ (one of the more extensively studied alkali dodecaborate species because of

its relatively larger cation radius) can be heated up to 810 °C under vacuum without undergoing any decomposition [90]. In contrast, hydrogen release from the smaller alkali dodecaborates has been observed at much lower temperatures. For example, $Na_2B_{12}H_{12}$ was observed to release hydrogen starting at around 450 °C under a helium flow [91]. Similar results have been reported for $K_2B_{12}H_{12}$ and $Li_2B_{12}H_{12}$, showing hydrogen release events beginning at 350 °C and 250 °C, respectively [92].

However, these low temperature hydrogen release steps have not been found to result in the decomposition of the dodecaborate species to smaller polyboranes or metal hydrides. Investigation of the decomposition mechanism of $Li_2B_{12}H_{12}$ carried out by XRD (Figure 7) revealed an increase in the amorphous character of the dodecaborate with increasing temperatures [92].



Figure 7. XRD data from thermally decomposed anhydrous crystalline Li₂B₁₂H₁₂ before and after the main H₂ evolution peak at ca. 440 °C. Reprinted from [92].

Furthermore, no evidence was identified for the formation of any other lithium containing phases, including LiH. From these observations, it was proposed that $Li_2B_{12}H_{12}$ decomposes via continuous hydrogen release, resulting in the formation of an amorphous hydrogen deficient dodecaborate species, $Li_2B_{12}H_{12-x}$ [92,93]. After the formation of this hydrogen deficient phase, shifts of the major resonance peaks of $[B_{12}H_{12}]^{2-}$ indicate that the icosahedral B_{12} skeleton of the anion may be polymerising, resulting in the formation of $(Li_2B_{12}H_z)_n$ polymers [94]. This polymerised phase was only observed to fully decompose to amorphous elemental boron when the temperature exceeded 650 °C [92]. This decomposition pathway has also been observed for NaB₁₂H₁₂, culminating in the formation of $(Na_2B_{12}H_z)_n$ polymers at around 700 °C [94].

Similar behaviour has been observed for the alkaline earth dodecaborates, $MgB_{12}H_{12}$ and $CaB_{12}H_{12}$. The decomposition of $MgB_{12}H_{12}$ is observed to begin at approximately 190 ° C, losing around 77% its theoretical hydrogen content between 190–800 °C [95]. Structural analysis by ¹¹B MAS-NMR (Figure 8) showed the formation of an amorphous hydrogen deficient dodecaborate species $MgB_{12}H_{12-x}$, analogous to $Li_2B_{12}H_{12-x}$, upon thermal decomposition.



Figure 8. ¹¹B MAS-NMR spectra of anhydrous MgB₁₂H₁₂ heated to respective temperatures between 190 and 800 °C. Reprinted from [95].

As the temperature increases, shifts of the major resonance peak of $[B_{12}H_{12}]^{2-}$ are also observed, indicating the polymerisation of the icosahedral B_{12} framework and the formation of $(MgB_yH_z)_n$ polymers. These intermediate products eventually decompose to amorphous elemental boron when the temperature exceeds 800 °C. These results are in agreement with an earlier study of $MgB_{12}H_{12}/carbon$ nanocomposites, with discrepancies in the temperatures of the intermediate transitions, possibly caused by an influence of the carbon on the decomposition process [96].

CaB₁₂H₁₂ has also been observed to undergo the same series of transformations during heating as MgB₁₂H₁₂, culminating in the formation of $(CaB_yH_z)_n$ polymers [95]. Unlike MgB₁₂H₁₂, amorphous elemental boron was not detected during the thermal treatment, even at temperatures greater than 750 °C. When considered collectively, these results are a strong indicator of the fundamental stability of the icosahedral molecular geometry of the dodecaborates, demonstrating that this structure persists even after intense thermal treatment.

The crystal structure and symmetry of the dodecaborates have been characterised for their ambient temperature polymorphs, summarised in Table 4. The high-temperature polymorphs of the alkali dodecaborates have also been found to display good ionic conduction and thus are potential candidates for solid-state electrolytes [97,98]. The thermodynamic stability of some of the dodecaborates has also been demonstrated theoretically by first-principles studies of their structure (Table 4). The extremely exothermic enthalpies of formation that have been calculated indicate that the dodecaborate species are very low energy state compounds and are therefore unlikely to react or decompose if formed.

Table 4. Structural and thermodynamic data reported for the common alkali and alkaline earth dodecaborates. The theoretically predicted enthalpy of formation ($\Delta H_{formation}^{T=0K}$) is given when values are available in literature. All given structures refer to the ambient temperature polymorph.

Species	$\Delta H_{formation}^{T=0K}$ (kJ mol ⁻¹)	Crystal System	Space Group
Li ₂ B ₁₂ H ₁₂	-945.95 [60]	Cubic [99]	Pa 3 [99]
	-	Monoclinic [34]	$P2_1/n$ [34]
$Na_2B_{12}H_{12}$	-1086.196 [91]	Cubic [91]	Pa3 [91]
	-1086.381 [91]	Monoclinic [100]	$P2_1/n$ [100]
$K_2B_{12}H_{12}$	-	Cubic [101]	$Fm\overline{3}$ [101]
$CaB_{12}H_{12}$	-	Monoclinic [102]	<i>C2/c</i> [102]
$MgB_{12}H_{12}$	-	Monoclinic [58]	C2/m [58]

3.2. Synthesis Methods

Dodecaborates were first synthesised in 1960 by Pitochelli and Hawthorne as a by-product of the reaction of 2-iododecaborane and triethylamine [103]. Since then, numerous synthetic methods have been developed specifically to produce dodecaborates in high yields [89,104]. Of particular significance to borohydride chemistry is the synthetic method first reported by Miller et al. in 1964. They achieved sodium dodecaborate yields of greater than 80% through the reaction of diborane and sodium borohydride in diethylamine at 180 °C [105].

$$2 \operatorname{NaBH}_4 + 5 \operatorname{B}_2 \operatorname{H}_6 \longrightarrow \operatorname{Na}_2 \operatorname{B}_{12} \operatorname{H}_{12} + 13 \operatorname{H}_2 \tag{19}$$

Based on their investigation, they proposed that polyborane species such as dodecaborates could be produced through a sequential addition of boron and hydrogen to an existing boron lattice, similar to a polymerisation reaction, as shown in the following scheme [105]:

$$aH^{-} + bB_{x}H_{y} \longrightarrow [B_{bx}H_{by+a-z}]^{a-} + (\frac{z}{2})H_{2}$$

$$(20)$$

This scheme is equivalent to the known boron addition Reactions (21a) and (21b) [105,106].

$$B_2H_6 + NaH \longrightarrow 2 NaBH_4$$
 (21a)

$$NaBH_4 + B_2H_6 \longrightarrow NaB_3H_8 + H_2$$
(21b)

Furthermore, through investigation of Reaction (19) in different solvents, Miller et al. found that the $[B_{11}H_{14}]^-$ anion was preferentially formed over $[B_{12}H_{12}]^{2-}$ under certain reaction conditions. For example, when Reaction (19) is conducted in a dioxane solvent at temperatures between 90–120 °C, $[B_{11}H_{14}]^-$ is the sole polyborane product. Conversely, they found that when the borohydride species was in excess and temperatures exceeded 130 °C, $Na_2B_{12}H_{12}$ was the sole product of Reaction (19), irrespective of solvent. Beyond these steps proposed by Miller et al., the mechanism of boron addition in a metal-boron-hydrogen system has not been conclusively determined, likely because of the emergence of more advantageous dodecaborate synthetic methods [89].

For example, a contemporary study by Adams et al. found that NaBH₄ reacts with $B_{10}H_{14}$ in diglyme at 160 °C to give dodecaborate yields of greater than 90% [107]. Because decaborane ($B_{10}H_{14}$) is stable under ambient conditions, it is preferred over diborane as a precursor in dodecaborate synthesis processes [89]. While it is possible that $B_{10}H_{14}$ is an intermediate compound in the reaction scheme proposed by Miller et al., its high stability makes it more likely to be an alternative terminal product. More recently, dodecaborates have been synthesised directly from gas–solid reactions between B_2H_6 and a metal borohydride [65,96]. As discussed in Section 2.1.1, these successful synthesis procedures have also been cited as evidence of the relevance of B_2H_6 to dodecaborate formation during borohydride decomposition [59].

3.3. Other $B_x H_y$ Compounds

The formation of other complex $[B_xH_y]^{n-}$ anions during borohydride decomposition has been investigated through experimental and theoretical means. Three species that are commonly discussed are the $[B_{10}H_{10}]^{2-}$ dianion and the $[B_{11}H_{14}]^-$ and $[B_3H_8]^-$ anions. $[B_{10}H_{10}]^{2-}$ and $[B_{11}H_{14}]^$ compounds have also been considered as potential hydrogen storage materials in their own right because of their ability to release hydrogen through transition metal-catalysed hydrolysis [108]. All three anions have been theoretically predicted as potential intermediate compounds in the desorption schemes of the most commonly investigated borohydrides (MBH₄, M = Li [34], Mg and Na [58]).

 $[B_3H_8]^-$ intermediate phases have also been observed experimentally during the thermal desorption of Y(BH₄)₃ [109] and Mg(BH₄)₂. When Mg(BH₄)₂ is desorbed at 200 °C, Mg(B₃H₈)₂ was identified as a reversible intermediate with a cycling capacity of 2.5 mass % [110]. Coordination of

Mg(BH₄)₂ with a THF adduct has also been found to result in the preferential formation of MgB₁₀H₁₀ as a product of desorption at 180 °C [111]. However, these observations for the Mg(BH₄)₂–THF system are anomalous, as the $[B_{12}H_{12}]^{2-}$ dianion has been recognised as the most energetically favourable and thermodynamically stable of the proposed polyborane intermediates. Therefore, it is considered to be both the most likely, and most problematic $[B_xH_y]^{n-}$ participant in the borohydride desorption scheme [34,58,112].

This is illustrated by the thermodynamic properties of $[B_xH_y]^{n-}$, summarised in Table 5. As NaB₃H₈ has been observed to decompose at temperatures as low as 100 °C [113], its formation during NaBH₄ thermolysis would not present the same challenges as the significantly more stable Na₂B₁₂H₁₂. Furthermore, although the energy state of the ionic salt varies with the metal species, the extremely exothermic gas phase enthalpy of formation of the $[B_{12}H_{12}]^{2-}$ dianion suggests that its formation is a more energetically favourable pathway when compared to the other polyborane species proposed as participants in borohydride decomposition.

Table 5. Key structural and thermodynamic properties tabulated for a range of polyborane anions that have been investigated as intermediate phases during borohydride decomposition. The theoretically predicted enthalpy of formation ($\Delta H_{\text{formation}}$) at T = 0 K is given for the gas phase formation of each anion. An approximate decomposition temperature (T_{dec}) is given for the sodium salt ($Na_n(B_xH_y)^{n-}$) of the given anion to allow for easy comparison between different species.

Anion	$\Delta H_{formation}^{T=0K}$ (kJ mol ⁻¹)	T_{dec} of $Na_n(B_xH_y)^{n-}$ (°C)	Anion Geometry [112]
[B ₁₂ H ₁₂] ²⁻	-328.4 [114]	612 (He flow) [115]	
$[B_{10}H_{10}]^{2-}$	-26.8 [114]	577 (He flow) [116]	
[B ₁₁ H ₁₄] ⁻	-200.4 [114]	127 (He flow) [117]	100 C
[B ₃ H ₈] ⁻	-72.8 [114]	100 (Ar flow) [113,118]	

Beyond their relevance to borohydride desorption, extensive independent investigation of the polyborane $(B_xH_y/[B_xH_y]^{n-})$ cluster compounds has been conducted to clarify the details of their unusual structural chemistry and properties. A significant volume of both neutral and anionic boron hydride cluster compounds have been identified. Their chemistry is relatively well understood and has been collected in numerous textbooks and reviews [90,104,119]. In general, the neutral polyborane clusters have been found to be highly reactive and prone to explosive oxidation by oxygen or water. They exhibit a unique form of electron-deficient bonding that can be described using polyhedral

skeletal electron pair theory, also known as Wade's rules [120,121]. A wide range of applications have been proposed for polyborane cluster compounds, including forms of optoelectronics, novel chemical synthesis methods and various medical technologies [122].

3.4. Role of $M_{n=1,2}B_{12}H_{12}$ in Borohydride Dehydrogenation

As discussed previously, the mechanism of dodecaborate formation during borohydride thermolysis has not been conclusively determined and is widely disputed within the field. Table 6 summarises the proposed mechanisms leading to the formation of dodecaborates, including enthalpies of reaction where available.

Metal Species	Reaction	$\Delta H_{reaction}^{T=0K}$ (kJ mol ⁻¹)	Reference
Li	$\text{LiBH}_4 \longrightarrow \frac{1}{12} \text{Li}_2 \text{B}_{12} \text{H}_{12} + \frac{5}{6} \text{LiH} + \frac{13}{12} \text{H}_2$	56	[34]
	$2 \operatorname{LiBH}_4 + 5 \operatorname{B}_2 \operatorname{H}_6 \longrightarrow \operatorname{Li}_2 \operatorname{B}_{12} \operatorname{H}_{12} + 13 \operatorname{H}_2$	Unspecified	[59]
	$12 \operatorname{LiBH}_4 \longrightarrow \operatorname{Li}_2 B_{12} H_{12} + 10 \operatorname{LiH} + 13 \operatorname{H}_2$	56.139	[60]
	$12 \operatorname{LiBH}_4 \longrightarrow \operatorname{Li}_2 B_{12} H_{12} + 10 \operatorname{Li} + 18 \operatorname{H}_2$	122.50	[60]
	$12 \operatorname{LiBH}_4 \longrightarrow \operatorname{Li}_2 B_{12} H_{12} + 10 \operatorname{LiH} + 13 \operatorname{H}_2$	40.9	[58]
Na	$2 \operatorname{NaBH}_4 + 5 \operatorname{B}_2\operatorname{H}_6 \longrightarrow \operatorname{Na}_2\operatorname{B}_{12}\operatorname{H}_{12} + 13 \operatorname{H}_2$	Unspecified	[64]
	$12 \operatorname{NaBH}_4 \longrightarrow 10 \operatorname{Na} + \operatorname{Na}_2 \operatorname{B}_{12} \operatorname{H}_{12} + 18 \operatorname{H}_2$	167.313	[91]
	$12 \operatorname{NaBH}_4 \longrightarrow 10 \operatorname{NaH} + \operatorname{Na}_2 \operatorname{B}_{12} \operatorname{H}_{12} + 13 \operatorname{H}_2$	129.386	[91]
К	$KBH_4 \longrightarrow \frac{1}{12} K_2 B_{12} H_{12} + \frac{5}{6} KH + \frac{13}{12} H_2$	117.5	[70]
Mg	$Mg(BH_4)_2 \xrightarrow{H_2} MgH_2 + \frac{1}{12}MgB_{12}H_{12} + MgB_4$	Unspecified	[76]
C	$6 \text{ Mg}(\text{BH}_4)_2 \longrightarrow \text{MgB}_{12}\text{H}_{12}^2 + 5 \text{ MgH}_2 + 13 \text{ H}_2$	25	[58]
Ca	$6 \operatorname{Ca}(BH_4)_2 \longrightarrow \operatorname{Ca}B_{12}H_{12} + 5 \operatorname{Ca}H_2 + 13 \operatorname{H}_2$	34.2	[58]
	$Ca(BH_4)_2 \longrightarrow \frac{2}{3}CaH_2 + \frac{1}{3}CaB_6 + \frac{10}{3}H_2$	35.2	[58]

Table 6. Summary of the metal borohydride decomposition mechanisms that result in dodecaborate formation.

Based on what is known of the thermolysis pathway, it is clear that by-products and intermediates, such as dodecaborate compounds, play an important role. Despite this, many investigations of borohydride decomposition fail to consider dodecaborates because of the sole use of XRD to identify reaction products. Furthermore, because of the unusual properties of dodecaborates, there is considerable controversy in the literature over their classification as a reaction intermediate versus a process by-product. However, from a practical perspective, this distinction has less relevance, as the formation of dodecaborates during dehydrogenation will present challenges either way. If any dodecaborates remain in the system after a dehydrogenation process, they can have a significant impact on the storage material's cycling efficiency and the overall reversibility of the dehydrogenation process (represented in Figure 9).

Dodecaborates, and other commonly reported by-products such as diborane, act as boron sinks, meaning that their formation will lead to a slow degradation of the capacity of a storage material over many dehydrogenation cycles. In the case of gaseous diborane, this is because boron is lost with the release of hydrogen, but the stability of dodecaborates means that boron is trapped in an unreactive decomposition product. This is illustrated by the hydrogen capacity degradation observed after multiple hydrogenation cycles of the reactive hydride composites LiBH₄–MgH₂–Al and LiBH₄–Al [123,124]. In both systems, Li₂B₁₂H₁₂ was observed to form during each decomposition step and accumulate with consecutive hydrogen release and uptake processes. In this way, the reversibility and storage capacity of a storage material is severely hindered by the formation of dodecaborates during thermolysis.



Figure 9. Schematic representation of the role of dodecaborates in the borohydride hydrogenation cycle.

4. Approaches to the Mitigation of M_{n=1,2}B₁₂H₁₂ Formation

Although most efforts in the field have focused on confirming the presence of dodecaborates in the dehydrogenation reaction scheme and clarifying their impact, some initial attempts have been made to improve hydrogen storage properties by specifically targeting dodecaborate formation. In general, the consequences of dodecaborate formation can be countered through one or more of the following mechanisms: $M_{n=1,2}B_{12}H_{12}$ destabilisation, improvement of $M_{n=1,2}B_{12}H_{12}$ rehydrogenation properties and alteration of decomposition pathways to inhibit the occurence of $M_{n=1,2}B_{12}H_{12}$ compounds altogether.

Of those three options, pathway alteration is the most holistic, and therefore most preferable approach. If decomposition can be forced through a kinetically and thermodynamically favourable mechanism that does not include $M_{n=1,2}B_{12}H_{12}$ formation, the entire hydrogenation cycle could be optimised while also addressing the problems posed specifically by dodecaborates. However, tuning of this pathway has proven challenging due to the sheer number of impactful variables that must be accounted for and controlled. This uncertainty must be considered when interpreting the results of investigations that report successful pathway alteration.

4.1. Catalysis of $M_{n=1,2}B_{12}H_{12}$ Dehydrogenation and Rehydrogenation

Multiple studies attempting to mitigate the impact of dodecaborates on borohydride thermolysis have focused on the use of some additive to destabilise and catalyse the dehydrogenation and rehydrogenation reactions of the dodecaborates. One of the first experimental studies that utilised this method was carried out on $CaB_{12}H_{12}$ synthesised through a wet chemistry procedure using a $Cs_2B_{12}H_{12}$ precursor [102]. Although the focus of this study was on elucidating the crystal structure of $CaB_{12}H_{12}$, milling of $CaB_{12}H_{12}$ with CaH_2 was also investigated as a possible method of improving the hydrogen cycling properties of the dodecaborate species.

Attempts were made to rehydrogenate the ball-milled material at 397 °C under 100 MPa of hydrogen pressure, but no Ca(BH₄)₂ formation was detected. However, thermal pretreatment of the ball-milled material at 597 °C under vacuum before following the same rehydrogenation procedure resulted in the production of small amounts of crystalline Ca(BH₄)₂. It was proposed that this Ca(BH₄)₂ formation might be the result of a reaction between CaH₂ and CaB₆ that could have been generated during the thermal pretreatment step. This aligns with a theoretical prediction of the following reaction between CaH₂ and CaB₁₂H₁₂ to produce CaB₆ ($\Delta H_{reaction}^{T=0K} = 38.6$ kJ mol⁻¹) [58].

$$CaB_{12}H_{12} + CaH_2 \longrightarrow 2CaB_6 + 7H_2$$
(22)

This finding has great significance, as the regeneration of $Ca(BH_4)_2$ from CaB_6 has been achieved up to around 60% by using various catalysts (including MgH₂ [40], and numerous transition metal compounds [125–127] and metal halides [128,129]) and shows much more potential for optimisation than the direct rehydrogenation of $CaB_{12}H_{12}$ [43,87]. Therefore, the identification of a mechanism for the conversion of $CaB_{12}H_{12}$ to the much more reactive CaB_6 is a potential step towards improved reversibility. In addition to that reaction during thermal treatment, ball-milling with CaH_2 also had a pronounced impact on the direct dehydrogenation of $CaB_{12}H_{12}$. When heated up to 597 °C, pure $CaB_{12}H_{12}$ experienced a total mass loss of less than 1.5% while the ball-milled mixture lost 6 mass% under the same treatment (Figure 10).



Figure 10. TGA curves for the desorption of $CaB_{12}H_{12}$ (green curve) and ball-milled $CaB_{12}H_{12}$:CaH₂ (1:1) (blue curve). Reprinted from [102].

A similar study was later carried out for the alkali borohydrides (M = K, Na, Li) and their analogous dodecaborate compounds ($K_2B_{12}H_{12}$, $Na_2B_{12}H_{12}$, and $Li_2B_{12}H_{12}$) [130]. The first method explored was the ball milling of the dodecaborate species with its corresponding metal hydride with the aim of facilitating the rehydrogenation of the system to give a metal borohydride (Reactions (23)–(25)).

$$Li_2B_{12}H_{12} + 10LiH + 13H_2 \longrightarrow 12LiBH_4$$

$$(23)$$

$$Na_2B_{12}H_{12} + 10 NaH + 13 H_2 \longrightarrow 12 NaBH_4$$

$$(24)$$

$$K_2 B_{12} H_{12} + 10 \text{ KH} + 13 \text{ H}_2 \longrightarrow 12 \text{ KBH}_4$$

$$(25)$$

Each of the rehydrogenation reactions was conducted at 500 °C under 100 MPa of H₂ pressure. XRD characterisation before and after rehydrogenation showed that rehydrogenated samples were primarily composed of crystalline MBH₄ (M = K, Na, Li), with small quantities of remaining M₂B₁₂H₁₂ and MH. Following from these results, a recent study attempted to clarify the mechanism of hydrogen uptake in the M₂B₁₂H₁₂–MH (M = Na, Li) system [131]. Under the milder conditions utilised in this investigation (400 °C under 54.7 MPa and 97 MPa of H₂), no reactions were observed in the Li₂B₁₂H₁₂-10LiH system.

During treatment of the Na₂B₁₂H₁₂-10NaH mixture at 400 °C under 54.7 MPa H₂, a pressure decrease was registered corresponding to a hydrogen sorption of approximately 1.5 mass% H₂. However, the phases produced during this hydrogenation process could not be conclusively identified and no NaBH₄ formation was observed. The same unidentifiable intermediates were detected in Na₂B₁₂H₁₂-10NaH samples treated under higher hydrogen pressure (400 °C under 97 MPa H₂). Although further investigation is required to clarify the composition of these intermediates, ¹¹B MAS NMR characterisation revealed structural similarities between the intermediates and [B₁₂H₁₂]²⁻,

suggesting that they could be some form of *closo*-polyborate anion or polymerised icosahedral B_{12} skeleton, as has been previously observed in studies of the thermal decomposition of NaB₁₂H₁₂ [94].

In another approach, the destabilisation of $Li_2B_{12}H_{12}$ using MgH₂ was investigated under the assumption that this system would form a reactive hydride composite in a similar manner as has been observed for LiBH₄ and MgH₂ [132]. Following this approach, $Li_2B_{12}H_{12}$ was ball-milled with MgH₂, with the aim of forming the more reactive binary compounds MgB₂ and LiH after H₂ desorption [130].

$$\operatorname{Li}_{2}B_{12}H_{12} + 6\operatorname{MgH}_{2} \longrightarrow 6\operatorname{MgB}_{2} + 2\operatorname{Li}H + 11\operatorname{H}_{2}$$

$$\tag{26}$$

The theoretical decomposition temperature of Reaction (26) is reported as 215 °C [58], but desorption of the as-synthesised $Li_2B_{12}H_{12}$ –MgH₂ composite did not begin until the temperature exceeded 380 °C and the rate of H₂ desorption did not peak until around 600 °C. Furthermore, the cumulative hydrogen release during this desorption only reached 5.9 mass %, significantly less than the 7.7 mass % theoretical capacity of the $Li_2B_{12}H_{12}$ –MgH₂ mixture.

The use of nanocrystalline cobalt boride (Co_{1.34}B) has also been proposed to catalyse the rehydrogenation of Li₂B₁₂H₁₂ [133], based on prior evidence of its catalytic properties in other borohydride systems such as the hydrolysis of NaBH₄ and the desorption of the LiNH₂–LiBH₄ composite material [134,135]. Hydrogen was desorbed from a ball-milled LiBH₄-Co_{1.34}B composite and the desorption products were then rehydrogenated at 400 °C under 10 MPa of H₂. The composite released 5.1 mass % H₂ after the first hydrogenation cycle and 3.6 mass % after a second. Hence the system achieved 68% reversibility at much more reasonable conditions than have been observed for the rehydrogenation of un-catalysed LiBH₄ (76% reversibility after one cycle when rehydrogenated at 600 °C under 15.5 MPa of H₂ [33]).

4.2. Reactive Hydride Composites

While metal hydrides catalysts could potentially solve the problem of dodecaborate boron sinks by allowing them to participate in borohydride regeneration reactions during rehydrogenation, other approaches aim to fully inhibit the formation of dodecaborates through an alteration of the desorption pathway. One such method is the combination of a borohydride species with another chemical hydride to form a eutectic mixture, resulting in the formation of a reactive composite with a lowered reaction enthalpy [136]. This enthalpy reduction is attributed to the exothermic formation of boron-containing intermediate phases, that decreases the cumulative reaction enthalpy of the endothermic desorption process [137].

While the conventional application of reactive hydride composites has been in the destabilisation of borohydrides to promote more thermodynamically favourable desorption [138], a similar concept has been proposed to prevent the formation of boron sinks such as dodecaborates [139]. In the context of dodecaborate inhibition, the secondary hydride species essentially acts as a reversible boron carrier (Figure 11). During the thermolysis of the composite material, this hydride reacts with the decomposing borohydride to form a boron-containing compound. During rehydrogenation, the newly formed boron-containing compound (e.g., MgNi_{2.5}B₂ in Figure 11) should be more prone to give up its boron than other stable boron phases such as $M_{n=1,2}B_{12}H_{12}$ that would occur otherwise.



Figure 11. Schematic representation of the function of the Mg₂NiH₄ boron carrier in the metal borohydride (MBH₄) hydrogenation cycle, shown without consideration of reaction stoichiometry.

Beyond acting as a boron carrier, the dopant hydride should also be lightweight and preferably contain hydrogen so that the overall gravimetric capacity of the storage material does not suffer. One such compound that has been proposed is the ternary hydride Mg₂NiH₄. In an extension of their previous work with LiBH₄ composites, Vajo et al. investigated the desorption reaction of a LiBH₄–Mg₂NiH₄ compound synthesised by ball-milling of the two compounds [140]. They found that the desorption of this composite material begins at a much lower temperature than either of the component hydrides (Figure 12).



Figure 12. Dehydrogenation of $4 \text{LiBH}_4 + 5 \text{Mg}_2 \text{NiH}_4$, Mg₂NiH₄, and LiBH₄ conducted using a 2 °C min⁻¹ temperature ramp under 4 bar of H₂. Reprinted from [140].

The first step of the hydrogen desorption is attributed to Reaction (27), which includes the formation of the boron containing ternary compound MgNi_{2.5}B₂. While a discussion of dodecaborate formation was not considered in this investigation, a small loss of hydrogen capacity was noted after the first cycle which could be attributed to the formation of a boron sink. However, the material was able to complete 10 hydrogenation cycles, which demonstrates the promise of borohydride–Mg₂NiH₄ composites, and validates the postulated advantages of a ternary boron carrier [140].

$$4 \operatorname{LiBH}_4 + 5 \operatorname{Mg}_2 \operatorname{NiH}_4 \longrightarrow \operatorname{MgNi}_{2.5} \operatorname{B}_2 + 4 \operatorname{LiH} + 8 \operatorname{MgH}_2 + 8 \operatorname{H}_2$$

$$(27)$$

These findings were further supported through similar results obtained for a NaBH₄–Mg₂NiH₄ composite material [141]. However, the most compelling evidence for the potential of borohydride–Mg₂NiH₄ composite materials is a study on Ca(BH₄)₂–Mg₂NiH₄ conducted with the goal of inhibiting the formation of stable boron sinks [139]. The Ca(BH₄)₂–Mg₂NiH₄ system was synthesised by ball-milling and then desorbed by ramping at 5 °C min⁻¹ from ambient temperature to 450 °C under 0.1 MPa H₂. The composite was characterised using ¹¹B MAS-NMR before dehydrogenation, after dehydrogenation and after an attempt to rehydrogenate desorption products under 39.5 MPa H₂ at a temperature of 400 °C.

In the NMR spectra, a peak at -141.5 ppm was attributed to the boron carrier MgNi_{2.5}B₂ (also observed in the LiBH₄–Mg₂NiH₄ system [140]) and a peak at -32.6 ppm to Ca(BH₄)₂. Beyond those major peaks, another small resonance peak was tentatively attributed to some B-H binary compound. Hence, it was concluded that Mg₂NiH₄ was able to successfully act as a boron carrier during the composite desorption reaction, as no other boron containing compounds were observed in the products beyond MgNi_{2.5}B₂ and the small peak at -14.7 ppm. Based on these findings and other characterisation by in-situ and ex-situ XRD, they proposed that the Ca(BH₄)₂–Mg₂NiH₄ composite desorbs according to the following reaction [139]:

$$Ca(BH_4)_2 + 2.5 Mg_2 NiH_4 \longrightarrow CaH_2 + MgNi_{2.5}B_2 + 4 Mg + 8 H_2$$
(28)

This successful inhibition of dodecaborate formation is significant, but the overall system requires further optimisation. During their attempts to rehydrogenate the desorption products, Bergemann et

al. estimated from NMR spectra that only around 1/3 of Ca(BH₄)₂ was reformed. It is believed that this low reversibility results from kinetic barriers that could be overcome using some form of catalysis or optimisation of reaction conditions. However, even if complete rehydrogenation could be achieved, the reduction of theoretical gravimetric hydrogen capacity between pure Ca(BH₄)₂ and the composite material is considerable.

Investigation of reactive hydride composite systems has also provided additional evidence that the application of hydrogen back-pressure during desorption can have an impact on the formation of dodecaborates. For a LiBH₄–MgH₂–Al composite, samples decomposed under a $p(H_2) = 0.5$ MPa back-pressure reversibly formed a larger proportion of LiBH₄ compared to those cycled under lower hydrogen pressure [123]. This was attributed to a decrease in the formation of Li₂B₁₂H₁₂, confirmed by XRD and ¹¹B MAS NMR. Similarly, in-situ measurements of the desorption of a LiBH₄–MgH₂ composite under $p(H_2) = 0.5$ MPa showed the composite preferentially decomposing to LiH and MgB₂ [142].

4.3. Nanoconfinement

Investigations of the catalysis of $M_{n=1,2}B_{12}H_{12}$ dehydrogenation/rehydrogenation and the use of boron carriers have often attributed issues to kinetic barriers that inhibit the progression of thermodynamically favourable reactions. Kinetic inefficiency is common in reactions with phase separations, especially gas–solid reactions wherein slow mass transport across the reacting solid can prove to be a limiting factor [7]. One widely utilised method of improving reaction kinetics is the nanosizing of solid materials, which has been observed to alter their properties significantly and cause them to react through different pathways than their bulk analogues.

However, the use of nanosizing to improve the properties of borohydride storage materials is challenging given the tendency of nanoparticles to agglomerate under heat treatment. One method of overcoming this tendency is to confine nanosized materials in a microporous matrix or other hollow nanostructures. These configurations have been described as "nano-reactors" wherein solid reactants are kept contained at nanoscale and improved reaction kinetics can be maintained after thermal cycling [143] (Figure 13).



Figure 13. Reversible behaviour of a sodium borohydride (NaBH₄) nanoparticle embedded in a nanoscale structure. In this scenario, the confined elements remain in close vicinity during hydrogen cycling, which should facilitate hydrogen reversibility.

For example, during an investigation of the dehydrogenation pathways of NaBH₄, reversible hydrogen storage in NaBH₄ confined in mesoporous carbon was attributed to the reduced diffusion distance between Na₂B₁₂H₁₂ and Na resulting from nanoconfinement [69]. Zhao-Karger et al. utilised a similar method, but considered the reactive hydride composite LiBH₄–Mg(BH₄)₂ instead of a single borohydride species, to investigate the interplay between the impacts of nanosizing and the property modifications observed in mixed hydrides [144]. In this system, diborane emission was found to be inhibited in the nanoconfined sample compared to the bulk LiBH₄–Mg(BH₄)₂. This finding is

significant, as diborane inhibition seems to be crucial to the viability and reversibility of a borohydride storage reaction, primarily because diborane emission results in boron loss from the system and presents a safety concern.

¹¹B MAS-NMR spectra were also produced for both the nanoconfined and bulk LiBH₄–Mg(BH₄)₂ at different temperatures within the desorption range to elucidate the reaction pathway and intermediates. The spectra suggested that at temperatures T > 280 °C, most of the borohydrides in the infiltrated samples had been converted to an amorphous elemental boron phase in a single reaction step. This is a significant deviation from the desorption mechanism observed for the bulk LiBH₄–Mg(BH₄)₂, which proceeds via several steps through the formation of other boron-containing intermediates, including MgB₂ [145].

Despite this observed pathway alteration, the presence of some $[B_{12}H_{12}]^{2-}$ anions was also detected in the desorbed nanoconfined samples. Zhao-Karger et al. proposed that the dodecaborate formation resulted from variation in pore size within the carbon matrix, such that some pores were large enough that the confined LiBH₄–Mg(BH₄)₂ displayed bulk behaviour. While these findings are compelling evidence of the effectiveness of nano-confinement, the system has fundamental gravimetric limitations. In the nanoconfined LiBH₄–Mg(BH₄)₂ samples investigated, the maximum gravimetric hydrogen capacity is only around 4 mass %, as the active borohydride-hydride only comprises 27% of the total mass of the carbon composite material.

4.4. Perspective

Because of the lack of specific research that has focused on dodecaborates within the borohydride system, there are a number of knowledge gaps that must be addressed. The underlying challenge is a fundamental lack of understanding of the borohydride decomposition mechanism, as evidenced by the number of conflicting pathways that have been proposed (see Section 2.1). Pathway alteration through nanosizing or the use of a catalyst/dopant could be the ultimate solution to the challenge of capacity loss during borohydride cycling. The suppression of dodecaborate formation that has been achieved in certain systems through the application of hydrogen back-pressure also raises the possibility of tuning the decomposition pathway by exerting fine control over the desorption conditions [88,123,142].

However, current attempts at alteration are exerted on a decomposition process that is essentially a black box, which is unlikely to yield comprehensive or reliable results. Therefore, it is unsurprising that none of the methods of dodecaborate mitigation that have been attempted have achieved completely satisfactory results. Of the techniques that focus on destabilising dodecaborates after they have formed, both investigations using alkali/alkaline earth hydrides reported sluggish rehydrogenation kinetics and capacity losses in the rehydrogenated materials [102,130]. Furthermore, both of these investigations attempted to directly rehydrogenate $M_{n=1,2}B_{12}H_{12}$ compounds and did not consider how the catalysts they used impact the overall dehydrogenation process.

The use of a "boron carrier", such as Mg₂NiH₄ [139], shows some potential, as it successfully forces the boron of the decomposing borohydride to react with the secondary species instead of forming dodecaborates [139–141]. However, this dehydrogenation process is not completely reversible (in the Ca(BH₄)₂–Mg₂NiH₄ system only 1/3 of the initial Ca(BH₄)₂ was regenerated [139]) and the composite materials also suffers from a severe degradation of gravimetric capacity compared to the un-doped borohydride species.

Nanoconfinement in mesoporous carbon results in similar gravimetric limitations, but the findings of Zhao-Karger show more potential as indicators of the underlying factors that impact the borohydride decomposition that could be exploited in other ways [144]. In particular, their conclusion that nanosizing successfully alters the borohydride thermolysis mechanism to prevent dodecaborate formation merits further investigation in a system wherein nanosizing impacts can be isolated from the interactions of the borohydride with the carbon host.

5. Applications of Dodecaborates and Their Derivatives

The identification of the relevance of $M_{n=1,2}B_{12}H_{12}$ compounds to borohydride thermolysis has sparked a renaissance in dodecaborate research that is currently ongoing. This research has the potential to yield exciting new technologies, especially in the development of new solid electrolytes and a variety of innovative medical applications.

5.1. Lithium-Ion Battery Technology

One of the most intriguing potential applications for the dodecaborates and their derivatives is as a solid-state electrolyte compatible with a variety of different battery configurations, including the dominant lithium-ion battery. Lithium-ion batteries are discharged through the migration of lithium cations from the anode to the cathode, liberating an electron that can be diverted to an external circuit to perform work [146] (Figure 14). Lithium ions are conducted within the battery cell by an electrolyte, which also serves to provide physical separation between the electrodes. In commercial lithium-ion batteries, this electrolyte is usually a liquid-phase solution of a lithium salt dissolved in some solvent.



Figure 14. Schematic representation of the working principle of a generic lithium-ion battery.

The most common solvents are organic liquid carbonates, which have a number of prohibitive drawbacks that have prompted a search for alternatives [147]. Their most critical weakness is their flammability, which presents a serious safety concern and has already resulted in numerous incidents of fire and explosion [148]. The development of an inorganic, solid-state electrolyte has the potential to increase the stability of a lithium-ion battery by eliminating the flammability risk and increasing the mechanical robustness of the cell. Beyond solving the safety issues, an entirely solid-state battery cell would also simplify the overall configuration and facilitate higher overall energy densities [149].

The application of the dodecaborates as solid-state electrolytes was first considered upon the discovery of a high-temperature order–disorder phase transition undergone by a number of alkali dodecaborates that was accompanied by a significant increase in ionic conductivity [97,98]. As shown in Figure 15, the cation sites of the low temperature structure are fully occupied. In contrast, the high-temperature cubic phase can accommodate a variety of off-centre cation positions, allowing the ions to be much more delocalised [150]. This cation delocalisation is the mechanism of conduction in most of the superior solid ionic conductors, including RbAg₄I₅, which has one of the highest room temperature conductivities reported for a solid material (0.12 S cm⁻¹ at 22 °C) [151,152].



Figure 15. Schematic representation of the high-temperature order–disorder phase transition of $Li_2B_{12}H_{12}$ and its impact on the ionic conductivity in a lithium ion battery; molecular geometries for the phases sourced from [115].

In these disordered phases, the $[B_{12}H_{12}]^{2-}$ anions were also found to undergo fast molecular reorientations within the cubic unit cell [150,153]. In addition to the cation delocalisation, the high reorientational mobility of the anions may also be contributing to the superior ionic conductivity of the disordered phase [154]. When considering conduction in the solid-state, it has been proposed that anions with high reorientational mobility move with the diffusing cation, thereby decreasing the system's resistance. In effect, these reorientations are thought to act as a "paddle wheel" that propels the cation through the solid matrix [155].

Despite these findings, the high temperatures (Table 7) required to stimulate the order–disorder phase transition in the pure alkali dodecaborates is an obstacle that must be overcome before these materials can be considered for practical application. To exploit the favourable properties of the disordered cubic phase, some method must be developed to stabilise it at moderate conditions and prevent its conversion back to the ambient temperature phase. Alternatively, chemical modifications could be considered to produce a dodecaborate derivative that achieves a lower transition temperature without compromising conductivity.

Species	Transition Temperature (°C)	Ionic Conductivity (S cm^{-1})
NaCB ₁₁ H ₁₂	107 [156]	0.15 (130 °C) [156]
$LiCB_{11}H_{12}$	127 [156]	0.12 (110 °C) [156]
$Ag_2B_{12}H_{12}$	200 [157]	0.035 (227 °C) [157]
LiNaB ₁₂ H ₁₂	215 [158]	0.79 (277 °C) [158]
$Na_2B_{12}H_{12}$	247 [97]	0.1 (267 °C) [154]
$Li_2B_{12}H_{12}$	355 [98]	0.07 (277 °C) [158]
$Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}$	N/A	0.0009 (20 °C) [159]
$Ag_{(2+x)}I_{x}B_{12}H_{12}$	N/A	0.002 (25 °C) [157]
$Cs_2B_{12}H_{12}$	256 [97]	-
$Rb_2B_{12}H_{12}$	469 [97]	-
$K_2B_{12}H_{12}$	538 [97]	-

Table 7. Tabulated values for the order–disorder transition temperature and the ionic conductivity reported at a given temperature for a selection of dodecaborates and dodecaborate derivatives.

Although this field of research has only recently attracted significant interest, several potential modifications have already been proposed and investigated. Duchêne et al. ball-milled an equimolar mixture of $Na_2B_{12}H_{12}$ and $Na_2B_{12}H_{10}$, resulting in the composite $Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}$ material. They found that this material did not undergo an order–disorder phase transition with heating, but still achieved a reasonable 0.9 mS cm⁻¹ sodium ion conductivity at ambient conditions.

He et al. considered the impacts of a system that includes multiple cation species through investigation of LiNaB₁₂H₁₂ [158]. This composite material was produced by sintering of LiBH₄, NaBH₄, and B₁₀H₁₄, resulting in the bimetallic LiNaB₁₂H₁₂ compound. This modification lowered the phase transition temperature compared to the Li/Na analagoues (Table 7) and showed an extreme peak in ionic conductivity to 0.79 S cm⁻¹ above 227 °C.

Beyond multi-cation systems, anion substitution has also been attempted as a method of modifying the crystal structure of a dodecaborate species to improve room temperature ion conductivity. The efficacy of this technique was demonstrated for $Ag_2B_{12}H_{12}$, which undergoes the characteristic polymorphic order–disorder transition and accompanying peak in ionic conductivity at around 200 °C (Table 7). In comparison, an iodide substituted composite (with the formula $Ag_{(2+x)}I_xB_{12}H_{12}$, where $x \approx 1$) displayed high ionic conductivity from room temperature (Figure 16) [157].



Figure 16. Ionic conductivities measured by Paskevicius et al. for silver dodecaborate and decaborate $Ag_2B_{12}H_{12}$ (red) and $Ag_2B_{10}H_{10}$ (blue) and the novel iodide substituted variations $Ag_{(2+x)}I_xB_{12}H_{12}$ (green) and $Ag_{(2+x)}I_xB_{10}H_{10}$ (purple), plotted with comparisons of other related materials [157]. Conductivities are plotted as a function of inverse temperature. Reprinted from [157].

When considering modifications to the dodecaborate cage itself, Tang et al. investigated the substitution of a boron atom with a carbon atom to give the carborane anion $[CB_{11}H_{12}]^-$ [156]. While $[CB_{11}H_{12}]^-$ and $[B_{12}H_{12}]^{2-}$ share very similar icosahedral structures, the carbon substitution results in a reduction in anionic charge from 2^- to 1^- and thereby halves number of alkali cation required for salt neutrality. Both of the two carborane species considered, NaCB₁₁H₁₂ and LiCB₁₁H₁₂, were found to experience an order–disorder phase transition at temperatures significantly lower than their pure dodecaborate analogues (Table 7). Most notably, it was also determined that the ionic conductivities of NaCB₁₁H₁₂ and LiCB₁₁H₁₂ far exceeded the pure dodecaborates for the entire range of temperatures probed. As shown in Figure 17, the carboranes show remarkably high ionic

conductivities, even at ambient temperature, and both peak in range of $0.1 \,\mathrm{S}\,\mathrm{cm}^{-1}$ after their respective phase transitions.



Figure 17. Ionic conductivities measured by Tang et al. for $LiCB_{11}H_{12}$ (blue) and $NaCB_{11}H_{12}$ (red), plotted with comparisons of other related materials. Conductivities are plotted as a function of inverse temperature. Circles and squares denote the conductivities of the respective 1st and 2nd temperature cycles. Closed and open symbols denote respective heating and cooling processes. Reprinted from [156].

Halogenation of the dodecaborate cage has also been considered, beginning as early as the 1980s with the investigation of perchlorinated lithium dodecaborate ($Li_2B_{12}Cl_{12}$) as a solvated electrolyte [160,161]. More recently, the thermal stability and conductive properties of the halogenated variations of Na₂B₁₂X₁₂ (where *X* = Cl, Br, I) have been characterised [162]. While the order–disorder transition temperatures for these compounds significantly exceed that of Na₂B₁₂H₁₂, their exceptional thermal stabilities indicate that they could be suitable for high temperature applications.

Although these preliminary observations are promising, all of the modifications discussed in this section are in the very early stages of experimental investigation. For each of these systems, overall battery chemistry and configuration must be considered, including the dodecaborate electrolyte's compatibility with commonly used electrode materials. While this specification will come with further electrochemical testing, a greater fundamental understanding of the origins of the conductivity of the dodecaborates is also required to aid in the optimisation of the properties of the dodecaborate electrolytes [163].

It is also interesting to note that the borohydrides themselves have also been considered as innovative alternatives to other components of battery chemistry [15]. LiBH₄ has been proposed as a conversion type anode material to replace the intercalation/insertion-type electrodes that are used in current lithium-ion battery configurations [164]. Conversion type electrodes are advantageous because of their high theoretical energy capacities (LiBH₄ has a theoretical capacity of 4992 mAh g⁻¹, compared to 372 mAh g⁻¹ for graphite, the most commonly commercialised anodic material [165]). Unfortunately, this application of LiBH₄ has not been extensively investigated and preliminary studies have reported low practical lithium capacities and poor reversibility of the electrochemical reactions [165,166].

5.2. Other Applications

Beyond their potential as solid-state electrolytes, the dodecaborates and their derivatives have been investigated for application in a number of other fields. However, the largest volume of research has been devoted to medical applications because of the low toxicity and resistance to hydrolysis of the dodecaborates and their derivatives [89]. In medicine, the most notable use that has been proposed is as a boron source in boron neutron capture therapy (BNCT), a novel cancer treatment that uses a boron-containing compound to "capture" neutron radiation and selectively target cancerous cells [167]. Sodium borocaptate, a thiol derivative of the $[B_{12}H_{12}]^{2-}$ anion with the chemical formula $Na_2B_{12}H_{11}SH$ (often abbreviated as BSH, as shown in Figure 18), is one of only two BNCT agents that have found extensive clinical application [168]. However, these clinical studies revealed a high degree of variability in the effectiveness of sodium borocaptate as a boron delivery agent, partially attributed to uneven uptake of the drug by tumour cells [169].

When considering dodecaborate derivatives, various materials have been proposed as carriers to enhance the delivery of boron-containing compounds to tumour cells. Conjugation of sodium borocaptate and other dodecaborate derivatives with organic polymers has been explored as a method of improving transport properties [170,171]. A range of nanosized delivery vehicles has also been investigated, including silicon nanowires [172] and boron cluster-containing redox nanoparticles [173].



Figure 18. Schematic view of the $[B_{12}H_{12}]^{2-}$ anion vs. the $[B_{12}H_{11}SH]^{2-}$ anion component of the BNCT agent, sodium borocaptate (BSH, Na₂B₁₂H₁₁SH). Pink spheres denote boron atoms and white spheres denote hydrogen atoms.

Liposomes, defined as an aqueous volume contained within lipid bilayer [169], are another notable carrier compound that are useful for selectively transporting materials into tumour cells [174]. Sodium borocaptate molecules can be contained in the aqueous volume and encapsulated by the liposome, allowing the selectivity of the delivery system to be tailored through the design of the lipid bilayer. For example, sodium borocaptate encapsulated in transferrin-PEG liposomes has shown effectiveness at treating solid tumours in mice [175]. Additionally, sodium borocaptate can be incorporated into the lipid bilayer, facilitating the synthesis of *closo*-dodecaborate lipid liposomes and maximising the boron-content of the system [176,177].

6. Conclusions

In this review, the origins of the irreversibility of the borohydride hydrogen storage cycle are investigated by analysing the mechanism of borohydride decomposition during thermolysis. The formation of exceptionally stable dodecaborate compounds during hydrogen desorption is identified as having serious implications for the reversibility of borohydride dehydrogenation. These dodecaborates act as boron sinks that cannot be rehydrogenated and decrease the overall hydrogen capacity of the material with each hydrogenation cycle. Review of the borohydride desorption mechanisms reported in literature also reveals numerous instances of contradiction between different investigations, indicating that the details of the decomposition process are not yet fully understood.

Furthermore, no mechanism for dodecaborate formation during borohydride dehydrogenation has ever been conclusively determined, though analysis of dodecaborate synthesis procedures suggests a possible route through polyborane intermediates. Adding another layer of complexity is the noted dependence of both the borohydride decomposition pathway and the dodecaborate formation mechanism on hydrogen back-pressure and desorption temperature. Based on these considerations, it is the recommendation of this review that future research focus on establishing a consensus opinion on the mechanism of hydrogen release from the borohydrides. Through an understanding of this mechanism, stable by-products such as dodecaborates can be inhibited by exerting fine control over the reactions and preventing decomposition via unfavourable pathways.

The unusual properties of dodecaborates also suggest a number of potential applications when considered independently, most notably as a solid-state superionic conductor. The current universal focus on identifying novel energy storage solutions could help to sustain the recent surge of research interest and progress in the development of dodecaborates and their derivatives as solid-state electrolytes. Further optimisation of BNCT technology also presents a dynamic research challenge with a dodecaborate derivative at its center. When considering the dodecaborate derivatives, carboranes in particular have been identified as a promising new iteration of *closo*-polyborate compounds that could ultimately find utility. Overall, the dodecahydro-*closo*-dodecaborates are an important facet of boron–hydride chemistry that will continue to have interdisciplinary relevance and intrigue into the future.

Author Contributions: The manuscript was written by A.G. and K.-F.A.-Z.

Funding: Financial support by the Office of Naval Research (Award No: ONRG-NICOP-N62909-16-1-2155) is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Lai, Q.; Paskevicius, M.; Sheppard Drew, A.; Buckley Craig, E.; Thornton Aaron, W.; Hill Matthew, R.; Gu, Q.; Mao, J.; Huang, Z.; Liu Hua, K.; et al. Hydrogen Storage Materials for Mobile and Stationary Applications: Current State of the Art. *ChemSusChem* 2015, *8*, 2789–2825. [CrossRef] [PubMed]
- 2. Bockris, J.O.M. The hydrogen economy: Its history. Int. J. Hydrog. Energy 2013, 38, 2579–2588. [CrossRef]
- 3. Andújar, J.M.; Segura, F. Fuel cells: History and updating. A walk along two centuries. *Renew. Sustain. Energy Rev.* 2009, 13, 2309–2322. [CrossRef]
- Ley, M.B.; Jepsen, L.H.; Lee, Y.S.; Cho, Y.W.; Bellosta von Colbe, J.M.; Dornheim, M.; Rokni, M.; Jensen, J.O.; Sloth, M.; Filinchuk, Y.; et al. Complex hydrides for hydrogen storage: new perspectives. *Mater. Today* 2014, 17, 122–128. [CrossRef]
- 5. Bockris, J.O.; Appleby, A.J. The hydrogen economy: an ultimate economy? *Environ. This Mon.* **1972**, *1*, 29–35. [CrossRef]
- 6. Makridis, S. Hydrogen storage and compression. In *Methane and Hydrogen for Energy Storage;* Carriveau, R., Ting, D.S.K., Eds.; IET Digital Library: Stevenage, UK, 2016; pp. 1–28.
- 7. Lèon, A. Hydrogen Storage. In *Hydrogen Technology: Mobile and Portable Applications.;* Lèon, A., Ed.; Springer: Dordrecht, The Netherlands, 2008.
- 8. Gray, E.M. Hydrogen storage status and prospects. Adv. Appl. Ceram. 2007, 106, 25–28. [CrossRef]
- 9. Klell, M. Storage of Hydrogen in the Pure Form. In *Handbook of Hydrogen Storage: New Materials for Future Energy Storage*; Hirscher, M., Ed.; Wiley Online Books, Wiley-VCH: Weinheim, Germany, 2010; pp. 1–36.
- 10. Krainz, G.; Bartlok, G.; Bodner, P.; Casapicola, P.; Doeller, C.; Hofmeister, F.; Neubacher, E.; Zieger, A. Development of Automotive Liquid Hydrogen Storage Systems. *AIP Conf. Proc.* **2004**, *710*, 35–40. [CrossRef]
- 11. Orimo, S.i.; Nakamori, Y.; Eliseo, J.R.; Züttel, A.; Jensen, C.M. Complex Hydrides for Hydrogen Storage. *Chem. Rev.* **2007**, *107*, 4111–4132. [CrossRef] [PubMed]
- Sun, Y.; Shen, C.; Lai, Q.; Liu, W.; Wang, D.W.; Aguey-Zinsou, K.F. Tailoring magnesium based materials for hydrogen storage through synthesis: Current state of the art. *Energy Storage Mater.* 2018, 10, 168–198. [CrossRef]
- Lai, Q.; Wang, T.; Sun, Y.; Aguey-Zinsou, K.F. Rational Design of Nanosized Light Elements for Hydrogen Storage: Classes, Synthesis, Characterization, and Properties. *Adv. Mater. Technol.* 2018, *3*, 1700298. [CrossRef]

- 14. Qiu, S.; Chu, H.; Zou, Y.; Xiang, C.; Xu, F.; Sun, L. Light metal borohydrides/amides combined hydrogen storage systems: composition, structure and properties. *J. Mater. Chem. A* 2017, *5*, 25112–25130. [CrossRef]
- 15. Møller, T.K.; Sheppard, D.; Ravnsbæk, B.D.; Buckley, E.C.; Akiba, E.; Li, H.W.; Jensen, R.T. Complex Metal Hydrides for Hydrogen, Thermal and Electrochemical Energy Storage. *Energies* **2017**, *10*. [CrossRef]
- 16. Yu, X.; Tang, Z.; Sun, D.; Ouyang, L.; Zhu, M. Recent advances and remaining challenges of nanostructured materials for hydrogen storage applications. *Prog. Mater. Sci.* **2017**, *88*, 1–48. [CrossRef]
- 17. Rusman, N.A.A.; Dahari, M. A review on the current progress of metal hydrides material for solid-state hydrogen storage applications. *Int. J. Hydrog. Energy* **2016**, *41*, 12108–12126. [CrossRef]
- Liu, B.H.; Li, Z.P. A review: Hydrogen generation from borohydride hydrolysis reaction. J. Power Sources 2009, 187, 527–534. [CrossRef]
- 19. Çakanyildirim, C.; Gürü, M. Hydrogen cycle with sodium borohydride. *Int. J. Hydrog. Energy* **2008**, *33*, 4634–4639. [CrossRef]
- Demirci, U.B.; Akdim, O.; Andrieux, J.; Hannauer, J.; Chamoun, R.; Miele, P. Sodium Borohydride Hydrolysis as Hydrogen Generator: Issues, State of the Art and Applicability Upstream from a Fuel Cell. *Fuel Cells* 2010, 10, 335–350. [CrossRef]
- 21. Ouyang, L.; Zhong, H.; Li, H.W.; Zhu, M. A Recycling Hydrogen Supply System of NaBH₄ Based on a Facile Regeneration Process: A Review. *Inorganics* **2018**, *6*. [CrossRef]
- 22. Kojima, Y.; Haga, T. Recycling process of sodium metaborate to sodium borohydride. *Int. J. Hydrog. Energy* **2003**, *28*, 989–993. [CrossRef]
- 23. Hsueh, C.L.; Liu, C.H.; Chen, B.H.; Chen, C.Y.; Kuo, Y.C.; Hwang, K.J.; Ku, J.R. Regeneration of spent-NaBH₄ back to NaBH₄ by using high-energy ball milling. *Int. J. Hydrog. Energy* **2009**, *34*, 1717–1725. [CrossRef]
- 24. Li, Z.P.; Liu, B.H.; Zhu, J.K.; Morigasaki, N.; Suda, S. NaBH₄ formation mechanism by reaction of sodium borate with Mg and H₂. *J. Alloys Compd.* **2007**, 437, 311–316. [CrossRef]
- 25. Suda, S.; Morigasaki, N.; Iwase, Y.; Li, Z.P. Production of sodium borohydride by using dynamic behaviors of protide at the extreme surface of magnesium particles. *J. Alloys Compd.* **2005**, 404–406, 643–647. [CrossRef]
- Ouyang, L.; Chen, W.; Liu, J.; Felderhoff, M.; Wang, H.; Zhu, M. Enhancing the Regeneration Process of Consumed NaBH4 for Hydrogen Storage. *Adv. Energy Mater.* 2017, 7, 1700299. [CrossRef]
- 27. Miwa, K.; Ohba, N.; Towata, S.I.; Nakamori, Y.; Orimo, S.I. First-principles study on lithium borohydride LiBH₄. *Phys. Rev. B* **2004**, *69*, 245120. [CrossRef]
- 28. Nakamori, Y.; Li, H.W.; Kikuchi, K.; Aoki, M.; Miwa, K.; Towata, S.; Orimo, S. Thermodynamical stabilities of metal-borohydrides. *J. Alloys Compd.* **2007**, 446–447, 296–300. [CrossRef]
- 29. Nakamori, Y.; Miwa, K.; Ninomiya, A.; Li, H.; Ohba, N.; Towata, S.I.; Züttel, A.; Orimo, S.I. Correlation between thermodynamical stabilities of metal borohydrides and cation electronegativites: First-principles calculations and experiments. *Phys. Rev. B* **2006**, *74*, 045126. [CrossRef]
- 30. Miwa, K.; Ohba, N.; Towata, S.; Nakamori, Y.; Orimo, S. First-principles study on copper-substituted lithium borohydride, (Li_{1-x}Cu_x)BH₄. *J. Alloys Compd.* **2005**, *404–406*, 140–143. [CrossRef]
- 31. Vajeeston, P.; Ravindran, P.; Kjekshus, A.; Fjellvåg, H. Structural stability of alkali boron tetrahydrides ABH₄ (A = Li, Na, K, Rb, Cs) from first principle calculation. *J. Alloys Compd.* **2005**, *387*, 97–104. [CrossRef]
- Paskevicius, M.; Jepsen, L.H.; Schouwink, P.; Cerny, R.; Ravnsbæk, D.B.; Filinchuk, Y.; Dornheim, M.; Besenbacherf, F.; Jensen, T.R. Metal borohydrides and derivatives: Synthesis, structure and properties. *Chem. Soc. Rev.* 2017, 46, 1565–1634. [CrossRef] [PubMed]
- 33. Mauron, P.; Buchter, F.; Friedrichs, O.; Remhof, A.; Bielmann, M.; Zwicky, C.N.; Züttel, A. Stability and Reversibility of LiBH₄. *J. Phys. Chem. B* **2008**, *112*, 906–910. [CrossRef] [PubMed]
- 34. Ohba, N.; Miwa, K.; Aoki, M.; Noritake, T.; Towata, S.I.; Nakamori, Y.; Orimo, S.I.; Züttel, A. First-principles study on the stability of intermediate compounds of LiBH₄. *Phys. Rev. B* **2006**, *74*, 075110. [CrossRef]
- 35. Martelli, P.; Caputo, R.; Remhof, A.; Mauron, P.; Borgschulte, A.; Züttel, A. Stability and Decomposition of NaBH₄. *J. Phys. Chem. C* 2010, *114*, 7173–7177. [CrossRef]
- 36. Smith, M.B.; Bass, G.E. Heats and Free Energies of Formation of the Alkali Aluminum Hydrides and of Cesium Hydride. *J. Chem. Eng. Data* **1963**, *8*, 342–346. [CrossRef]
- 37. Matsunaga, T.; Buchter, F.; Mauron, P.; Bielman, M.; Nakamori, Y.; Orimo, S.; Ohba, N.; Miwa, K.; Towata, S.; Züttel, A. Hydrogen storage properties of Mg[BH4]2. *J. Alloys Compd.* **2008**, 459, 583–588. [CrossRef]

- Li, H.W.; Kikuchi, K.; Nakamori, Y.; Ohba, N.; Miwa, K.; Towata, S.; Orimo, S. Dehydriding and rehydriding processes of well-crystallized Mg(BH₄)₂ accompanying with formation of intermediate compounds. *Acta Mater.* 2008, *56*, 1342–1347. [CrossRef]
- 39. Mao, J.; Guo, Z.; Poh, C.K.; Ranjbar, A.; Guo, Y.; Yu, X.; Liu, H. Study on the dehydrogenation kinetics and thermodynamics of Ca(BH₄)₂. *J. Alloys Compd.* **2010**, *500*, 200–205. [CrossRef]
- 40. Kim, Y.; Reed, D.; Lee, Y.S.; Lee, J.Y.; Shim, J.H.; Book, D.; Cho, Y.W. Identification of the Dehydrogenated Product of Ca(BH₄)₂. *J. Phys. Chem. C* **2009**, *113*, 5865–5871. [CrossRef]
- Severa, G.; Rönnebro, E.; Jensen, C.M. Direct hydrogenation of magnesium boride to magnesium borohydride: demonstration of >11 weight percent reversible hydrogen storage. *Chem. Commun.* 2010, *46*, 421–423. [CrossRef] [PubMed]
- 42. Li, H.W.; Miwa, K.; Ohba, N.; Fujita, T.; Sato, T.; Yan, Y.; Towata, S.; Chen, M.W.; Orimo, S. Formation of an intermediate compound with a B₁₂H₁₂ cluster: experimental and theoretical studies on magnesium borohydride Mg(BH₄)₂. *Nanotechnology* **2009**, *20*, 204013. [CrossRef] [PubMed]
- 43. Rönnebro, E.; Majzoub, E.H. Calcium Borohydride for Hydrogen Storage: Catalysis and Reversibility. *J. Phys. Chem. B* 2007, *111*, 12045–12047. [CrossRef] [PubMed]
- 44. Ngene, P.; van Zwienen, M.; de Jongh, P.E. Reversibility of the hydrogen desorption from LiBH4: a synergetic effect of nanoconfinement and Ni addition. *Chem. Commun.* **2010**, *46*, 8201–8203. [CrossRef] [PubMed]
- 45. Orimo, S.; Nakamori, Y.; Kitahara, G.; Miwa, K.; Ohba, N.; Towata, S.; Züttel, A. Dehydriding and rehydriding reactions of LiBH₄. *J. Alloys Compd.* **2005**, 404–406, 427–430. [CrossRef]
- Wang, H.; Lin, H.J.; Cai, W.T.; Ouyang, L.Z.; Zhu, M. Tuning kinetics and thermodynamics of hydrogen storage in light metal element based systems: A review of recent progress. J. Alloys Compd. 2016, 658, 280–300. [CrossRef]
- 47. Rude Line, H.; Nielsen Thomas, K.; Ravnsbæk Dorthe, B.; Bösenberg, U.; Ley Morten, B.; Richter, B.; Arnbjerg Lene, M.; Dornheim, M.; Filinchuk, Y.; Besenbacher, F.; et al. Tailoring properties of borohydrides for hydrogen storage: A review. *Phys. Status Solidi A* **2011**, *208*, 1754–1773. [CrossRef]
- 48. Soulié, J.P.; Renaudin, G.; Černý, R.; Yvon, K. Lithium boro-hydride LiBH₄: I. Crystal structure. *J. Alloys Compd.* **2002**, *346*, 200–205. [CrossRef]
- 49. Pistorius Carl, W.F.T. Melting and Polymorphism of LiBH₄ to 45 kbar. *Z. Phys. Chem.* **1974**, *88*, 253–263. [CrossRef]
- 50. Filinchuk, Y.; Chernyshov, D.; Nevidomskyy, A.; Dmitriev, V. High-Pressure Polymorphism as a Step towards Destabilization of LiBH₄. *Angew. Chem. Int. Ed.* **2007**, *47*, 529–532. [CrossRef] [PubMed]
- 51. Abrahams, S.C.; Kalnajs, J. The Lattice Constants of the Alkali Borohydrides and the Low-Temperature Phase of Sodium Borohydride. *J. Chem. Phys.* **1954**, *22*, 434–436. [CrossRef]
- 52. Allis, D.G.; Hudson, B.S. Inelastic neutron scattering spectra of NaBH₄ and KBH₄: reproduction of anion mode shifts via periodic DFT. *Chem. Phys. Lett.* **2004**, *385*, 166–172. [CrossRef]
- 53. Filinchuk, Y.; Talyzin, A.V.; Chernyshov, D.; Dmitriev, V. High-pressure phase of NaBH₄: Crystal structure from synchrotron powder diffraction data. *Phys. Rev. B* **2007**, *76*, 092104. [CrossRef]
- 54. Renaudin, G.; Gomes, S.; Hagemann, H.; Keller, L.; Yvon, K. Structural and spectroscopic studies on the alkali borohydrides MBH₄ (M = Na, K, Rb, Cs). *J. Alloys Compd.* **2004**, *375*, 98–106. [CrossRef]
- 55. Kumar, R.S.; Kim, E.; Cornelius, A.L. Structural Phase Transitions in the Potential Hydrogen Storage Compound KBH₄ under Compression. *J. Phys. Chem.* C 2008, *112*, 8452–8457. [CrossRef]
- 56. Züttel, A.; Wenger, P.; Rentsch, S.; Sudan, P.; Mauron, P.; Emmenegger, C. LiBH₄ a new hydrogen storage material. *J. Power Sources* **2003**, *118*, 1–7. [CrossRef]
- Mosegaard, L.; Møller, B.; Jørgensen, J.E.; Filinchuk, Y.; Cerenius, Y.; Hanson, J.C.; Dimasi, E.; Besenbacher, F.; Jensen, T.R. Reactivity of LiBH4: In-Situ Synchrotron Radiation Powder X-ray Diffraction Study. *J. Phys. Chem. C* 2008, *112*, 1299–1303. [CrossRef]
- Ozoliņš, V.; Majzoub, E.H.; Wolverton, C. First-Principles Prediction of Thermodynamically Reversible Hydrogen Storage Reactions in the Li-Mg-Ca-B-H System. J. Am. Chem. Soc. 2009, 131, 230–237. [CrossRef] [PubMed]
- 59. Friedrichs, O.; Borgschulte, A.; Kato, S.; Buchter, F.; Gremaud, R.; Remhof, A.; Züttel, A. Low-Temperature Synthesis of LiBH₄ by Gas-Solid Reaction. *Chem. A Eur. J.* **2009**, *15*, 5531–5534. [CrossRef] [PubMed]
- 60. Caputo, R.; Züttel, A. First-principles study of the paths of the decomposition reaction of LiBH₄. *Mol. Phys.* **2010**, *108*, 1263–1276. [CrossRef]

- Santos, D.M.F.; Sequeira, C.A.C. Sodium borohydride as a fuel for the future. *Renew. Sustain. Energy Rev.* 2011, 15, 3980–4001. [CrossRef]
- 62. Muir, S.S.; Yao, X. Progress in sodium borohydride as a hydrogen storage material: Development of hydrolysis catalysts and reaction systems. *Int. J. Hydrog. Energy* **2011**, *36*, 5983–5997. [CrossRef]
- Kim, E.; Kumar, R.; Weck, P.F.; Cornelius, A.L.; Nicol, M.; Vogel, S.C.; Zhang, J.; Hartl, M.; Stowe, A.C.; Daemen, L.; et al. Pressure-Driven Phase Transitions in NaBH₄: Theory and Experiments. *J. Phys. Chem. B* 2007, 111, 13873–13876. [CrossRef] [PubMed]
- 64. Çakir, D.; de Wijs, G.A.; Brocks, G. Native Defects and the Dehydrogenation of NaBH₄. *J. Phys. Chem. C* **2011**, *115*, 24429–24434. [CrossRef]
- 65. Friedrichs, O.; Remhof, A.; Hwang, S.J.; Züttel, A. Role of Li₂B₁₂H₁₂ for the Formation and Decomposition of LiBH₄. *Chem. Mater.* **2010**, *22*, 3265–3268. [CrossRef]
- 66. Urgnani, J.; Torres, F.J.; Palumbo, M.; Baricco, M. Hydrogen release from solid state NaBH₄. *Int. J. Hydrog. Energy* **2008**, *33*, 3111–3115. [CrossRef]
- 67. Mao, J.; Guo, Z.; Yu, X.; Liu, H. Improved Hydrogen Storage Properties of NaBH₄ Destabilized by CaH₂ and Ca(BH₄)₂. *J. Phys. Chem. C* 2011, *115*, 9283–9290. [CrossRef]
- Garroni, S.; Milanese, C.; Pottmaier, D.; Mulas, G.; Nolis, P.; Girella, A.; Caputo, R.; Olid, D.; Teixdor, F.; Baricco, M.; et al. Experimental Evidence of Na₂B₁₂H₁₂ and Na Formation in the Desorption Pathway of the 2NaBH₄ + MgH₂ System. *J. Phys. Chem. C* 2011, *115*, 16664–16671. [CrossRef]
- Ngene, P.; van den Berg, R.; Verkuijlen, M.H.W.; de Jong, K.P.; de Jongh, P.E. Reversibility of the hydrogen desorption from NaBH₄ by confinement in nanoporous carbon. *Energy Environ. Sci.* 2011, *4*, 4108–4115. [CrossRef]
- 70. Kim, K.C.; Sholl, D.S. Crystal Structures and Thermodynamic Investigations of LiK(BH₄)₂, KBH₄, and NaBH₄ from First-Principles Calculations. *J. Phys. Chem. C* **2010**, *114*, 678–686. [CrossRef]
- 71. Černý, R.; Filinchuk, Y.; Hagemann, H.; Yvon, K. Magnesium Borohydride: Synthesis and Crystal Structure. *Angew. Chem. Int. Ed.* **2007**, *46*, 5765–5767. [CrossRef] [PubMed]
- Her, J.H.; Stephens, P.W.; Gao, Y.; Soloveichik, G.L.; Rijssenbeek, J.; Andrus, M.; Zhao, J.C. Structure of unsolvated magnesium borohydride Mg(BH₄)₂. *Acta Crystallogr. Sect. B* 2007, *63*, 561–568. [CrossRef] [PubMed]
- 73. Filinchuk, Y.; Richter, B.; Jensen Torben, R.; Dmitriev, V.; Chernyshov, D.; Hagemann, H. Porous and Dense Magnesium Borohydride Frameworks: Synthesis, Stability, and Reversible Absorption of Guest Species. *Angew. Chem. Int. Ed.* 2011, 50, 11162–11166. [CrossRef] [PubMed]
- 74. Filinchuk, Y.; Rönnebro, E.; Chandra, D. Crystal structures and phase transformations in Ca(BH₄)₂. *Acta Mater.* **2009**, *57*, 732–738. [CrossRef]
- 75. Buchter, F.; Lodziana, Z.; Remhof, A.; Friedrichs, O.; Borgschulte, A.; Mauron, P.; Züttel, A.; Sheptyakov, D.; Barkhordarian, G.; Bormann, R.; et al. Structure of Ca(BD₄)₂ beta-phase from combined neutron and synchrotron X-ray powder diffraction data and density functional calculations. *J. Phys. Chem. B* 2008, 112, 8042–8048. [CrossRef] [PubMed]
- 76. Soloveichik, G.L.; Gao, Y.; Rijssenbeeka, J.; Andrusa, M.; Kniajanskia, S.; Bowman, R.C., Jr.; Hwang, S.J.; Zhao, J.C. Magnesium borohydride as a hydrogen storage material: Properties and dehydrogenation pathway of unsolvated Mg(BH₄)₂. *Int. J. Hydrog. Energy* **2009**, *34*, 916–928. [CrossRef]
- 77. Chłopek, K.; Frommen, C.; Leon, A.; Zabara, O.; Fichtner, M. Synthesis and properties of magnesium tetrahydroborate, Mg(BH₄)₂. *J. Mater. Chem.* **2007**, *17*, 3496–3503. [CrossRef]
- 78. Yang, J.; Zhang, X.; Zheng, J.; Song, P.; Li, X. Decomposition pathway of Mg(BH₄)₂ under pressure: Metastable phases and thermodynamic parameters. *Scr. Mater.* **2011**, *64*, 225–228. [CrossRef]
- 79. Paskevicius, M.; Pitt, M.P.; Webb, C.J.; Sheppard, D.A.; Filsø, U.; Gray, E.M.; Buckley, C.E. In-Situ X-ray Diffraction Study of Mg(BH₄)₂ Decomposition. *J. Phys. Chem. C* **2012**, *116*, 15231–15240. [CrossRef]
- 80. Miwa, K.; Aoki, M.; Noritake, T.; Ohba, N.; Nakamori, Y.; Towata, S.I.; Züttel, A.; Orimo, S.I. Thermodynamical stability of calcium borohydride. *Phys. Rev. B* **2006**, *74*, 155122. [CrossRef]
- 81. Kim, J.H.; Jin, S.A.; Shim, J.H.; Cho, Y.W. Thermal decomposition behavior of calcium borohydride Ca(BH₄)₂. *J. Alloys Compd.* **2008**, *461*, L20–L22. [CrossRef]
- Sahle, C.J.; Sternemann, C.; Giacobbe, C.; Yan, Y.; Weis, C.; Harder, M.; Forov, Y.; Spiekermann, G.; Tolan, M.; Krisch, M.; et al. Formation of CaB₆ in the thermal decomposition of the hydrogen storage material Ca(BH₄)₂. *Phys. Chem. Chem. Phys.* **2016**, *18*, 19866–19872. [CrossRef] [PubMed]

- 83. Yan, Y.; Remhof, A.; Rentsch, D.; Züttel, A.; Giri, S.; Jena, P. A novel strategy for reversible hydrogen storage in Ca(BH₄)₂. *Chem. Commun.* **2015**, *51*, 11008–11011. [CrossRef] [PubMed]
- 84. Riktor, M.D.; Sørby, M.H.; Chłopek, K.; Fichtner, M.; Hauback, B.C. The identification of a hitherto unknown intermediate phase CaB₂H_x from decomposition of Ca(BH₄)₂. *J. Mater. Chem.* **2009**, *19*, 2754–2759. [CrossRef]
- 85. Aoki, M.; Miwa, K.; Noritake, T.; Ohba, N.; Matsumoto, M.; Li, H.W.; Nakamori, Y.; Towata, S.; Orimo, S. Structural and dehydriding properties of Ca(BH₄)₂. *Appl. Phys. A* **2008**, *92*, 601–605. [CrossRef]
- Wang, L.L.; Graham, D.D.; Robertson, I.M.; Johnson, D.D. On the Reversibility of Hydrogen-Storage Reactions in Ca(BH₄)₂: Characterization via Experiment and Theory. *J. Phys. Chem. C* 2009, 113, 20088–20096. [CrossRef]
- Kim, Y.; Hwang, S.J.; Shim, J.H.; Lee, Y.S.; Han, H.N.; Cho, Y.W. Investigation of the Dehydrogenation Reaction Pathway of Ca(BH₄)₂ and Reversibility of Intermediate Phases. *J. Phys. Chem. C* 2012, 116, 4330–4334. [CrossRef]
- 88. Kim, Y.; Hwang, S.J.; Lee, Y.S.; Suh, J.Y.; Han, H.N.; Cho, Y.W. Hydrogen Back-Pressure Effects on the Dehydrogenation Reactions of Ca(BH₄)₂. *J. Phys. Chem. C* **2012**, *116*, 25715–25720. [CrossRef]
- Sivaev, I.B.; Bregadze, V.I.; Sjöberg, S. Chemistry of closo-Dodecaborate Anion [B₁₂H₁₂]²⁻: A Review. *Collect. Czech. Chem. Commun.* 2002, 67. [CrossRef]
- 90. Muetterties, E.L. Boron Hydride Chemistry; Academic Press Inc.: London, UK, 1975.
- 91. Caputo, R.; Garroni, S.; Olid, D.; Teixidor, F.; Surinach, S.; Baro, M.D. Can Na₂B₁₂H₁₂ be a decomposition product of NaBH₄? *Phys. Chem. Chem. Phys.* **2010**, *12*, 15093–15100. [CrossRef] [PubMed]
- 92. Pitt, M.P.; Paskevicius, M.; Brown, D.H.; Sheppard, D.A.; Buckley, C.E. Thermal Stability of Li₂B₁₂H₁₂ and its Role in the Decomposition of LiBH₄. *J. Am. Chem. Soc.* **2013**, *135*, 6930–6941. [CrossRef] [PubMed]
- Yan, Y.; Remhof, A.; Hwang, S.J.; Li, H.W.; Mauron, P.; Orimo, S.i.; Züttel, A. Pressure and temperature dependence of the decomposition pathway of LiBH₄. *Phys. Chem. Chem. Phys.* 2012, 14, 6514–6519. [CrossRef] [PubMed]
- 94. He, L.; Li, H.W.; Akiba, E. Thermal Decomposition of Anhydrous Alkali Metal Dodecaborates M₂B₁₂H₁₂ (M = Li, Na, K). *Energies* **2015**, *8*. [CrossRef]
- 95. He, L.; Li, H.W.; Tumanov, N.; Filinchuk, Y.; Akiba, E. Facile synthesis of anhydrous alkaline earth metal dodecaborates MB₁₂H₁₂ (M = Mg, Ca) from M(BH₄)₂. *Dalton Trans.* 2015, 44, 15882–15887. [CrossRef] [PubMed]
- 96. Remhof, A.; Yan, Y.; Rentsch, D.; Borgschulte, A.; Jensen, C.M.; Züttel, A. Solvent-free synthesis and stability of MgB₁₂H₁₂. *J. Mater. Chem. A* **2014**, *2*, 7244–7249. [CrossRef]
- 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. *J. Solid State Chem.* 2011, 184, 3110–3116. [CrossRef]
- Paskevicius, M.; Pitt, M.P.; Brown, D.H.; Sheppard, D.A.; Chumphongphan, S.; Buckley, C.E. First-order phase transition in the Li₂B₁₂H₁₂ system. *Phys. Chem. Chem. Phys.* **2013**, *15*, 15825–15828. [CrossRef] [PubMed]
- Her, J.H.; Yousufuddin, M.; Zhou, W.; Jalisatgi, S.S.; Kulleck, J.G.; Zan, J.A.; Hwang, S.J.; Bowman, R.C.; Udovic, T.J. Crystal Structure of Li₂B₁₂H₁₂: a Possible Intermediate Species in the Decomposition of LiBH₄. *Inorg. Chem.* 2008, 47, 9757–9759. [CrossRef] [PubMed]
- 100. Her, J.H.; Zhou, W.; Stavila, V.; Brown, C.M.; Udovic, T.J. Role of Cation Size on the Structural Behavior of the Alkali-Metal Dodecahydro-closo-Dodecaborates. *J. Phys. Chem. C* 2009, *113*, 11187–11189. [CrossRef]
- 101. Tiritiris, I.; Schleid, T. Die Dodekahydro-closo-Dodekaborate $M_2[B_{12}H_{12}]$ der schweren Alkalimetalle (M⁺ = K⁺, Rb⁺, NH⁴⁺, Cs⁺) und ihre formalen Iodid-Addukte $M_3I[B_{12}H_{12}]$ (MI- $M_2[B_{12}H_{12}]$). Z. Anorg. Allg. Chem. **2003**, 629, 1390–1402. [CrossRef]
- Stavila, V.; Her, J.H.; Zhou, W.; Hwang, S.J.; Kim, C.; Ottley, L.A.M.; Udovic, T.J. Probing the structure, stability and hydrogen storage properties of calcium dodecahydro-closo-dodecaborate. *J. Solid State Chem.* 2010, 183, 1133–1140. [CrossRef]
- Pitochelli, A.R.; Hawthorne, F.M. THE ISOLATION OF THE ICOSAHEDRAL B₁₂H₁₂²⁻ ION. J. Am. Chem. Soc. 1960, 82, 3228–3229. [CrossRef]
- 104. Hansen, B.R.S.; Paskevicius, M.; Li, H.W.; Akiba, E.; Jensen, T.R. Metal boranes: Progress and applications. *Coord. Chem. Rev.* 2016, 323, 60–70. [CrossRef]

- Miller, H.C.; Miller, N.E.; Muetterties, E.L. Chemistry of Boranes. XX. Syntheses of Polyhedral Boranes. *Inorg. Chem.* 1964, *3*, 1456–1463. [CrossRef]
- 106. Brown, H.C.; Tierney, P.A. The Reaction of Lewis Acids of Boron with Sodium Hydride and Borohydride. *J. Am. Chem. Soc.* **1958**, *80*, 1552–1558. [CrossRef]
- 107. Adams, R.M.; Siedle, A.R.; Grant, J. Convenient Preparation of the Dodecahydrododecaborate Ion. *Inorg. Chem.* **1964**, *3*, 461–461. [CrossRef]
- 108. Safronov, A.V.; Jalisatgi, S.S.; Lee, H.B.; Hawthorne, M.F. Chemical hydrogen storage using polynuclear borane anion salts. *Int. J. Hydrog. Energy* **2011**, *36*, 234–239. [CrossRef]
- 109. Yan, Y.; Remhof, A.; Rentsch, D.; Lee, Y.S.; Whan Cho, Y.; Züttel, A. Is Y₂(B₁₂H₁₂)₃ the main intermediate in the decomposition process of Y(BH₄)₃? *Chem. Commun.* **2013**, *49*, 5234–5236. [CrossRef] [PubMed]
- Chong, M.; Karkamkar, A.; Autrey, T.; Orimo, S.i.; Jalisatgi, S.; Jensen, C.M. Reversible dehydrogenation of magnesium borohydride to magnesium triborane in the solid state under moderate conditions. *Chem. Commun.* 2011, 47, 1330–1332. [CrossRef] [PubMed]
- 111. Chong, M.; Autrey, T.; Jensen, M.C. Lewis Base Complexes of Magnesium Borohydride: Enhanced Kinetics and Product Selectivity upon Hydrogen Release. *Inorganics* **2017**, *5*. [CrossRef]
- 112. Zhang, Y.; Majzoub, E.; Ozoliņš, V.; Wolverton, C. Theoretical Prediction of Metastable Intermediates in the Decomposition of Mg(BH₄)₂. *J. Phys. Chem. C* **2012**, *116*, 10522–10528. [CrossRef]
- 113. Huang, Z.; Eagles, M.; Porter, S.; Sorte, E.G.; Billet, B.; Corey, R.L.; Conradi, M.S.; Zhao, J.C. Thermolysis and solid state NMR studies of NaB₃H₈, NH₃B₃H₇, and NH₄B₃H₈. *Dalton Trans.* **2013**, 42, 701–708. [CrossRef] [PubMed]
- 114. Nguyen, M.T.; Matus, M.H.; Dixon, D.A. Heats of Formation of Boron Hydride Anions and Dianions and Their Ammonium Salts $[B_nH_m^{y-}][NH_4^+]_y$ with y = 1-2. *Inorg. Chem.* **2007**, *46*, 7561–7570. [CrossRef] [PubMed]
- 115. Verdal, N.; Her, J.H.; Stavila, V.; Soloninin, A.V.; Babanova, O.A.; Skripov, A.V.; Udovic, T.J.; Rush, J.J. Complex high-temperature phase transitions in Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂. *J. Solid State Chem.* **2014**, 212, 81–91. [CrossRef]
- 116. Udovic Terrence, J.; Matsuo, M.; Tang Wan, S.; Wu, H.; Stavila, V.; Soloninin Alexei, V.; Skoryunov Roman, V.; Babanova Olga, A.; Skripov Alexander, V.; Rush John, J.; et al. Exceptional Superionic Conductivity in Disordered Sodium Decahydro-closo-decaborate. *Adv. Mater.* 2014, *26*, 7622–7626. [CrossRef] [PubMed]
- 117. Tang, W.S.; Dimitrievska, M.; Stavila, V.; Zhou, W.; Wu, H.; Talin, A.A.; Udovic, T.J. Order-Disorder Transitions and Superionic Conductivity in the Sodium nido-Undeca(carba)borates. *Chem. Mater.* 2017, 29, 10496–10509. [CrossRef]
- 118. Bykov, A.Y.; Zhizhin, K.Y.; Kuznetsov, N.T. The chemistry of the octahydrotriborate anion [B₃H₈]⁻. *Russ. J. Inorg. Chem.* **2014**, *59*, 1539–1555. [CrossRef]
- 119. Driess, M.; Nöth, H. Molecular Clusters of the Main Group Elements; Wiley-VCH: Berlin, Germany, 2008.
- Wade, K. Structural and Bonding Patterns in Cluster Chemistry. In Advances in Inorganic Chemistry and Radiochemistry; Emelèus, H.J., Sharpe, A.G., Eds.; Academic Press: Cambridge, MA, USA, 1976; Volume 18, pp. 1–66. [CrossRef]
- 121. Mingos, D.M.P. A General Theory for Cluster and Ring Compounds of the Main Group and Transition Elements. *Nat. Phys. Sci.* **1972**, *236*, 99–102.
- 122. Schubert, D.M. Boron Chemistry for Hydrogen Storage. In *Boron Science: New Technologies and Applications;* Hosmane, N.S., Ed.; CRC Press: Boca Raton, FL, USA, 2012; pp. 393–397. [CrossRef] [PubMed]
- 123. Hansen, B.R.S.; Ravnsbæk, D.B.; Skibsted, J.; Jensen, T.R. Hydrogen reversibility of LiBH₄-MgH₂-Al composites. *Phys. Chem. Chem. Phys.* **2014**, *16*, 8970–8980. [CrossRef]
- 124. Hansen, B.R.S.; Ravnsbæk, D.B.; Reed, D.; Book, D.; Gundlach, C.; Skibsted, J.; Jensen, T.R. Hydrogen Storage Capacity Loss in a LiBH₄-Al Composite. *J. Phys. Chem. C* 2013, *117*, 7423–7432. [CrossRef]
- Kim, J.H.; Shim, J.H.; Cho, Y.W. On the reversibility of hydrogen storage in Ti- and Nb-catalyzed Ca(BH₄)₂. J. Power Sources 2008, 181, 140–143. [CrossRef]
- 126. Kim, J.H.; Jin, S.A.; Shim, J.H.; Cho, Y.W. Reversible hydrogen storage in calcium borohydride Ca(BH₄)₂. *Scr. Mater.* **2008**, *58*, 481–483. [CrossRef]
- 127. Rongeat, C.; D'Anna, V.; Hagemann, H.; Borgschulte, A.; Züttel, A.; Schultz, L.; Gutfleisch, O. Effect of additives on the synthesis and reversibility of Ca(BH₄)₂. *J. Alloys Compd.* **2010**, *493*, 281–287. [CrossRef]

- 128. Gosalawit-Utke, R.; Suarez, K.; Bellosta von Colbe, J.M.; Bösenberg, U.; Jensen, T.R.; Cerenius, Y.; Bonatto Minella, C.; Pistidda, C.; Barkhordarian, G.; Schulze, M.; et al. Ca(BH4)2-MgF2 Reversible Hydrogen Storage: Reaction Mechanisms and Kinetic Properties. *J. Phys. Chem. C* 2011, 115, 3762–3768. [CrossRef]
- 129. Lee, J.Y.; Lee, Y.S.; Suh, J.Y.; Shim, J.H.; Cho, Y.W. Metal halide doped metal borohydrides for hydrogen storage: The case of Ca(BH₄)₂-CaX₂ (X = F, Cl) mixture. *J. Alloys Compd.* **2010**, *506*, 721–727. [CrossRef]
- White, J.L.; Newhouse, R.J.; Zhang, J.Z.; Udovic, T.J.; Stavila, V. Understanding and Mitigating the Effects of Stable Dodecahydrocloso-dodecaborate Intermediates on Hydrogen-Storage Reactions. *J. Phys. Chem. C* 2016, 120, 25725–25731. [CrossRef] [PubMed]
- 131. Jensen, S.R.H.; Paskevicius, M.; Hansen, B.R.S.; Jakobsen, A.S.; Møller, K.T.; White, J.L.; Allendorf, M.D.; Stavila, V.; Skibsted, J.; Jensen, T.R. Hydrogenation properties of lithium and sodium hydride—*closo*-borate, [B₁₀H₁₀]^{2–} and [B₁₂H₁₂]^{2–}, composites. *Phys. Chem. Chem. Phys.* **2018**, 20, 16266–16275. [CrossRef]
- 132. Bonatto Minella, C.; Garroni, S.; Olid, D.; Teixidor, F.; Pistidda, C.; Lindemann, I. Experimental Evidence of CaB₁₂H₁₂ Formation During Decomposition of a Ca(BH₄)₂ + MgH₂ Based Reactive Hydride Composite. *J. Phys. Chem. C* 2011, *115*, 18010–18014. [CrossRef]
- Yan, Y.; Wang, H.; Zhu, M.; Cai, W.; Rentsch, D.; Remhof, A. Direct Rehydrogenation of LiBH₄ from H-Deficient Li₂B₁₂H_{12-x}. *Crystals* 2018, *8*. [CrossRef] [PubMed]
- 134. Tang, W.S.; Wu, G.; Liu, T.; Wee, A.T.S.; Yong, C.K.; Xiong, Z.; Hor, A.T.S.; Chen, P. Cobalt-catalyzed hydrogen desorption from the LiNH₂-LiBH₄ system. *Dalton Trans.* **2008**, pp. 2395–2399. [CrossRef]
- 135. Wu, C.; Wu, F.; Bai, Y.; Yi, B.; Zhang, H. Cobalt boride catalysts for hydrogen generation from alkaline NaBH₄ solution. *Mater. Lett.* **2005**, *59*, 1748–1751. [CrossRef] [PubMed]
- Paskevicius, M.; Ley, M.B.; Sheppard, D.A.; Jensen, T.R.; Buckley, C.E. Eutectic melting in metal borohydrides. *Phys. Chem. Chem. Phys.* 2013, 15, 19774–19789. [CrossRef]
- Dornheim, M.; Doppiu, S.; Barkhordarian, G.; Boesenberg, U.; Klassen, T.; Gutfleisch, O.; Bormann, R. Hydrogen storage in magnesium-based hydrides and hydride composites. *Scr. Mater.* 2007, *56*, 841–846. [CrossRef] [PubMed]
- Vajo, J.J.; Skeith, S.L.; Mertens, F. Reversible Storage of Hydrogen in Destabilized LiBH₄. J. Phys. Chem. B 2005, 109, 3719–3722. [CrossRef] [PubMed]
- Bergemann, N.; Pistidda, C.; Milanese, C.; Emmler, T.; Karimi, F.; Chaudhary, A.L.; Chierotti, M.R.; Klassen, T.; Dornheim, M. Ca(BH4)2-Mg2NiH4: On the pathway to a Ca(BH4)2 system with a reversible hydrogen cycle. *Chem. Commun.* 2016, *52*, 4836–4839. [CrossRef] [PubMed]
- 140. Vajo, J.J.; Li, W.; Liu, P. Thermodynamic and kinetic destabilization in LiBH₄/Mg₂NiH₄: Promise for borohydride-based hydrogen storage. *Chem. Commun.* **2010**, *46*, 6687–6689. [CrossRef]
- 141. Afonso, G.; Bonakdarpour, A.; Wilkinson, D.P. Hydrogen Storage Properties of the Destabilized 4NaBH4/5Mg2NiH4 Composite System. *J. Phys. Chem. C* **2013**, *117*, 21105–21111. [CrossRef]
- 142. Bösenberg, U.; Doppiu, S.; Mosegaard, L.; Barkhordarian, G.; Eigen, N.; Borgschulte, A.; Jensen, T.R.; Cerenius, Y.; Gutfleisch, O.; Klassen, T.; et al. Hydrogen sorption properties of MgH₂-LiBH₄ composites. *Acta Mater.* 2007, 55, 3951–3958.
- 143. Maximilian, F. Properties of nanoscale metal hydrides. Nanotechnology 2009, 20, 204009. [CrossRef]
- 144. Zhao-Karger, Z.; Witter, R.; Bardaji, E.G.; Wang, D.; Cossement, D.; Fichtner, M. Altered reaction pathways of eutectic LiBH₄-Mg(BH₄)₂ by nanoconfinement. *J. Mater. Chem. A* **2013**, *1*, 3379–3386. [CrossRef]
- 145. Nale, A.; Catti, M.; Bardají, E.G.; Fichtner, M. On the decomposition of the 0.6LiBH₄-0.4Mg(BH₄)₂ eutectic mixture for hydrogen storage. *Int. J. Hydrog. Energy* **2011**, *36*, 13676–13682. [CrossRef]
- 146. Etacheri, V.; Marom, R.; Elazari, R.; Salitra, G.; Aurbach, D. Challenges in the development of advanced Li-ion batteries: a review. *Energy Environ. Sci.* **2011**, *4*, 3243–3262. [CrossRef]
- 147. Goodenough, J.B.; Kim, Y. Challenges for Rechargeable Li Batteries. *Chem. Mater.* **2010**, 22, 587–603. [CrossRef]
- 148. Wang, Q.; Ping, P.; Zhao, X.; Chu, G.; Sun, J.; Chen, C. Thermal runaway caused fire and explosion of lithium ion battery. *J. Power Sources* **2012**, *208*, 210–224.
- Xiayin, Y.; Bingxin, H.; Jingyun, Y.; Gang, P.; Zhen, H.; Chao, G.; Deng, L.; Xiaoxiong, X. All-solid-state lithium batteries with inorganic solid electrolytes: Review of fundamental science. *Chin. Phys. B* 2016, 25, 018802. [CrossRef]

- 150. Skripov, A.V.; Babanova, O.A.; Soloninin, A.V.; Stavila, V.; Verdal, N.; Udovic, T.J.; Rush, J.J. Nuclear Magnetic Resonance Study of Atomic Motion in A₂B₁₂H₁₂ (A = Na, K, Rb, Cs): Anion Reorientations and Na+ Mobility. *J. Phys. Chem. C* 2013, 117, 25961–25968. [CrossRef]
- 151. Kumar, P.P.; Yashonath, S. Ionic conduction in the solid state. J. Chem. Sci. 2006, 118, 135–154. [CrossRef]
- 152. Chandra, A. Ion conduction in crystalline superionic solids and its applications. *Eur. Phys. J.-Appl. Phys.* **2014**, *66*, 30905. [CrossRef]
- Tiritiris, I.; Schleid, T.; Müller, K. Solid-State NMR Studies on Ionic closo-Dodecaborates. *Appl. Magn. Reson.* 2007, 32, 459–481. [CrossRef] [PubMed]
- Udovic, T.J.; Matsuo, M.; Unemoto, A.; Verdal, N.; Stavila, V.; Skripov, A.V.; Rush, J.J.; Takamura, H.; Orimo, S.I. Sodium superionic conduction in Na₂B₁₂H₁₂. *Chem. Commun.* 2014, *50*, 3750–3752. [CrossRef]
- 155. Uvarov, N.F.; Ulikhin, A.S.; Iskakova, A.A.; Medvedev, N.N.; Anikeenko, A.V. Ionic conductivity in orientationally disordered phases. *Russ. J. Electrochem.* **2011**, *47*, 404. [CrossRef] [PubMed]
- 156. Tang, W.S.; Unemoto, A.; Zhou, W.; Stavila, V.; Matsuo, M.; Wu, H.; Orimo, S.i.; Udovic, T.J. Unparalleled lithium and sodium superionic conduction in solid electrolytes with large monovalent cage-like anions. *Energy Environ. Sci.* 2015, *8*, 3637–3645. [CrossRef] [PubMed]
- 157. Paskevicius, M.; Hansen, B.R.S.; Jørgensen, M.; Richter, B.; Jensen, T.R. Multifunctionality of silver *closo*-boranes. *Nat. Commun.* **2017**, *8*, 15136. [CrossRef]
- He, L.; Li, H.W.; Nakajima, H.; Tumanov, N.; Filinchuk, Y.; Hwang, S.J.; Sharma, M.; Hagemann, H.; Akiba, E. Synthesis of a Bimetallic Dodecaborate LiNaB₁₂H₁₂ with Outstanding Superionic Conductivity. *Chem. Mater.* 2015, 27, 5483–5486. [CrossRef] [PubMed]
- Duchene, L.; Kuhnel, 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]
- 160. Johnson, J.W.; Thompson, A.H. Lithium Closoboranes II. Stable Nonaqueous Electrolytes for Elevated Temperature Lithium Cells. *J. Electrochem. Soc.* **1981**, *128*, 932–933. [CrossRef]
- Dey, A.N.; Miller, J. Primary Li/SOCl₂ Cells: VII. Effect of Li₂B₁₀Cl₁₀ and Li₂B₁₂Cl₁₂ Electrolyte Salts on the Performance. J. Electrochem. Soc. 1979, 126, 1445–1451. [CrossRef]
- Hansen, B.R.S.; Paskevicius, M.; Jørgensen, M.; Jensen, T.R. Halogenated Sodium-closo-Dodecaboranes as Solid-State Ion Conductors. *Chem. Mater.* 2017, 29, 3423–3430. [CrossRef]
- Kweon, K.E.; Varley, J.B.; Shea, P.; Adelstein, N.; Mehta, P.; Heo, T.W.; Udovic, T.J.; Stavila, V.; Wood, B.C. Structural, Chemical, and Dynamical Frustration: Origins of Superionic Conductivity in closo-Borate Solid Electrolytes. *Chem. Mater.* 2017, 29, 9142–9153. [CrossRef] [PubMed]
- 164. Oumellal, Y.; Rougier, A.; Nazri, G.A.; Tarascon, J.M.; Aymard, L. Metal hydrides for lithium-ion batteries. *Nat. Mater.* **2008**, *7*, 916–921. [CrossRef]
- 165. Meggiolaro, D.; Farina, L.; Silvestri, L.; Panero, S.; Brutti, S.; Reale, P. Lightweight Borohydrides Electro-Activity in Lithium Cells. *Energies* **2016**, *9*. [CrossRef]
- 166. Mason, T.H.; Liu, X.; Hong, J.; Graetz, J.; Majzoub, E.H. First-Principles Study of Novel Conversion Reactions for High-Capacity Li-Ion Battery Anodes in the Li-Mg-B-N-H System. J. Phys. Chem. C 2011, 115, 16681–16687. [CrossRef]
- 167. Valliant, J.F.; Guenther, K.J.; King, A.S.; Morel, P.; Schaffer, P.; Sogbein, O.O.; Stephenson, K.A. The medicinal chemistry of carboranes. *Coord. Chem. Rev.* 2002, 232, 173–230. [CrossRef] [PubMed]
- 168. Barth, R.F.; Zhang, Z.; Liu, T. A realistic appraisal of boron neutron capture therapy as a cancer treatment modality. *Cancer Commun.* **2018**, *38*, 36. [CrossRef] [PubMed]
- Barth, R.F.; Mi, P.; Yang, W. Boron delivery agents for neutron capture therapy of cancer. *Cancer Commun.* 2018, 38, 35. [CrossRef] [PubMed]
- 170. Mi, P.; Yanagie, H.; Dewi, N.; Yen, H.C.; Liu, X.; Suzuki, M.; Sakurai, Y.; Ono, K.; Takahashi, H.; Cabral, H.; et al. Block copolymer-boron cluster conjugate for effective boron neutron capture therapy of solid tumors. *J. Control. Release* 2017, 254, 1–9. [CrossRef] [PubMed]
- 171. Kikuchi, S.; Kanoh, D.; Sato, S.; Sakurai, Y.; Suzuki, M.; Nakamura, H. Maleimide-functionalized closo-dodecaborate albumin conjugates (MID-AC): Unique ligation at cysteine and lysine residues enables efficient boron delivery to tumor for neutron capture therapy. *J. Control. Release* **2016**, *237*, 160–167. [CrossRef]

- 172. Jiang, K.; Coffer, J.L.; Gillen, J.G.; Brewer, T.M. Incorporation of Cesium Borocaptate onto Silicon Nanowires as a Delivery Vehicle for Boron Neutron Capture Therapy. *Chem. Mater.* 2010, 22, 279–281. [CrossRef] [PubMed]
- 173. Gao, Z.; Horiguchi, Y.; Nakai, K.; Matsumura, A.; Suzuki, M.; Ono, K.; Nagasaki, Y. Use of boron cluster-containing redox nanoparticles with ROS scavenging ability in boron neutron capture therapy to achieve high therapeutic efficiency and low adverse effects. *Biomaterials* 2016, 104, 201–212. [CrossRef] [PubMed]
- 174. Deshpande, P.P.; Biswas, S.; Torchilin, V.P. Current trends in the use of liposomes for tumor targeting. *Nanomedicine* **2013**, *8*. [CrossRef] [PubMed]
- 175. Maruyama, K.; Ishida, O.; Kasaoka, S.; Takizawa, T.; Utoguchi, N.; Shinohara, A.; Chiba, M.; Kobayashi, H.; Eriguchi, M.; Yanagie, H. Intracellular targeting of sodium mercaptoundecahydrododecaborate (BSH) to solid tumors by transferrin-PEG liposomes, for boron neutron-capture therapy (BNCT). *J. Control. Release* 2004, *98*, 195–207.
- 176. Nakamura, H. Chapter 10—Liposomal Boron Delivery for Neutron Capture Therapy. In *Methods in Enzymology*; Academic Press: Cambridge, MA, USA, 2009; Volume 465, pp. 179–208. [CrossRef] [PubMed]
- Lee, J.D.; Ueno, M.; Miyajima, Y.; Nakamura, H. Synthesis of Boron Cluster Lipids: closo-Dodecaborate as an Alternative Hydrophilic Function of Boronated Liposomes for Neutron Capture Therapy. *Org. Lett.* 2007, *9*, 323–326.

 \odot 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).