Effects of LiBF$_4$ Addition on the Lithium-Ion Conductivity of LiBH$_4$

Laura M. de Kort$^1$, Valerio Gulino$^1$, Didier Blanchard$^2$ and Peter Ngene$^1$*

1 Materials Chemistry and Catalysis, Department of Chemistry, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CS Utrecht, The Netherlands; l.m.dekort@uu.nl (L.M.d.K.); v.gulino@uu.nl (V.G.)
2 The European Synchrotron Facility (ESRF), 71 Avenue des Martyrs, 38000 Grenoble, France; didier.blanchard@esrf.fr
* Correspondence: p.ngene@uu.nl

Abstract: Complex hydrides, such as LiBH$_4$, are a promising class of ion conductors for all-solid-state batteries, but their application is constrained by low ion mobility at room temperature. Mixing with halides or complex hydride anions, i.e., other complex hydrides, is an effective approach to improving the ionic conductivity. In the present study, we report on the reaction of LiBH$_4$ with LiBF$_4$, resulting in the formation of conductive composites consisting of LiBH$_4$, LiF and lithium closo-borates. It is believed that the in-situ formation of closo-borate related species gives rise to highly conductive interfaces in the decomposed LiBH$_4$ matrix. As a result, the ionic conductivity is improved by orders of magnitude with respect to the Li-ion conductivity of the LiBH$_4$, up to $0.9 \times 10^{-5}$ S cm$^{-1}$ at 30 $^\circ$C. The insights gained in this work show that the incorporation of a second compound is a versatile method to improve the ionic conductivity of complex metal hydrides, opening novel synthesis pathways not limited to conventional substituents.

Keywords: solid-state electrolytes; complex hydrides; lithium borohydride; ionic conductivity; ion substitution; interface effects

1. Introduction

In our current society, rechargeable lithium-ion batteries are crucial energy storage devices for a wide variety of applications, ranging from small portable electronics to electric vehicles. The performance and safety requirements for automotive electrification and grid-energy storage systems, however, cannot be met by the commercially available batteries [1,2]. Hence, the development of batteries with higher energy densities and improved safety is crucial. The performance limitations in commercial Li-ion batteries are caused by their organic liquid electrolytes that often suffer from poor electrochemical and thermal stability, which poses safety risks and limits storage capacity [3]. Replacement of the liquid electrolyte with a solid electrolyte could overcome these persistent problems. Solid-state electrolytes (SSEs) are inherently safer and, in many cases, compatible with high energy density electrodes, such as metallic lithium [4]. Consequently, the realization of all-solid-state batteries implementing SSEs can lead to safer batteries that store more energy.

The anticipated benefits of SSEs has led to a growing number of studies on inorganic lithium ion conductors [5], such as garnet-type [6,7], perovskite-type [8,9] and sulphide-type materials [10,11]. The research scope on potential Li-ion conductors was recently extended to complex metal hydrides following the surprising discovery of fast Li-ion mobility in LiBH$_4$ [12]. Complex metal hydrides exhibit several unique material properties that are interesting for battery application, i.e., low molecular weight, easy deformability and high compressibility, and compatibility with a lithium metal anode [13–16]. Among others, these benefits have spurred research on complex metal hydrides as promising SSEs for all-solid-state Li-ion batteries.
A main disadvantage for metal hydrides, and many other solid electrolytes, is their low room temperature (RT) ionic conductivity. Complex hydrides typically exhibit high ionic conductivity as a result of a reversible structural phase change that requires high temperatures [12,17,18]. For example, fast lithium-ion mobility and high conductivity (\(10^{-3} \, \text{S cm}^{-1}\)) in LiBH\(_4\) is only observed after a phase transition from the orthorhombic to the hexagonal phase at 110 °C [12]. Therefore, the development of strategies that enhance RT Li-ion conductivity is of major importance for the application of metal hydride-based ion conductors.

From various methods developed to boost ionic conductivity in complex hydrides, e.g., nanoconfinement and interface engineering [19–22], partial ionic substitution has proven to be particularly useful [23–28]. Previous reports reveal that the incorporation of lithium halides (LiX, with X = Br\(^-\), I\(^-\)) or lithium amide (LiNH\(_2\)) in the LiBH\(_4\) crystal structure leads to significant improvement in ionic transport. Depending on the substituting anion, partial anionic substitution of BH\(_4^-\) either leads to stabilization of the conductive hexagonal phase at lower temperatures (\(h\)-Li(BH\(_4\))\(_{1−x}\)(X\(_x\)) [15,29,30]) or to the formation of a new highly conductive crystal structure, e.g., Li\(_2\)(BH\(_4\))(NH\(_2\)) [27,28].

The use of anion substitution for conductivity enhancement in LiBH\(_4\) has so far been limited to the addition of halides and other complex hydrides. A complex anion that could also be interesting as a partial substituent for [BH\(_4^-\)]\(^-\) is the [BF\(_4^-\)]\(^-\) anion. LiBF\(_4\) is a well-known Li-ion conductor for liquid electrolytes, but it has not been investigated as SSE because it exhibits very poor conductivity as a solid electrolyte. Partial ionic substitution of BF\(_4^-\) in LiBH\(_4\) has been investigated as a method to improve the hydrogen storage properties of metal borohydrides [31–35]. Different from LiX and LiNH\(_2\), in this case, it was reported that F\(^-\) is exchanged for H\(^-\), forming a [BH\(_4-x,F_x\)]\(^-\) complex. Theoretical studies proposed that intramolecular hydrogen-fluorine exchange in MBH\(_4\)-MBF\(_4\) systems (M = Li, Na, K) significantly alters the borohydride structure [31–33]. It has been speculated that the strong electronegativity of the fluoride atom weakens the force of attraction between the B and the H in the complex anion [36]. Similarly, electrostatic interactions between the [BH\(_4-x,F_x\)]\(^-\) anion with the Li\(^+\) cation could be attenuated, thereby improving Li-ion mobility. The predicted effects in the LiBH\(_4\)-LiBF\(_4\) system for hydrogen storage have been experimentally reported by Richter et al. [36]. However, it was demonstrated that the formation of [BH\(_4-x,F_x\)]\(^-\) causes a strong destabilization of LiBF\(_4\), leading to a decomposition pathway forming diborane gas and solid decomposition products such as LiF and Li\(_2\)B\(_2\)H\(_2\). This decomposition reaction pathway led the authors to conclude that this system does not hold promise of any practical usage in hydrogen desorption/absorption cycling [36]. Even if the conclusion of the authors can be considered correct, the studied system could be of interest in the SSE research field. In fact, it has been suggested that closo-borate anions (e.g., B\(_{12}\)H\(_{22}^2\)^-\) have lower reduction ability than BH\(_4^-\) and thus show higher electrochemical stability, in addition to a higher RT Li-ion conductivity [37].

Recently, Zhu et al. [36] reported that partial dehydrogenation of LiBH\(_4\) results in the in-situ formation of highly conductive Li–B–H complexes, containing LiBH\(_4\), [Li\(_2\)B\(_2\)H\(_{11+1/n}\)]\(_n\) and LiH. A dramatic increase in Li-ion conductivity to \(2.7 \times 10^{-4} \, \text{S cm}^{-1}\) at 35 °C is observed, likely due to the presence of a highly conductive interface between [Li\(_2\)B\(_2\)H\(_{11+1/n}\)]\(_n\) and LiBH\(_4\) [38]. Although the exact phase is still under debate, these Li–B–H complexes are believed to contain closo-borates [39]. We expect that similar in-situ formed Li–B–H complexes can be derived from the destabilization of LiBH\(_4\) caused by LiBF\(_4\), which may exhibit superior Li-ion conducting performances.

In this work, we explore the impact of LiBF\(_4\) incorporation on LiBH\(_4\), especially looking into the ionic conductivity of in-situ formed Li-B-H complexes. The structural properties and ionic conductivity of the synthetized mixtures are analysed to investigate how the presence of BF\(_4^-\) in the mixtures affects the Li-B-H complex composition and structure, as well as the lithium-ion mobility.
2. Experimental Section

2.1. Solid-State Synthesis

Several LiBH₄-LiBF₄ and LiBH₄-Li₂B₁₂H₁₂ mixtures were prepared by physically mixing LiBH₄ (purity > 95%, Sigma-Aldrich, St. Louis, MO, USA) with either 20 mol% of LiBF₄ (purity > 98%, Sigma-Aldrich) or 25 mol% of anhydrous Li₂B₁₂H₁₂ (purity > 98%, Katchem, Prague, Czech Republic) in an agate mortar approximately 5 min. The physical mixtures were transferred into a stainless-steel reactor, which was placed in a stainless-steel high-pressure autoclave (Parr, 250 mL). After pressurizing the autoclave with 50 bar of H₂, the physical mixtures were heated to 150 °C or 280 °C (heating rate 2.5 °C min⁻¹) for 30 min. The samples were collected from the autoclave after the heat treatment and analysed further. An overview of all prepared samples is provided in Table S1. All storage and handling of the chemicals and prepared samples was carried out in an argon-filled glovebox (H₂O and O₂ < 0.1 ppm).

2.2. Structural Characterization

X-ray powder diffraction (XRD) analysis was performed with a Bruker-AXS D8 Advance X-ray diffractometer (Co Kα = 1.78897 Å). The samples were placed in an airtight sample holder, preventing air and moisture exposure. Diffractograms were recorded at RT from 20° to 80° 2θ range.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed on a Perkin-Elmer 2000 spectrometer equipped with an MCT detector. Using an airtight sample holder with KBr windows, samples were measured without any air or moisture exposure. Spectra were acquired from 900 cm⁻¹ to 4500 cm⁻¹ with a resolution of 4 cm⁻¹.

2.3. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were performed using a Princeton Applied Research Parstat 2273 connected to a custom-made measurement cell in a Büchi B-585 glass oven. Two stainless steel cylinders with Li foil (Sigma-Aldrich, purity 99.9%, 0.38 mm thick) were placed on one side and configured as electrodes. Using a standard 13 mm pellet press, an approximately 80–150 mg sample was pressed between the electrodes with a pressure of approximately 1.5 ton cm⁻². During a typical conductivity measurement, the measurement cell was incrementally heated to 130 °C (∆T = 10 °C) and incrementally cooled to room temperature (∆T = 20 °C). At each increment the temperature was allowed to equilibrate before an EIS measurement was performed using a 10 mV of amplitude and with frequencies from 1 MHz to 1 Hz.

2.4. Linear Sweep Voltammetry

Linear sweep voltammetry (LSV) was used to determine the oxidative stability of the LiBH₄–20% LiBF₄ sample. The sample was mixed with carbon black (CB, Ketjenblack EC600JD) in a weight ratio of 90:10 using an agate mortar. A pellet was obtained by pressing approximately 5 mg of electrolyte-carbon mixture and 50 mg of the electrolyte at 1.5 ton cm⁻². After compressing, a cell was formed with stainless-steel as the working electrode in contact with the electrolyte-carbon mixture and a lithium disk as the counter electrode in contact with the solid electrolyte. The linear sweep measurement was performed at 60 °C with a voltage range from 1.0 V to 5.0 V versus Li⁺/Li at a scanning rate of 0.1 mVs⁻¹.

3. Results and Discussion

3.1. Structural Characterization and Conductivity of LiBH₄–LiBF₄ Mixtures

The impact of the addition of LiBF₄ on the crystal structure of the Li-B-H complexes has been determined using XRD. In Figure 1a, the diffractograms of a mixture consisting of 80 mol% of LiBH₄ and 20 mol% LiBF₄ prepared via solid-state reaction at 150 °C and 280 °C are shown. The XRD patterns of LiBH₄ and LiBF₄ are provided for comparison. In
the diffraction pattern of the LiBH₄-LiBF₄ mixture heated at 150 °C, the main diffraction peaks characteristic of both starting compounds are still observed. Additionally, two new peaks have appeared at 45 and 53 2θ, that correspond to cubic (Fm-3m) LiF. This can be explained considering that the decomposition of LiBH₄ in the presence of LiBF₄ starts at 80 °C and LiF has been reported as a decomposition product [36]. During the reaction, hydrogen-fluorine exchange results in the formation of LiBHₓ₋ₓFₓ [36], which is not stable and decomposes to form LiF.

![Figure 1](image_url)

Figure 1. (a) X-ray powder diffraction patterns, (b) DRIFTS spectra and (c) Arrhenius conductivity plots of LiBH₄-LiBF₄ mixtures prepared at 150 °C and 280 °C. For comparison, LiBH₄, LiBF₄ and LiF are included in the XRD patterns; the spectra of LiBH₄, LiBF₄ and LiF are shown in the DRIFTS spectra and the ionic conductivity of pristine LiBH₄ is added to the Arrhenius plots. Relevant reflections are highlighted in grey.

Similarly, the diffraction pattern of the LiBH₄-LiBF₄ mixture prepared at 280 °C predominantly contains peaks related to LiF; however, in this case no clear diffraction peaks of the starting compounds can be identified. Thus, at a reaction temperature of 280 °C, the decomposition reaction proceeds further in agreement with results reported by Richter et al. [36]. Note that with XRD only crystalline compounds can be identified. Therefore, it is not clear whether LiF is the only solid decomposition product or if an unidentified amorphous phase is formed as well. For example, Zhu et al. reported that highly conductive amorphous Li-B-H complexes can form during the LiBH₄ decomposition [38].

Because with the XRD analysis the presence of possible amorphous Li-B-H complexes could not be confirmed, the structural properties of the LiBH₄-LiBF₄ mixtures were further analysed using DRIFTS measurements. This technique is not limited to crystalline compounds, which means that it can be used to identify the composition of the crystalline and amorphous phases present in the LiBH₄-LiBF₄ mixtures. The DRIFTS absorbance spectra obtained for LiBH₄-LiBF₄ synthesized at 150 °C and 280 °C are shown in Figure 1b, as well as the spectra for pristine LiBH₄ and LiBF₄. Pristine LiBH₄ typically shows several characteristic absorption bands. The most predominant bands, corresponding to [BH₄⁻] stretching vibrations, can be seen between 2000 and 2800 cm⁻¹. Other characteristic LiBH₄ vibrations can be seen between 1000 and 1300 cm⁻¹ ([BH₄⁻] bending) and 3200 and 3700 cm⁻¹ ([OH] stretching from adsorbed moisture) [40–42]. Though less intense, these characteristic bands are seen in the spectra of both LiBH₄-LiBF₄ mixtures, indicating that LiBH₄ is still present in both mixed compounds, hence the starting compounds have not completely decomposed. Note that the bands related to LiBH₄ vibrations are especially pronounced in the DRIFTS spectrum of LiBH₄-LiBF₄ prepared at 280 °C, even though no peaks related to crystalline LiBH₄ were present in the diffractogram, suggesting that residual amorphous LiBH₄ is present in the compound.

Besides the LiBH₄ vibrations, multiple unidentified peaks are present in both LiBH₄-LiBF₄ spectra, specifically around 2500 cm⁻¹ and at 1800 cm⁻¹. Surprisingly, none of these peaks is related to the presence of LiBF₄ or LiF (Figure 1b) [40,43]. Clearly, decomposition of the unstable LiBHₓ₋ₓFₓ complex does not only result in the formation of LiF, but also...
in an unidentified amorphous compound. Similar to the Li-B-H complexes obtained during LiBH₄ decomposition described by Zhu et al., this unidentified compound could be beneficial for the overall conductivity of the LiBH₄-LiBF₄ compounds [38]. Therefore, the nature of this compound has been studied in more detail, which will be discussed later in this work.

The impact of the decomposition reaction on Li-ion conductivity in the prepared LiBH₄-LiBF₄ mixed compounds is determined using electrochemical impedance spectroscopy (EIS). The obtained Nyquist plots display single semicircles that could be analysed with a simple one-phase model, as is shown in Figure S1. Additionally, exemplary Bode plots corresponding to the data are shown in Figure S2. In this way, the resistance and corresponding conductivity are determined over a temperature range from room temperature to 130 °C. In Figure 1c and Figure S3, the temperature dependence of the ionic conductivity of the LiBH₄-LiBF₄ mixtures prepared at 150 °C and 280 °C is displayed using an Arrhenius plot. Comparison to the ionic conductivity of LiBH₄ shows that ion transport in the LiBH₄-LiBF₄ mixtures prepared at 280 °C has improved at temperatures lower than 100 °C, reaching 0.9 × 10⁻⁶ S cm⁻¹ at 30 °C, which is three orders of magnitude higher than that of LiBH₄. In contrast, the mixture prepared with a lower reaction temperature exhibits a conductivity lower than that of LiBH₄ over the entire temperature range.

At temperatures above 110 °C, the same temperature-dependent Li-ion conductivity behaviour as LiBH₄ has been measured for the mixture treated at 150 °C, i.e., a drastic increase of the Li-ion conductivity. This behaviour indicates that the sample contains unreacted LiBH₄ that undergoes a phase transition from the orthorhombic to the hexagonal phase, increasing the Li-ion conductivity. These results agree with both the diffraction and IR data reported in Figure 1. The lower ion conductivity with respect to pure LiBH₄ can be explained considering that the sample also contains non-conductive phases, i.e., unreacted LiBF₄ and LiF. The LiBH₄-LiBF₄ mixture prepared at 280 °C also exhibits a conductivity enhancement above 110 °C related to the phase transition of LiBH₄, though it is not as pronounced. The conductivity above 110 °C is lower than that of pristine LiBH₄, which again can be attributed to the presence of non-conductive LiF.

The difference in conductivity between the mixtures prepared with different reaction temperatures (see also Figure S4) indicates that the reaction temperature of the prepared LiBH₄-LiBF₄ system plays an important role. It is not likely that LiF predominantly contributes to the enhanced conductivity, as it does not exhibit high room temperature conductivity by itself, typically below 10⁻⁷ S cm⁻¹ [44,45]. On the other hand, the incorporation of LiF could lead to the formation of a LiF-substituted LiBH₄ solid solution in which the hexagonal LiBH₄ phase is stabilized at lower temperatures. However, previous studies on halide substituted LiBH₄ demonstrated that the RT stability range of the hexagonal phase decreases with the anionic radius. In fact, it has been reported that h-Li(BH₄)₁₋ₓ(I)ₓ solid solutions are stable at RT in the range of 0.18 ≤ x ≤ 0.50 [46,47] h-Li(BH₄)₁₋ₓ(Br)ₓ in the range 0.3 ≤ x ≤ 0.55 [29], while Cl⁻ is not able to stabilize the high temperature phase at RT [46]. The ionic size of F⁻ is considerably smaller with respect to BH₄⁻ as well as to the other halides, i.e., r(F⁻) = 1.33 Å, r(Cl⁻) = 1.81 Å, r(Br⁻) = 1.96 Å, r(I⁻) = 2.20 Å and r(BH₄⁻) = 2.03 Å [48], which makes stabilization of the hexagonal phase at ambient temperature unlikely. This hypothesis is further confirmed by the absence of reflections related to hexagonal LiBH₄ in the LiBH₄-LiBF₄ diffraction patterns (Figure 1a). Consequently, it is not expected that the formation of LiF contributes to conductivity enhancement in the LiBH₄-LiBF₄ compound.

Nevertheless, it is clear that a highly conductive compound forms after the solid-state reaction occurring at 280 °C, during which hydrogen-fluoride substitution and subsequent decomposition of LiBH₄₋ₓFₓ occur. Because an improved conductivity is only seen in this case, it seems that the decomposition reaction that results in the presence of amorphous LiBH₄ and the formation of the unidentified compound (only observed in DRIFTS) is of vital importance to the conductivity enhancement. Richter et al. established a decomposition
pathway of LiBH$_3$F (Figure 2) that could explain the conductivity enhancement in the LiBH$_4$-LiBF$_4$ mixture [36].

![Diagram](https://via.placeholder.com/150)

**Figure 2.** Reaction overview for LiBH$_4$-LiBF$_4$ solid solutions as proposed by Richter et al. [36]. (a) Hydrogen-fluorine exchange of LiBF$_4$ with LiBH$_4$ to form LiBH$_3$F. (b) Decomposition of the substituted material yielding LiF and B$_2$H$_6$. (c) Reaction of B$_2$H$_6$ with excess LiBH$_4$ forming Li$_2$B$_{12}$H$_{12}$. Reaction stoichiometry not taken in account in this overview.

Their analysis illustrates that the formation of LiBH$_3$F from hydrogen-fluorine substitution does not solely result in the formation of LiF. The highly unstable LiBH$_3$F compound decomposes to form both LiF and diborane (B$_2$H$_6$). Finally, diborane can react with an excess of LiBH$_4$ to form Li$_2$B$_{12}$H$_{12}$. Because the studied composition consists of 80 mol% of LiBH$_4$, it is possible for this final reaction (Figure 2c) to occur. This decomposition pathway can support our observations on the effect of hydrogen-fluorine exchange and decomposition of the LiBH$_4$-LiBF$_4$ mixtures together with the enhancement of the Li-ion conductivity.

3.2. LiBH$_4$-Li$_2$B$_{12}$H$_{12}$ Composites

To investigate if the high ionic conductivity is related to the formation of Li$_2$B$_{12}$H$_{12}$-like or LiBH$_4$-Li$_2$B$_{12}$H$_{12}$ composites during the decomposition reaction, mixtures of LiBH$_4$ with 10 to 75 mol% Li$_2$B$_{12}$H$_{12}$ (see Table S1) were prepared following the synthetic procedure used for the mixture LiBH$_4$-LiBF$_4$ synthetized at 280 °C. The composition based on 25 mol% Li$_2$B$_{12}$H$_{12}$ will be discussed below because it resembles the composition of the LiBH$_4$-LiBF$_4$ mixture. The DRIFTS and XRD spectra of the LiBH$_4$-25% Li$_2$B$_{12}$H$_{12}$ sample prepared are shown in Figure 3, together with those obtained from the LiBH$_4$-LiBF$_4$ system, while in Figure S5 the other LiBH$_4$-Li$_2$B$_{12}$H$_{12}$ samples are presented. In Figure 3a, the DRIFTS spectra of both LiBH$_4$-LiBF$_4$ and LiBH$_4$-Li$_2$B$_{12}$H$_{12}$ contain strong absorption bands at 2535 cm$^{-1}$ and 2480 cm$^{-1}$. The previously unidentified peaks in the LiBH$_4$-LiBF$_4$ spectrum can thus be associated with the presence of Li$_2$B$_{12}$H$_{12}$, which displays characteristic [B-H] stretching vibrations exactly at these wavenumbers [49–51]. Other similarities in the DRIFTS spectra of LiBH$_4$-LiBF$_4$ and LiBH$_4$-Li$_2$B$_{12}$H$_{12}$ are also observed. The comparison reveals that, in addition to the pronounced bands around 2500 cm$^{-1}$, smaller peaks between 3700 and 3000 cm$^{-1}$, at 1835 cm$^{-1}$ and at 1015 cm$^{-1}$, can also be explained by the presence of Li$_2$B$_{12}$H$_{12}$ [49–51]. Together with the XRD results discussed previously (Figure 1b), this illustrates that the prepared LiBH$_4$-LiBF$_4$ mixtures decompose to form crystalline LiF and likely amorphous closo-borate-related compounds with residual LiBH$_4$. 
LiBH₄ and Li₂B₁₂H₁₂ are included for comparison. In the DRIFTS, spectra peaks related to Li₂B₁₂H₁₂ or [Li₂B₁₂H₁₁+1/n]ₙ, further indicating that the highly conductivity phase data reported by Zhu et al. [38], e.g., 0.43 and 0.44 eV for the samples containing amorphous Li₂B₁₂H₁₂ or [Li₂B₁₂H₁₁+1/n]ₙ, further indicating that the highly conductivity phase formed during reaction with LiBF₄ could be amorphous Li₂B₁₂H₁₂ or a related compound. It is also good to note that the oxidative stability of 4.0 V determined for the LiBH₄-LiBF₄ mixture (Figure S7) is similar to the value reported for other closo-borate-related compounds [13,38,57].

This assertion is further investigated by comparing the XRD patterns of LiBH₄-LiBF₄ to that of LiBH₄-Li₂B₁₂H₁₂ shown in Figure 3b. Notably, the pattern collected for the LiBH₄-Li₂B₁₂H₁₂ contains characteristic diffraction peaks related to both starting compounds, which clearly demonstrates that both phases are still present and crystalline. This is different from the pattern of LiBH₄-LiBF₄, where, besides LiF, no other crystalline phase is detected. Note that a small peak indicative of Li₂B₁₂H₁₂ can be observed at 24 20° in the LiBH₄-LiBF₄ mixture pattern, strengthening the possibility that Li₂B₁₂H₁₂ has formed. However, in general it seems that the reaction between LiBF₄ and LiBH₄ leads to partial decomposition forming crystalline LiF and amorphous Li₂B₁₂H₁₂. Several studies have shown that the incorporation of Li₂B₁₂H₁₂ in the LiBH₄ matrix could lead to enhanced lithium-ion mobility [38,52–54]. Similar to the Li-B-H compound proposed by Zhu et al. [38], after reaction the LiBH₄-LiBF₄ mixture consists of residual LiBH₄ in contact with LiF and amorphous Li₂B₁₂H₁₂. Accordingly, the conductivity enhancement could originate from the in-situ formation of Li₂B₁₂H₁₂.

To further investigate this hypothesis, electrochemical impedance spectroscopy was used to determine the conductivity of LiBH₄-Li₂B₁₂H₁₂. Interestingly, in Figure 3c and Figure S6, it can be seen that the conductivity of LiBH₄-Li₂B₁₂H₁₂ (0.5 × 10⁻⁶ S cm⁻¹ at RT) is improved compared to both pristine LiBH₄ and Li₂B₁₂H₁₂ (2.5 × 10⁻⁸ S cm⁻¹ at RT) [55]. The improvement in ionic conductivity can be attributed again to a partial LiBH₄ decomposition, to form some amorphous Li₂B₁₂H₁₂ or [Li₂B₁₂H₁₁+1/n]ₙ and undecomposed LiBH₄ (see also next paragraph). Consequently, the improved cation mobility observed in the LiBH₄-LiBF₄ mixture prepared at 280 °C can be attributed to the formation of Li₂B₁₂H₁₂ and its interaction with residual LiBH₄, while the presence of LiF likely has a minor or no impact.

Table 1 shows the values of the activation energies (Eₐ) obtained by a linear fit of the Arrhenius plot. The Eₐ of the orthorhombic LiBH₄ is in good agreement with the calculated average value using all values reported in the literature by Gulino et al. [56], i.e., 0.75 ± 0.07 eV. The Eₐ obtained for the mixtures LiBH₄-LiBF₄ and LiBH₄-Li₂B₁₂H₁₂ are lower compared to that of pure LiBH₄, indicating a more facile conduction mechanism, in agreement with the higher Li-ion conductivity. In addition, these values are in agreement with the data reported by Zhu et al. [38], e.g., 0.43 eV and 0.44 eV for the samples containing amorphous Li₂B₁₂H₁₂ or [Li₂B₁₂H₁₁+1/n]ₙ, further indicating that the highly conductivity phase formed during reaction with LiBF₄ could be amorphous Li₂B₁₂H₁₂ or a related compound. It is also good to note that the oxidative stability of 4.0 V determined for the LiBH₄-LiBF₄ mixture (Figure S7) is similar to the value reported for other closo-borate-related compounds [13,38,57].
Table 1. Activation energies (eV) calculated from a linear plot of \(\ln(\sigma T)\) and 1000/T of the EIS data reported in Figure 3c. The standard deviation is based on the 99% confidence interval of the linear fit.

| Sample                        | \(E_a\) (eV) | Pre-Exponential Factor |
|-------------------------------|--------------|------------------------|
| LiBH4 (orthorhombic)          | 0.68 (±0.05) | 15 (±2)                |
| LiBH4-LiBF4 (280 °C)          | 0.44 (±0.01) | 11.1 (±0.3)            |
| LiBH4-Li2B12H12 (280 °C)      | 0.41 (±0.01) | 11.8 (±0.4)            |

3.3. Alternative Decomposition Pathway

Although it seems clear that the formation of a Li\(_2\)B\(_{12}\)H\(_{12}\)-like compound is responsible for the enhancement in ionic conductivity for LiBH\(_4\)-LiBF\(_4\), this could not explain the behaviour of the system completely. Surprisingly, comparison of the respective conductivities of LiBH\(_4\)-Li\(_2\)B\(_{12}\)H\(_{12}\) and LiBH\(_4\)-LiBF\(_4\) mixtures (Figure 3c) illustrates that the latter has the highest conductivity. If the conductivity enhancement is solely related to the formation of Li\(_2\)B\(_{12}\)H\(_{12}\), this would not be the case. However, as our structural analysis did not yield any other compounds or phases, the unidentified conductive phase is likely very similar to amorphous Li\(_2\)B\(_{12}\)H\(_{12}\).

Interestingly, it has been proposed that the combination of different closo-borate complex anions could lead to improved ion transport in metal hydride-based ion conductors [38,54,58,59]. Toyama et al. prepared complex hydrides containing three closo-borate-type anions, e.g., [B\(_{12}\)H\(_{12}\)]\(^{2-}\), [B\(_{11}\)H\(_{11}\)]\(^{2-}\) and [B\(_{10}\)H\(_{12}\)]\(^{2-}\), from LiBH\(_4\) and B\(_{10}\)H\(_{14}\) as the starting materials [54]. They observed that with increasing amount of [B\(_{11}\)H\(_{11}\)]\(^{2-}\) and [B\(_{10}\)H\(_{10}\)]\(^{2-}\), ionic conductivity improves. Remarkably, under the reaction conditions used during our synthesis, pyrolysis of B\(_2\)H\(_6\) to B\(_{10}\)H\(_{14}\) can occur [60,61]. The in-situ generated B\(_{10}\)H\(_{14}\) can then react with LiBH\(_4\) to form several closo-borate anions, similar to the synthesis performed by Toyama et al. [54] The reaction scheme discussed here is presented in Figure 4.

![Figure 4](image-url)  
**Figure 4.** Reaction scheme proposed for the synthesis of LiBH\(_4\)-LiBF\(_4\) solid solutions constituted of multiple closo-borate phases. (a) Reaction between LiBF\(_4\) and LiBH\(_4\) yielding unstable LiBH\(_3\)F followed by (b) decomposition to form LiF and B\(_2\)H\(_6\). (c) Pyrolysis of B\(_2\)H\(_6\) generating B\(_{10}\)H\(_{14}\) in-situ. (d) Reaction of B\(_{10}\)H\(_{14}\) with LiBH\(_4\) forming several lithium closo-borates. Reaction stoichiometry not taken in account in this overview.

The conductivity enhancement achieved in decomposed LiBH\(_4\) in the presence of LiBF\(_4\) that forms multiple closo-borate phases would be higher than expected for a mixture consisting solely of LiBH\(_4\) and Li\(_2\)B\(_{12}\)H\(_{12}\). Consequently, the reaction process described in Figure 4 provides a possible explanation for an increased conductivity in LiBH\(_4\)-LiBF\(_4\) compared to LiBH\(_4\)-Li\(_2\)B\(_{12}\)H\(_{12}\) through the introduction of different lithium closo-borate compounds. A detailed investigation of this hypothesis will require solid-state \(^{11}\)B-MAS-NMR measurements, which is the subject of an ongoing study.

Another explanation for the enhanced conductivity could be the formation of highly conductive interfaces between the amorphous LiBH\(_4\)-Li\(_2\)B\(_{12}\)H\(_{12}\) solid solution and the in-situ formed nanocrystalline LiF particles. The melting of the undecomposed LiBH\(_4\)
will likely lead to strong interface interactions with LiF and Li$_2$B$_{12}$H$_{12}$, thereby enhancing the ionic conductivity of the composite. Recent studies by Yan and Zhao reported on similar systems in which LiBH$_4$ xNH$_3$ was stabilized in an amorphous (molten-like) state on (inert) Li$_2$O nanoparticles that were formed in-situ via a decomposition pathway [62,63]. Even in compounds with a high weight percentage (78 wt%) of the non-conducting metal oxide, a high room temperature conductivity has been obtained. Likewise, in our case, the amorphous LiBH$_4$-Li$_2$B$_{12}$H$_{12}$ phase could benefit from the presence of LiF particles, for example by stabilizing the amorphous form or even by beneficial interface interactions, thereby forming a conductive space-charge layer.

4. Conclusions

In conclusion, the impact of LiBF$_4$ addition on the ionic transport in LiBH$_4$ was explored by correlating the physical properties and ionic conductivity of LiBH$_4$-LiBF$_4$ mixtures. After synthesis at 280 °C, the LiBH$_4$-LiBF$_4$ sample contains LiF and amorphous lithium closo-borate, such as Li$_2$B$_{12}$H$_{12}$. The presence of this phase is in line with the fact that partial substitution of the BH$_4$ anion in LiBH$_4$ with BF$_4$ anion yields unstable LiBH$_3$F, which decomposes into LiF and B$_2$H$_6$. The latter may react further to form B$_{10}$H$_{14}$, which in turn leads to the formation of [B$_{12}$H$_{12}$]$^{2-}$, [B$_{11}$H$_{11}$]$^{2-}$ and [B$_{10}$H$_{10}$]$^{2-}$ complex anions by reacting with excess LiBH$_4$.

Interestingly, a conductivity enhancement of over two orders of magnitude (to 0.9 x 10$^{-5}$ S cm$^{-1}$ at 30 °C) is achieved for the LiBH$_4$-LiBF$_4$ mixture reacted at 280 °C. The formation of LiF does not seem to lead to any improvement in conductivity, while the presence of solely Li$_2$B$_{12}$H$_{12}$ leads to a minor enhancement. Thus, the improved lithium-ion mobility in LiBH$_4$ through decomposition reaction with LiBF$_4$ may be attributed to the formation of a lithium closo-borate-like phase, i.e., amorphous Li$_2$B$_{12}$H$_{12}$ or [Li$_2$B$_{12}$H$_{11}$+1/n$]^n_-$.

The insights provided in this work highlight the versatility of LiBH$_4$ as a promising solid-state electrolyte, considering that several different strategies can be exploited to increase the ionic conductivity of the compound. Our work demonstrates that decomposition reactions is a promising approach to enhancing ionic conductivity in LiBH$_4$. This approach might be applicable to other complex hydrides and other classes of inorganic solid electrolytes.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27072187/s1, Table S1: Overview of the sample compositions, Figure S1: Nyquist plots of two exemplary samples, Figure S2: Bode plots of two exemplary samples, Figures S3 and S4: conductivity data of LiBH$_4$-LiBF$_4$ samples prepared with different compositions and under varying synthesis conditions, Figures S5 and S6: characterization of LiBH$_4$-Li$_2$B$_{12}$H$_{12}$ samples with varying composition and Figure S7: a linear sweep voltammogram of LiBH$_4$-LiBF$_4$.

**Author Contributions:** Conceptualization, P.N. and L.M.d.K.; formal analysis, P.N., L.M.d.K. and D.B.; data curation, L.M.d.K., P.N. and D.B.; writing—review and editing, P.N., L.M.d.K., V.G. and D.B.; project administration, P.N. All authors have read and agreed to the published version of the manuscript.

**Funding:** Dutch Research Council (NWO) Materials for sustainability Mat4Sus (739.017.009) grant.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available in supplementary material.

**Acknowledgments:** The authors greatly appreciate the fruitful discussions with Petra de Jongh, Jan Willem de Rijk is acknowledged for technical support.

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

1. Lach, J.; Wröbel, K.; Wröbel, J.; Czerwiński, A. Applications of carbon in rechargeable electrochemical power sources: A review. 
Molecules 2022, 27, 2187. [CrossRef]

2. Li, C.; Wang, Z.Y.; He, Z.J.; Li, Y.J.; Mao, J.; Dai, K.H.; Yan, C.; Zheng, J.C. An advance review of solid-state battery: Challenges, 
progress and prospects. Sustain. Mater. Technol. 2021, 29, e00297. [CrossRef]

3. Tarascon, J.M.; Armand, M. Issues and challenges facing rechargeable lithium batteries. 
Nature 2001, 414, 359–367. [CrossRef] [PubMed]

4. Janek, J.; Zeier, W.G. A solid future for battery development. 
Nat. Energy 2016, 1, 16141. [CrossRef]

5. Manthiram, A.; Yu, X.; Wang, S. Lithium battery chemistries enabled by solid-state electrolytes. 
Nat. Rev. Mater. 2017, 2, 16103. [CrossRef]

6. Thangadurai, V.; Narayanan, S.; Pinzaru, D. Garnet-type solid-state fast Li ion conductors for Li batteries: Critical review. 
Chem. Soc. Rev. 2014, 43, 4714–4727. [CrossRef]

7. Subramanian, K.; Alexander, G.V.; Karthik, K.; Indu, M.S.; Sreejith, O.V.; Viswanathan, R.; Narayanasamy, J.; Murugan, R. 
A brief review of recent advances in garnet structured solid electrolyte based lithium metal batteries. 
J. Energy Storage 2021, 33, 102157. [CrossRef]

8. Thangadurai, V.; Weppner, W. Recent progress in solid oxide and lithium ion conducting electrolytes research. 
Ionics 2006, 12, 81–92. [CrossRef]

9. Itoh, M.; Inaguma, Y.; Jung, W.H.; Chen, L.; Nakamur, T. High lithium ion conductivity in the perovskite-type compounds 
Li$_2$Li$_2$TiO$_3$ (ln=La,Pr,Nd,Sm). Solid State Ion. 1994, 70–71, 203–207. [CrossRef]

10. Seino, Y.; Ota, T.; Takada, K.; Hayashi, A.; Tatsumisago, M. A sulphide lithium super ion conductor is superior to liquid 
ion conductors for use in rechargeable batteries. Energy Environ. Sci. 2014, 7, 627–631. [CrossRef]

11. Rangasamy, E.; Liu, Z.; Gobet, M.; Pilar, K.; Sahu, G.; Zhou, W.; Wu, H.; Greenbaum, S.; Liang, C. An iodide-based Li$_2$P$_2$S$_4$ 
superionic conductor. J. Am. Chem. Soc. 2015, 137, 1384–1387. [CrossRef] [PubMed]

12. Matsuo, M.; Nakamori, Y.; Orimo, S.I.; Maekawa, H.; Takamura, H. Lithium superionic conduction in lithium borohydride 
accompanied by structural transition. Appl. Phys. Lett. 2007, 91, 2–5. [CrossRef]

13. Lu, Z.; Ciucci, F. Metal Borohydrides as Electrolytes for Solid-State Li, Na, Mg, and Ca Batteries: A First-Principles Study. 
Chem. Mater. 2017, 29, 9308–9319. [CrossRef]

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

15. Kim, S.; Oguchi, H.; Toyama, N.; Orimo, S.I. Interfacial stability between LiBH$_4$-based complex hydride solid electrolytes 
and Li metal anode for all-solid-state Li batteries. J. Power Sour. 2019, 436, 226821. [CrossRef]

16. Duchène, L.; Remhof, A.; Hagemann, H.; Battaglia, C. Status and prospects of borohydride electrolytes for all-solid-state batteries. 
Energy Storage Mater. 2020, 25, 782–794. [CrossRef]

17. Verdal, N.; Udovic, T.J.; Stavila, V.; Tang, W.S.; Rush, J.J.; Skripov, A.V. Anion reorientations in the superionic conducting phase 
of Na$_2$B$_2$H$_6$-Li$_2$H$_4$. J. Phys. Chem. C 2014, 118, 17483–17489. [CrossRef]

18. Tang, W.S.; Matsuo, M.; Wu, H.; Stavila, V.; Zhou, W.; Talin, A.A.; Solominin, A.V.; Skoryunov, R.V.; Babanova, O.A.; 
Skripov, A.V.; et al. Liquid-Like Ionic Conduction in Solid Lithium and Sodium Monocarba-closo-Decaborates Near or at Room 
Temperature. Adv. Energy Mater. 2016, 6, 1502237. [CrossRef]

19. Gulino, V.; Brighi, M.; Murgia, F.; Ngene, P.; De Jongh, P.; Cerny, R.; Baricco, M. Room temperature Solid-State Lithium-ion 
Battery using LiBH$_4$-Mo composite Electrolyte. ACS Appl. Energy Mater. 2021, 4, 1228–1236. [CrossRef]

20. Zettl, R.; De Kort, L.; Komotz, M.; Wilkening, H.M.; De Jongh, P.E.; Ngene, P. Combined Effects of Anion Substitution and 
Nanoconfinement on the Ionic Conductivity of Li-Based Complex Hydrides. J. Phys. Chem. C 2020, 124, 2806–2816. [CrossRef]

21. De Kort, L.M.; Harmel, J.; De Jongh, P.E.; Ngene, P. The effect of nanoscaffold porosity and surface chemistry on the Li-ion 
conductivity of LiBH$_4$-Li$_2$O metal oxide nanocomposites. J. Mater. Chem. A 2020, 8, 20687–20697. [CrossRef]

22. De Kort, L.M.; Gulino, V.; De Jongh, P.E.; Ngene, P. Ionic conductivity in complex metal hydride-based nanocomposite materials: 
The impact of nanostructuring and nanocomposite formation. J. Alloys Compd. 2021, 901, 163474. [CrossRef]

23. Oguchi, H.; Matsuo, M.; Hummelshej, J.S.; Vegge, T.; Norskov, J.K.; Sato, T.; Miura, Y.; Takamura, H.; Maekawa, H.; Orimo, S. 
Experimental and computational studies on structural transitions in the LiBH$_4$-Li$_2$ metallophosphide system. 
Appl. Phys. Lett. 2009, 94, 2–5. [CrossRef]

24. Matsuo, M.; Takamura, H.; Maekawa, H.; Li, H.-W.; Orimo, S. Stabilization of lithium superionic conduction phase and 
enhancement of conductivity of LiBH$_4$ by Li$_2$O addition. Appl. Phys. Lett. 2009, 94, 084103. [CrossRef]

25. Maekawa, H.; Matsuo, M.; Takamura, H.; Ando, M.; Noda, Y. Halide-Stabilized LiBH$_4$, a Room-Temperature Lithium Fast-Ion 
Conductor. J. Am. Chem. Soc. 2009, 131, 894–895. [CrossRef]

26. Rude, L.H.; Groppo, E.; Arnberg, L.M.; Ravnbaek, D.B.; Malmkjaer, R.A.; Filinchuk, Y.; Baricco, M.; Besenbacher, F.; Jensen, T.R. 
Iodide substitution in lithium borohydride, LiBH$_4$-LiI. J. Alloys Compd. 2011, 509, 8299–8305. [CrossRef]

27. Matsuo, M.; Remhof, A.; Martelli, P.; Caputo, R.; Ernst, M.; Miura, Y.; Sato, T.; Oguchi, H.; Maekawa, H.; Takamura, H. Complex 
hydrides with (BH$_4^-$) and (NH$_4^+$) anions as new lithium fast-ion conductors. J. Am. Chem. Soc. 2009, 131, 16389–16391. [CrossRef]

28. Yan, Y.; Kühnel, R.S.; Remhof, A.; Duchène, L.; Reyes, E.C.; Rentsch, D.; Lodziana, Z.; Battaglia, C. A Lithium Amidoborohydride 
Solid-State Electrolyte with Lithium-Ion Conductivities Comparable to Liquid Electrolytes. Adv. Energy Mater. 2017, 7, 1700294. [CrossRef]
29. Gulino, V.; Dematteis, E.M.; Corno, M.; Palumbo, M.; Baricco, M. Theoretical and Experimental Studies of LiBH₄-LiBr Phase Diagram. *ACS Appl. Energy Mater.* 2021, 4, 7327–7337.

30. Gulino, V.; Brighi, M.; Dematteis, E.M.; Murgia, F.; Nervi, C.; Cerny, R.; Baricco, M. Phase Stability and Fast Ion Conductivity in the Hexagonal LiBH₄-LiBr-LiCl Solid Solution. *Chem. Mater.* 2019, 31, 5133–5144. [CrossRef]

31. Rude, L.H.; Filso, U.; D’Anna, V.; Spyratou, A.; Richter, B.; Hino, S.; Zavorotynska, O.; Baricco, M.; Sorby, M.H.; Hauback, B.C. Hydrogen-fluorine exchange in NaBH₄-NaBF₄. *Phys. Chem. Chem. Phys.* 2013, 15, 18185–18194. [CrossRef] [PubMed]

32. Yin, L.; Wang, P.; Fang, Z.; Cheng, H. Thermodynamically tuning LiBH₄ by fluorine anion doping for hydrogen storage: A density functional study. *Chem. Lett.* 2008, 450, 318–321. [CrossRef]

33. Corno, M.; Pinatel, U.; Ugliengo, P.; Baricco, M. A computational study on the effect of fluorine substitution in LiBH₄. *J. Alloy. Compd.* 2011, 509, S679–S683. [CrossRef]

34. Heyn, R.H.; Saldan, I.; Sorby, M.H.; Frommen, C.; Arstad, B.; Bougza, A.M.; Fjellvåg, H.; Hauback, B.C. Structural and spectroscopic characterization of potassium fluoroborohydrides. *Phys. Chem. Chem. Phys.* 2013, 15, 11226–11230. [CrossRef]

35. Saldin, VI.; Sukhovey, V.V.; Savchenko, N.N.; Slobodyuk, A.B.; Ignatieva, L.N. Thermal studies of sodium tetrahydroborate–potassium tetrafluoroborate mixtures. *Russ. J. Inorg. Chem.* 2016, 61, 630–637. [CrossRef]

36. Richter, B.; Ravnsvæk, D.B.; Sharma, M.; Spyratou, A.; Hagemann, H.; Jensen, T.R. Fluoride substitution in LiBH₄: Destabilization and decomposition. *Phys. Chem. Chem. Phys.* 2017, 19, 30175–30185. [CrossRef]

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

38. Zhu, M.; Pang, Y.; Lu, F.; Shi, X.; Yang, J.; Zheng, S. In Situ Formed Li-B-H Complex with High Li-Ion Conductivity as a Potential Solid Electrolyte for Li Batteries. *ACS Appl. Mater. Interfaces* 2019, 11, 14136–14141. [CrossRef]

39. 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]

40. Zavorotynska, O.; Corno, M.; Damin, A.; Spoto, G.; Ugliengo, P.; Baricco, M. Vibrational properties of MBH₄ and MBF₄ crystals (M = Li, Na, K): A combined DFT, infrared, and Raman study. *J. Phys. Chem. C* 2011, 115, 18890–18890. [CrossRef]

41. D’Anna, V.; Spyratou, A.; Sharma, M.; Hagemann, H. FT-IR spectra of inorganic borohydrides. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 2014, 128, 902–906. [CrossRef] [PubMed]

42. Filinchuk, Y.; Hagemann, H. Structure and properties of NaBH₄·2H₂O and NaBH₄. *Eur. J. Inorg. Chem.* 2008, 112, 3217–3233. [CrossRef]

43. Rahman, C.V. The vibration spectrum of lithium fluoride and the evaluation of its specific heat. *Proc. Indian Acad. Sci. Sect. A* 1962, 55, 131–152. [CrossRef]

44. Breuer, S.; Pregartner, V.; Lunghammer, S.; Wilkening, H.M.R. Dispersed Solid Conductors: Fast Interface Li-Ion Dynamics in Nanostructured LiF and LiF·γ-Al₂O₃ Composites. *J. Phys. Chem. C* 2013, 123, 5222–5230. [CrossRef]

45. Li, C.; Gu, L.; Maier, J. Enhancement of the Li conductivity in LiF by introducing glass/crystal interfaces. *Adv. Funct. Mater.* 2012, 22, 1145–1149. [CrossRef]

46. Miyazaki, R.; Karahashi, T.; Kumatani, N.; Noda, Y.; Ando, M.; Takamura, H.; Matsuo, M.; Orimo, S.I.; Maekawa, H. Room temperature lithium fast-ion conduction and phase relationship of Li stabilized LiBH₄. *Solid State Ion.* 2011, 192, 143–147. [CrossRef]

47. Sveinbjörnsson, D.; Myrdal, J.S.; Blanchard, D.; Bentzen, J.J.; Hirata, T.; Mogensen, M.B.; Norby, P.; Orimo, S.I.; Vegge, T. Effect of Heat Treatment on the Lithium Ion Conduction of the LiBH₄-LiSolid Solution. *J. Phys. Chem. C* 2013, 117, 3249–3257. [CrossRef]

48. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. Sect. A* 1976, 32, 751–767. [CrossRef]

49. Muettterties, E.L.; Merrifield, R.E.; Miller, H.C.; Knoth, W.H.; Downing, J.R. Chemistry of Boranes. III. 1 The Infrared and Raman Spectra of Bi2HfN 4 (12-N)2-. *J. Hydrogen Energy 2015*, 40, 12721–12726. [CrossRef]

50. Sharma, M.; Sethio, D.; D’Anna, V.; Hagemann, H. Theoretical study of Bi2HfN 4 (12-N)2-. *Int. J. Hydrogen Energy* 2015, 40, 12721–12726. [CrossRef]

51. Jensen, S.R.; Paskevicius, M.; Hansen, B.R.; Jakobsen, A.S.; Müller, K.T.; White, J.L.; Allendorf, M.D.; Stavila, V.; Skibsted, J.; Jensen, T.R. Hydrogen properties of lithium and sodium hydride–closo-borate, [BiO(H)O]2- and [Bi2H12]2-, composites. *Phys. Chem. Chem. Phys.* 2018, 20, 16266–16275. [CrossRef] [PubMed]

52. Sadikin, Y.; Brighi, M.; Schouwink, P.; Cerny, R. Superionic Conduction of Sodium and Lithium in Anion-Mixed Hydrotorodes Na₅BH₄B₂H₁₂ and (Li₇Na₄O₃)BH₂B₁₂H₁₁. *Adv. Energy Mater.* 2015, 5, 1501016. [CrossRef]

53. Sadikin, Y.; Skoryunov, R.V.; Babanova, O.A.; Solonin, A.V.; Lodziana, Z.; Brighi, M.; Skripov, A.V.; Cerny, R. Anion Disorder in K₃BH₂B₁₂H₁₁ and Its Effect on Cation Mobility. *J. Phys. Chem. C* 2017, 121, 5503–5514. [CrossRef]

54. Toyama, N.; Kim, S.; Oguchi, H.; Sato, T.; Takagi, S.; Tajawa, M.; Nogami, G.; Orimo, S.I. Lithium ion conductivity of complex hydrides incorporating multiple closo-type complex anions. *J. Energy Chem.* 2019, 38, 84–87. [CrossRef]

55. Friedricks, O.; Remhof, A.; Hwang, S.-J.; Züttel, A. Role of Li₂B₁₂H₂₃ for the Formation and Decomposition of LiBH₄. *Chem. Mater.* 2010, 22, 3265–3268. [CrossRef]

56. Gulino, V.; Wolczyk, A.; Golov, A.A.; Eremin, R.A.; Palumbo, M.; Nervi, C.; Blatov, V.A.; Proserpio, D.M.; Baricco, M. Combined DFT and geometrical–topological analysis of Li-ion conductivity in complex hydrides. *Inorg. Chem. Front.* 2020, 7, 3115–3125. [CrossRef]
57. Asakura, R.; Reber, D.; Duchêne, L.; Payandeh, S.; Remhof, A.; Hagemann, H.; Battaglia, C. 4 V Room-Temperature All-Solid-State Sodium Battery Enabled By a Passivating Cathode/Hydroborate Solid Electrolyte Interface. *Energy Environ. Sci.* 2020, 13, 5048–5058. [CrossRef]

58. Yoshida, K.; Sato, T.; Unemoto, A.; Matsuo, M.; Ikeshoji, T.; Udovic, T.J.; Orimo, S.I. Fast sodium ionic conduction in Na2B10H10-Na2B12H12 pseudo-binary complex hydride and application to a bulk-type all-solid-state battery. *Appl. Phys. Lett.* 2017, 110, 103901. [CrossRef]

59. Duchêne, L.; Kühnel, 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]

60. Polak, R.J.; Obenland, C. Pyrolysis of diborane. *Ind. Eng. Chem. Prod. Res. Dev.* 1964, 3, 234–238.

61. Dobson, J.; Maruca, R.; Schaeffer, R. Studies of Boranes. XXX. Reaction of Pentaborane (9) with Diborane (6). Isolation of Several New Boron Hydrides. *Inorg. Chem.* 1970, 9, 2161–2166. [CrossRef]

62. Zhao, W.; Zhang, R.; Li, H.; Zhang, Y.; Wang, Y.; Wu, C.; Yan, Y.; Chen, Y. Li-Ion Conductivity Enhancement of LiBH4·xNH3 with in Situ Formed Li2O Nanoparticles. *ACS Appl. Mater. Interfaces* 2021, 13, 31635–31641. [CrossRef] [PubMed]

63. Yan, Y.; Grinderslev, J.B.; Lee, Y.S.; Jørgensen, M.; Cho, Y.W.; Černý, R.; Jensen, T.R. Ammonia-assisted fast Li-ion conductivity in a new hemiammine lithium borohydride, LiBH4·1/2NH3. *Chem. Commun.* 2020, 56, 3971–3974. [CrossRef] [PubMed]