Journal of Alloys and Compounds 895 (2021) 162659

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Metal hydroborates: From hydrogen stores to solid electrolytes

Radovan Černý*, Fabrizio Murgia, Matteo Brighi

Laboratory of Crystallography, DQMP, University of Geneva, 24 quai E. Ansermet, CH-1211 Geneva, Switzerland

A R T I C L E I N F O

Article history:
Received 4 October 2021
Received in revised form 29 October 2021
Accepted 4 November 2021
Available online 8 November 2021

Keywords:
Hydroborate
Hydrogen storage
Solid electrolyte
Carboranate

A B S T R A C T

The last twenty years of an intense research on metal hydroborates as solid hydrogen stores and solid electrolytes are reviewed. It is shown that from the most promising application in hydrogen storage due to their high gravimetric and volumetric capacities, the focus has moved to solid electrolytes due to high cation mobility in disordered structures with rotating or tumbling anions-hydroborate clusters. Various strategies of overcoming the strong covalent bonding of hydrogen in hydroborates for hydrogen storage and disordering their structures at room temperature for solid electrolytes are discussed. The important role of crystal chemistry and crystallography knowledge in material design can be read in the cited literature.

1. Introduction

Hydroborates are anions containing hydrogen bonded to boron. By substituting one or more boron atom with a carbon, the carboranates are obtained [1], which we will also call hydroborates unless specified. They are also sometimes referred to as "boranes" and "carboranes"; this term is, however, used for neutral molecules according to IUPAC [2]. Inorganic hydroborates are salts or coordination compounds where one of the ligands is the hydroborate. The bonding in boron clusters of boranes and hydroborates was explained by Lipscomb [3] using the concept of a three-electron-two-center bond. The concept was further developed in the Polyhedral Skeletal Electron Pair theory (PSEPT) also known as Wade–Mingos rules based on a molecular orbital treatment of the bonding [4,5]. The naming of the boron and hydroborate clusters, used in this review, follows the Wade–Mingos rules: (i) the number of vertices in the polyhedral boron cluster, *i.e.*, dodecaborate for $B_{12}H_{12}^{2-}$ anion, and (ii) the name that describes the topology of the polyhedral cluster, *i.e.*, *closo*-, *nido*- and *arachno*-borates for all polyhedron vertices occupied by boron, and one or two boron atoms missing, respectively.

Inorganic hydroborates were studied as fuels for military applications [6], reducing agents in organic syntheses [7], weakly coordinating anions in catalysis [8,9], for the delivery of ^{10}B for Boron Neutron Capture Therapy (BNCT) [10], as nanocarriers for the delivery of various chemotherapy drugs [11], magnetic resonance imaging (MRI) agents [12], liquid electrolytes [13], and more recently as hydrogen stores [14] and solid ionic conductors [15,16]. We will concentrate in this review to the last two applications.

2. Hydrogen storage

Inorganic salts based on the smallest hydroborate BH_4^- are correctly called tetrahydroborates but commonly as borohydrides [17,18]. Their usage as solid-state hydrogen stores, owing to the high hydrogen densities (up to 24.5 wt% in NH_4BH_4), was proposed by Schlapbach and Züttel [19], and initiated extensive efforts in the discovery, characterization and the understanding of novel single-, double- and triple-cation borohydrides [20]. Only few metal borohydrides, but of high technological importance, have been known before, such as $LiBH_4$, $NaBH_4$, $Al(BH_4)_3$, $Be(BH_4)_2$ and $U(BH_4)_4$, resulting from the search for boron and hydrogen-rich or volatile uranium compounds with the Manhattan project. Results of this wartime research were declassified and published in 1953 [21]. Salts based on bigger hydroborate clusters such as the dodecaborate $B_{12}H_{12}^{2-}$ anion are too stable for the hydrogen storage applications and are generally considered as hydrogen sinks.

The first application of a metal borohydride as a hydrogen store dates back to World War II, when the hydrolysis of a $NaBH_4$ suspension was used in hydrogen production for weather balloons. Hydrogen-rich lithium borohydride, $LiBH_4$ was discovered in 1940 [22], but its structural characterization had to wait till 2002 [23,24]. The compound was studied as source of hydrogen [25], motivated by a successful cycling of titanium-catalyzed alanate $NaAlH_4$ between 180 and 210 °C [26]. The advantage of metal borohydrides for

---

* Corresponding author.
E-mail addresses: Radovan.Cerny@unige.ch (R. Černý), Fabrizio.Murgia@unige.ch (F. Murgia), Matteo.Brighi@unige.ch (M. Brighi).

https://doi.org/10.1016/j.jallcom.2021.162659
0925-8388/

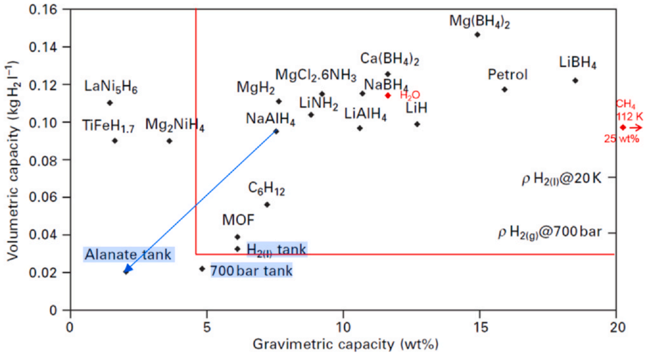

Fig. 1. Volumetric and gravimetric hydrogen storage capacity of selected hydrogen stores. Modified from [28]. Red lines refer to minimal capacities fixed by US Department of Energy as targets for practical application.

hydrogen storage compared to metal hydrides such as $LaNi_5H_6$ is their high volumetric and gravimetric hydrogen storage capacities (Fig. 1). However, due to covalent B-H bonding, the hydrogen storage is usually non-reversible. Several ways have been investigated to overcome this difficulty (for recent overview, see [27]).

2.1. Thermolysis

Thermolysis denotes the decomposition of a substance upon heat treatment. Monometallic borohydrides may release hydrogen and, in some cases, also diborane, B_2H_6, during the formation of higher metal hydroborates, metal borides or even pure boron upon thermolysis. Physical conditions such as partial pressures and temperatures also influence the mechanism of decomposition, *i.e.*, the decomposition pathway.

Direct thermal decomposition of the most hydrogen-rich borohydride, $LiBH_4$, leads to the release of 13.1 wt% hydrogen according to.

$$LiBH_4(s) \rightarrow LiH(s) + B(s) + 3/2H_2(g) \quad (1)$$

The enthalpy and entropy of the decomposition reaction (1) have been measured as $\Delta H_{dec} = 66.6–74\ kJ\ mol^{-1}\ H_2$ and $\Delta S_{dec} = 97.3–115\ J\ K\ mol^{-1}\ H_2$, respectively, using van't Hoff method (upper limit) and calorimetry (lower limit) [29,30]. Partial dehydrogenation can also occur, forming lithium *closo*-hydroborate, $Li_2B_{12}H_{12}$, *via* less endothermic reaction, with a calculated reaction enthalpy of 56 kJ mol^{-1} H_2 [31] according to.

$$LiBH_4(s) \rightarrow 5/6\ LiH(s) + 1/12\ Li_2B_{12}H_{12}(s) + 13/12H_2(g) \quad (2)$$

The formation of $LiBH_4$ from the elements has also been attempted, which is equivalent to re-hydrogenation or reversing reaction (1), however, temperatures as high as 500 °C and hydrogen gas pressures of 180 bar has been used and a complete reaction was not achieved [32]. The hydrogen desorption and absorption has been studied also for many other monometallic borohydrides, such as $NaBH_4$, KBH_4, $Mg(BH_4)_2$, $Ca(BH_4)_2$, facing similar problems as $LiBH_4$ (for more details, see [27]). As for the molecular metal borohydrides, such as $Al(BH_4)_3$, $Ti(BH_4)_3$, or $Zr(BH_4)_4$, they first sublime at low temperatures. In the gas phase, the compounds tend to release diborane *via* polymerization [33,34]. The re-hydrogenation may be promoted by reaction between an ionic hydride and diborane resulting in a borohydride [35].

The multi-metallic borohydrides $M_xM'_y(BH)_z$ usually decompose *via* splitting into the individual borohydrides. The thermolysis then continue *via* their usual decomposition routes when either the thermal stability of the products is comparable or the less stable multi-metallic borohydride immediately decomposes at higher temperature than monometallic compounds [36]. An inversed empirical correlation between the decomposition temperature of metal borohydrides and metal Pauling electronegativity was suggested in 1955 [37] and has been further developed into the correlation with ionic potential of the metal [38]. In the multi-metallic borohydrides it means that the more electronegative metal will control the stability of the borohydride by destabilization of the BH_4^- anion. It is similar to alloying a stable hydride such as LaH_3 with an unstable one, such as $NiH_{0.8}$ resulting in $LaNi_5H_6$, with the stability favorable for reversible hydrogen storage. The concept is further illustrated on bimetallic borohydrides with high difference in electronegativity of metals leading to complex anions such as $[Sc(BH_4)_4]^-$, $[Zn(BH_4)_3]^-$ or $[Al(BH_4)_4]^-$ where the decomposition temperature practically does not vary with the less electronegative metal [39]. In some cases, the multi-metallic borohydrides form eutectic melting mixture, and kinetic or thermodynamic (chemical) effects lower the decomposition temperature of the eutectic [40].

2.2. Catalysis

Additives to borohydrides may significantly change the reaction mechanism of their decomposition. The addition of small amounts of additives in the range of a few mol% has been considered for possible catalytic effects and will be discussed in this chapter, while larger amounts of additives may react with the metal borohydrides and form reactive hydride composites, which will be the object of the next chapter.

Catalysis has been widely investigated in an attempt to overcome kinetic barriers and reduce the activation energy for hydrogen release and uptake in metal borohydrides. Mainly lithium and magnesium borohydrides have been examined systematically. A range of transition metals have been considered as additives in MBH_4 systems, *e.g.*, Sc, Ti, V, Cr with reported decreases of ~ 50 °C in their decomposition temperatures [41]. The non-metallic additives such as carbon, sulfur, various hydrides, oxides, halides and borides have been tested too, but generally speaking, their effect is observed rather when present in higher content, *i.e.*, as reactive mixtures than as catalyzers (see [27] and references therein). Overall, no real catalyst for B—H bond breaking or formation has been identified.

2.3. Reactive mixtures

Larger amounts of additives may lead to stoichiometric reactions among the components in a system, denoted Reactive Hydride Composites (RHC). This approach, known already from metal amides, was later on extended to borohydrides [42,43]. Many two component reactions between metal borohydrides and metal hydrides, alanates or metals have been investigated leading to lower reaction enthalpies than for borohydride thermolysis (see [27] and references therein) as proposed by a computational screening in [44]. As an example we may give the following reaction [45].

$$LiBH_4(s) + 1/2\ MgH_2(s) \rightarrow LiH(s) + 1/2\ MgB_2(s) + 2H_2(g) \quad (3)$$

with reaction enthalpy lowered to 46 kJ mol^{-1} H_2 compared to reaction (1) and still important gravimetric hydrogen capacity of 11.6 wt% instead of 13.4 wt% of the reaction (1). The RHC approach seems to be the most promising approach for enhancing the hydrogen storage performance of metal hydrides allowing their onboard application. The thermodynamics and kinetics of the RHC is improved through the metathesis reaction that occurred between the hydrides [46].

Hydrogen can be released from borohydrides also in a reaction with water (hydrolysis) [47]. An advantage is that half of the released hydrogen originates from the water and increases the hydrogen capacity of the system. The ideal reaction for $NaBH_4$ hydrolysis.

$$NaBH_4(aq) + 2H_2O(l) \rightarrow NaBO_2(s) + 4H_2(g) \qquad (4)$$

can theoretically release 10.8 wt% hydrogen, but is limited by the lower concentration of $NaBH_4$ in the water solution, in order to limit the rapid precipitation of $NaBO_2$ that may block the hydrolysis reaction. A significant handicap of the hydrolysis, an excellent RT source of hydrogen, is that the dehydrogenated product is typically a stable metal oxide, *i.e.*, the off-board regeneration is required to reverse the hydrolysis reaction.

2.4. Physical activation

Variation of physical parameters such as temperature or pressure is used for hydrogen release from hydrides, for example in thermolysis. Another physical parameter that may be tuned is a size of hydride crystalline domains. Decreasing the domain size down to nanoparticles facilitate the release and uptake of hydrogen from borohydrides and enhance reaction kinetics due to increased particle surface-area/volume ratio and modified crystal structure in the grain boundaries [48,49]. The most widely employed technique for the preparation of hydride nanoparticles is the mechanical treatment such as high-energy ball-milling, also used as mechanochemistry for borohydride synthesis [50]. Nanoparticles of the size below 100 nm are easily obtained, but the ball-milled product may be contaminated with trace materials from the milling vials and balls [51].

Nano-sized materials may be directly synthesized and stabilized in a nanoporous carbon or SiO_2 scaffold, *i.e.*, nanoconfinement. Moreover, the nanoconfinement hinders the particle growth, change the decomposition reaction avoiding hydrogen sinks and keeps the various desorption products in a close contact. A carbon scaffold, contrary to hydrides, is a good thermal conductor allowing also for dissipation of the heat produced during hydrogen release or uptake. Various single-phase borohydrides and mixtures have been nanoconfined with different positive effects on the desorption reaction: more significant for $NaBH_4$ [52] and $Mg(BH_4)_2$ [53] while less improving the desorption temperature and kinetics in $LiBH_4$ [54].

3. Solid-electrolytes

Difficulty in making the hydrogen storage in hydroborates fully reversible led the researchers to investigate other energy storage applications using hydroborates. In 2007 the fast Li^+ motion has been discovered in HT hexagonal $LiBH_4$ phase above 110 °C leading to superionic conductivity of $2 \cdot 10^{-3}$ S cm^{-1} [55]. Since then, many others single and poly-cation solid-electrolytes (SE) based on borohydrides or bigger hydroborate poly-anions have been discovered, characterized and tested in all-solid-state batteries (ASSB). There are several valid reasons to replace the current generation of Li-ion batteries using the liquid electrolyte (LE) by ASSB [56,57]:

(1) Safety aspects in replacing inflammable LE by inert SE;
(2) Increase of energy storage capacity by using metallic negative electrode and higher potential positive electrode;
(3) Battery less prone to dendritic growth of the metallic negative electrode;
(4) More compact battery design by removing separator and current collector on the negative electrode;
(5) Simpler and cheaper battery production.

Replacing Li by other metals such as Na in negative electrode is an additional motivation for ASSB and was made possible due to novel SEs for Na^+ and Co-free positive electrodes. Sodium (23,000 ppm in Earth's crust) is also much more abundant and geopolitically more homogeneously available compared to lithium (20 ppm) [58].

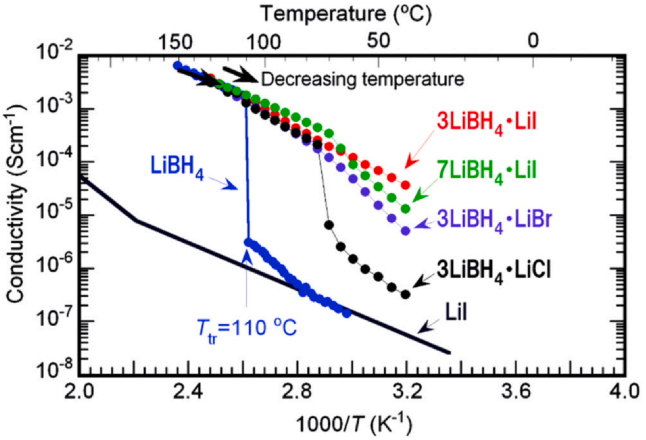

Fig. 2. Electrical conductivities of anionic mixtures $LiBH_4$-LiX (X = Cl, Br and I) measured by electrical impedance spectroscopy.
Reproduced from [61].

Hydroborates provide several benefits as SEs compared to other materials such as oxides, sulfides, halides or polymers: (i) high thermal, chemical, reduction and oxidation stability, (ii) high ionic and low electronic conductivities, (iii) more suitable mechanical properties (soft materials) for low cost and stable fabrication and (iv) comparable density to current LEs (~ 1.1 g cm^{-3}) [59,60].

3.1. $LiBH_4$

After the discovery of high Li^+ mobility in the HT phase of $LiBH_4$, an intense effort has been spent to bring its superionicity down to RT. Substitution of BH_4^- anions by halides stabilizes the HT hexagonal phase at RT (Fig. 2) [61].

The oxidation stability of $LiBH_4$ has been initially overestimated, and finally has been resized about 2 V *vs.* Li^+/Li, in agreement with first principle calculations [62]. A trianionic mixture $LiBH_4$-LiBr-LiCl has been studied in [63] resulting in the HT phase stabilized at RT with an optimal composition of $Li(BH_4)_{0.7}Br_{0.2}Cl_{0.1}$ as a compromise between the oxidation stability (effect of Br), ionic conductivity (effect of BH_4) and density (effect of Cl). An alternative method to improve the Li^+ conductivity of the RT orthorhombic $LiBH_4$ is by nanoconfinement in suitable scaffolds or mixing it with oxides, forming oxide-based composites [64,65]. In this case, the improved Li^+ conductivity relies on the formation of a conductive interface, described by a core-shell model. The fraction of $LiBH_4$ (the core) in direct contact with the oxide (the shell) forms an interfacial layer, exhibiting a Li^+ conductivity enhancement.

Several ASSBs have been tested with $LiBH_4$ as SE [66] and operating in superionic regime of SE at 120 °C. Lithium metal has been used as the negative electrode and either TiS_2 [67] or sulfur [68] as the positive one. Using the metal hydride as negative electrode has increased the energy storage capacity of the battery, but simultaneously deteriorated its cyclability [69]. For the first time the battery has been operated at RT by using a $LiBH_4$-MgO composite SE [70].

3.2. Other borohydrides

Amongst the numerous candidate SE materials the garnet-type metal oxides have received increased attention in the recent past after their discovery as Li-ion conductors owed to their huge chemical flexibility, resulting from variable cation distributions on three different sites and providing sufficient structural flexibility to allow for important heterovalent doping. The first garnet-type borohydride SE have been prepared and characterized with the composition $Li_3K_3Ce_2(BH_4)_{12}$ and $Li_3K_3La_2(BH_4)_{12}$ [71]. These mixed cation SEs show unexpectedly high RT Li^+ ionic conductivity (compared to the reported isostructural garnet oxide Li-conductor) of $3\cdot10^{-7}$ and $6\cdot10^{-7}$ S cm^{-1} with corresponding activation energies of 0.79 and 0.67 eV, respectively, which result from large bottleneck windows in the conduction path. Doping with divalent Sr^{2+} and Eu^{2+} shows that Li^+ conductivity can be increased by one order of magnitude.

The oxides with spinel type of structure AB_2X_4 such as $LiMn_2O_4$ have been mostly studied as electrode materials [72]. A mixed cation and anion borohydride $LiM(BH_4)_3Cl$, M = La, Gd, has been shown to have spinel-like structure where the ratio between the basic building units, cubanes B_4X_4 and tetrahedra AX_4 is different than in true spinel resulting in the composition ABX_4 [73]. Their RT Li^+ ion conductivity amounts to $2.3\cdot10^{-4}$ and $3.5\cdot10^{-4}$ S cm^{-1}.

Borohydrides were often mixed with amides to form mixed anion compounds in the view to stabilize new structures with perturbed energy landscape of the cation leading to its higher mobility at RT. $Li_4(BH_4)(NH_2)_3$ shows high RT ionic conductivities of $6.4\cdot10^{-3}$ S cm^{-1}, but a stability window of only 0.7–2.0 V *vs.* Li^+/Li [74]. Its crystal structure may be compared with sphalerite, but the distribution of the filled tetrahedral sites in the cubic close packing (*ccp*) of anions is more complex than in the sphalerite [75].

The disordered anti-perovskite $Na_2(BH_4)(NH_2)$ and tetragonal $Mg(BH_4)(NH_2)$ were also recently shown to have a Na^+ ion conductivity of $2\cdot10^{-6}$ S cm^{-1} [76] and Mg^{2+} ion conductivity of $1\cdot10^{-6}$ S cm^{-1} [77] at RT and 150 °C, respectively.

3.3. SEs based on larger hydroborate anions

Superionicity in solid hydroborates based on larger poly-anion than borohydride was for the first time discovered in $Na_2B_{12}H_{12}$ [15], but the first test with solution of halogenated *closo*-borates $Li_2B_{12}Cl_{12}$ and $Li_2B_{10}Cl_{10}$ as LE in Li-TiS_2 cells have been done already in 1980 [78]. Soon after the discovery of superionicity in $Na_2B_{12}H_{12}$, many other *closo*-borates of lithium and sodium have been presented as SE (Fig. 3).

All hydroborates and carborane $C_2B_{10}H_{12}$ present a phase transition from the LT ordered to HT disordered phase. The origin of this transition has been studied using solid state NMR [80], quasi-elastic neutron scattering [81] and dielectric spectroscopy [82]. The transition is of the order/disorder type and is related to the rotation of the boron(carbon)-hydrogen clusters, which trigger afterwards the cation mobility in the salts leading to superionic state in the HT disordered phase. Such order/disorder transition is situated for $Na_2B_{12}H_{12}$ at 540 K, which is too high for mobile applications of ASSBs [83]. The HT disordered phases of hydroborate salts and carborane may be called rotatory phases or plastic crystals [84]. The most studied compounds in the view of their use as SE are based on three similar topologies of the boron cage (Fig. 4): *closo*-dodecaborates with icosahedral cage, *closo*-decaborates with bi-capped square antiprismatic cage and *nido*-borates with an open cage.

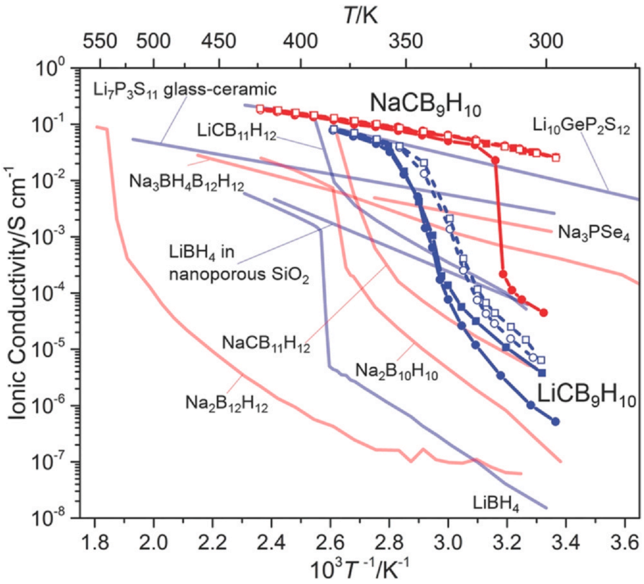

Fig. 3. Ionic conductivities of selected hydride materials as functions of inverse temperature, Li^+ conductors in blue, Na^+ conductors in red. For the best materials, $NaCB_9H_{10}$ and $LiCB_9H_{10}$, the circles and squares denote the conductivities of the respective first and second temperature cycles. Closed and open symbols denote respective heating and cooling regimens. For comparison, conductivities of select non-hydridic polycrystalline electrolytes are also shown (From Ref. [79]).

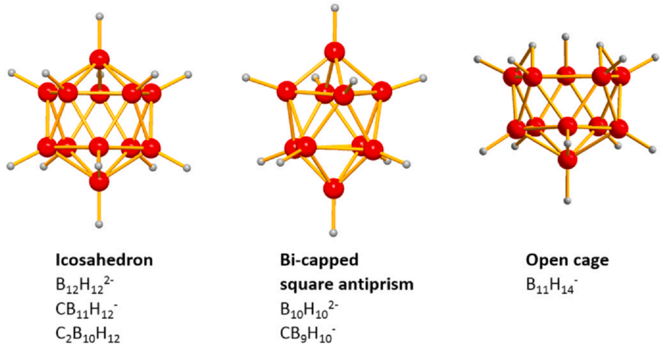

Fig. 4. Panoply of hydrogen – (carba-)boron clusters for designing the hydroborate solid electrolytes.

Similarly, to $LiBH_4$ lot of effort has been devoted to bring the order/disorder transition down to RT or to suppress it completely. For the first time, the transition has been suppressed in an anion-mixed superionic $Na_3BH_4B_{12}H_{12}$ with RT ionic conductivity of $1\cdot10^{-3}$S cm^{-1}, which however suffers from low oxidative stability with the limit of 1.9 V [85]. The strategies used to bring the superionicity down to RT are similar to those used for modification of hydrogen release temperature: cation mixing, anion modification [86], anion mixing [87], nanoconfinement [88] and physical activation [89].

Anion mixing, represented by alio- or isovalent anion mixing of the boron cluster *closo*-hydroborates, maintains the same chemistry and does not affect negatively the electrochemical window. Several SEs obtained in this way, such as $Li_2(CB_9H_{10})(CB_{11}H_{12})$, $Na_4(B_{10}H_{10})(B_{12}H_{12})$, and $Na_3(CB_{11}H_{12})(B_{12}H_{12})$, showed not only high RT ionic conductivity but also do not have a structural phase transition over a very wide temperature range [90–93]. High ionic conductivity is achieved also by combining *nido*-$B_{11}H_{14}^{-}$ with *closo*-$B_{12}H_{12}^{2-}$ or *closo*-$CB_{11}H_{12}^{-}$ anions into cubic unit cell in Li- and Na-salts [94,95]. Six combinations of four *closo*-anions from the Fig. 4 in ratio 1:1 have been studied in details for sodium salts [96]. In all mixtures the phase transition is suppressed and orientation of the anions is disordered already at RT. Their crystal structure is based on one of the three common packing types, *i.e.*, cubic or hexagonal close packing and body centered cubic (*ccp*, *hcp* and *bcc*), see Fig. 5. It follows that all three types of anions packing may provide pathways suitable for Na^+ conduction.

The drop of the ionic conductivity below the phase transition temperature in single anion compounds (Fig. 3) is related to lowering of the crystal symmetry, which closes the conduction pathways. In the same time the anion reorientation rate drops of nearly three orders of magnitude (from 10^{11} to 10^8 s^{-1}) [97]. The degree of lattice distortion in sodium *closo*-borate mixtures has been shown as small [96] compared to ionic conductors based on similar anion packing such as AgI or Ag_2S. This suggests that a small increase of the entropy of mixing (or configurational entropy) due to the adoption of at least two different anions may stabilize the high

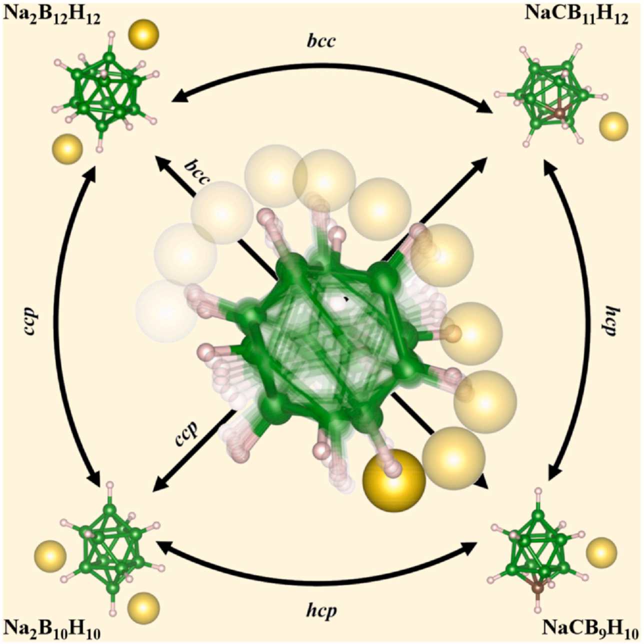

Fig. 5. Resulting anions packing in binary mixtures of *closo*-hydroborates sodium salts.

symmetry polymorph, as happens in the so-called high-entropy alloys. This is in line with the analysis of cation mobility in *closo*-hydroborates suggesting the crystal structure, local cation-hydrogen interaction and anion's dynamics as three ways of frustrating the structure, resulting in a flattening of the energy landscape for the mobile cation [98]. The first parameter, *i.e.*, the crystal symmetry and anions packing, for all hydroborates has been recently analysed and reviewed [99].

Other poly-anions have been also considered for designing SEs such as *nido*-borates of lithium and sodium and their carbon substituted analogs [100] or *arachno*-borates AB_3H_8 (A = Na, K) [101]. Their open cages, however, suffer from lower oxidative stability.

Not only high ionic conductivity ($> 10^{-3}$ S cm^{-1}), but also other parameters play an important role in application of a compounds as SE. The performance parameters as presented for hydrides in Ref. [102], Fig. 6, may be improved for *closo*-borates according to latest results on ionic Area Specific Resistance (ASR) [103], oxidation, chemical and thermal stability [99] and mechanical properties [104]. Due to the three-dimensional, aromatic-like electronic distribution in the anions, the hydroborates have been shown to be unchanged up to 600 °C or even up to 800 °C in the case of cesium hydroborates [83,105,106]. This makes the *closo*-borates, especially the sodium dodecahedral ones, very promising candidates for SE.

The stability against the reduction in contact with low electrical potential anode and oxidation in contact with high potential cathode is crucial parameter for the application of SEs in ASB. The reduction is usually not a problem for the hydroborates as they are used as reducing agents in organic syntheses. As far as for the oxidation, hydroborates have been demonstrated to be rather electrochemically robust: Wiersema et al. [107] showed that the oxidative limit increases following the series $B_{10}H_{10}^{2-} < B_{12}H_{12}^{2-} < CB_9H_{10}^{-} < CB_{11}H_{12}^{-}$ (respectively at +0.4, +1.4, +1.85 and > +2.4 *versus* SCE). The systematic study of the electrochemical stability in solid sodium salts partly confirms this stability scale but shows a superior robustness of dodecahedral clusters over the decahedral ones, mainly due to isotropic delocalization of σ electrons. The large increase of the resonance energy, which stands for the extra stabilization energy provided by the electron delocalization along the σ molecular orbitals in the cage. The resonance energy rises with the cage size and almost doubles from 10 to 12-vertex polyhedron [108]. Moreover, C-containing anions seem to be more robust than their corresponding boron clusters. This could be due to the different acidity of the C-H hydrogen. A higher acidity corresponds to a higher stability of the conjugated base; therefore, the corresponding anion is less prone to oxidation, leading to a higher decomposition voltage for the C-substituted anions with respect to their unsubstituted counterparts.

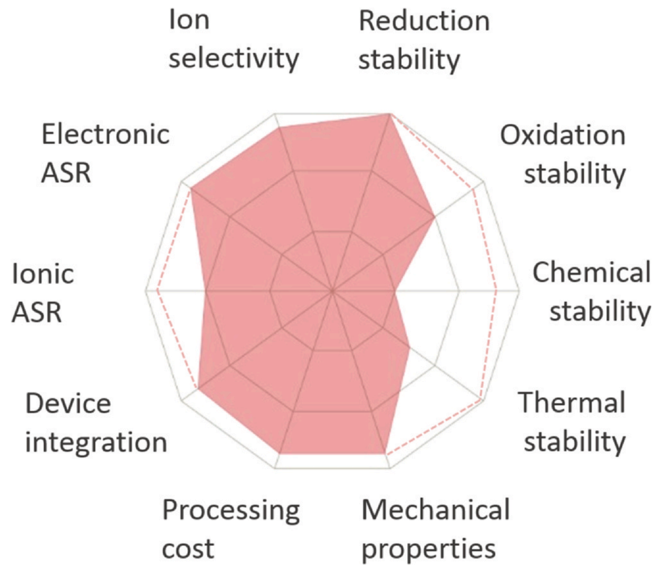

Fig. 6. Performance parameters for hydride based SE as presented in Ref. [102] and modified (dashed lines) according to latest results.

From the electrochemical stability results, it follows that the most stable among sodium salts is $NaCB_{11}H_{12}$. It redirected the research effort into the stabilization of disordered HT phase [109] down to RT. Recently, a nano-confinement of $NaCB_{11}H_{12}$, within porous, high-surface-area silica *via* salt-solution infiltration stabilized the HT cubic phase with anions *ccp* at RT providing the ionic conductivity of $3{\cdot}10^{-4}$ S cm^{-1} [88].

A potential commercial application of hydroborates as SE is currently hindered by the difficult, low-yielding, and expensive synthetic pathways. Nonetheless, several reports proposed novel and cost-effective synthetic methods for $B_{11}H_{14}^{-}$ based salts [94] as a precursor for cheap syntheses of $B_{12}H_{12}^{2-}$ [110,111] and $CB_1H_{12}^{-}$ [112] based salts.

3.4. ASSBs based on closo-hydroborate SE

Several proofs-of-concept of ASSBs featuring *closo*-hydroborates as SE have been assembled and tested. Mixed anion $Li(CB_9H_{10})_{0.7}(CB_{11}H_{12})_{0.3}$ as SE, metallic lithium as negative and sulfur as positive electrode were cycled at 25 °C with the charging/discharging rate of up to 1 C and good capacity retention during 100 cycles [90]. Replacing the carbon substituted anions with $B_{12}H_{12}^{2-}$ led to a cheaper SE, but with lower charging/discharging rate of only 0.05 C due to lower ionic conductivity of SE. Such battery has been tested with metallic lithium as negative and $LiCoO_2$ as positive (4 V *vs.* Li^+/Li) electrode at 30 °C. As high potential positive electrode would oxidize the SE, a $LiNbO_3$ has been used as a protective layer [113].

Better performances have been achieved with Na-ion batteries. Two batteries using sodium metal as negative and $NaCrO_2$ as positive electrode have been assembled with two different SEs,

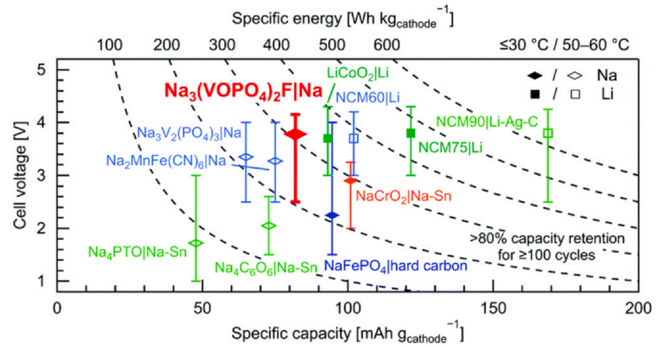

Fig. 7. Comparison of state-of-the-art all-solid sodium and lithium battery performance. The abbreviations stand for: PTO = pyrene-4,5,9,10-tetraone, NCM90 = $Li[Ni_{0.90}Co_{0.05}Mn_{0.05}]O_2$, NCM75 = $Li[Ni_{0.751}Co_{0.101}Mn_{0.148}]O_2$, and NCM60 = $Li[Ni_{0.60}Co_{0.20}Mn_{0.20}]O_2$.
Reproduced from [117].

$Na_4(B_{10}H_{10})(B_{12}H_{12})$ [114] and $Na_4(CB_{11}H_{12})_2(B_{12}H_{12})$ [115]. While the former was operated at 60 °C to prevent the dendritic growth of sodium in the SE cracks, the latter was operated at RT. The $NaCrO_2$ positive electrode operates at 3 V *vs.* Na^+/Na and delivers the capacity close to 100 mA h g^{-1} at the charge/discharge rate of C/5 in both experiments. Better cyclability has been achieved in the first experiment by more homogeneous positive electrode prepared by infiltration method [116]. The carba-borate based electrolyte $Na_4(CB_{11}H_{12})_2(B_{12}H_{12})$ has been used also in preparation of a 4 V battery using $Na_3(VOPO_4)_2F$ as positive electrode without any artificial protective coating [117]. The battery's capacity is close to 100 mA h g^{-1} at C/5 rate with excellent capacity retention over 800 cycles. Higher cycling rates has been obtained by applying a pressure of 3.2 MPa on the battery stack. Such 4 V ASSB shows the capacity of energy storage comparable to current generation of Li-ion batteries (Fig. 7) showing a high potential of *closo*-hydroborates for designing post-lithium ASBs.

4. Other applications of borohydrides related to energy conversion

Luminescence has been studied among other properties in borohydride-perovskites [118]. The non-spherical shape of BH_4^- anion compared to oxides or halides results in different crystal field effect and consequently in shift of the luminescence spectrum as it was observed in $CsEu(BH_4)_3$. The reducing nature of the borohydride anion may be utilized to stabilize low oxidation states in perovskites that are labile with respect to oxidation such as Yb(II). The optical properties may be also tuned by halide-borohydride substitution.

Gadolinium-based mono- and bimetallic borohydrides, with a general formula $A_nGd(BH_4)_{n+3}$ (A = K, Cs; n = 0–3), have been studied in view of their magnetic cooling properties at cryogenic temperatures [119]. The results suggest that paramagnetic metal borohydride salts may approach the expected maximum values for isolated Gd^{3+} ions. The isolated Gd-centers in five-fold coordination in $K_2Gd(BH_4)_5$, the first representative of a new structure type, lead to exceptionally high mass magnetic entropy change of 54.6 J kg^{-1} K^{-1} at the maximum field change of 9 T.

5. Conclusions and outlook

Metal borohydrides, the salts based on a simplest hydroborate BH_4^-, have found in last twenty years a large interest as solid stores of hydrogen due to their high gravimetric and volumetric storage capacity. Contrary to classical metal hydrides based on interstitial hydrogen, the latter is bonded covalently in borohydride crystals leading to rather complex chemical reactions related to desorption and re-absorption of hydrogen. This handicap can be minimized by various methods including catalysis, reactive mixtures of borohydrides with other metal hydrides and physical methods based on nano-sizing of active material.

The discovery of high cation mobility in disordered hydroborates including also bigger anionic *closo*-clusters in 2007, has started another intense energy storage related research of hydroborates as solid electrolytes for application in all-solid-state batteries. The mobility of Li^+ and Na^+ cations increases by several orders of magnitude when these crystals transform into disordered phases with rotating or tumbling anions. Several approaches succeeded to move the temperature of the transition close to the room temperature or to suppress it completely. Among them the anion mixing and nano-sizing showed to be the most promising. The peculiarity of the hydroborate anion is its shape close to a sphere when orientationally disordered which stabilizes high-symmetry structures with favorable conduction pathways for cations. On the other side, the deviation of the anion's charge distribution from an ideal sphere frustrates the energy landscape seen locally by the cation further promoting its mobility.

The non-spherical shape of the borohydride anion leads to deformed variants of known structure types such as perovskites or garnets observed in borohydride crystals. The deformation modifies consequently physical properties such as luminescence or magnetocaloric effect.

As a consequence of these findings, we expect an increase of interest in the scientific community in order to investigate the fundamental theoretical aspects of hydroborate structure-property relation in more detail. Novel and cheap synthetic ways must be developed allowing to decrease their high price on the market penalizing the hydroborates from a broader application. Their sensitivity to a prolonged air exposure must be treated by novel technologies of production and final product packaging. The novel synthetic ways will also allow for stabilizing various oxidation states of transition metals in these salts with highly reducing anion. This will allow to investigate properties related to spontaneous polarization in the crystal or to spin ordering as in the oxide perovskites and their derivatives. The chemical and thermal stability of the hydroborates, albeit not so high as of the oxides, qualifies the former for applications where the different chemistry of the hydroborate anion results in different values of physical properties. Waiting for such achievements, we see the most mature application of the hydroborates as solid electrolytes. Due to their large oxidative window and low gravimetric density, this family of compounds represents a substantial breakthrough in the search for feasible solid electrolytes in all-solid rechargeable batteries.

CRediT authorship contribution statement

Radovan Černý: Writing – original draft. **Fabrizio Murgia and Matteo Brighi:** Completing and correcting the draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] R.N. Grimes, Carboranes, Elsevier, 2011.
[2] R.M. Adams, Nomenclature of inorganic boron compounds, Pure Appl. Chem. 30 (1972) 681–710.
[3] W.N. Lipscomb, Boron Hydrides, W.A. Benjamin Inc., New York, NY, USA, 1963.
[4] K. Wade, The structural significance of the number of skeletal bonding electron-pairs in carboranes, the higher boranes and borane anions, and various transition-metal carbonyl cluster compounds, J. Chem. Soc. D Chem. Commun. (1971) 792–793.

[5] D.M.P. Mingos, A general theory for cluster and ring compounds of the main group and transition elements, Nat. Phys. Sci. 236 (1972) 99–102.
[6] J.D. Clark, Ignition!: An Informal History of Liquid Rocket Propellants, Rutgers University Press, New Brunswick, NJ, USA, 1972.
[7] H.C. Brown, Hydroboration, W.A. Benjamin Inc., New York, NY, USA, 1962.
[8] C. Douvris, O.V. Ozerov, Hydrodefluorination of perfluoroalkyl groups using silylium-carborane catalysts, Science 321 (2008) 1188–1190.
[9] B. Shao, A.L. Bagdasarian, S. Popov, H.M. Nelson, Arylation of hydrocarbons enabled by organosilicon reagents and weakly coordinating anions, Science 355 (2017) 1403–1407.
[10] R.F. Barfh, A.H. Soloway, R.G. Fairchild, R.M. Brugger, Boron neutron capture therapy for cancer. Realities and prospects, Cancer 70 (1992) 2995–3007.
[11] O. Bondarev, A.A. Khan, X. Tu, Y.V. Sevryugina, S.S. Jalisatgi, M.F. Hawthorne, Synthesis of $[\text{closo-}B_{12}(OH)_{11}NH_3]^-$: a new heterobifunctional dodecaborane scaffold for drug delivery applications, J. Am. Chem. Soc. 135 (2013) 13204–13211.
[12] L.N. Goswami, L. Ma, S. Chakravarty, Q. Cai, S.S. Jalisatgi, M.F. Hawthorne, Discrete nanomolecular polyhedral borane scaffold supporting multiple gadolinium(III) complexes as a high performance MRI contrast agent, Inorg. Chem. 52 (2013) 1694–1700.
[13] J.W. Johnson, J.F. Brody, Lithium closoborane electrolytes: III. Preparation and characterization, J. Electrochem. Soc. 129 (1982) 2213–2219.
[14] L.H. Rude, T.K. Nielsen, D.B. Ravnsbæk, U. Bösenberg, M.B. Ley, B. Richter, L.M. Arnbjerg, M. Dornheim, Y. Filinchuk, F. Besenbacher, T.R. Jensen, Tailoring properties of borohydrides for hydrogen storage: a review, Phys. Status Solidi A 208 (2011) 1754–1773.
[15] T.J. Udovic, M. Matsuo, A. Unemoto, N. Verdal, V. Stavila, A.V. Skripov, J.J. Rush, H. Takamura, S. Orimo, Sodium superionic conduction in $Na_2B_{12}H_{12}$, Chem. Commun. 50 (2014) 3750–3752.
[16] T.J. Udovic, M. Matsuo, W.S. Tang, H. Wu, V. Stavila, A.V. Soloninin, R.V. Skoryunov, O.A. Babanova, A.V. Skripov, J.J. Rush, Exceptional superionic conductivity in disordered sodium decahydro-closo-decaborate, Adv. Mater. 26 (2014) 7622–7626.
[17] B.D. James, M.G.H. Wallbridge, Metal tetrahydroborates, Prog. Inorg. Chem. 11 (1970) 99–231.
[18] T.J. Marks, J.R. Kolb, Covalent transition metal, lanthanide, and actinide tetrahydroborate complexes, Chem. Rev. 77 (1977) 263–293.
[19] L. Schlapbach, A. Züttel, Hydrogen-storage materials for mobile applications, Nature 414 (2001) 353–358.
[20] R. Černý, P. Schouwink, The crystal chemistry of inorganic metal borohydrides and their relation to metal oxides, Acta Crystallogr. B 71 (2015) 619–640.
[21] H.I. Schlesinger, H.C. Brown, B. Abraham, A.C. Bond, N. Davidson, A.E. Finholt, J.R. Gilbreath, H. Hoekstra, L. Horvitz, E.K. Hyde, J.J. Katz, J. Knight, R.A. Lad, D.L. Mayfield, L. Rapp, D.M. Ritter, A.M. Schwartz, I. Sheft, L.D. Tuck, A.O. Walker, New developments in the chemistry of diborane and the borohydrides, J. Am. Chem. Soc. 75 (1953) 186–190.
[22] H.I. Schlesinger, H.C. Brown, Metallo borohydrides. III lithium borohydride, J. Am. Chem. Soc. 62 (1940) 3429–3435.
[23] J.P. Soulié, G. Renaudin, R. Černý, K. Yvon, Lithium boro-hydride, LiBH4: I. Crystal structure, J. Alloy. Compd. 346 (2002) 200–205.
[24] Ya Filinchuk, D. Chernyshov, R. Černý, Lightest borohydride probed by synchrotron X-ray diffraction: experiment calls for a new theoretical revision, J. Phys. Chem. C 112 (2008) 10579–10584.
[25] A. Züttel, S. Rentsch, P. Fischer, P. Wenger, P. Sudan, P. Mauron, C. Emmenegger, Hydrogen storage properties of $LiBH_4$, J. Alloy. Compd. 356–357 (2003) 515–520.
[26] B. Bogdanovic, M. Schwickardi, Ti-doped alkali metal aluminium hydrides as potential novel reversible hydrogen storage materials, J. Alloy. Compd. 253–254 (1997) 1–9.
[27] M. Paskevicius, L.H. Jepsen, P. Schouwink, R. Černý, D. Ravnsbaeck, Y. Filinchuk, M. Dornheim, F. Besenbacher, T.R. Jensen, Metal borohydrides and derivatives – synthesis, structure and properties, Chem. Soc. Rev. 46 (2017) 1565–1634.
[28] G. Walker (Ed.), Solid-State Hydrogen Storage, Materials and Chemistry, Woodhead Publishing Ltd, 2008, p. 12.
[29] P. Mauron, F. Buchter, O. Friedrichs, A. Remhof, M. Bielmann, C.N. Zwicky, A. Zuttel, Stability and reversibility of $LiBH_4$, J. Phys. Chem. B 112 (2008) 906–910.
[30] W.D. Davis, L.S. Mason, G. Stegeman, The heats of formation of sodium borohydride, lithium borohydride and lithium aluminum hydride, J. Am. Chem. Soc. 71 (1949) 2775–2781.
[31] N. Ohba, K. Miwa, M. Aoki, T. Noritake, S. Towata, Y. Nakamori, S. Orimo, A. Züttel, First-principles study on the stability of intermediate compounds of $LiBH_4$, Phys. Rev. B Condens. Matter 74 (2006) 075110.
[32] O. Friedrichs, F. Buchter, A. Borgschulte, A. Remhof, C.N. Zwicky, P. Mauron, M. Bielmann, A. Züttel, Direct synthesis of $Li[BH_4]$ and $Li[BD_4]$ from the elements, Acta Mater. 56 (2008) 949–954.
[33] H.I. Schlesinger, R.T. Sanderson, A.B. Burg, Metallo borohydrides. I. Aluminum borohydride, J. Am. Chem. Soc. 62 (1940) 3421–3425.
[34] L.H. Rude, M. Corno, P. Ugliengo, M. Baricco, Y.S. Lee, Y.W. Cho, F. Besenbacher, J. Overgaard, T.R. Jensen, Synthesis and structural investigation of $Zr(BH_4)_4$, J. Phys. Chem. C 116 (2012) 20239–20245.
[35] B.R.S. Hansen, M. Paskevicius, H.W. Li, E. Akiba, T.R. Jensen, Metal boranes: progress and applications, Coord. Chem. Rev. 323 (2016) 60–70.
[36] P. Schouwink, M.B. Ley, A. Tissot, H. Hagemann, T.R. Jensen, L. Smrčok, R. Černý, Structure and properties of complex hydride perovskite materials, Nat. Commun. 5 (2014) 5706.
[37] G.N. Schrauzer, Über ein Periodensystem der Metallboranate, Naturwissenschaften 42 (1955) 438.
[38] P. Blonski, Z. Łodziana, Correlation between the ionic potential and thermal stability of metal borohydrides: first-principles investigations, Phys. Rev. B 90 (2014) 054114.
[39] D.B. Ravnsbak, L.H. Sorensen, Y. Filinchuk, F. Besenbacher, T.R. Jensen, Screening of metal borohydrides by mechanochemistry and diffraction, Angew. Chem. Int. Ed. 51 (2012) 3582–3586.
[40] M. Paskevicius, M.B. Ley, D.A. Sheppard, T.R. Jensen, C.E. Buckley, Eutectic melting in metal borohydrides, Phys. Chem. Chem. Phys. 15 (2013) 19774–19789.
[41] J. Yang, A. Sudik, C. Wolverton, Destabilizing $LiBH_4$ with a metal (M = Mg, Al, Ti, V, Cr, or Sc) or metal hydride ($MH_2 = MgH_2$, TiH_2, or CaH_2), J. Phys. Chem. C 111 (2007) 19134–19140.
[42] G. Barkhordarian, T. Klassen, M. Dornheim, R. Bormann, Unexpected kinetic effect of MgB_2 in reactive hydride composites containing complex borohydrides, J. Alloy. Compd. 440 (2007) L18–L21.
[43] J.J. Vajo, F. Mertens, C.C. Ahn, R.C. Bowman, B. Fultz, Altering hydrogen storage properties by hydride destabilization through alloy formation: LiH and MgH_2 destabilized with Si, J. Phys. Chem. B 108 (2004) 13977–13983.
[44] K.Ch. Kim, A.D. Kulkarni, J.K. Johnson, D.S. Sholl, Large-scale screening of metal hydrides for hydrogen storage from first-principles calculations based on equilibrium reaction thermodynamics, Phys. Chem. Chem. Phys. 13 (2011) 7218–7229.
[45] J.J. Vajo, S.L. Skeith, F. Mertens, Reversible storage of hydrogen in destabilized $LiBH_4$, J. Phys. Chem. B 109 (2005) 3719–3722.
[46] N.A. Ali, N.A. Sazelee, M. Ismail, An overview of reactive hydride composite (RHC) for solid-state hydrogen storage materials, Int. J. Hydrog. Energy 46 (2021) 31674–31698.
[47] H.I. Schlesinger, H.C. Brown, A.E. Finholt, J.R. Gilbreath, H.R. Hoekstra, E.K. Hyde, Sodium borohydride, Its hydrolysis and its use as a reducing agent and in the generation of hydrogen, J. Am. Chem. Soc. 75 (1953) 215–219.
[48] V. Berube, G. Chen, M.S. Dresselhaus, Impact of nanostructuring on the enthalpy of formation of metal hydrides, Int. J. Hydrog. Energy 33 (2008) 4122–4131.
[49] A. Schneemann, J.L. White, S.Y. Kang, S. Jeong, L.F. Wan, E.S. Cho, T.W. Heo, D. Prendergast, J.J. Urban, B.C. Wood, M.D. Allendorf, V. Stavila, Nanostructured metal hydrides for hydrogen storage, Chem. Rev. 118 (2018) 10775–10839.
[50] J. Huot, D.B. Ravnsbæk, J. Zhang, F. Cuevas, M. Latroche, T.R. Jensen, Mechanochemical synthesis of hydrogen storage materials, Prog. Mater. Sci. 58 (2013) 30–75.
[51] J. Huot, F. Cuevas, S. Deledda, K. Edalati, Y. Filinchuk, T. Grosdidier, B.C. Hauback, M. Heere, T.R. Jensen, M. Latroche, S. Sartori, Mechanochemistry of metal hydrides: recent advances, Materials 12 (2019) 2778.
[52] P. Ngene, R. van den Berg, M.H.W. Verkuijlen, K.P. de Jong, P.E. de Jongh, Reversibility of the hydrogen desorption from $NaBH_4$ by confinement in nanoporous carbon, Energy Environ. Sci. 4 (2011) 4108–4115.
[53] Y. Yan, Y.S. Au, D. Rentsch, A. Remhof, P.E. de Jongh, A. Zuttel, Reversible hydrogen storage in $Mg(BH_4)_2$/carbon nanocomposites, J. Mater. Chem. A 1 (2013) 11177–11183.
[54] S. Cahen, J.B. Eymery, R. Janot, J.M. Tarascon, Improvement of the $LiBH_4$ hydrogen desorption by inclusion into mesoporous carbons, J. Power Sources 189 (2009) 902–908.
[55] M. Matsuo, Y. Nakamori, S.I. Orimo, H. Maekawa, H. Takamura, Lithium superionic conduction in lithium borohydride accompanied by structural transition, Appl. Phys. Lett. 91 (2007) 224103.
[56] J. Janek, W.G. Zeier, A solid future for battery development, Nat. Energy 1 (2016) (16141).
[57] Y. Tian, G. Zeng, A. Rutt, T. Shi, H. Kim, J. Wang, J. Koettgen, Y. Sun, B. Ouyang, T. Chen, Z. Lun, Z. Rong, K. Persson, G. Ceder, Promises and challenges of next-generation "beyond li-ion" batteries for electric vehicles and grid decarbonization, Chem. Rev. 121 (2021) 1623–1669.
[58] K. Barbalace, Periodic Table of Elements, EnvironmentalChemistry.com, 1995–2021. Accessed on-line: 9/14/2021.
[59] J. Cuan, Y. Zhou, T. Zhou, S. Ling, K. Rui, Z. Guo, H. Liu, X. Yu, Borohydride-scaffolded Li/Na/Mg fast ionic conductors for promising solid-state electrolytes, Adv. Mater. 31 (2019) 1803533.
[60] Z. Lu, F. Ciucci, Metal borohydrides as electrolytes for solid-state Li, Na, Mg, and Ca batteries: a first-principles study, Chem. Mater. 29 (2017) 9308–9319.
[61] H. Maekawa, M. Matsuo, H. Takamura, M. Ando, Y. Noda, T. Karahashi, S.I. Orimo, Halide-stabilized LiBH4, a room-temperature lithium fast-ion conductor, J. Am. Chem. Soc. 131 (2009) 894–895.
[62] R. Asakura, L. Duchêne, R.S. Kühnel, A. Remhof, H. Hagemann, C. Battaglia, Electrochemical oxidative stability of hydroborate-based solid-state electrolytes, ACS Appl. Energy Mater. 2 (2019) 6924–6930.
[63] V. Gulino, M. Brighi, E.M. Dematteis, F. Murgia, C. Nervi, R. Černý, M. Baricco, Phase stability and fast ion conductivity in the hexagonal $LiBH_4$-LiBr-LiCl solid solution, Chem. Mater. 31 (2019) 5133–5144.
[64] D. Blanchard, A. Nale, D. Sveinbjörnsson, T.M. Eggenhuisen, M.H.W. Verkuijlen, Suwarno, T. Vegge, A.P.M. Kentgens, P.E. de Jongh, Nanoconfined $LiBH_4$ as a fast lithium ion conductor, Adv. Funct. Mater. 25 (2015) 184–192.
[65] V. Gulino, L. Barberis, P. Ngene, M. Baricco, P.E. de Jongh, Enhancing li-ion conductivity in $LiBH_4$-based solid electrolytes by adding various nanosized oxides, ACS Appl. Energy Mater. 3 (2020) 4941–4948.
[66] M. Latroche, D. Blanchard, F. Cuevas, A. El Kharbachi, B.C. Hauback, T.R. Jensen, P.E. de Jongh, S. Kim, N.S. Nazer, P. Ngene, S.I. Orimo, D.B. Ravnsbæk, V.A. Yartys,

Full-cell hydride-based solid-state Li batteries for energy storage, Int. J. Hydrog. Energy 44 (2019) 7875–7887.

[67] A. Unemoto, T. Ikeshoji, S. Yasaku, M. Matsuo, V. Stavila, T.J. Udovic, S.I. Orimo, Stable interface formation between TiS_2 and $LiBH_4$ in bulk-type all-solid-state lithium batteries, Chem. Mater. 27 (2015) 5407–5416.

[68] A. Unemoto, S. Yasaku, G. Nogami, M. Tazawa, M. Taniguchi, M. Matsuo, T. Ikeshoji, S.I. Orimo, Development of bulk-type all-solid-state lithium-sulfur battery using $LiBH_4$ electrolyte, Appl. Phys. Lett. 105 (2014) 083901.

[69] P. Lopez-Aranguren, N. Berti, A.H. Dao, J. Zhang, F. Cuevas, M. Latroche, Ch Jordy, An all-solid-state metal hydride – sulfur lithium-ion battery, J. Power Sources 357 (2017) 56–60.

[70] V. Gulino, M. Brighi, F. Murgia, P. Ngene, P. de Jongh, R. Černý, M. Baricco, Room-temperature solid-state lithium-ion battery using a $LiBH_4$-MgO composite electrolyte, ACS Appl. Energy Mater. 4 (2021) 1228–1236.

[71] M. Brighi, P. Schouwink, Y. Sadikin Y, R. Černý, Fast ion conduction in garnet-type metal borohydrides $Li_3K_3Ce_2(BH_4)_{12}$ and $Li_3K_3La_2(BH_4)_{12}$, J. Alloy. Compd. 662 (2016) 388–395.

[72] M.M. Thackaray, A. de Kock, W.I.F. David, Synthesis and structural characterization of defect spinels in the lithium-manganese-oxide system, Mater. Res. Bull. 28 (1993) 1041–1049.

[73] M.B. Ley, S. Boulineau, R. Janot, Y. Filinchuk, T.R. Jensen, New li ion conductors and solid state hydrogen storage materials: $LiM(BH_4)_3Cl$, M = La, Gd, J. Phys. Chem. C 116 (2012) 21267–21276.

[74] Y. Yan, R.S. Kühnel, A. Remhof, L. Duchêne, E. Cuervo Reyes, D. Rentsch, Z. Łodziana, C. Battaglia, A lithium amide-borohydride solid-state electrolyte with lithium-ion conductivities comparable to liquid electrolytes, Adv. Energy Mater. 114 (2017) 1700294–1704618.

[75] Y. Filinchuk, K. Yvon, G.P. Meisner, F.E. Pinkerton, M.P. Balogh, On the composition and crystal structure of the new quaternary hydride phase $Li_4BN_3H_{10}$, Inorg. Chem. 45 (2006) 1433–1435.

[76] M. Matsuo, S. Kuromoto, T. Sato, H. Oguchi, H. Takamura, S.I. Orimo, Sodium ionic conduction in complex hydrides with $[BH_4]^-$ and $[NH_2]^-$ anions, Appl. Phys. Lett. 100 (2012) 203904.

[77] S. Higashi, K. Miwa, M. Aoki, K. Takechi, A novel inorganic solid state ion conductor for rechargeable Mg batteries, Chem. Commun. 50 (2014) 1320–1322.

[78] J.W. Johnson, S. Whittingham, Lithium closoboranes as electrolytes in solid cathode lithium cells, J. Electrochem. Soc. 127 (1980) 1653–1654.

[79] W.S. Tang, M. Matsuo, H. Wu, V. Stavila, W. Zhou, A.A. Talin, A.V. Soloninin, R.V. Skoryunov, O.A. Babanova, A.V. Skripov, A. Unemoto, S.I. Orimo, T.J. Udovic, Liquid-like ionic conduction in solid lithium and sodium monocarba- closo -decaborates near or at room temperature, Adv. Energy Mater. 6 (2016) 1502237.

[80] A.V. Skripov, A.V. Soloninin, O.A. Babanova, R.V. Skoryunov, Anion and cation dynamics in polyhydroborate salts: NMR studies, Molecules 25 (2020) (2940).

[81] N. Verdal, T.J. Udovic, V. Stavila, W.S. Tang, J.J. Rush, A.V. Skripov, Anion reorientations in the superionic conducting phase of $Na_2B_{12}H_{12}$, J. Phys. Chem. C 118 (2014) 17483–17489.

[82] P. Lunkenheimer, A. Loidl, Molecular reorientation in *ortho*-carborane studied by dielectric spectroscopy, J. Chem. Phys. 104 (1996) 4324–4329.

[83] N. Verdal, J.H. Her, V. Stavila, A.V. Soloninin, O.A. Babanova, A.V. Skripov, T.J. Udovic, J.J. Rush, Complex high-temperature phasetransitions in $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$, J. Solid State Chem. 212 (2014) 81–91.

[84] J. Timmermans, Plastic crystals: a historical review, J. Phys. Chem. Solids 18 (1961) 1–8.

[85] Y. Sadikin, M. Brighi, P. Schouwink, R. Černý, Superionic conduction of sodium and lithium in anion-mixed hydroborates $Na_3BH_4B_{12}H_{12}$ and $(Li_{0.7}Na_{0.3})_3BH_4B_{12}H_{12}$, Adv. Energy Mater. 5 (2015) 1501016.

[86] Y. Sadikin, P. Schouwink, M. Brighi, Z. Lodziana, R. Černý, Modified anion packing of $Na_2B_{12}H_{12}$ in close to room temperature superionic conductors, Inorg. Chem. 56 (2017) 5006–5016.

[87] W.S. Tang, K. Yoshida, A.V. Soloninin, R.V. Skoryunov, O.A. Babanova, A.V. Skripov, M. Dimitrievska, V. Stavila, S.I. Orimo, T.J. Udovic, Stabilizing superionic-conducting structures via mixed-anion solid solutions of monocarba-closo-borate salts, ACS Energy Lett. 1 (2016) 659–664.

[88] M.S. Andersson, V. Stavila, A.V. Skripov, M. Dimitrievska, M.T. Psurek, J.B. Leão, O.A. Babanova, R.V. Skoryunov, A.V. Soloninin, M. Karlsson, T.J. Udovic, Promoting persistent superionic conductivity in sodium monocarba-closo-dodecaborate $NaCB_{11}H_{12}$ via confinement within nanoporous silica, J. Phys. Chem. C 125 (2021) 16689–16699.

[89] W.S. Tang, M. Matsuo, H. Wu, V. Stavila, A. Unemoto, S.I. Orimo, T.J. Udovic, Stabilizing lithium and sodium fast-ion conduction in solid polyhedral-borate salts at device-relevant temperatures, Energy Storage Mater. 4 (2016) 79–83.

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

[91] L. Duchêne, R.-S. Kühnel, D. Rentsch, A. Remhof, H. Hagemann, C. Battaglia, A highly stable sodium solid-state electrolyte based on a dodeca/deca-borate equimolar mixture, Chem. Commun. 53 (2017) 4195–4198.

[92] K. Yoshida, T. Sato, A. Unemoto, M. Matsuo, T. Ikeshoji, T.J. Udovic, S.I. Orimo, Fast sodium ionic conduction in $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride and application to a bulk-type all-solid-state battery, Appl. Phys. Lett. 110 (2017) 103901.

[93] M. Brighi, F. Murgia, Z. Łodziana, P. Schouwink, A. Wołczyk, R. Černý, A mixed anion hydroborate/carba-hydroborate as a room temperature Na-ion solid electrolyte, J. Power Sources 404 (2018) 7–12.

[94] S. Payandeh, R. Asakura, P. Avramidou, D. Rentsch, Z. Łodziana, R. Černý, A. Remhof, C. Battaglia, Nido-borate/closo- borate mixed-anion electrolytes for all-solid-state batteries, Chem. Mater. 32 (2020) 1101–1110.

[95] S. Payandeh, D. Rentsch, Z. Łodziana, R. Asakura, L. Bigler, R. Černý, C. Battaglia, A. Remhof, *Nido*-hydroborate-based electrolytes for all-solid-state lithium batteries, Adv. Funct. Mater. 31 (2021) 2010046.

[96] M. Brighi, F. Murgia, R. Černý, Closo-hydroborate sodium salts as an emerging class of room-temperature solid electrolytes, Cell Rep. Phys. Sci. 1 (2020) 100217.

[97] A.V. Skripov, O.A. Babanova, A.V. Soloninin, V. Stavila, N. Verdal, T.J. Udovic, J.J. Rush, Nuclear magnetic resonance study of atomic motion in $A_2B_{12}H_{12}$ (A = Na, K, Rb, Cs): anion reorientations and Na^+ mobility, J. Phys. Chem. C 117 (2013) 25961–25968.

[98] K.E. Kweon, J.B. Varley, P. Shea, N. Adelstein, P. Mehta, T.W. Heo, T.J. Udovic, V. Stavila, B.C. Wood, Structural, chemical, and dynamical frustration: origins of superionic conductivity in closo-borate solid electrolytes, Chem. Mater. 29 (2017) 9142–9153.

[99] R. Černý, M. Brighi, F. Murgia, The crystal chemistry of inorganic hydroborates, Chemistry 2 (2020) 805–826.

[100] W.S. Tang, M. Dimitrievska, V. Stavila, W. Zhou, H. Wu, A.A. Talin, T.J. Udovic, Order–disorder transitions and superionic conductivity in the sodium nido-undeca(carba)borates, Chem. Mater. 29 (2017) 10496–10509.

[101] M.S. Andersson, J.B. Grinderslev, X.-M. Chen, X. Chen, U. Häussermann, W. Zhou, T.R. Jensen, M. Karlsson, T.J. Udovic, Interplay between the reorientational dynamics of the $B_3H_8^-$ anion and the structure in KB_3H_8, J. Phys. Chem. C 125 (2021) 3716–3724.

[102] A. Manthiram, X. Yu, S. Wang, Lithium battery chemistries enabled by solid-state electrolytes, Nat. Rev. 2 (2017) (16103).

[103] M. Brighi, F. Murgia, R. Černý, Mechanical behavior and dendrite resistance of *closo*-hydroborates solid-electrolyte, Adv. Mater. Interfaces 31 (18) (2021).

[104] R. Moury, Z. Łodziana, A. Remhof, L. Duchêne, E. Roedern, A. Gigantea, H. Hagemann, Pressure-induced phase transitions in $Na_2B_{12}H_{12}$, structural investigation on a candidate for solid state electrolyte, Acta Crystallogr. B 75 (2019) 406–413.

[105] E.L. Muetterties, J.H. Balthis, Y.T. Chia, W.H. Knoth, H.C. Miller, Chemistry of boranes. VIII. Salts and acids of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$, Inorg. Chem. 3 (1964) 444–451.

[106] L. He, H.W. Li, E. Akiba, Thermal decomposition of anhydrous alkali metal dodecaborates $M_2B_{12}H_{12}$ (M = Li, Na, K), Energies 8 (2015) 12429–12438.

[107] R.J. Wiersema, M.F. Hawthorne, Electrochemistry and boron-11 nuclear magnetic resonance spectra of monocarbon carboranes, Inorg. Chem. 12 (1973) 785–788.

[108] J. Aihara, Three-dimensional aromaticity of polyhedral boranes, J. Am. Chem. Soc. 100 (1978) 3339–3342.

[109] W.S. Tang, A. Unemoto, W. Zhou, V. Stavila, M. Matsuo, H. Wu, S.I. Orimo, T.J. Udovic, Unparalleled lithium and sodium superionic conduction in solid electrolytes with large monovalent cage-like anions, Energy Environ. Sci. 8 (2015) 3637–3645.

[110] S. Pylypko, S. Ould-Amara, A. Zadick, E. Petit, M. Chatenet, M. Cretin, U.B. Demirci, The highly stable aqueous solution of sodium dodecahydro-closo-dodecaborate $Na_2B_{12}H_{12}$ as a potential liquid anodic fuel, Appl. Catal. B 222 (2018) 1–8.

[111] R. Moury, A. Gigante, H. Hagemann, An alternative approach to the synthesis of NaB_3H_8 and $Na_2B_{12}H_{12}$ for solid electrolyte applications, Int. J. Hydrog. Energy 42 (2017) 22417–22421.

[112] A. Berger, C.E. Buckley, M. Paskevicius, Synthesis of closo-$CB_{11}H_{12}$ – salts using common laboratory reagents, Inorg. Chem. 60 (2021) 14744–14751.

[113] S. Kim, K. Harada, N. Toyama, H. Oguchi, K. Kisu, S.I. Orimo, Room temperature operation of all-solid-state battery using a *closo* -type complex hydride solid electrolyte and a $LiCoO_2$ cathode by interfacial modification, J. Energy Chem. 43 (2020) 47–51.

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

[115] F. Murgia, M. Brighi, R. Černý, Room-temperature-operating Na solid state battery with complex hydride as electrolyte, Electrochem. Commun. 106 (2019) 106534.

[116] L. Duchêne, D.H. Kim, Y.B. Song, S. Jun, R. Moury, A. Remhof, H. Hagemann, Y.S. Jung, C. Battaglia, Crystallization of *closo*-borate electrolytes from solution enabling infiltration into slurry casted porous electrodes for all-solid-state batteries, Energy Storage Mater. 26 (2020) 543–549.

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

[118] P. Schouwink, M.B. Ley, A. Tissot, H. Hagemann, T.R. Jensen, L. Smrčok, R. Černý, Structure and properties of a new class of complex hydride perovskite materials, Nat. Commun. 5 (2014) (5706).

[119] P. Schouwink, E. Didelot, Y.S. Lee, T. Mazet, R. Černý, Large magnetocaloric effect and magneto-structural correlations in novel gadolinium borohydrides, J. Alloy. Compd. 664 (2016) 378–384.