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Hydrides for solid-state batteries: A review

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ABSTRACT

Solid-state batteries (SSBs) are one of the most promising candidates for the next generation energy storage devices due to their huge potential for higher safety and energy density. Polymers, oxides and sulfides have been extensively investigated as electrolytes and electrodes for SSBs. Recently, hydrides have attracted much attention as both electrolytes and electrodes for SSBs owing to the existence of unique $H^{\delta-}$ in hydrides. In this review, we provide an overview of the borohydride-based solid electrolytes (SEs) as well as binary hydride- and alanate-based anode materials. Finally, perspectives on the design concept, processing technology and ion insertion/extraction mechanism are provided for the development of hydride-based key components towards practical high-performance SSBs.

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1. Introduction

Solid-state batteries (SSBs) are the most promising candidates for next-generation energy storage devices. The replacement of liquid electrolytes by solid electrolytes (SEs) can not only improve safety by avoiding combustion but also increase the energy density by utilizing more aggressive electrodes [1,2].

SEs and electrodes are the key components for SSBs, which are mainly responsible for ionic conduction and storage, respectively [3]. For SEs, high ionic conduction and wide electrochemical stability window are the main challenges [4]. For electrodes, appropriate electrochemical reaction potential, fast reaction kinetics and large reversible ion storage capacity are more favorable [5,6]. It is obvious that the requirements for SEs and electrodes are quite different, but many classes of materials, such as polymers, oxides and sulfides, can fulfill requirements of either SE or electrode by appropriate compositional and structural tailoring.

Polymers, such as poly (ethylene oxide), can conduct ions through segmental motion, showing good mechanical flexibility. Meanwhile, some conducting polymers, such as poly (pyrrole), can reversibly store high-capacity ions as electrodes [7,8]. Oxides are extensively explored as SEs and electrodes due to their air stability.

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discharge [18]. To comprehensively understand the excellent properties and corresponding mechanisms, we herein review the state-of-art on the hydride SEs and electrodes for SSBs, including typical compounds, improving strategies and SSB performances. Perspectives for future investigations are also provided based on the above discussions for pushing SSBs towards practical applications.

For example, garnet $Li_7La_3Zr_2O_{12}$ has high ionic conductivity and chemical stability; layered $LiCoO_2$ is the most widely used cathode material [9,10]. As for sulfides, $Li_{10}GeP_2S_{12}$ is the first SE that ex-

hibits comparable conductivity to the organic liquid electrolyte $(10^{-2} \text{ S cm}^{-1})$, and TiS₂ can react with ions and electrons via

intercalation reactions, demonstrating stable ionic storage perfor-

reported as electrolytes and electrodes for SSBs (Fig. 1) [13]. For

hydride SEs, beneficial from the lightweight H atoms in the polyanions (such as $[BH_4]^-$ and $[B_{12}H_{12}]^{2-}$), the rotation of polyanions is

much easier, resulting in an effective ion transfer through the paddle-wheel mechanism [14]. In addition, $H^{\delta-}$ is highly reductive,

making hydride SEs more compatible with the metal anodes and/or

leading to more appropriate interphases [15]. As electrodes, some

hydrides can electrochemically react with ions via conversion reactions [16]. The theoretical specific capacities of these hydrides are

therefore much higher than those of typical conversion-type elec-

trodes due to the existence of lightweight H element [17]. More-

over, the small H atoms in the hydride electrodes can diffuse

quickly, leading to a small polarization voltage between charge and

Recently, hydrides, featured by the content of unique $H^{\delta-}$, are





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Fig. 1. Schematic illustration of applications of hydrides as electrode and electrolyte in SSBs.

2. Hydride electrolytes

Hydride with a high ionic conductivity was first reported by Matsuo et al. [19] in 2007, demonstrating that LiBH₄ can rapidly conduct Li⁺ in the *P*6₃*mc* phase. Then, numerous borohydride-based SEs with fast ionic conductivities and high stabilities with metal anodes were developed in SSBs. In this section, two types of anion-based borohydride SEs, i.e., $[BH_4]^-$ and $[B_nH_n]^{2-}$ were reviewed, and the corresponding strategies for performance improvement for SSBs have also been discussed, as seen in Table 1.

2.1. [BH₄]⁻ anion-based electrolytes

 $[BH_4]^-$ is the most simple and common borohydride anion, in which one B atom and four H atoms construct a regular tetrahedron. $[BH_4]^-$ can form stable compounds with alkali or alkaline earth cations, which have great potentials for rapidly conducting ions due to their unique structures, and thus draw intense interest in the recent decade.

2.1.1. Typical compounds

In 2007, Matsuo et al. [19] found for the first time that when LiBH₄ undergoes a structural transition from the orthorhombic *Pnma* phase to hexagonal *P6*₃*mc* phase at 120 °C, the Li⁺ conductivity can be increased by three orders of magnitude (from 10^{-6} to 10^{-3} S cm⁻¹) due to the disorganization of anionic orientation after phase transition. The activation energies of *Pnma* and *P6*₃*mc* phases were 0.69 and 0.53 eV, respectively. Ikeshoji et al. [20] proposed a novel interstitialcy-based mechanism for the fast ionic conductivity process based on first-principles molecular dynamics (FPMD) simulations over LiBH₄ structures (Fig. 2a,b). Due to the double splitting (dumbbell type) of Li atoms, the metastable interstitial sites with a hexagonal center composed of three Li⁺ ions and three

[BH₄]⁻ ions in the *a*-*b* plane and the connection path between the two nearest Li sites are generated. Li atom moves to metastable interstitial sites by thermal excitation, meanwhile leaving a vacancy, thus realizing the rapid diffusion of Li⁺ [21].

The electrochemical stability window of LiBH₄ is investigated by cyclic voltammetry (CV) of a Li|LiBH₄|Mo cell [22]. The results show that no current signals can be detected in the potential range of 0-5 V and the electrochemical stability window is wide enough for SSBs. However, the first principle calculations indicate that the window for LiBH₄ should be in the range of 0.2-2 V, much narrower than the experimental result [23]. Moreover, LiBH₄ is proved to be a good SE to prevent Li dendrite formation, which may be attributed to the in-situ formation of the lowly electron conductive and highly Li⁺ conductive solid electrolyte interphase (SEI) at the interface [24]. On the other hand, LiBH₄ is not compatible with high potential cathodes, such as LiFePO₄ and LiCoO₂, which is the main drawback as a SE.

Since the discovery of the rapid diffusion of Li⁺ in LiBH₄, other [BH₄]⁻-based compounds have also been investigated. NaBH₄ has different crystal structures at different temperatures and pressures (*P*-42₁*c*, *Fm*-3*m*, and *F*-43*m*) [25]. Li et al. [26] firstly used density functional theory (DFT) to fully characterize the *Fm*-3*m* structure of NaBH₄. Half of the lattice sites of H atom in *Fm*-3*m* structure are occupied with the occupancy factor of 0.5, which means that four H atoms in the [BH₄]⁻ group have eight possible positions, the Na⁺ performs octahedral coordination with [BH₄]⁻ exhibits certain disorder (Fig. 2c). Matsuo et al. [27] investigated the Na⁺ conductivity of NaBH₄ by alternating current impedance measurements, which showed very low conductivity of 2×10^{-10} S cm⁻¹ at room temperature (RT) and activation energy of 0.61 eV.

For Mg(BH₄)₂, its polymorphism was observed experimentally, among which the ones with good stability are the $P6_122$, Fddd, Id-3a and $P4_2nm$ phases [28,29]. Matsuo et al. [27] evaluated the Mg²⁺ conductivity capability by calculating the model structure of the

Table 1

Performance comparison of hydride-based electrolytes and corresponding SSBs. LCO represents LiCoO2, LTO represents Li4Ti5O12 and LFP represents LiFePO4.

SSEs	Conductivity (S cm ⁻¹)	Electrochemical Window (V)	Cell	References
LiBH ₄	10 ^{−8} (30 °C) 10 ^{−3} (120 °C)	0–1.8 (theoretical) 0-5 (experimental)	TiS ₂ Li (205 mAh g ⁻¹ @ 0.2 C and 120 °C) S Li (1140 mAh g ⁻¹ @ 0.05 C and 120 °C) LCO Li (89 mAh g ⁻¹ @ 0.05 mA cm ⁻² and 120 °C)	[19,22,23,75,80,81]
Li ₄ (BH ₄) ₃ I	$2\times10^{-4}(30~^\circ\text{C})$	0-5 (experimental)	TiS ₂ Li (141 mAh g ⁻¹ @ 0.05 C and 120 $^{\circ}$ C) LTO Li (122 mAh g ⁻¹ @ 0.02 C and 20 $^{\circ}$ C)	[31,73,79]
$Li(BH_4)_{0.7}(Br)_{0.2}(Cl)_{0.1}$	$1.3 imes 10^{-5} (30 \ ^{\circ}\text{C})$	0-1.8 (experimental)	_	[33]
LiCe(BH ₄) ₃ Cl	10 ^{−4} (20 °C)	0-7 (experimental)	S Li–In (141 mAh g ⁻¹ @ 0.05 C and 120 °C)	[34]
Li(BH ₄) _{1/3} (NH ₂) _{2/3}	6.4 × 10 ^{−3} (40 °C)	0.7-2 (experimental)	LTO Li (101 mAh g ⁻¹ @ 5 C and 40 °C)	[41]
LiBH ₄ ·NH ₃	$2.2 \times 10^{-3} (40 \ ^{\circ}\text{C})$	0-4 (experimental)	-	[47]
Li(BH ₄)·AB	$4 \times 10^{-4} (25 \ ^{\circ}\text{C})$	0-2 (experimental)	_	[48]
90LiBH4 · 10P2S5	10 ^{−3} (27 °C)	0-5 (experimental)	TiS ₂ Li (192 mAh g ⁻¹ @ 0.1 C and 27 °C)	[45]
1/3LiBH ₄ ·2/3 (0.75Li ₂ S·0.25P ₂ S ₅)	$1.6 imes 10^{-3} (25 \ ^{\circ}C)$	0-5 (experimental)	TiS ₂ Li (223 mAh g^{-1} @ 0.064 mA cm ⁻² and 25 °C)	[44]
$Li(BH_4)_{0.75}I_{0.25} \cdot (0.75Li_2S \cdot 0.25P_2S_5)$	10 ^{−3} (30 °C)	0-5 (experimental)	TiS ₂ Li (210 mAh g ⁻¹ @ 0.05 C and 50 °C)	[46]
LiBH ₄ -SiO ₂	10 ⁻⁴ (25 °C)	-	S Li (1500 mAh g ⁻¹ @ 0.03 C and 55 °C)	[55]
Li ₄ (BH ₄) ₃ I-MoS ₂	$2.78 imes 10^{-4} (30 \ ^{\circ}\text{C})$	1-5 (experimental)	-	[60]
LiBH ₄ @MCM41	10 ^{−4} (30 °C)	0-3.5 (experimental)	-	[61]
Li ₄ (BH ₄) ₃ I@SBA-15	$2.5 \times 10^{-4} (35 \ ^{\circ}\text{C})$	0-5 (experimental)	LTO Li (166 mAh g ⁻¹ @ 0.05 C and 55 °C) S Li (1397 mAh g ⁻¹ @ 0.05 C and 55 °C) LCO Li (122 mAh g ⁻¹ @ 0.05 C and 55 °C)	[62]
$M\sigma(BH_4)(NH_2)$	10 ^{−6} (150 °C)	0-3 (experimental)		[66]
$Mg(en)_1(BH_4)_2$	$6 \times 10^{-5} (70 ^{\circ}\text{C})$	0-1.2 (experimental)	_	[67]
$Mg(BH_4)_2(NH_2BH_2)_2$	$1.3 \times 10^{-5} (30 ^{\circ}\text{C})$	0-1.2 (experimental)	LTOIIMg (17 mAh g^{-1} @ 0.01 C and 30 °C)	[69]
$Mg(BH_4)_2 \cdot NH_2$	$3.3 \times 10^{-4} (80 ^{\circ}\text{C})$	0.5-1.2 (experimental)		[70]
Li ₂ B ₁₂ H ₁₂	$3.1 \times 10^{-4} (30 ^{\circ}\text{C})$	0-6 (experimental)	TiS ₂ Li (217 mAh g ⁻¹ @ 0.05C and 60 °C) TiS ₂ Li (228 mAh g ⁻¹ @ 0.05C and 80 °C) LFP Li (129 mAh g ⁻¹ @ 75 °C)	[86,112–114]
Na ₂ B ₁₂ H ₁₂	10 ⁻² (110 °C)	0-4 (experimental)	_	[93]
$Na_2B_{10}H_{10}$	10 ^{−6} (30 °C) 10 ^{−1} (265 °C)	0-4 (experimental)	-	[95]
Na3NH2B12H12	10 ⁻⁴ (100 °C)	0-10 (experimental)	TiS ₂ Na (146 mAh g ⁻¹ @ 0.1 C and 80 $^{\circ}$ C)	[64]
LiCB ₁₁ H ₁₂	$1.5 \times 10^{-1} (130 \ ^{\circ}\text{C})$	_	TiS ₂ Li (175 mAh g ⁻¹ @ 0.2 C and 60 °C)	[84]
LiCB ₉ H ₁₀	10 ^{−1} (110 °C)	_	-	[85]
NaCB ₁₂ H ₁₂	1.2 × 10 ⁻¹ (110 °C)	_	_	[84]
NaCB9H10	10 ^{−1} (100 °C)	_	_	[85]
$Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}$	$9 \times 10^{-4} (20 ^\circ C)$	0–6.5 (experimental)	NaCrO ₂ Na (80 mAh g ⁻¹ @ 0.2 C and 60 °C) NaCrO ₂ Na—Sn (118 mAh g ⁻¹ @ 0.1 C and 30 °C)	[100]
Na4(CB11H12)2(B12H12)	$2 \times 10^{-4} (25 \ ^\circ C)$	0-4.1 (experimental)	Na ₃ (VOPO ₄) ₂ F Na (104 mAh g ⁻¹ @ 0.1 C and 30 °C)	[102,117]
Na ₂ (CB ₉ H ₁₀)(CB ₁₁ H ₁₂)	$7 \times 10^{-2} (27 \ ^{\circ}C)$	_	-	[103]
Li ₂ (CB ₉ H ₁₀)(CB ₁₁ H ₁₂)	$4 imes 10^{-2}$ (77 °C)	_	-	[103]
$Li(CB_9H_{10})_{0.7}(CB_{11}H_{12})_{0.3}$	$6.7\times10^{-3}(25\ ^\circ C)$	0-5 (experimental)	TiS ₂ Li (229.5 mAh g ^{-1} @ 0.1 C and 60 °C) S Li (1618 mAh g ^{-1} @ 0.03 C and 25 °C)	[104,105]

Fddd phase using the FPMD simulation method (Fig. 2d). The strong Coulombic interaction locking of the Mg^{2+} in a narrow tetrahedral cage of four [BH₄]⁻ results in conductivity of less than 10^{-10} S cm⁻¹ at RT (Fig. 2e) [30]. It is hypothesized that a significant improvement in ionic conductivity is expected if Mg^{2+} is located in a larger cage, just like the LiBH₄ *P*6₃mc phase.

2.1.2. Strategies for improving ionic conductivities

The typical [BH₄]⁻ containing compounds all show great potentials as SEs, but they still cannot meet the requirements for practical use. For LiBH₄, lowering the Li⁺ diffusion barrier at RT can be achieved by bulk phase modifications and/or phase boundary engineering.

Ion substitution and ligand complexation are effective strategies for bulk phase modification. Maekawa et al. [31] doped lithium halide LiX (X = Cl, Br and I) in LiBH₄, significantly reducing the phase transition temperature and stabilizing the LiBH₄ $P6_3mc$ phase to RT. Among these solid solutions, embedding highly polarized I⁻ of the maximum radius may help to broaden Li⁺ diffusion channels and reduce electrostatic interactions between anions and cations (Fig. 3a). Li₄(BH₄)₃I displays the highest conductivity (above 10⁻⁵ S cm⁻¹) at RT and the lowest activation energy (0.56 eV), as summarized in Fig. 3b. After that, the DFT calculations and experiments show that increasing the concentration of substituents can improve the stabilization of the $P6_3mc$ phase [32]. The most effective way to stabilize the $P6_3mc$ phase at the same substituent concentration is to use I⁻ instead of [BH₄]⁻ or K⁺ instead of Li⁺. I⁻ substitution has been proved to be effective, but K⁺ substitution blocks the diffusion path of Li⁺ and leads to a narrow diffusion channel, and thus the conductivity of Li⁺ obtained by K⁺ substitution is very low. The LiBH₄ with more than 15% LiI can stabilize the *P6*₃*mc* phase down to RT. Higher ion content leads to larger lattice parameter, which may weaken the Li–H interaction and facilitate the transition of Li. Gulino et al. [33] found that the presence of Br⁻ in the solid solution facilitated the solubilization of \mbox{Cl}^- with up to 30% through the $\mbox{LiBH}_4\mbox{-LiBr}-\mbox{LiCl}$ ternary phase diagrams at RT. Based on that, their group first reported that the Li(BH₄)_{0.7}Br_{0.2}Cl_{0.1} ternary hexagonal solid solution has the highest ionic conductivity of 1.3×10^{-5} S cm⁻¹ for ternary samples at 30 °C.

The binary alkali/lanthanide borohydride chlorides LiM(BH₄)₃Cl (M = Ge, La, Gd) systems also exhibit reformative Li⁺ conduction properties [34,35]. Lee et al. [36] studied the diffusion mechanism of Li⁺ in LiGe(BH₄)₃Cl, and this unique mechanism leads to rapid Li⁺ conduction. For LiLa(BH₄)₃X (X = Cl, Br, I), the new addition reaction of La(BH₄)₃ and LiX can obtain LiLa(BH₄)₃X much easier than the LaX₃-LiBH₄ reaction [37]. By adjusting the anion size of halide, LiLa(BH₄)₃Br compound has the highest ionic conductivity of



Fig. 2. (a, b) FPMD calculations of the free energy (0.05 eV, 0.30 eV, 0.31 eV and 0.32 eV) on the surface of Li and H atoms in the LiBH₄ *P6*₃*mc* phase [20]. Copyright 2011 American Physical Society. (c) Unit cells of NaBH₄ *P42*₁*c* phase [25]. Copyright 2004 Elsevier. (d) FPMD calculations of free energy (0.18 eV) on the surface of Mg and H atom in the Mg(BH₄)₂ *fdd* phase at 230 °C [27]. Copyright 2013 Elsevier. (e) Temperature-dependent conductivities of LiBH₄, NaBH₄ and Mg(BH₄)₂ [19,25,30].

 7.74×10^{-5} S cm $^{-1}$ at RT. To further optimize the bimetallic borohydrides system, the other ingredient such as KBH₄, Mn(BH₄)₂, Mg(BH₄)₂, Ce(BH₄)₃, CeCl₃, or ZnCl₂, were added to the LiBH₄ to form trimetallic borohydrides. Cerny et al. [38] and Brighi et al. [39] synthesized a series of SEs like Li₃MgZn₅(BH₄)₁₅ and Li₃MnZn₅(BH₄)₁₅ Li₃K₃Ce₂(BH₄)₁₂ and Li₃K₃La₂(BH₄)₁₂, of which the highest conductivity can reach 6×10^{-7} S cm $^{-1}$ at RT.

Motoaki et al. [40] developed two compounds with the general formula Li(BH₄)_{1-x} (NH₂)_x with cubic I2₁3 phase x = 3/4 and trigonal *R*-3 phase x = 1/2, exhibited high Li⁺ conductivity at RT around 10^{-4} S cm⁻¹ higher than those of both parent hydrides (Fig. 3c,d). The activation energy for conduction significantly decreased at 95 °C from 0.56 eV (30-75 °C) to 0.24 eV (above 95 °C). Alternatively, the optimal Li⁺ conductivity of 6.4×10^{-3} S cm⁻¹ at RT was reached for a new lithium amide-borohydride of $Li(BH_4)_{1-x}$ (NH₂)_x, (x = 2/3) through increasing the precursor ratio LiBH₄:LiNH₂ to 1:2 [41]. The activation energy is 0.30 eV above 40 °C. The $I2_13$ phase of the material remains unchanged, but the lattice parameter is larger than for the x = 3/4 phase, the existence of additional $[BH_4]^-$ within $I2_13$ phase or the existence of a disordered side phase enables Li^+ to diffuse rapidly. In addition, LiBH₄ and Li₂NH can also react with each other to form a new Pna21 phase by ball milling more than 24 h or heating to 150 °C, which exhibited a conductivity of about 10^{-5} S cm⁻¹ at RT [42].

Generally, glass electrolytes have higher ionic conductivities than crystal ones. It was reported that the $(100-x) \cdot (0.75 \text{Li}_2 \text{S} \cdot 0.25 \text{P}_2 \text{S}_5) \cdot x \text{LiBH}_4$ ($0 \le x \le 33$) glass SE can be prepared by a mechanochemical method [43,44]. Due to the reduced electrostatic interaction by S^{2-/} [BH₄]⁻ random distribution, the samples with x = 33 exhibit conductivities as high as 1.6×10^{-3} S cm⁻¹ at 25 °C, and presented a wide apparent electrochemical window of 0–5 V. Unemoto et al. [45] and Kharbachi et al. [46] further investigated 90LiBH₄ · 10P₂S₅ and Li(BH₄)_{0.75}I_{0.25} · (0.75Li₂S · 0.25P₂S₅) hydride-sulfide system SEs, which showed the ionic conductivity of 10^{-3} S cm⁻¹ at RT and low activation energy of 0.38 and 0.30 eV, respectively. Quasielastic

neutron scattering (QENS) and elastic scattering fixed window scans (FWSs) reveal that the rapid reorientation of the anionic group may be a key factor in altering the ionic conductivity of borohydride.

More recently, the new concept of ionic conductivity enhancement by complexation with neutral ligands has also been proposed. Zhang et al. [47] systematically investigated the ammonia absorption properties of LiBH₄. LiBH₄·(NH₃)_x (0 < x < 2) exhibited a high ionic conductivity of 2.21×10^{-3} S cm⁻¹ at 40 °C (Fig. 3e,f). As the volume density of Li⁺ decreases and the atomic arrangement changes, the activation energy of Li⁺ migration decreases, and the defects generated in the deformation process are expected to improve its Li⁺ conductivity replacing substituting an element by introducing gas. Moreover, Liu et al. [48] developed LiBH₄ ammonia borane (AB) complexes by incorporation of AB into the LiBH₄ structure. The molecular volume of AB is much larger than that of NH₃, which will lead to larger volume expansion and lower volume density of Li⁺. The conductivity of LiBH₄·AB at RT is as high as 4×10^{-4} S cm⁻¹. The activation energy of (LiBH₄)₂·AB is 0.25 eV, while LiBH₄ · AB is only half of it (0.12 eV), which results in ultrafast Li⁺ conduction of lithium borohydride ammonia borane complex at RT. In addition, CV result indicates that the apparent electrochemical stability window of (LiBH₄)₂·AB and LiBH₄·AB is 0–2 V.

 $[BH_4]^-$ anion-based electrolytes were also investigated as lithium salt in the composite polymer electrolytes [49]. The PEO-LiBH₄ SE has a relatively high Li⁺ transference number of 0.62 probably attributed to the interaction between $[BH_4]^-$ and terminal hydroxyl groups of PEO. In contrast, PEO-Li₄(BH₄)₃I–SiO₂ exhibited higher ionic conductivity and better mechanical properties, and the addition of ceramic filler SiO₂ prevented the formation and growth of lithium dendrites. PEO-Li₄(BH₄)₃I–SiO₂ exhibited a Li⁺ conductivity of 4.28 × 10⁻⁴ S cm⁻¹ at 70 °C. The corresponding electrochemical window and Li⁺ transference number are 3.6 V and 0.42, respectively.

From the above, new single-phase SEs are developed via ion substitution and ligand complexation. These single-phase SEs already exhibit comparable Li⁺ conductivities to polymer, oxide



Fig. 3. (a) Crystal structure of $\text{Li}_4(\text{BH}_4)_3\text{I}$ [22]. Copyright 2019 Elsevier. (b) Temperature-dependent conductivities of LiBH₄-LiX (X = Cl, Br and I) [31]. Copyright 2009 American Chemical Society. (c) Crystal structure of Li(BH₄)_{1-x} (NH₂)_x (x = 2/3) and its symmetry-related dual structure. (d) Temperature-dependent conductivities of Li(BH₄)_{1-x} (NH₂)_x and their precursors LiBH₄ and LiNH₂ [41]. Copyright 2017 Wiley-VCH. (e) Crystal structure of LiBH₄·NH₃. (f) Temperature-dependent conductivities of LiBH₄·NH₃ [47]. Copyright 2018 Elsevier.

and sulfide SEs, but the introduction of additional ions and ligands in the crystal structure may degrade their electrochemical stability and electrode compatibility. Therefore, further improving the [BH₄]⁻based SEs by composition with other functional components to form Li⁺ fast conduction channels at the phase boundary is another successful approach.

Dual-cation borohydride (1-x)LiBH₄-xCa(BH₄)₂ composites were prepared by ball milling of different ratios of LiBH₄ and Ca(BH₄)₂ [50]. No solid solution was observed in the composites, which was proved to be a physical mixture of Ca(BH₄)₂ and LiBH₄ Pnma phase by synchrotron radiation X-ray diffraction (XRD), showing an ionic conductivity of 8.8 \times 10⁻⁶ S cm⁻¹ at 40 °C. Subsequently, the LiBH₄-NaBH₄ system and the LiBH₄-MgH₂ system were also developed with enhanced ionic conductivity (10^{-2} S cm⁻¹ at above 100 °C) compared to the pristine LiBH₄ and showed an apparent potential window of wider than 0–4 V [51,52]. Inspired by this, Xiang et al. [53] developed a LiBH₄-NaBH₄-MgH₂ ternary composite SE with high Li⁺ conductivity. For the 4LiBH₄-NaBH₄-30% MgH_2 composite, the ionic conductivity reached $1.12\times10^{-2}\,S\,cm^{-1}$ at 110 °C and an apparent potential window from 0–4 V, indicating the NaBH₄-MgH₂ co-additive can effectively stabilize the P6₃mc phase of LiBH₄. They further combined the strategies of the LiBH₄-NaBH₄ eutectic system and halide substitution to jointly facilitate the diffusion of the ions in the system.

Ball-milled LiBH₄-NaX (X = Cl, I) composites achieve coexistence of halide solid solution and LiBH₄-NaBH₄ composite, achieving an ionic conductivity up to 10^{-2} S cm⁻¹ above 100 °C, which is approximately two orders of magnitude higher than the pristine LiBH₄ [54]. The formation of a highly defective interface between phases is favorable for Li⁺ diffusion. A series of fast-ionic conductors of LiBH₄oxide systems were developed by making LiBH₄ and oxides form an interface to improve ionic conductivity. Adding nano-oxides such as SiO₂, Al₂O₃, CaO, MgO, TiO₂, ZrO₂, etc., into LiBH₄ by ball milling can greatly improve the conductivity of Li⁺ at RT (Fig. 4a,b) [55–57]. The presence of oxide nanoparticles forms a defective highly conductive layer at the interface between LiBH₄ and the oxide, and the volume fraction and particle size of the insulating phase determine the enhancement. Recently, Zhao et al. [58] reported the in-situ formation of nanocrystalline Li₂O by mechanically milling different stoichiometric ratios of LiBH₄, LiNH₂, and LiOH. By the conversion of the crystalline LiBH₄ \cdot (NH₃)_x to the amorphous state on the surface of Li₂O particles and the interfacial layer formed between the two amorphous phases, the thermal stability and electrochemical properties of LiBH₄·(NH₃)_x-78 wt% Li₂O was further enhanced, the ionic conductivity was increased to 5.4×10^{-4} S cm⁻¹ at 20 °C.

Apart from that, MoS₂ with layered structure and high surface areas also offer alternative opportunities. Liu et al. proved the feasibility of the MoS₂ scaffold for borohydride SEs [59,60]. LiBH₄–MoS₂ and Li₄(BH₄)₃I–MoS₂ composites were synthesized by ball milling, the ionic conductivity at RT reached 1 × 10⁻⁴ and 2.78 × 10⁻⁴ S cm⁻¹ respectively, and both CV curves indicate an electrochemical stability window of 1–5 V. It was suggested that the aligned interface effect between the borohydride and 2D layered material may help to reduce the migration energy barrier and lead to improved Li⁺ mobility.

The formation of interfaces with high surface area 3D materials to facilitate ionic conduction was also investigated. Silica has very low electron conductivity, which makes it an ideal nano-scaffold. Blanchard and coworkers [61] propose that confinement of LiBH₄ in mesoporous silica scaffold (MCM-41) by melt-infiltration, in which conductivity of LiBH₄@MCM41 is 1×10^{-4} S cm⁻¹ at 40 °C (Fig. 4d), due to the rapid migration of Li⁺ in the interface layer between LiBH₄ and SiO₂. Solid-state ⁷Li nuclear magnetic resonance (NMR) reveals the presence of two different components of LiBH₄ in mesoporous MCM-41, as described in Fig. 4c: i) the wide line represents the slow Li⁺ mobility component, which may originate from the crystalline bulk LiBH₄ in the pore and does not contribute to the high conductivity at RT; ii) the narrow line indicates the presence of a high Li⁺ mobility component, which may originate from the LiBH₄ at the MCM-41 interface, contributing to the high ionic conductivity in the entire temperature range. The ratio of the high mobility phase to the low mobility phase is roughly calculated to be 3:7 based on the spectral areas of the two components. The interfacial interaction between LiBH₄ and mesoporous SiO₂ may be the main reason for the rapid Li⁺ migration in LiBH₄@MCM41. Inspired by this, Lu and co-workers [62] have successfully confined the highly conductive Li₄(BH₄)₃I into mesoporous silica SBA-15 via the combination of halide substitution and scaffold nanoconfinement (Fig. 4e). The results show that the conductivity is as high as 2.5×10^{-4} S cm⁻¹ at 35 °C (Fig. 4f) and an apparent potential window from 0–5 V. The solid-state ⁷Li NMR spectroscopy of Li₄(BH₄)₃I@SBA-15 showed that the slow Li⁺ mobility component and the high Li⁺ mobility component each accounted for 50%, indicating that Li₄(BH₄)₃I in the mesoporous SiO₂ interfacial layer significantly enhanced the Li⁺ mobility.

Moreover, a series of Na and Mg fast ion conductor materials have been studied to solve the problem of low ionic conductivity of NaBH₄ and Mg(BH₄)₂ at RT. Matsuo et al. [27,63] compared various combinations of NaBH₄-NaNH₂-NaI systems in terms of structures and Na^+ conductivity properties. Among them, $Na(BH_4)_{0.5}(NH_2)_{0.5}$, with an antiperovskite-type structure provides a large number of vacancies to facilitate fast Na⁺ migration exhibiting the relatively excellent Na⁺ conductivity of 2×10^{-6} S cm⁻¹ at RT and an apparent electrochemical stability window of up to 6 V. Sadikin et al. [64] prepared the Na₃BH₄B₁₂H₁₂ metal borane-borohydride via ball milling a mixture of NaBH₄ and Na₂B₁₂H₁₂ during and heat treatment. The Na₃BH₄B₁₂H₁₂ conduction pathways indicate that the Na-rich region containing [BH₄]⁻ ions and the Na-free region constructed by *closo*-borohydride anion alternately appear without interconnection. This lavered character is also reflected in the fact that the thermal expansion of the *b*-axis is lower than that of the *a*and *c*-axes, indicating that there is a continuous 2D migration path of Na⁺ along the (010) planes. The RT Na⁺ conductivity of Na₃BH₄B₁₂H₁₂ is about 5×10^{-4} S cm⁻¹, which is more than two orders of magnitude higher than that of $Na(BH_4)_{0.5}(NH_2)_{0.5}$.

 $Mg(BH_4)_2$ has a large bandgap, and there are ionic bonds between Mg^{2+} and $[BH_4]^-$ and strong covalent bonds in each anionic complex, resulting in a strong Coulomb interaction and low Mg²⁺ mobility $(10^{-12} \text{ S cm}^{-1} \text{ at RT})$ [65]. Multiple [BH₄]⁻-based Mg²⁺ ionic conductors were reported to improve the unsatisfactory conductivity of Mg(BH₄)₂, as summarized in Fig. 5a. In 2014, Higashi et al. [66] first developed $Mg(BH_4)(NH_2)$ as a SE, in which Mg^{2+} is coordinated tetrahedrally by two [BH₄]⁻ and two [NH₂]⁻ groups. Benefiting from the Mg zigzag chain and tunnel structure (Fig. 5b), the distance (3.59 Å) between adjacent Mg atoms in Mg(BH₄)(NH₂) is less than that of $Mg(BH_4)_2$ (4.32 Å) facilitating Mg^{2+} diffusion with high ionic conductivity of $1 \times 10^{-6}~\text{S}~\text{cm}^{-1}$ at 150 °C, and with an oxidative decomposition potential of about 3 V. Beside, Roedern et al. [67], Burankova et al. [68] and Kisu et al. [69] have investigated the coordination of Mg^{2+} with $NH_2CH_2CH_2NH_2$ (en), diglyme, and AB. Enabling Mg²⁺ to enter the environment of partial chelation and asymmetric coordination thus speeding up the mobility of Mg^{2+} , The conductivity of Mg (en)₁(BH₄)₂, Mg(BH₄)₂-diglyme_{0.5} and Mg(BH₄)₂(NH₃BH₃)₂ are up to 6×10^{-5} (70 °C), 2×10^{-5} (75 °C), and 1.3×10^{-5} S cm⁻¹ (30 °C), respectively, and an apparent electrochemical window of 1.2 V. To further enhance the Mg²⁺ conductivity within the [BH₄]⁻ group, Yan et al. [70] developed a ammoniacal magnesium borohydride Mg(BH₄)₂·NH₃ (Fig. 5c), which exhibited an advanced Mg²⁺ conductivity of 3.3×10^{-4} S cm⁻¹ at 80 °C, about 8 orders of magnitude higher than for Mg(BH₄)₂. The high conductivity of Mg(BH₄)₂·NH₃ is attributed to form a network of dihydrogen bonds by the combination of complex anion and neutral ligand, which promotes the rapid conduction of Mg^{2+} (Fig. 5d). Moreover, these authors further explored the conductivity of $Mg(BH_4)_2 \cdot xNH_3$ composites with non-integer x value, and combined the conductive material with MgO nanoparticles to make it



Fig. 4. (a) Schematic illustration of ion migration in LiBH₄-oxide systems. (b)Temperature-dependent conductivities of LiBH₄-oxide systems [57]. Copyright 2020 American Chemical Society. (c) The solid-state ⁷Li NMR spectroscopy at different temperatures. (d) Temperature-dependent conductivities of LiBH₄-SiO₂ nanocomposites and bulk LiBH₄. (Circles: 90% melt-infiltrated sample; squares: 60% melt-infiltrated sample, green diamonds: physical-mixture, red triangles: bulk LiBH₄) [61]. Copyright 2014 Wiley-VCH. (e) Schematic illustration of synthesis procedures for Li₄(BH₄)₃@SBA-15. (f) Temperature-dependent conductivities of LiBH₄, Li₄(BH₄)₃I, LiBH₄@SBA-15, and Li₄(BH₄)₃]@SBA-15 [62]. Copyright 2019 Wiley-VCH. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

amorphous to further improve the ionic conductivity [71]. For the Mg(BH₄)₂·1.6NH₃@MgO composite, the ionic conductivity reached 10^{-3} S cm⁻¹ at 70 °C and stable magnesium plating/stripping in symmetrical cells for at least 100 cycles.

2.1.3. Strategies for improving compatibility to electrodes

With the above methods to enhance ionic conductivity, [BH₄] anion-based SEs have basically reached the requirements for practical use in terms of conductivity, but problems in electrode



Fig. 5. (a) Reported ionic conductivity of Mg-ion hydride conductors as a function of temperature [27,66–71]. (b) Crystal structure (left) and Mg zigzag arrangement (right) of Mg(BH₄)(NH₂) [66]. Copyright 2014 Royal Society of Chemistry. (c) Crystal structures of Mg(BH₄)₂·NH₃. (d) The energy profile of interstitial Mg²⁺ migrating along the *b*-axis calculated by FPMD [70]. Copyright 2020 Royal Society of Chemistry.

compatibility still need to be solved for configuration into SSBs for commercial applications.

The $H^{\delta-}$ in $[BH_4]^-$ has high reducibility, and thus is expected to be stable to metal anodes. Mo et al. [15] compared the cycling stability of Li|LiBH4|Li and Li|LiBH4-30LiF|Li symmetrical cells (Fig. 6a). The smaller overpotential indicates that no significant side reactions occur between LiBH₄ and Li metal, and with the addition of LiF, the cell cycling duration is extended by 250% compared to that of the pure LiBH₄, the critical current density (CCD) rises from 2.8 to 6.6 mA cm⁻². As shown in Fig. 6b, the added LiF with insulator nature is in the voids/grain boundary of LiBH₄, interrupting the encounter of electron and Li⁺ to prevent the formation of Li dendrites, ensuring structural stability during cycling. It should be noted that, up to now, LiBH₄ exhibits the highest CCD among the reported SEs (all without modifications). We think this advantage can be mainly ascribed to the better intrinsic electrochemical stability and more appropriate SEIs. This phenomenon can also be found for other hydride SEs (such as Li₂B₁₂H₁₂, as illustrated in Section 2.2.3), indicating that this is a general advantage for hydride SEs.

On the other hand, $[BH_4]^-$ is liable to be oxidized at higher potentials, and thus maybe not be stable enough for some cathode materials. TiS₂ has relatively low working potential at around 2 V, but LiBH₄ is still found to be unstable to TiS₂ [72]. Unemoto et al. [73] investigated the interface between TiS₂ and LiBH₄ and found that L_{i2}B₁₂H₁₂ is in-situ formed as stable interphase. This interphase can enable the stable cycling of TiS₂|LiBH₄|Li SSBs for 300 cycles in the voltage range of 1.6–2.7 V at 125 °C and 0.2 C with an available discharge capacity of 205 mAh g⁻¹ after the 2nd cycle and high Coulombic efficiency of near 100% (Fig. 6c,d). They also assembled SSBs in TiS₂ (Li₄(BH₄)₃I as conductor)|Li₄(BH₄)₃I|Li and TiS₂ (LiBH₄

I[−] doping on the electrolyte stability and battery performance. It should be noted that, in the description of SSBs, the conductors are only shown when they play important roles. They found that the interface between Li₄(BH₄)₃I and TiS₂ is not as stable as that between LiBH₄ and TiS₂, leading to a remarkable capacity decay in the reversible capacity. In addition, the low initial discharge capacity can be attributed to the direct solid-state reaction between [BH₄][−] and TiS₂ to form Li_xTiS₂; the initial charge capacity that is higher than the theoretical value can be ascribed to the decomposition of [BH₄][−] to form interphase.

S has high theoretical capacity (1675 mAh g^{-1}) and acceptable working potential (around 2.1 V), which is one of the most promising cathodes for SSBs [74]. The exploration of [BH₄]⁻ anion-based SEs in Li-S batteries were therefore performed. LiBH₄ is investigated as SE in Li-S battery, which is high-energy ball milled with various carbon materials, such as Ketjen Black (KB), Maxsorb, et al., to form continuous ion/electron conducting pathways in the cathode [75]. The S (KB-Maxsorb-LiBH₄ as conductor)|LiBH₄|Li delivered a discharge capacity of 1140 mAh g⁻¹ under 120 °C and 0.025 mA cm^{-2} in the first cycle, equivalent to 70% of the sulfur utilization ratio, and also exhibited a discharge capacity of 730 mAh g⁻¹ after 45th cycles (Fig. 6e,f), which was superior to both reference S (Maxsorb-LiBH4 as conductor)|LiBH4|Li and S (KB-LiBH4 as conductor)|LiBH₄|Li (950 mAh g^{-1}). To enable the cycling of the Li-S SSBs at lower temperatures, Unemoto et al. [76] use Cl⁻ doped LiBH₄ as SE and construct the S|Li₄(BH₄)₃Cl|Li SSBs. A capacity of 1377 mAh g⁻¹ is achieved at a current density of 150 μ A cm⁻², corresponding to 80% sulfur utilization ratio. Alternatively, Lefevr et al. [77] designed a solid-state Li-S battery using a 30/70 wt% LiBH₄/SiO₂ SE. When this SSB was cycled at 55 °C and 0.03 C, Coulombic efficiency recorded in the first 10 cycles was about 88.8%, and the discharge capacity at this moment was 794 mAh g^{-1} .



Fig. 6. (a) Electrochemical cycling curves of Li|LiBH₄–LiF|Li cells at 1.0 mA cm⁻² and 125 °C [15]. (b) Schematic illustration of Li dendrite suppression mechanism in LiF-modified electrolyte system [15]. Copyright 2019 Wiley-VCH. Galvanostatic charge/discharge curves (c) and cycling stability (d) of TiS₂|LiBH₄|Li SSB at 0.2 C and 120 °C [81]. Copyright 2015 American Chemical Society. Galvanostatic charge/discharge curves (e) and cycling stability (f) of S|LiBH₄|Li SSB at 0.05 C and 120 °C [75]. Copyright 2014 AIP Publishing. Galvanostatic charge/discharge curves (g) and cycling stability (h) of LiCoO₂|Li₄(BH₄)₃|Li SSB at 0.05 C and 55 °C [62]. Copyright 2019 Wiley-VCH.

Capacity attenuation may be caused by the loss of contact between electrolyte and electrode interface due to the expansion of cathode electrode volume (80%) during circulation. Lu et al. [62] assembled a Li–S SSB utilizing an SBA-15-confined Li₄(BH₄)₃I SE, which was successfully operated at 55 °C and 0.05 C, showing an initial discharge capacity of 1397 mAh g⁻¹, equivalent to 90% of the sulfur utilization ratio, and a Coulombic efficiency near 100% after the 2nd cycle. Zhang et al. [49] evaluated the suitability of a hydride containing composite SE in Li-sulfurized pyrolyzed poly (acrylonitrile) (SPAN) SSBs. The SPAN|PEO-Li₄(BH₄)₃I–SiO₂|Li configuration of the SSB provided a specific capacity of 967 mAh g⁻¹ after 75th cycles of stabilization at 70 °C.

Li₄Ti₅O₁₂ is usually an anode material due to its low lithiation/ delithiation potential (1.55 V) [78]. This value is low enough to avoid apparent decomposition of $[BH_4]^-$ anion-based SEs, and thus Li₄Ti₅O₁₂ is a good electrode choice for investigating the cycling stability of $[BH_4]^-$ anion-based SEs. Yoshida et al. [79] assembled Li₄Ti₅O₁₂|Li₄(BH₄)₃|Li SSBs, which were operated in the potential range of 1–2 V. The SSBs delivered excellent cycling performance (170 mAh g⁻¹, 1st cycle; and 140 mAh g⁻¹, 100th cycle) at 150 °C and 0.2 C and (122 mAh g⁻¹, 1st cycle; and 111 mAh g⁻¹, 5th cycle) at 23 °C and 0.02 C with nearly 100% Coulombic efficiency.

[BH₄]⁻ anion-based SEs are generally not compatible with higher potential oxide cathodes, which may lead to the formation of inert interphase and prevent the ion transfer. Takahashi and co-workers

[80] studied LiCoO₂|LiBH₄|Li SSBs. They found that this type of SSB cannot cycle without interface modification. A Li₃PO₄ intermediate layer is then introduced to the LiBH₄/LiCoO₂ interface, which can prevent the side reaction and result in a reversible capacity of 89 mAh g⁻¹ at 120 °C with a capacity retention ratio of 97% at 0.05 mA cm⁻² after 30th cycles of the SSBs. Lu et al. [62] introduced LiNbO₃ and sulfide in the composite cathode to block the direct contact between [BH₄]⁻ anion-based SEs and LiCoO₂. The assembled LiCoO₂@LiNbO₃-Li₂S·P₂S₅|Li₄(BH₄)₃I@SBA-15|Li SSB achieved a discharge capacity of 122 mAh g⁻¹ in the first cycle at 0.05 C and 55 °C and presented a stable capacity over 28 discharge-charge cycles, with a Coulombic efficiency close to 100% (Fig. 6g,h).

2.2. $[B_nH_n]^{2-}$ anion-based electrolytes (n = 10, 12)

Structurally, the *closo*-type $[B_nH_n]^{2-}$ anion (in this review, n = 10,12) exhibits a higher diameter and lower reactivity than $[BH_4]^-$ anion, which have closed polyhedral clusters of n boron atoms and terminal hydrogen atoms [82,83]. These unique structures of large cage-like $[B_nH_n]^{2-}$ anion give their compounds the great potential for fast ionic conductivity (Fig. 7a) [84,85].

2.2.1. Typical compounds

 $Li_2B_{12}H_{12}$ was first found to exhibit high ionic conduction $(10^{-4} \text{ S cm}^{-1} \text{ at RT} \text{ with an activation energy of 0.34 eV})$ by

Teprovich et al. [86] in 2015. Li₂B₁₂H₁₂ can be synthesized by the reaction between LiBH₄ and B₂H₆ [87], or B₁₀H₁₄ [88]. Paskeviciu et al. [89] proposed that Li₂B₁₂H₁₂ is *Pa*-3 structure at below 355 °C, in which the presence of a frustrated Li⁺ lattice indicate Li⁺ conduction.

 $Li_2B_{10}H_{10}$ is another relatively stable $[B_nH_n]^{2-}$ anion-based SE, which shows a $P6_422$ structure at below 367 °C [90]. Varley et al. [91] predict that $Li_2B_{10}H_{10}$ may possess promising Li^+ conduction properties according to the ab initio molecular dynamics simulation (AIMD) calculation results. However, the experimental

 ${\rm Li}^+$ conductivity of ${\rm Li}_2{\rm B}_{10}{\rm H}_{10}$ has not been reported yet, which may be due to the difficulty of synthesis.

Other alkali-metal *closo*-borohydrides are also investigated as corresponding ion conductors. Na₂B₁₂H₁₂ shows a *P*2₁/*n* structure at RT and changes into *Im*-3*m* structure at 256 °C with a significant Na⁺ conductivity increase to 10^{-4} S cm⁻¹ [92]. During the cooling process, the superionic conductivity can be maintained until the temperature falls below 205 °C due to the structural hysteresis (Fig. 7b) [93]. NMR spectra studies showed that the jump in Na⁺ mobility is concomitant with the [B₁₂H₁₂]²⁻



Fig. 7. (a) Geometric shapes and Mulliken charges of $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ [84,85]. Copyright 2015 Royal Society of Chemistry. Copyright 2016 Wiley-VCH. (b) Temperaturedependent conductivities of Li₂B₁₂H₁₂ [89], Na₂B₁₂H₁₂ [93], and Na₂B₁₀H₁₀ [95]. (c) Effect of structural, chemical, and dynamical frustration on ultrafast ion conduction [14]. Copyright 2017 American Chemical Society. (d) Decomposition products of Li₂B₁₂H₁₂ (left) and Na₂B₁₂H₁₂ (right) at different voltages [23]. Copyright 2017 American Chemical Society.

reorientation, and the corresponding activation energy for Na⁺ diffusion is about 0.41 eV [94].

Na₂B₁₀H₁₀ has a much lower order-disorder phase transition temperature than $Na_2B_{12}H_{12}$ [95]. The ordered $P2_1/c$ phase transforms to disordered Fm-3m phase at 87 °C [96], and then exhibits remarkable superionic conductivity, reaching 10^{-2} S cm⁻¹ at $110 \degree$ C. Different saddle points inherent within the disordered Fm-3m Na₂B₁₀H₁₀ and Im-3m Na₂B₁₂H₁₂ structures are mainly responsible for the different Na⁺ conduction properties, i.e., the activation energy of Na⁺ diffusion in Na₂B₁₀H₁₀ (0.19 eV) is less than half of that in Na₂B₁₂H₁₂ (0.41 eV), and the phase transition temperature of $Na_2B_{10}H_{10}$ (87 °C) is lower than that of $Na_2B_{12}H_{12}$ (256 °C). It should be noted that the maximum size and packing radii (3.5 Å) of ellipsoidal-shaped $B_{10}H_{10}^{2-}$ and near-spherical $B_{12}H_{12}^{2-}$ anions are similar. These anions can act as the "lubricant" of cation diffusion movement. It is the overly large size and spheroidal structure of the $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$ anions that cause the Na⁺ high mobility in the interstitial network formed by the anion sublattices, thus reducing the diffusion bottlenecks between different Na⁺ and providing abundant Na⁺ diffusion sites.

Based on AIMD and DFT calculation, the basic mechanism of ultrafast ion conduction is further revealed [14]. It is found that the superionic behavior of $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ is the result of intrinsic frustration and disorder caused by the combined action of structural, chemical, and kinetic factors shown in (Fig. 7c). Structurally, the intrinsic vacancies and high density of accessible interstitial sites contribute to flattening the whole energy landscape and reducing the trend of cation ordering. Chemically, the cations closest to anions tend to arrange themselves according to the symmetry of anions, which is incompatible with the preferred symmetry occupying the lattice gap position, thus bringing an intrinsic frustration, which reduces the obstacles to the formation of coordination defects and helps the cation migration. Dynamically, the reorientation of negative ions and other low-frequency thermal vibrations generate fluctuations in the local potential force to enhance the mobility of cations. This is closely related to the "paddle-wheel" mechanism of ionic conductivity [97]. Analysis of the decomposition products of Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂ under high pressure indicates that the phase containing $[B_nH_n]^{2-}$ has a large apparent electrochemical window as 5 V (Fig. 7d) [23].

2.2.2. Strategies for improving ionic conductivities

The typical $[B_nH_n]^{2-}$ containing compounds all show better intrinsic ionic conduction properties than $[BH_4]^-$ containing compounds, but further improvement is still highly needed for practical use. Various successful strategies have been proposed to further optimize *closo*-borohydrides in terms of ionic conductivities, including atomic substitution, anion mixing, composition and defect engineering.

Atomic substitutions are a potential chemical modification to $[B_nH_n]^{2-}$ anion. Carba-*closo*-borohydride anions $[CB_{n-1}H_n]^{-}$ are synthesized via the replacement of an apical boron atom by an isoelectronic carbon atom, thus having a very similar size and geometric structure and pseudoaromantic nature (Fig. 8a). In 2015, Tang et al. [84] first explored the carba-closo-borohydride (LiCB₁₁H₁₂ and NaCB₁₁H₁₂) as SEs, which show organic liquid electrolyte like ionic conductivities (1.5 \times 10 $^{-1}$ S cm $^{-1}$ at 130 $^{\circ}$ C and 1.2×10^{-1} S cm⁻¹ at 110 °C) after ordered-disordered transitions (120 °C and 100 °C) (Fig. 8b). Moreover, their activation energies are both as low as 0.22 eV, which are typical activation energies of superconductors (below 0.5 eV). One year later, the [CB₉H₁₀]⁻-based superionic conductors were further investigated [85]. Compared to LiCB₁₁H₁₂ and NaCB₁₁H₁₂, LiCB₉H₁₀ and NaCB₉H₁₀ have similar ionic conductivity as well as temperature-dependent conductivity behavior, and encouragingly, their ordered-disordered transition

temperatures are much lower (80 and 50 °C). The conductivity of LiCB₉H₁₀ is closed to 10⁻¹ S cm⁻¹ at 110 °C, while NaCB₁₁H₁₂ reaches 10⁻¹ S cm⁻¹ at 100 °C, and both have low activation energies (0.29 and 0.20 eV). The carbon atom substitution patterns in closoborohydride anions $[B_nH_n]^{2-}$ lead to faster anion reorientation and higher cation mobility, which is determined by the crystal structure, anion packing, cation density, and interaction between carbon atoms and nearby cations [98]. The uniquely superionic conductivity of carba-closo-borohydride SEs in the hydride family may be attributed to their intrinsic properties and the inherited merits of $[B_nH_n]^{2-}$. Not only inherits the high mobility of cations in interstitial networks and abundant cation diffusion sites in large anions, but also the halved negative charges of carba-closo-borohydride anions $[CB_{n-1}H_n]^-$, the stoichiometric ratio of anions and cations decreases, and the Coulomb attraction of single charge $[CB_{n-1}H_n]^-$ anions to the surrounding cations is decreased, which may also help to reduce the barriers of activation energy barrier and hindered cation transfer

Anion mixing is also a successful strategy for improving ionic conductivity. Mixing compounds tend to stabilize the hightemperature phase of precursor materials. He et al. [99] reported the fast Na⁺ conduction in the Na₃NH₂B₁₂H₁₂ complex. The ionic conductivity of Na₃NH₂B₁₂H₁₂ is 1×10^{-4} S cm⁻¹ at 100 °C, which is several orders of magnitude higher than for both precursors $NaNH_2$ and $Na_2B_{12}H_{12}.$ Moreover, $Na_3NH_2B_{12}H_{12}$ has high apparent electrochemical stability of at 10 V. In 2017, the mixture of equimolar 1:1 Na₂B₁₀H₁₀ and Na₂B₁₂H₁₂ was reported to exhibit a unique fast-rotating anion and a new highly stable phase, $Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}$, which has high Na^+ conductivity of $9\times 10^{-4}\,S\,cm^{-1}$ at 20 $^\circ C$ and the high electrochemical stability of 3 V [100]. XRD patterns only show the *Fm*-3*m* phase of $Na_2B_{10}H_{10}$, which indicates that $[B_{12}H_{12}]^{2-}$ incorporates in and stabilizes the Na₂B₁₀H₁₀ highly conducting phase [101]. Inspired by these results, a series of new mixed anionic compounds, Na_{2-x} (CB₁₁H₁₂)_x $(B_{12}H_{12})_{1-x}$, have been developed, which have fast Na⁺ conductivity of 2 \times 10⁻³ S cm⁻¹ at RT and low activation energy of 0.314 eV and can be used as a potential SE [102]. To further improve the ionic conductivity, Tang et al. developed two intimately anion-mixed solid solutions Li₂(CB₉H₁₀)(CB₁₁H₁₂) and Na₂(CB₉H₁₀)(CB₁₁H₁₂) with disordered superionic structures at RT, which were prepared by mixing and drying two equimolar aqueous solutions of carbo-closo-borohydride anions ([CB₉H₁₀] and [CB₁₁H₁₂]⁻) (Fig. 8c) [103]. The ionic conductivity of Li₂(CB₉H₁₀)(CB₁₁H₁₂) was higher than that of disordered LiCB₉H₁₀ at 75 °C and slightly lower than that of $LiCB_{11}H_{12}$ at 105 °C. Impressively, $Na_2(CB_9H_{10})(CB_{11}H_{12})$ is more conductive than its two precursor materials NaCB9H10 and NaCB11H12 over all temperature ranges. Because Li₂(CB₉H₁₀)(CB₁₁H₁₂) mainly forms two kinds of disorder phases, one is the hexagonal structure dominated by [CB₉H₁₀]⁻, the other is the smaller face-centered cubic structure dominated by [CB₁₁H₁₂]⁻. However, for Na₂(CB₉H₁₀)(CB₁₁H₁₂), only one disordered hexagonal phase with $[CB_9H_{10}]^-$ as the main phase is formed. The mixed anions with slightly different geometry sizes will produce an enthalpy penalty when forming any possible ordered phase, which will cause some degree of geometric frustration with the surrounding cations. Therefore, the disorder similarity is favored, which can successfully inhibit the formation of possible ordered phases and promote the formation of disordered and rapid ionic conductive phases. By testing various content levels of $[CB_{11}H_{12}]^-$ anions, it was found that lower content (0.1 M fraction) would lead to the instability of the high conductive phase, while higher content (0.5 M fraction) would cause the increase of other impurity phases. Therefore, Kim et al. [104] proposed that a 0.3 M fraction of $[CB_{11}H_{12}]^{-}$ is the optimal composition to stabilize the high conductive phase. Li(CB₉H₁₀)_{0.7}(CB₁₁H₁₂)_{0.3}



Fig. 8. (a) Geometric shapes and Mulliken charges of $[CB_{11}H_{12}]^{-}$ and $[CB_{9}H_{10}]^{-}$ [84,85]. Copyright 2015 Royal Society of Chemistry. (b) Temperature-dependent conductivities of *closo*-borohydrides, Na₃PSe₄, Li₁₀GeS₂P₁₂, and Li₇P₃S₁₁ glass-ceramic SEs [85]. Copyright 2016 Wiley-VCH. (c) The disordered hexagonal structure via the mixing of two different *closo*-borohydride anions $[CB_{11}H_{12}]^{-}$ and $[CB_{9}H_{10}]^{-}$ [103]. Copyright 2016 American Chemical Society. (d) Temperature-dependent conductivities of LiCB₉H₁₀ and Li(CB₉H_{10)0.7}(CB₁₁H₁₂)_{0.3} [104]. Copyright 2019 Springer Nature. (e) Schematic illustration of improving ionic conductivity via ball milling [110]. (f) Temperature-dependent conductivities of pristine and ball-milled Li₂B₁₂H₁₂ [112]. Copyright 2018 American Chemical Society.

has the highest RT ionic conductivity among all hydride SEs, with 25 °C being 6.7×10^{-3} S cm⁻¹ (Fig. 8d), which is already comparable to the organic liquid electrolytes. Structural characterization and electrochemical impedance spectroscopy (EIS) measurements reveal that the stabilization of LiCB₉H₁₀ high conductive phase is due to the formation of a solid solution, and the effect of the solid solution on the phase transformation mainly depends on the

structural difference between the two matrix anions [105]. Therefore, more accurate atomic-level and/or in-situ characterization is needed to clarify the influence of the structural phase interaction between multiple composite anions on the phase transition temperature [106,107].

Recently, studies on the use of *closo*-borohydrides as active fillers in composite polymer electrolytes have been reported. Bao

et al. [108] introduced Li₂B₁₂H₁₂ into poly (vinylidene fluoride)-Li bis-(trifluoromethanesulfonyl) imide (PVDF-LiTFSI) to form a new composite polymer electrolyte (CPE). The CPE achieves a conductivity of 1.43×10^{-4} S cm⁻¹ and a Li⁺ transfer number of 0.34 at 25 °C. The improved conductivity can be attributed to the electron-deficient multicenter bonds of Li₂B₁₂H₁₂ that promote the dissociation of LiTFSI and enhance the immobilization of [TFSI]⁻. In addition, the addition of Li₂B₁₂H₁₂ helps to protect the anode/electrolyte interface and prevent further side reactions from occurring.

Besides stabilizing the superionic disordered structure by appropriate chemical modification, interfacial and morphological modifications have also been proved to be an effective strategy to improve electrical conductivity. It is known that LiBH₄ can be decomposed to form different Li–B–H complexes by adjusting the temperature above 280 °C. Zhu et al. [109] prepared and investigated the partial dehydrogenation of LiBH₄ to form the Li–B–H complex in-situ. The LiBH_{4-x} (i.e., HP-LiBH_{2.4}) with 7.5 wt% H₂ desorption under 3 bar H₂ is found to show a highly Li⁺ conductivity of 2.7 × 10⁻⁴ S cm⁻¹ at 35 °C, and the activation energy of HP-LiBH_{2.4} is calculated to be 0.43 eV. In-depth characterizations show that the fast Li⁺ mobility in the interface layer between LiBH₄ and (Li₂B₁₂H_{11+1/n})_n is the reason for its high Li⁺ conductivity.

Additionally, ball milling can decrease the grain size and induce defects in the crystal structures of *closo*-borohydride, leading to improvement in the ionic conduction properties (Fig. 8e). Tang et al. [110] proposed that ball milling may not have positive effect on the ion conduction in lattice, but it is helpful for the stabilization of highly conductive disordered phase. This phenomenon is also observed for ball milled Na2B10H10-Na2B12H12 pseudo-binary hydride SE. Therefore, they think nanosizing is a good strategy for obtaining RT SEs [111]. In addition, another conductivity enhancing mechanism by ball milling is proposed, which related to the atom deficiency in the lattice [112]. As the content of Li and H is reduced by simple ball milling to form atomic defects, the increased carrier concentration of these defects significantly increases the conductivity of Li⁺. The ionic conductivity (2.0×10^{-5} S cm⁻¹ at 30 °C) of the atom-deficient $Li_2B_{12}H_{12}$ is almost 1000 times higher than that of the pristine Li₂B₁₂H₁₂ (Fig. 8f), although its activation energy is not apparently lowered.

2.2.3. Strategies for improving compatibility to electrodes

So far, after the optimization of $[B_nH_n]^{2-}$ anion-based SEs by the above methods, a series of *closo*-borohydrides containing complex polyanions such as $[B_{12}H_{12}]^{2-}$, $[CB_{11}H_{12}]^{-}$, and $[CB_9H_{10}]^{-}$ have largely reached the threshold of practicality in terms of conductivity, and SSBs have been assembled to investigate the compatibility issues aspects with electrodes for achieving the purpose of commercial application.

To investigate the Li dendrite suppression capability of *closo*borohydride and the principle of improving its anode compatibility. Shi et al. [113] compared the ability of Li|Li₂B₁₂H₁₂|Li and Li|Li₂B₁₂H₁₂-LiF|Li symmetrical cells to show the effect of LiF in Li₂B₁₂H₁₂ on suppressing the Li dendrites (Fig. 9a). The CCD of LiF-modified Li₂B₁₂H₁₂ symmetric cells forming lithium dendrites is 3.6 mA cm⁻², which is 80% higher than that of pure Li₂B₁₂H₁₂. The in-situ formed ultrafine LiF nanoparticles formed anodic electrolyte interphase and cathodic electrolyte interphase films at the electrolyte/electrode interface, respectively, which prevented the rapid growth of lithium dendrites in the electrolyte (Fig. 9b).

For the cathode, *closo*-borohydride SEs match well with TiS_2 cathode with relatively low working potential (2 V). Unemoto et al. [114] have assembled a typical SSB constituted of $TiS_2|Li_2B_{12}H_{12}|Li$ working at 120 °C. The initial discharge capacity was 207 mAh g⁻¹

at 0.2 C, and the high discharge capacity of 190 mAh g^{-1} was maintained after 10th cycles. Kim et al. [112] investigated the cycling performance of an SSB utilizing atom-deficient Li₂B₁₂H₁₂ as the SE, and the SSB with the ball-milled TiS_2 |ball-milled $Li_2B_{12}H_{12}$ | Li configuration exhibited an initial discharge capacity of 228 mAh g⁻¹ (80 °C and 0.05 C), which shows good capacity retention over 20 cycles (Fig. 9c). Zhu et al. [109] developed a TiS₂-based SSB utilizing an HP-LiBH_{2.4} SE formed by partial dehydrogenation of LiBH₄ was successfully operated at 35 °C, in the following 50 cycles, high Coulombic efficiency (near 100%) and capacity (200 mAh g⁻¹ were achieved. Apart from SSEs with $[B_{12}H_{12}]^{2-}$ groups, the feasibility of carba-closo-borohydride SEs paired with a TiS₂ electrode was also probed. Tang and coworkers [84] assembled an SSB in the TiS₂|LiCB₁₁H₁₂|Li configuration, which was operated at 130 °C. This SSB delivered a discharge capacity surpassing 175 mAh g^{-1} in the 3rd cycle, with approximately 95% Coulombic efficiency. Recently, Kim et al. [105] fabricated a TiS₂-based SSB utilizing the Li(CB9H10)0.7(CB11H12)0.3 compound as SE, which exhibited the highest ionic conductivity in the (1-x)Li(CB₉H₁₀)-xLi(CB₁₁H₁₂) series $(6.7 \times 10^{-3} \text{ S cm}^{-1}, 25 \text{ °C})$, and operated successfully at 60 °C and 0.1 C. An SSB in the TiS₂|Li(CB₉H₁₀)_{0.7}(CB₁₁H₁₂)_{0.3}|Li configuration showed an initial discharge and charge capacity of 238.5 and 229.5 mAh g^{-1} , respectively. Then, it showed a capacity of 230.5 mAh g^{-1} (96.4% of the theoretical capacity) and Coulombic efficiency of near 100% at the 2nd cycle, and the rate and cycle performance were also excellent.

The electrochemical investigation of *closo*-borohydride SEs was extended to SSB with the S electrode as the cathode. Kim and coworkers [104] studied an S|Li(CB₉H₁₀)_{0.7}(CB₁₁H₁₂)_{0.3}|Li SSB, which presented the discharge capacity of the second cycle was 1618 mAh g⁻¹, corresponding to the utilization rate of 96.8% sulfur under a current density of 50.2 mA g⁻¹ (0.03 C) at 25 °C. Then, the rate performance of the SSB was tested at different current loads from 0.03 C to 1 C at 25 °C. When the current density changed from 0.03 C to 1 C, only 24% capacity loss was observed in the 2nd cycle, and this SSB presented about 100% capacity retention after 10th and 20th cycles at 0.1 C and 1 C in subsequent cycling, respectively. After rate testing, the SSB was further cycled under a discharging rate of 5 C and a charging rate of 1 C at 60 °C, and it demonstrated very excellent cycling stability up to 100th cycles with a capacity of 1017 mAh g⁻¹ (Fig. 9d,e).

 $[B_nH_n]^{2^-}$ anion-based SEs have lower reducibility than $[BH_4]^$ anion-based SEs, thus it possesses better cathode compatibility, which can be further enhanced by interfacial modifications. Shi et al. [113] assembled a LiFePO₄||Li SSB using LiF-decorated Li₂B₁₂H₁₂ SE prepared in-situ from a solid-state reaction, which was successfully operated at 75 °C. An SSB in the LiFePO₄|LiFdecorated Li₂B₁₂H₁₂|Li configuration showed an initial reversible specific capacity of 129 mAh g⁻¹ and 84% capacity retention after 30 cycles. The LiFePO₄||Li SSB assembled with Li₂B₁₂H₁₂/PVDF-LiTFSI composite polymer electrolyte (LBH-CPE) by Bao et al. [108] exhibited excellent cycling performance, achieving a reversible specific capacity of 140 mAh g⁻¹ after 200th cycles under a current density of 1 C at 25 °C.

For Na *closo*-borohydride SEs, stable cycling of SSBs have also been reported. The SSB with a $TiS_2|Na_3NH_2B_{12}H_{12}|Na$ configuration presented stable capacity retention of more than 50% over 200 discharge-charge cycles [99]. Yoshida et al. [111] assembled a bulk-type $TiS_2|Na_2B_{10}H_{10}-3Na_2B_{12}H_{12}|Na$ SSB, which was operated at 30 °C and 0.02 C, employing ball-milled mixtures of Na *closo*-borohydride mixture as SE to provide excellent electrochemical stability and compatibility for Na metal electrodes (Fig. 9f). In 2017, Duchene and coworkers [115] first investigated the excellent material properties of the Na *closo*-borohydride as SE in high-voltage batteries. They fabricated an SSB in the NaCrO₂]

Fig. 9. (a) Galvanostatic charge/discharge curves of LiF-decorated $Li_2B_{12}H_{12}$ symmetrical cell at increasing current densities [113]. (b) Schematic illustration of the mechanism on LiF-decorated $Li_2B_{12}H_{12}$ to stabilize the electrolyte/electrode interface [113]. Copyright 2020 Elsevier. (c) Galvanostatic charge/discharge curves of TiS₂|ball-milled $Li_2B_{12}H_{12}|Li$ SSB at 0.05 C and 80 °C [112]. Copyright 2017 American Chemical Society. Charge/discharge curves at different rates (d) and cycling stability (e) of S|Li(CB₃H₁₀)_{0.7}(CB₁₁H₁₂)_{0.3}|Li SSB at 55 °C [104]. Copyright 2019 Springer Nature. (f) Galvanostatic charge/discharge curves of SSB with NaCrO₂|Na₂(B₁₂H₁₂)_{0.5}(B₁₀H₁₀)_{0.5}|Na configuration in different cycles [115]. Copyright 2017 Royal Society of Chemistry. Charge/discharge curves at different rates (g) and long-term cycling stability (h) of Na₃(VOPO₄)₂F|Na₄(CB₁₁H₁₂)₂(B₁₂H₁₂)|Na SSB at 0.2 C and RT [117]. Copyright 2020 Royal Society of Chemistry.

 $Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}|Na$ configuration, which maintained a stable and effective cycle at 3 V and 60 °C with reversible capacities of 85 mAh g^{-1} and 80 mAh g^{-1} at 0.05 C and 0.2 C respectively, and a capacity retention rate of 85% after 250th cycles at 0.05 C. To investigate the stability of the material at lower temperatures and higher current densities. Duchene et al. [116] used direct infiltration of Na₂(B₁₂H₁₂)_{0.5}(B₁₀H₁₀)_{0.5} in porous electrodes to construct convenient ion and electron conduction channels and used Na-Sn alloy anode to prevent inhomogeneous Na plating. The SSB with a $NaCrO_2|Na_2(B_{12}H_{12})_{0.5}(B_{10}H_{10})_{0.5}|Na-Sn configu$ ration operated successfully at 4.5 mA cm⁻² (5 C) and 30 °C. Asakura et al. [117] further investigated the stability of the materials at higher voltage to pursue higher specific energy. A 4 Vclass SSB utilizing a Na₃(VOPO₄)₂F cathode and a Na metal anode was successfully operated at RT for the first time, and it delivered a discharge capacity of 104 mAh g^{-1} at 0.1 C and 99 mAh g^{-1} at 0.2 C in the first cycle, equivalent to 78% and 76% of the theoretical capacity. In the following 800 cycles, high Na-storage capacity (78 mAh g^{-1}) and capacity retention (78%) were achieved (Fig. 9g,h). In addition, Niitani et al. [118] assembled a Na_{0.7}Mn_{0.5}Ni_{0.2}Co_{0.3}O₂| Na(CB₉H₁₀)_{0.7}(CB₁₁H₁₂)_{0.3}|hard carbon SSB, which exhibited good fast charging performance by charging over 1 mA h cm^{-2} . The successful operation of the above SSBs verified the potential of Na closo-borohydride as SE in SSBs. Notably, Sun et al. [119] demonstrated by synchrotron X-ray tomography that electrochemically inactive Na⁰ or Na⁺ compounds are generated during the electrochemical cycling of Na SSBs using *closo*-borohydride SE, and they make Na⁺ transport blocked, and methods to eliminate or inhibit their appearance need to be further explored.

3. Hydride-based electrodes

Hydrides were first found to exhibit reversible ion storage properties in 2008 using organic liquid electrolytes [120], in which the presence of light H element and the rapid diffusion of small H atoms lead to high theoretical capacity and low polarization voltage, as shown in Fig. 10 [121]. However, severe side reactions between hydrides and organic liquid electrolytes lead to inferior cycling performances. Therefore, the investigations on hydrides as electrode materials in SSBs become a research hot spot in recent years. In this section, binary hydrides and alanates are mainly introduced, focusing on the typical compounds and corresponding improving strategies in SSBs, as seen in Table 2.

3.1. Binary hydrides

Binary hydrides, consisting of two elements (one element is H, the other element can be Mg, Ti, Zr or Cs et al.), are the simplest and most common hydrides. They can reversibly store ions via conversion reactions, and attract great interest in the last decade due to their unique electrochemical performances.

Fig. 10. Gravimetric and volumetric theoretical specific capacities for binary and complex hydrides [121]. Copyright 2012 Royal Society of Chemistry.

Fable 2
Performance comparison of hydride-based electrodes and SSBs based on them.

Anode	Theoretical Capacity (mAh g^{-1})	Average Voltage (V)	Cell Performance	References
MgH ₂	2038	0.5	MgH ₂ LiBH ₄ Li (1572 mAh g ^{-1} @ 0.1 A g ^{-1} and 120 °C)	[120,123]
Nb ₂ O ₅ - MgH ₂	2018	0.5	$MgH_2 LiBH_4 Li$ (1650 mAh g ⁻¹ @ 0.1 A g ⁻¹ and 120 °C)	[125]
TiH ₂ -MgH ₂	1728	0.5	MgH ₂ LiBH ₄ Li (1100 mAh g ⁻¹ @ 0.02C and 120 $^{\circ}$ C)	[127]
VGCF-MgH ₂	2038	0.5	MgH ₂ LiBH ₄ Li (1000 mAh g^{-1} @ 1 A g^{-1} and 120 °C) after 50 cycles	[126]
LiAlH ₄	2119	0.25	-	[132,133]
Li ₃ AlH ₆	1493	0.25	-	[132,133]
Li ₃ AlH ₆ -Al	1548	0.25	Li ₃ AlH ₆ –Al LiBH ₄ Li (1416 mAh g ⁻¹ @ 0.5 A g ⁻¹ and 120 °C) after 100 cycles	[141]
			LCO LiBH4 Li3AlH6-Al (102 mAh g ⁻¹ @ 0.2C and 120 °C)	
$NaAlH_4$	1985	0.25	-	[135]
Na ₃ AlH ₆	1576	0.25	-	[135]
LiNa ₂ AlH ₆	1558	0.25	LiNa_2AlH_6-3DG LiBH_4 Li (861 mAh g^{-1} @ 1 A g^{-1} and 120 $^\circ\text{C})$ after 100 cycles	[140]

*These theoretical capacities are calculated from the conversion reactions only (excluding the alloying reactions).

3.1.1. Typical compounds

MgH₂ is known as a hydrogen storage material, which can store 7.6 wt% hydrogens through chemical reactions. Since Oumellal et al. [120] found that hydrides can lithiation/delithiation through a conversion reaction, MgH₂ becomes one of the most extensively studied hydride-based anode materials due to its high theoretical capacity and excellent cycling stability.

Structurally, five polymorphs ($P4_2/mnm$, Pa, Pbcn, $Pbc2_1$ and Pnma) of MgH₂ exist at different pressures and temperatures, in which $P4_2/mnm$ is the most stable phase at RT [122]. Oumellal and co-workers proposed that the theoretical gravimetric capacity of MgH₂ is 2038 mAh g⁻¹ (for conversion reaction) and found that a large reversible capacity of 1480 mAh g⁻¹ can be obtained at an average voltage of 0.5 V with a small polarization and voltage hysteresis (~0.2 V) (Fig. 11a,b). Brutti et al. [121] further investigated the reaction mechanism of the MgH₂ by a combined analysis of electrochemical measurements, ex-situ XRD and transmission electron microscopy (TEM), demonstrating that the lithiation/

delithiation reaction of MgH₂ is not only a simple conversion pathway but also involves Li alloying and possibly the formation of intermediate Li–Mg–H phases. The reversible Li⁺ storage reaction of MgH₂ is shown as follows:

$$MgH_2 + 2Li^+ + 2e^- \leftrightarrow 2Mg + 2LiH, \tag{1}$$

$$Mg + xLi^{+} + xe^{-} \leftrightarrow MgLi_{x}, \ x \le 0.15,$$
(2)

$$MgLi_{0.15} + 0.2Li^{+} + 0.2e^{-} \leftrightarrow MgLi_{0.35}, \qquad (3)$$

$$MgLi_{0.35} + yLi^{+} + ye^{-} \leftrightarrow MgLi_{0.35+\nu}$$
(4)

At least four reaction steps are involved: i) the conversion of MgH₂ to Mg and LiH; ii) alloying of Li in Mg to form MgLix; iii) conversion of Li–Mg solid solution to MgLi_{0.35}; iv) further incorporation of Li⁺ into MgLi_{0.35} by a topological reaction.

Fig. 11. Voltage profile (a) and XRD patterns (b) of MgH₂ electrode at various stages of the conversion processes [120]. Copyright 2008 Springer Nature. (c) Expected volume variation of the MgH₂ electrode at various stages of the conversion processes [121]. Copyright 2012 Royal Society of Chemistry. (d) Galvanostatic charge/discharge curves and cycling performance of doped-MgH₂|LiBH₄|Li SSB under a current density of 100 mA g⁻¹ at 120 °C [125]. Copyright 2015 Royal Society of Chemistry. (e) Galvanostatic charge/discharge curves at different rates of MgH₂(VGCF-LiBH₄ as conductor)|LiBH₄|Li SSB in different cycles at 120 °C [126]. Copyright 2017 American Chemical Society. (f) Galvanostatic charge/discharge/discharge curves at different rates of MgH₂-TiH₂|LiBH₄|Li SSB at 120 °C [127]. Copyright 2017 Elsevier.

The above investigations mainly use organic liquid electrolytes, which usually leads to severe side reactions and thus results in significant capacity decay during cycling (1480 mAh g⁻¹ for the first cycle reduces to 200 mAh g⁻¹ after 10 cycles). Aiming at this critical issue, Zeng et al. [123]. Proposed that using SEs (such as LiBH₄) instead of organic liquid electrolytes can avoid the apparent side reactions between electrolytes and electrodes. With the MgH₂ and LiBH₄ composite working electrode, the SSB delivers an initial reversible capacity of 1572 mAh g⁻¹ under a current density of 100 mA g⁻¹ at 120 °C, which then reduces to over 1100 mAh g⁻¹ after 10 cycles and 270 mAh g⁻¹ after 93 cycles. [BH₄]⁻ groups participate in the conversion reaction, which significantly promotes the conductivity of Li⁺ and H⁻, and its good compatibility with MgH₂ accelerates H⁻ transmission in MgH₂ and Li⁺ conduction in LiBH₄ [124]. The excellent hydrogen exchange effect of borohydrides SSEs with MgH₂ electrode can improve the shortcomings of the slow kinetics of \mbox{MgH}_2 to a certain extent.

This electrochemical performance is still not satisfactory due to the following reasons: i) after complete lithiation, the volume change of the MgH₂ electrode is over 200% (Fig. 11c) [121], which is a very large value and may lead to considerable electrochemical grinding and electrical contact loses; ii) the rough morphology and the inevitable oxide layer on the surface of MgH₂ also lead to the loss of electrochemical activity of MgH₂ in batteries.

3.1.2. Improving strategies

To overcome the critical issues of unsatisfactory initial Coulombic efficiency and poor recyclability of MgH₂ electrode materials, a series of modification strategies are proposed.

The addition of catalysts facilitates the improvement of the reaction kinetics of MgH₂ electrodes. Zeng et al. [125] assembled

Fig. 12. (a) Crystal structures of LiAlH₄, Li₃AlH₆, NaAlH₄, and Na₃AlH₆ [139]. Copyright 2012 AIP Publishing. Phase transition (b) and in-operando XRD diffraction patterns (c) during the first discharge of LiAlH₄. Phase transition (d) and in-operando XRD diffraction patterns (e) during the first discharge of NaAlH₄ [133]. Copyright 2015 American Chemical Society.

Nb₂O₅-doped MgH₂|LiBH₄|Li configurations, which presents a higher initial capacity of around 1650 mAh g⁻¹ and stabilized to 924 mAh g⁻¹ after 50 cycles, with Coulombic efficiency up to 94.7% (Fig. 11d). The above results are attributed to the improved reaction kinetics by doping 1 mol% Nb₂O₅ catalyst into MgH₂, which leads to the enhancement in reversibility and initial Coulombic efficiency. In their later research, carbon modification was used to increase the electrical conductivity of insulating MgH₂ thus solving the problem of relatively low utilization of active materials [126]. They used vapor-grown carbon nanofibers (VGCF) to form continuous electron conduction paths in the composite electrode and assembled an SSB of MgH₂ (VGCF-LiBH₄ as conductor)|LiBH₄|Li configuration at a cut-off voltage of 0.3~1 V to avoid the formation of Li–Mg alloy (0.1 V) and Mg(BH₄)₂ (above 1.0 V). The SSB has capacity retention of 75.6% (1221 mAh g⁻¹) after 50th cycles (Fig. 11e). The cycling

performance of MgH₂ can also be improved by mixing with other metal hydrides. Dao et al. [127] and Aranguren et al. [128] improved the MgH₂ hydrogen transport and prevented the growth of Mg particles during cycling by adding TiH₂ with high electrical conductivity and fast hydrogen transport. For SSB with MgH₂–TiH₂/LiBH₄/Li configuration subjected to galvanostatic cycling at 120 °C (Fig. 11f). The Mg-rich nanocomposite (0.7MgH₂+0.3TiH₂) exhibited a higher specific capacity (above 1700 mAh g⁻¹), while the Tirich nanocomposite (0.2MgH₂+0.8TiH₂) had a better cycling performance (capacity after 10th cycles retention rate of about 100%). To reduce the operating temperature of SSBs to RT, Cano-Banda et al. [129] tested different combinations of LiBH₄, Li₄(BH₄)₃I and Li₂S–P₂S₅ as SEs. The MgH₂ (Li₄(BH₄)₃I-acetylene carbon black as conductor)|Li₂S–P₂S₅|Li SSB has an initial capacity of 1570 mAh g⁻¹

Fig. 13. (a) Schematic illustration of synthesis procedures for LiNa₂AlH₆/3DG. Cycling stability (b) and rate capability (c) of LiNa₂AlH₆/3DG|LiBH₄|Li SSB at 125 °C [140]. Copyright 2019 Elsevier. (d) Schematic illustration of the structural evolution of the Li₃AlH₆–Al nanocomposites anode and LiAlH₄ anode during cycling. (e) Photographs of the LiCoO₂|LiBH₄| Li₃AlH₆–Al SSB. (f) Cycling stability of the Li₃AlH₆–Al anode and LiAlH₄ anode [141]. Copyright 2020 Wiley-VCH.

3.2. Alanates

Alanates usually possess higher H content than binary hydrides because they are composed of polyanions formed by tetrahedra AlH₄⁻ or octahedra AlH₆²⁻ (Fig. 12a) [130]. Alanates have been studied in-depth as a hydrogen storage system, while the application as anode materials for SSB is still in the initial stage of research. As conversion-type electrodes, higher H content in hydrides means a higher theoretical specific capacity. Moreover, alanates also show excellent electrochemical behaviors in terms of appropriate potentials and fast kinetics [131]. Therefore, alanates become promising electrode candidates.

3.2.1. Typical compounds

LiAlH₄ is in $P2_1/c$ phase at RT, which has a high H₂ capacity of 10.5 wt% and can allow 3 Li⁺ insertions (corresponding to a theoretical capacity of 2119 mAh g⁻¹) through a series of electrochemical conversion reactions [132]. From the thermodynamic point of view, the conversion process takes place in a three-step path involving the formation of Li₃AlH₆ followed by the conversion to LiH and Al and finally the alloying Li into Al (Fig. 12b,c) [133].

$$3\text{LiAlH}_4 + 6\text{Li}^+ + 6\text{e}^- \rightarrow \text{Li}_3\text{AlH}_6 + 2\text{Al} + 6\text{LiH}$$
(5)

$$Li_3AlH_6 + 3Li^+ + 3e^- \leftrightarrow 6LiH + Al$$
(6)

$$AI + Li^{+} + e^{-} \leftrightarrow AILi$$
(7)

These reactions correspond to three plateaus at 0.78, 0.27, and 0.15 V in the initial discharge process. It should be noted that Reaction (5) is irreversible because LiAlH₄ is thermodynamically unstable. According to Reaction (5) and (6), Li₃AlH₆ (*R*3 phase at RT) is the intermediate product during lithiation of LiAlH₄, which can reversibly store 3 Li⁺ (corresponding to a theoretical capacity of 1493 mAh g⁻¹) through the conversion reaction.

Moreover, LiAlH₄ can conduct Li⁺ to some extent, which is beneficial to its Li⁺ storage. The conductivity of Li⁺ increases almost linearly from 8.7×10^{-9} S cm⁻¹ at RT to 4.6×10^{-6} S cm⁻¹ at 120 °C and the activation energy is 0.76 eV [134]. Li₃AlH₆ has higher Li⁺ conductivity and smaller activation energy than LiAlH₄, which range from 1.4×10^{-7} to 1.6×10^{-5} S cm⁻¹ between RT and 120 °C with an activation energy of 0.61 eV.

NaAlH₄ shows a structure of $I4_1/a$, in which 4 Li⁺ can be incorporated in the conversion reaction in the potential range of 0.01–0.7 V (Fig. 12d,e), corresponding to a theoretical capacity of 1985 mAh g⁻¹ [135]. In the beginning, NaAlH₄ decomposes to LiH, Al and the *Fm3m* phase LiNa₂AlH₆ instead of the expected $P2_1/n$ phase Na₃AlH₆ phase [133].

$$2NaAlH_4 + 3Li \rightarrow LiNa_2AlH_6 + Al + 2LiH$$
(8)

$$LiNa_2AlH_6 + 5Li \rightarrow 2Na + Al + 6LiH$$
(9)

Finally, the decomposition produces Al reacts with Li to form AlLi (Reaction 7). As an intermediate product, $LiNa_2AlH_6$ shows a theoretical capacity of 1558 mAh g⁻¹ for the conversion reaction, also a promising electrode candidate. Moreover, Sartori et al. [131] calculations show that Na_3AlH_6 can reversibly store 6 Li⁺ (theoretical capacity of 1576 mAh g⁻¹), which has not been confirmed experimentally.

It should be noted that NaAlH₄ can also be applied as electrodes as Na⁺ batteries [136–138]. The reaction pathways are expected to be similar to those of Reaction (5–7). These reactions can be beneficial from the Na⁺ conductivity of NaAlH₄ (2.1×10^{-10} S cm⁻¹

at RT with activation energy of 0.79 eV) and Na_3AlH_6 $(6.4\times10^{-7}~S~cm^{-1}$ at RT with activation energy of 0.62 eV) [139].

The above works reveal the electrochemical reactions between alanates and Li⁺ and Na⁺. However, these investigations all use organic liquid electrolytes, which leads to more severe side reactions due to the more aggressive reducibility of alanates than that of metal hydrides, resulting in a low reversibility and cycling performance. Therefore, using SEs instead of organic liquid electrolytes is expected to be a promising strategy to solve this problem. Mo et al. [140] first used LiBH₄ as SE and LiNa₂AlH₆ as electrode to construct SSBs, which shows greatly improved electrochemical performances. Moreover, other alanate hydrides, such as LiAlH₄ [141], Li₃AlH₆ [142], were then explored as electrodes in SSBs, all showing better performances than those using organic liquid electrolytes. The interactions between the hydride electrodes and hydride electrolytes are believed to be mainly responsible for these improvements.

To realize the successful application of alanate electrodes in SSBs, the following issues should be further overcome: i) poor kinetics derived from the large-scale structural reorganization and volume change during the conversion process, ii) highly reductive nature that makes it extremely sensitive to many SEs, iii) irreversible insertion/extraction of ions and formation of H₂ according to the thermodynamic properties.

3.2.2. Improving strategies

Strategies for materials and structural designs, such as mechanochemical treatment and nanosizing methods, are proposed to alleviate the drawbacks of the mechanical instability and the consumption of active substances caused by hydrogen release or unstable SEI of Li alanates.

In 2019, a 3D hierarchical complex hydride/graphene composite anode material (LiNa₂AlH₆/3DG) with excellent performance was exhibited (Fig. 13a) [140]. LiNa₂AlH₆ with an optimal Δ H value $(53.0 \text{ kJ mol}^{-1})$, which is beneficial to reversible dehydrogenation and hydrogenation. The LiNa₂AlH₆/3DG, with LiBH₄ as a SE, provides a high capacity of 861 mAh g^{-1} under a current density of 5 A g⁻¹ at 125 °C and can reversibly circulates for 500 times under a current density of 1 A g^{-1} with a capacity retention of 97% (Fig. 13b,c). Pang et al. [141] in-situ prepared dispersed Al nanograins and amorphous Li₃AlH₆ matrix by a short-circuited electrochemical reaction between LiAlH₄ and Li with the help of fast electron and Li-ion conductors (Fig. 13d). This Li-Al-H composite electrode exhibits good overall electrochemical performances in terms of specific capacity (2266 mAh g^{-1} for the first cycle), Coulombic efficiency (88%), cycling stability (71% retention after 100 cycles) and rate capability (1429 mAh g^{-1} at 1 A g^{-1}), enabling the stable cycling of full SSBs (Fig. 13e,f). The above improvements can be attributed to the enhanced reaction kinetics from the diffusion distance reduction and defect proliferation. This solidstate prelithiation approach can also be applied to other Li-poor electrode materials. Furthermore, a Li₃AlH₆-LiBH₄-NaBH₄ composite electrode was prepared using the reaction between Na₃AlH₆ and LiBH₄ [142]. This structure can ensure the tight contact between Li₃AlH₆ and electrolyte, and can enhance the ionic conductivity by Na⁺ partial substitution. As a result, this Li₃AlH₆ composite electrode exhibit an initial discharge capacity of 1722 mAh g^{-1} and retains at 990 mAh g^{-1} after 150 cycles, 30% higher than the simply mixed counterpart.

4. Conclusions and outlook

The introduction of hydrides as SEs and electrodes into SSBs brings new opportunities towards practical applications. As SEs, borohydrides, i.e., $[BH_4]^-$ and $[B_nH_n]^{2-}$ containing compounds, can

rapidly conduct ions due to the effective paddle-wheel mechanism. After being improved in ionic conductivities and electrode compatibilities, these compounds can enable stable cycling of various SSBs, showing competitive performances to other SEs. As electrodes, binary hydrides and alanates can react with Li (or Na) through conversion reactions, delivering ultrahigh theoretical specific capacities. After being improved by rational compositional and structural design, these hydrides exhibit high specific reversible capacities as well as excellent rate capabilities and cycling stabilities. Nevertheless, further exploration of hydrides as key components for SSBs is still highly desirable in the following recommended aspects.

- (1) Balance the ionic conductivity and electrode compatibility of hydride SEs to enable the use of more aggressive electrodes at RT. Only high ionic conductivity is not enough for a practical SE. Insights into the electrolyte/electrode interfaces are also of great importance for hydride SEs, such as effective contact, intrinsic electrochemical stability, interphases, Li dendrite suppression.
- (2) Develop fabrication technology for thin, large, uniform and dense hydride SE film to enable the scale-up production of high energy density SSBs. Current cold pressing technology cannot fulfill the requirements for high energy density SSBs, which is a critical barrier that prevents hydride SEs from industrial use.
- (3) Understand the conversion reaction mechanism of hydride electrodes to improve the reversible ion storage capacity, velocity and durability. The H^{δ -} involved conversion reaction has unique advantages, and further optimizing the hydride electrodes by doping, nanosizing and coating may be a promising way to push them towards applications.

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.

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References

- X. Yang, K.R. Adair, X. Gao, X. Sun, Recent advances and perspectives on thin electrolytes for high-energy-density solid-state lithium batteries, Energy Environ. Sci. 14 (2) (2021) 643–671, https://doi.org/10.1039/D0EE02714F.
- [2] X. Feng, H.-H. Wu, B. Gao, M. Świętosławski, X. He, Q. Zhang, Lithiophilic Ndoped carbon bowls induced Li deposition in layered graphene film for advanced lithium metal batteries, Nano Res. 15 (1) (2022) 352–360, https:// doi.org/10.1007/s12274-021-3482-0.
- [3] X. Zhang, J. Meng, X. Wang, Z. Xiao, P. Wu, L. Mai, Comprehensive insights into electrolytes and solid electrolyte interfaces in potassium-ion batteries, Energy Storage Mater. 38 (2021) 30–49, https://doi.org/10.1016/ j.ensm.2021.02.036.
- [4] Z. Gao, H. Sun, L. Fu, F. Ye, Y. Zhang, W. Luo, Y. Huang, All-solid-state batteries: promises, challenges, and recent progress of inorganic solid-state

electrolytes for all-solid-state lithium batteries, Adv. Mater. 30 (17) (2018) 1870122, https://doi.org/10.1002/adma.201870122.

- [5] Y. Kuang, C. Chen, D. Kirsch, L. Hu, Thick electrode batteries: principles, opportunities, and challenges, Adv. Energy Mater. 9 (33) (2019) 1901457, https://doi.org/10.1002/aenm.201901457.
- [6] B.X. Chengzhi Ke, J.L. Miao Li, L.Z. Yang He, Q. Zhang, Research progress in understanding of lithium storage behavior and reaction mechanism of electrode materials through in situ transmission electron microscopy, Energy Storage Sci. and Technol. 10 (4) (2021) 1219–1236, https://doi.org/10.19799/ j.cnki.2095-4239.2021.0042.
- [7] S. Xu, Z. Sun, C. Sun, F. Li, K. Chen, Z. Zhang, G. Hou, H.M. Cheng, F. Li, Homogeneous and fast ion conduction of PEO-based solid-state electrolyte at low temperature, Adv. Funct. Mater. 30 (51) (2020) 2007172, https://doi.org/ 10.1002/adfm.202007172.
- [8] C. Peng, G.-H. Ning, J. Su, G. Zhong, W. Tang, B. Tian, C. Su, D. Yu, L. Zu, J. Yang, M.-F. Ng, Y.-S. Hu, Y. Yang, M. Armand, K.P. Loh, Reversible multi-electron redox chemistry of *π*-conjugated N-containing heteroaromatic molecule-based organic cathodes, Nat. Energy 2 (7) (2017) 17074–17083, https://doi.org/10.1038/nenergy.2017.74.
 [9] Y. Tian, F. Ding, H. Zhong, C. Liu, Y.-B. He, J. Liu, X. Liu, Q. Xu,
- [9] Y. Tian, F. Ding, H. Zhong, C. Liu, Y.-B. He, J. Liu, X. Liu, Q. Xu, Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂@amorphous Li₃OCl composite electrolyte for solid state lithium-metal batteries, Energy Storage Mater. 14 (2018) 49–57, https://doi.org/10.1016/j.ensm.2018.02.015.
- [10] Y. Lyu, X. Wu, K. Wang, Z. Feng, T. Cheng, Y. Liu, M. Wang, R. Chen, L. Xu, J. Zhou, Y. Lu, B. Guo, An overview on the advances of LiCoO₂ cathodes for lithium-ion batteries, Adv. Energy Mater. 11 (2) (2021) 2000982, https:// doi.org/10.1002/aenm.202000982.
- [11] Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, R. Kanno, High-power all-solid-state batteries using sulfide superionic conductors, Nat. Energy 1 (4) (2016) 16030, https://doi.org/10.1038/ nenergy.2016.30.
- [12] T. Liu, X. Zhang, M. Xia, H. Yu, N. Peng, C. Jiang, M. Shui, Y. Xie, T.-F. Yi, J. Shu, Functional cation defects engineering in TiS₂ for high-stability anode, Nano Energy 67 (2020) 104295, https://doi.org/10.1016/j.nanoen. 2019.104295.
- [13] 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 (1) (2019) 1803533, https://doi.org/10.1002/adma.201803533.
- [14] 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 (21) (2017) 9142–9153, https://doi.org/10.1021/acs.chemmater.7b02902.
- [15] F. Mo, J. Ruan, S. Sun, Z. Lian, S. Yang, X. Yue, Y. Song, Y.N. Zhou, F. Fang, G. Sun, S. Peng, D. Sun, Inside or outside: origin of lithium dendrite formation of all solid-state electrolytes, Adv. Energy Mater. (2019), https://doi.org/ 10.1002/aenm.201902123.
- [16] R. Mohtadi, S.-i. Orimo, The renaissance of hydrides as energy materials, Nat. Rev. Mater. 2 (3) (2016) 16091, https://doi.org/10.1038/natrevmats.2016.91.
- [17] N.V. Belkova, L.M. Epstein, O.A. Filippov, E.S. Shubina, Hydrogen and dihydrogen bonds in the reactions of metal hydrides, Chem. Rev. 116 (15) (2016) 8545–8587, https://doi.org/10.1021/acs.chemrev.6b00091.
- [18] T. He, H. Cao, P. Chen, Complex hydrides for energy storage, conversion, and utilization, Adv. Mater. 31 (50) (2019) 1902757, https://doi.org/10.1002/ adma.201902757.
- [19] 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 (22) (2007) 224103, https://doi.org/10.1063/ 1.2817934.
- [20] T. Ikeshoji, E. Tsuchida, T. Morishita, K. Ikeda, M. Matsuo, Y. Kawazoe, S.i. Orimo, Fast-ionic conductivity of Li⁺ in LiBH₄, Phys. Rev. B 83 (14) (2011) 144301, https://doi.org/10.1103/PhysRevB.83.144301.
- [21] P.C. Aeberhard, S.R. Williams, D.J. Evans, K. Refson, W.I.F. David, Ab initio nonequilibrium molecular dynamics in the solid superionic conductor LiBH₄, Phys. Rev. Lett. 108 (9) (2012), 095901, https://doi.org/10.1103/ PhysRevLett.108.095901.
- [22] K. Kisu, S. Kim, H. Oguchi, N. Toyama, S.-i. Orimo, Interfacial stability between LiBH₄-based complex hydride solid electrolytes and Li metal anode for all-solid-state Li batteries, J. Power Sources 436 (2019) 226821, https:// doi.org/10.1016/j.jpowsour.2019.226821.
- [23] 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 (9) (2019) 6924–6930, https://doi.org/ 10.1021/acsaem.9b01487.
- [24] M. Matsuo, H. Oguchi, T. Sato, H. Takamura, E. Tsuchida, T. Ikeshoji, S.i. Orimo, Sodium and magnesium ionic conduction in complex hydrides, J. Alloys Compd. 580 (2013) S98–S101, https://doi.org/10.1016/ j.jallcom.2013.01.058.
- [25] D.G. Allis, B.S. Hudson, Inelastic neutron scattering spectra of NaBH₄ and KBH₄: reproduction of anion mode shifts via periodic DFT, Chem. Phys. Lett. 385 (3–4) (2004) 166–172, https://doi.org/10.1016/j.cplett.2003.12.046.
- [26] P. Li, Phase Behavior and Reaction Mechaism Study of Hydrogen Storage in Sodium Borohydride, Ph.D Thesis, University of Pittsburgh, 2013.
- [27] M. Matsuo, S.-i. Orimo, Lithium fast-ionic conduction in complex hydrides: review and prospects, Adv. Energy Mater. 1 (2) (2011) 161–172, https:// doi.org/10.1002/aenm.201000012.

- [28] E.R. Pinatel, E. Albanese, B. Civalleri, M. Baricco, Thermodynamic modelling of Mg(BH₄)₂, J. Alloys Compd. 645 (2015) S64–S68, https://doi.org/10.1016/ j.jallcom.2015.01.199.
- [29] Y. Filinchuk, B. Richter, T.R. Jensen, V. Dmitriev, D. Chernyshov, H. Hagemann, Porous and dense magnesium borohydride frameworks: synthesis, stability, and reversible absorption of guest species, Angew. Chem. Int. Ed. 50 (47) (2011) 11162–11166, https://doi.org/10.1002/anie.201100675.
- [30] O. Zavorotynska, A. El-Kharbachi, S. Deledda, B.C. Hauback, Recent progress in magnesium borohydride Mg(BH₄)₂: fundamentals and applications for energy storage, Int. J. Hydrogen Energy 41 (32) (2016) 14387–14403, https://doi.org/10.1016/j.ijhydene.2016.02.015.
- [31] M.M. Hideki Maekawa, M.A. Hitoshi Takamura, T.K. Yasuto Noda, S.-i. Orimo, Halide-stabilized LiBH₄, a room-temperature lithium fast-ion conductor, J. Am. Chem. Soc. 131 (2008) 894–895.
- [32] Z. Yao, S. Kim, K. Michel, Y. Zhang, M. Aykol, C. Wolverton, Stability and conductivity of cation- and anion-substituted LiBH₄-based solid-state electrolytes, Phys. Rev. Mater. 2 (6) (2018), 065402, https://doi.org/10.1103/ PhysRevMaterials.2.065402.
- [33] V. Gulino, M. Brighi, E.M. Dematteis, F. Murgia, C. Nervi, R. Černý, M. Baricco, Phase stability and fast ion conductivity in the hexagonal LiBH₄–LiBr–LiCl solid solution, Chem. Mater. 31 (14) (2019) 5133–5144, https://doi.org/ 10.1021/acs.chemmater.9b01035.
- [34] M.B. Ley, D.B. Ravnsbæk, Y. Filinchuk, Y.-S. Lee, R. Janot, Y.W. Cho, J. Skibsted, T.R. Jensen, LiCe(BH₄)₃Cl, a new lithium-ion conductor and hydrogen storage material with isolated tetranuclear anionic clusters, Chem. Mater. 24 (9) (2012) 1654–1663, https://doi.org/10.1021/cm300792t.
- [35] M.B. Ley, S. Boulineau, R. Janot, Y. Filinchuk, T.R. Jensen, New Li ion conductors and solid state hydrogen storage materials: LiM(BH4)₃Cl, M = La, Gd, J. Phys. Chem. C 116 (40) (2012) 21267–21276, https://doi.org/10.1021/ jp307762g.
- [36] Y.-S. Lee, M.B. Ley, T.R. Jensen, Y.W. Cho, Lithium ion disorder and conduction mechanism in LiCe(BH₄)₃Cl, J. Phys. Chem. C 120 (34) (2016) 19035–19042, https://doi.org/10.1021/acs.jpcc.6b06564.
- [37] S. Payandeh GharibDoust, M. Brighi, Y. Sadikin, D.B. Ravnsbæk, R. Černý, J. Skibsted, T.R. Jensen, Synthesis, structure, and Li-ion conductivity of LiLa(BH4)₃X, X = Cl, Br, I, J. Phys. Chem. C 121 (35) (2017) 19010–19021, https://doi.org/10.1021/acs.jpcc.7b04905.
- [38] R. Cerny, P. Schouwink, Y. Sadikin, K. Stare, L. Smrcok, B. Richter, T.R. Jensen, Trimetallic borohydride Li₃MZn₅(BH₄)₁₅ (M = Mg, Mn) containing two weakly interconnected frameworks, Inorg. Chem. 52 (17) (2013) 9941–9947, https://doi.org/10.1021/ic401139k.
- [39] M. Brighi, P. Schouwink, Y. Sadikin, R. Černý, Fast ion conduction in garnettype metal borohydrides Li₃K₃Ce₂(BH₄)₁₂ and Li₃K₃La₂(BH₄)₁₂, J. Alloys Compd. 662 (2016) 388–395, https://doi.org/10.1016/j.jallcom.2015.11.218.
- [40] A.R. Motoaki Matsuo, R.C. Pascal Martelli, S.-i. Orimo, Complex hydrides with (BH₄)⁻ and (NH₂)⁻ anions as new lithium fast-ion conductors, J. Am. Chem. Soc. 131 (2009) 16389–16391.
- [41] Y. Yan, R.-S. Kühnel, A. Remhof, L. Duchêne, E.C. 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. 7 (19) (2017) 1700294–1700301, https://doi.org/10.1002/ aenn.201700294.
- [42] H. Wang, H. Cao, W. Zhang, J. Chen, H. Wu, C. Pistidda, X. Ju, W. Zhou, G. Wu, M. Etter, T. Klassen, M. Dornheim, P. Chen, Li₂NH-LiBH₄ : a complex hydride with near ambient hydrogen adsorption and fast lithium ion conduction, Chemistry 24 (6) (2018) 1342–1347, https://doi.org/10.1002/ chem.201703910.
- [43] A. Yamauchi, A. Sakuda, A. Hayashi, M. Tatsumisago, Preparation and ionic conductivities of (100-x)(0.75Li₂S·0.25P₂S₅)·xLiBH₄ glass electrolytes, J. Power Sources 244 (2013) 707–710, https://doi.org/10.1016/ j.jpowsour.2012.12.001.
- [44] A. Sakuda, A. Yamauchi, S. Yubuchi, N. Kitamura, Y. Idemoto, A. Hayashi, M. Tatsumisago, Mechanochemically prepared Li₂S-P₂S₅-LiBH₄ solid electrolytes with an argyrodite structure, ACS Omega 3 (5) (2018) 5453–5458, https://doi.org/10.1021/acsomega.8b00377.
- [45] A. Unemoto, H. Wu, T.J. Udovic, M. Matsuo, T. Ikeshoji, S. Orimo, Fast lithiumionic conduction in a new complex hydride-sulphide crystalline phase, Chem Commun (Camb). 52 (3) (2016) 564–566, https://doi.org/10.1039/ c5cc07793a.
- [46] A. El kharbachi, Y. Hu, K. Yoshida, P. Vajeeston, S. Kim, M.H. Sørby, S.i. Orimo, H. Fjellvåg, B.C. Hauback, Lithium ionic conduction in composites of Li(BH₄)_{0.75}I_{0.25} and amorphous 0.75Li₂S·0.25P₂S₅ for battery applications, Electrochim. Acta 278 (2018) 332–339, https://doi.org/10.1016/ j.electacta.2018.05.041.
- [47] T. Zhang, Y. Wang, T. Song, H. Miyaoka, K. Shinzato, H. Miyaoka, T. Ichikawa, S. Shi, X. Zhang, S. Isobe, N. Hashimoto, Y. Kojima, Ammonia, a switch for controlling high ionic conductivity in lithium borohydride ammoniates, Joule 2 (8) (2018) 1522–1533, https://doi.org/10.1016/j.joule.2018.04.015.
- [48] H. Liu, Z. Ren, X. Zhang, J. Hu, M. Gao, H. Pan, Y. Liu, Incorporation of ammonia borane groups in the lithium borohydride structure enables ultrafast lithium ion conductivity at room temperature for solid-state batteries, Chem. Mater. 32 (2) (2019) 671–678, https://doi.org/10.1021/ acs.chemmater.9b03188.
- [49] X. Zhang, T. Zhang, Y. Shao, H. Cao, Z. Liu, S. Wang, X. Zhang, Composite electrolytes based on poly(ethylene oxide) and lithium borohydrides for all-

solid-state lithium–sulfur batteries, ACS Sustain. Chem. Eng. 9 (15) (2021) 5396–5404, https://doi.org/10.1021/acssuschemeng.1c00381.

- [50] D. Sveinbjörnsson, D. Blanchard, J.S.G. Myrdal, R. Younesi, R. Viskinde, M.D. Riktor, P. Norby, T. Vegge, Ionic conductivity and the formation of cubic CaH₂ in the LiBH₄-Ca(BH₄)₂ composite, J. Solid State Chem. 211 (2014) 81–89, https://doi.org/10.1016/j.jssc.2013.12.006.
- [51] M. Xiang, Y. Zhang, L. Zhan, Y. Zhu, X. Guo, J. Chen, Z. Wang, L. Li, Study on xLiBH₄-NaBH₄ (x = 1.6, 2.3, and 4) composites with enhanced lithium ionic conductivity, J. Alloys Compd. 729 (2017) 936–941, https://doi.org/10.1016/ j.jallcom.2017.08.253.
- [52] L Zhan, Y. Zhang, M. Xiang, Y. Zhu, X. Guo, J. Chen, Z. Wang, L. Li, The lithium ionic conductivity of 2LiBH₄-MgH₂ composite as solid electrolyte, Inorg. Chem. Commun. 83 (2017) 62–65, https://doi.org/10.1016/j.inoche.2017.05.010.
- [53] M. Xiang, Y. Zhang, Y. Zhu, X. Guo, J. Chen, L. Li, Ternary LiBH₄-NaBH₄-MgH₂ composite as fast ionic conductor, Solid State Ionics 324 (2018) 109–113, https://doi.org/10.1016/j.ssi.2018.06.015.
- [54] M. Xiang, Y. Zhang, H. Lin, Y. Zhu, X. Guo, J. Chen, L. Li, LiBH₄-NaX (X=Cl, I) composites with enhanced lithium ionic conductivity, J. Alloys Compd. 764 (2018) 307–313, https://doi.org/10.1016/j.jallcom.2018.06.091.
- [55] Y.S. Choi, Y.S. Lee, K.H. Oh, Y.W. Cho, Interface-enhanced Li ion conduction in a LiBH₄-SiO₂ solid electrolyte, Phys. Chem. Chem. Phys. 18 (32) (2016) 22540–22547, https://doi.org/10.1039/c6cp03563a.
- [56] Y.S. Choi, Y.-S. Lee, D.-J. Choi, K.H. Chae, K.H. Oh, Y.W. Cho, Enhanced Li ion conductivity in LiBH₄-Al₂O₃ mixture via interface engineering, J. Phys. Chem. C 121 (47) (2017) 26209–26215, https://doi.org/10.1021/ acs.jpcc.7b08862.
- [57] V. Gulino, L. Barberis, P. Ngene, M. Baricco, P.E. de Jongh, Enhancing Li-ion conductivity in LiBH₄-based solid electrolytes by adding various nanosized oxides, ACS Appl. Energy Mater. 3 (5) (2020) 4941–4948, https://doi.org/ 10.1021/acsaem.9b02268.
- [58] W. Zhao, R. Zhang, H. Li, Y. Zhang, Y. Wang, C. Wu, Y. Yan, Y. Chen, Li-ion conductivity enhancement of LiBH₄xNH₃ with in situ formed Li₂O nanoparticles, ACS Appl. Mater. Interfaces 13 (27) (2021) 31635–31641, https:// doi.org/10.1021/acsami.1c06164.
- [59] Z. Liu, M. Xiang, Y. Zhang, H. Shao, Y. Zhu, X. Guo, L. Li, H. Wang, W. Liu, Lithium migration pathways at the composite interface of LiBH₄ and twodimensional MoS₂ enabling superior ionic conductivity at room temperature, Phys. Chem. Chem. Phys. 22 (7) (2020) 4096–4105, https://doi.org/ 10.1039/C9CP06090A.
- [60] Z. Liu, Y. Zhang, J. Hao, Y. Zhu, X. Guo, L. Li, G. Sly, High ionic conductivities of composites of Li₄(BH₄)₃l with two-dimensional MoS₂ at room temperature, J. Alloys Compd. 815 (2020), https://doi.org/10.1016/j.jallcom.2019.152353.
- [61] 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 LiBH₄ as a fast lithium ion conductor, Adv. Funct. Mater. 25 (2) (2015) 184–192, https://doi.org/10.1002/adfm.201402538.
- [62] F. Lu, Y. Pang, M. Zhu, F. Han, J. Yang, F. Fang, D. Sun, S. Zheng, C. Wang, A high-performance Li–B–H electrolyte for all-solid-state Li batteries, Adv. Funct. Mater. 29 (15) (2019) 1809219–1809226, https://doi.org/10.1002/ adfm.201809219.
- [63] M. Matsuo, S. Kuromoto, T. Sato, H. Oguchi, H. Takamura, S.-i. Orimo, Sodium ionic conduction in complex hydrides with [BH₄]⁻ and [NH₂]⁻ anions, Appl. Phys. Lett. 100 (20) (2012) 203904, https://doi.org/10.1063/1.4716021.
- [64] Y. Sadikin, M. Brighi, P. Schouwink, R. Černý, Superionic conduction of sodium and lithium in anion-mixed hydroborates Na₃BH₄B₁₂H₁₂and (Li_{0,7}Na_{0,3})₃BH₄B₁₂H₁₂, Adv. Energy Mater. 5 (21) (2015) 1501016–1501022, https://doi.org/10.1002/aenm.201501016.
- [65] R. Mohtadi, M. Matsui, T.S. Arthur, S.J. Hwang, Magnesium borohydride: from hydrogen storage to magnesium battery, Angew. Chem. Int. Ed. 51 (39) (2012) 9780–9783, https://doi.org/10.1002/anie.201204913.
- [66] S. Higashi, K. Miwa, M. Aoki, K. Takechi, A novel inorganic solid state ion conductor for rechargeable Mg batteries, Chem Commun (Camb). 50 (11) (2014) 1320–1322, https://doi.org/10.1039/c3cc47097k.
- [67] E. Roedern, R.S. Kuhnel, A. Remhof, C. Battaglia, Magnesium ethylenediamine borohydride as solid-state electrolyte for magnesium batteries, Sci. Rep. 7 (2017) 46189, https://doi.org/10.1038/srep46189.
- [68] T. Burankova, E. Roedern, A.E. Maniadaki, H. Hagemann, D. Rentsch, Z. Lodziana, C. Battaglia, A. Remhof, J.P. Embs, Dynamics of the coordination complexes in a solid-state mg electrolyte, J. Phys. Chem. Lett. 9 (22) (2018) 6450–6455, https://doi.org/10.1021/acs.jpclett.8b02965.
- [69] K. Kisu, S. Kim, M. Inukai, H. Oguchi, S. Takagi, S.-i. Orimo, Magnesium borohydride ammonia borane as a magnesium ionic conductor, ACS Appl. Energy Mater. 3 (4) (2020) 3174–3179, https://doi.org/10.1021/acsaem.0c00113.
- [70] Y. Yan, W. Dononelli, M. Jorgensen, J.B. Grinderslev, Y.S. Lee, Y.W. Cho, R. Cerny, B. Hammer, T.R. Jensen, The mechanism of Mg²⁺ conduction in ammine magnesium borohydride promoted by a neutral molecule, Phys. Chem. Chem. Phys. 22 (17) (2020) 9204–9209, https://doi.org/10.1039/ d0cp00158a.
- [71] Y. Yan, J.B. Grinderslev, M. Jørgensen, L.N. Skov, J.r. Skibsted, T.R. Jensen, Ammine magnesium borohydride nanocomposites for all-solid-state magnesium batteries, ACS Appl. Energy Mater. 3 (9) (2020) 9264–9270, https:// doi.org/10.1021/acsaem.0c01599.
- [72] M.S. Whittingham, Electrical energy storage and intercalation chemistry, Science 192 (4244) (1976) 1126–1127, https://doi.org/10.1126/ science.192.4244.1126.

- [73] A. Unemoto, G. Nogami, M. Tazawa, M. Taniguchi, S.-i. Orimo, Development of 4V-class bulk-type all-solid-state lithium rechargeable batteries by a combined use of complex hydride and sulfide electrolytes for room temperature operation, Mater. Trans. 58 (7) (2017) 1063–1068, https://doi.org/ 10.2320/matertrans.M2017022.
- [74] S.-E. Cheon, K.-S. Ko, J.-H. Cho, S.-W. Kim, E.-Y. Chin, H.-T. Kim, Rechargeable lithium sulfur battery, J. Electrochem. Soc. 150 (6) (2003) A796, https:// doi.org/10.1149/1.1571532.
- [75] A. Unemoto, S. Yasaku, G. Nogami, M. Tazawa, M. Taniguchi, M. Matsuo, T. Ikeshoji, S.-i. Orimo, Development of bulk-type all-solid-state lithiumsulfur battery using LiBH₄ electrolyte, Appl. Phys. Lett. 105 (8) (2014), 083901, https://doi.org/10.1063/1.4893666.
- [76] A. Unemoto, C. Chen, Z. Wang, M. Matsuo, T. Ikeshoji, S. Orimo, Pseudo-binary electrolyte, LiBH₄-LiCl, for bulk-type all-solid-state lithium-sulfur battery, Nanotechnology 26 (25) (2015) 254001, https://doi.org/10.1088/0957-4484/26/25/254001.
- [77] J. Lefevr, L. Cervini, J.M. Griffin, D. Blanchard, Lithium conductivity and ions dynamics in LiBH₄/SiO₂ solid electrolytes studied by solid-state NMR and quasi-elastic neutron scattering and applied in lithium-sulfur batteries, J. Phys. Chem. C 122 (27) (2018) 15264–15275, https://doi.org/10.1021/ acs.jpcc.8b01507.
- [78] K.-S. Park, A. Benayad, D.-J. Kang, S.-G. Doo, Nitridation-driven conductive Li₄Ti₅O₁₂ for lithium ion batteries, J. Am. Chem. Soc. 130 (45) (2008) 14930–14931, https://doi.org/10.1021/ja806104n.
- [79] K. Yoshida, S. Suzuki, J. Kawaji, A. Unemoto, S.-i. Orimo, Complex hydride for composite negative electrode-applicable to bulk-type all-solid-state Li-ion battery with wide temperature operation, Solid State Ionics 285 (2016) 96–100, https://doi.org/10.1016/j.ssi.2015.07.013.
- [80] K. Takahashi, K. Hattori, T. Yamazaki, K. Takada, M. Matsuo, S. Orimo, H. Maekawa, H. Takamura, All-solid-state lithium battery with LiBH₄ solid electrolyte, J. Power Sources 226 (2013) 61–64, https://doi.org/10.1016/ j.jpowsour.2012.10.079.
- [81] T.I. Atsushi Unemoto, M.M. Syun Yasaku, T.J. Vitalie Stavila, Stable interface formation between TiS2 and LiBH₄ in bulk-type allsolid-state lithium batteries, Chem. Mater. 27 (2015) 5407–5417, a.S.-i.O. Udovic.
- [82] 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, https:// doi.org/10.1016/j.ccr.2015.12.003.
- [83] 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 nidoundeca(carba)borates, Chem. Mater. 29 (24) (2017) 10496–10509, https:// doi.org/10.1021/acs.chemmater.7b04332.
- [84] 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 (12) (2015) 3637–3645, https://doi.org/10.1039/C5EE02941D.
- [85] 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 (8) (2016) 1502237, https://doi.org/10.1002/aenm.201502237.
- [86] J.A. Teprovich, H. Colón-Mercado, A.L. Washington Ii, P.A. Ward, S. Greenway, D.M. Missimer, H. Hartman, J. Velten, J.H. Christian, R. Zidan, Bi-functional Li₂B₁₂H₁₂ for energy storage and conversion applications: solid-state electrolyte and luminescent down-conversion dye, J. Mater. Chem. 3 (45) (2013) 22853–22859, https://doi.org/10.1039/c5ta06549f.
- [88] L. He, H. Shao, M. Felderhoff, H.-W. Li, X. Li, Q. Zhu, D. Zhang, D. Wu, Y. Fu, Y. Deng, Z. Lu, Facile synthesis of anhydrous Li₂B₁₂H₁₂ with high purity by solvent-free method, Inorg. Chim. Acta. 464 (2017) 147–151, https://doi.org/ 10.1016/j.ica.2017.05.025.
- [89] M. Paskevicius, M.P. Pitt, D.H. Brown, D.A. Sheppard, S. Chumphongphan, C.E. Buckley, First-order phase transition in the Li₂B₁₂H₁₂ system, Phys. Chem. Chem. Phys. 15 (38) (2013) 15825–15828, https://doi.org/10.1039/ c3cp53090f.
- [90] H. Wu, W.S. Tang, V. Stavila, W. Zhou, J.J. Rush, T.J. Udovic, Structural behavior of Li₂B₁₀H₁₀, J. Phys. Chem. C 119 (12) (2015) 6481–6487, https:// doi.org/10.1021/acs.jpcc.5b00533.
- [91] J.B. Varley, K. Kweon, P. Mehta, P. Shea, T.W. Heo, T.J. Udovic, V. Stavila, B.C. Wood, Understanding ionic conductivity trends in polyborane solid electrolytes from ab initio molecular dynamics, ACS Energy Lett. 2 (1) (2016) 250–255, https://doi.org/10.1021/acsenergylett.6b00620.
- [92] W.Z. Jae-Hyuk Her, Vitalie Stavila, Craig M. Brown, Terrence J. Udovic, Role of cation size on the structural behavior of the alkali-metal dodecahydro-closododecaborates, J. Phys. Chem. C 113 (2009) 11187–11189.
- [93] 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 Na₂B₁₂H₁₂, Chem Commun (Camb). 50 (28) (2014) 3750–3752, https://doi.org/10.1039/ c3cc49805k.
- [94] 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 A₂B₁₂H₁₂ (A = Na, K, Rb, Cs): anion reorientations and Na⁺ mobility, J. Phys. Chem. C 117 (49) (2013) 25961–25968, https://doi.org/10.1021/jp4106585.

- [95] 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, A. Unemoto, H. Takamura, S. Orimo, Exceptional superionic conductivity in disordered sodium decahydro-closo-decaborate, Adv. Mater. 26 (45) (2014) 7622–7626, https://doi.org/10.1002/adma.201403157.
- [96] B.A. Kathrin Hofmann, Crystal structures of M₂[B₁₀H₁₀] (M = Na, K, Rb) via real-space simulated annealing powder techniques, Z. Kristallogr. 220 (2005) 142–146, https://doi.org/10.1524/zkri.220.2.142.59144.
- [97] M. Paskevicius, B.R.S. Hansen, M. Jørgensen, B. Richter, T.R. Jensen, Multifunctionality of silver closo-boranes, Nat. Commun. 8 (1) (2017) 15136, https://doi.org/10.1038/ncomms15136.
- [98] M. Dimitrievska, P. Shea, K.E. Kweon, M. Bercx, J.B. Varley, W.S. Tang, A.V. Skripov, V. Stavila, T.J. Udovic, B.C. Wood, Carbon incorporation and anion dynamics as synergistic drivers for ultrafast diffusion in superionic LiCB₁₁H₁₂ and NaCB₁₁H₁₂, Adv. Energy Mater. 8 (15) (2018) 1703422, https:// doi.org/10.1002/aenm.201703422.
- [99] L. He, H. Lin, H.-F. Li, Y. Filinchuk, J. Zhang, Y. Liu, M. Yang, Y. Hou, Y. Deng, H.-W. Li, H. Shao, L. Wang, Z. Lu, Na3NH2B12H12 as high performance solid electrolyte for all-solid-state Na-ion batteries, J. Power Sources 396 (2018) 574–579, https://doi.org/10.1016/j.jpowsour.2018.06.054.
- [100] L. Duchene, R.S. Kuhnel, 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 (Camb). 53 (30) (2017) 4195–4198, https://doi.org/10.1039/c7cc00794a.
- [101] L. Duchêne, S. Lunghammer, T. Burankova, W.-C. Liao, J.P. Embs, C. Copéret, H.M.R. Wilkening, A. Remhof, H. Hagemann, C. Battaglia, Ionic conduction mechanism in the Na₂(B₁₂H₁₂)_{0.5}(B₁₀H₁₀)_{0.5} closo-borate solid-state electrolyte: interplay of disorder and ion-ion interactions, Chem. Mater. 31 (9) (2019) 3449–3460, https://doi.org/10.1021/acs.chemmater.9b00610.
- [102] M. Brighi, F. Murgia, Z. Łodziana, P. Schouwink, A. Wołczyk, R. Cerny, A mixed anion hydroborate/carba-hydroborate as a room temperature Naion solid electrolyte, J. Power Sources 404 (2018) 7–12, https://doi.org/ 10.1016/j.jpowsour.2018.09.085.
- [103] 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 (4) (2016) 659–664, https://doi.org/10.1021/acsenergylett.6b00310.
- [104] 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 (1) (2019) 1081, https://doi.org/10.1038/s41467-019-09061-9.
- [105] S. Kim, K. Kisu, S. Takagi, H. Oguchi, S.-i. Orimo, Complex hydride solid electrolytes of the Li(CB₉H₁₀)-Li(CB₁₁H₁₂) quasi-binary system: relationship between the solid solution and phase transition, and the electrochemical properties, ACS Appl. Energy Mater. 3 (5) (2020) 4831–4839, https://doi.org/ 10.1021/acsaem.0c00433.
- [106] Q. Zhang, Z. Gong, Y. Yang, Advance in interface and characterizations of sulfide solid electrolyte materials, Acta Phys. Sin. 69 (22) (2020) 228803-228811, https://doi.org/10.7498/aps.69.20201581.
- [107] J. Lu, C. Ke, Z. Gong, D. Li, L. Ci, L. Zhang, Q. Zhang, Application of in-situ characterization techniques in all-solid-state lithium batteries, Acta Phys. Sin. 70 (19) (2021) 198102–198111, https://doi.org/10.7498/ aps.70.20210531.
- [108] K. Bao, Y. Pang, J. Yang, D. Sun, F. Fang, S. Zheng, Modulating composite polymer electrolyte by lithium closo-borohydride achieves highly stable solid-state battery at 25°C, Sci. China Mater. (2021), https://doi.org/10.1007/ s40843-021-1740-7.
- [109] M. Zhu, Y. Pang, F. Lu, X. Shi, J. Yang, S. Zheng, In situ formed Li-B-H complex with high Li-ion conductivity as a potential solid electrolyte for Li batteries, ACS Appl. Mater. Interfaces 11 (15) (2019) 14136–14141, https://doi.org/ 10.1021/acsami.9b01326.
- [110] 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 polyhedralborate salts at device-relevant temperatures, Energy Storage Mater. 4 (2016) 79–83, https://doi.org/10.1016/j.ensm.2016.03.004.
- [111] K. Yoshida, T. Sato, A. Unemoto, M. Matsuo, T. Ikeshoji, T.J. Udovic, S.i. Orimo, Fast sodium ionic conduction in Na₂B₁₀H₁₀-Na₂B₁₂H₁₂ pseudobinary complex hydride and application to a bulk-type all-solid-state battery, Appl. Phys. Lett. 110 (10) (2017) 103901, https://doi.org/10.1063/ 1.4977885.
- [112] S. Kim, N. Toyama, H. Oguchi, T. Sato, S. Takagi, T. Ikeshoji, S.-i. Orimo, Fast lithium-ion conduction in atom-deficient closo-type complex hydride solid electrolytes, Chem. Mater. 30 (2) (2018) 386–391, https://doi.org/10.1021/ acs.chemmater.7b03986.
- [113] X. Shi, Y. Pang, B. Wang, H. Sun, X. Wang, Y. Li, J. Yang, H.W. Li, S. Zheng, In situ forming LiF nanodecorated electrolyte/electrode interfaces for stable allsolid-state batteries, Mater. Today Nano 10 (2020) 100079, https://doi.org/ 10.1016/j.mtnano.2020.100079.
- [114] A. Unemoto, K. Yoshida, T. Ikeshoji, S.-i. Orimo, Bulk-type all-solid-state lithium batteries using complex hydrides containing cluster-anions, Mater. Trans. 57 (9) (2016) 1639–1644, https://doi.org/10.2320/matertrans.MAW201601.
- [115] L. Duchêne, R.S. Kühnel, E. Stilp, E. Cuervo Reyes, A. Remhof, H. Hagemann, C. Battaglia, A 3 V all-solid-state sodium—ion battery based on a closo-borate

electrolyte, Energy Environ. Sci. 10 (12) (2017) 2609–2615, https://doi.org/ 10.1039/c7ee02420g.

- [116] L. Duchene, 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-solidstate batteries, Energy Storage Mater. 26 (2020) 543–549, https://doi.org/ 10.1016/j.ensm.2019.11.027.
- [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 (12) (2020) 5048–5058, https://doi.org/10.1039/d0ee01569e.
- [118] K. Niitani, S. Ushiroda, H. Kuwata, H.N. Ohata, Y. Shimo, M. Hozumi, T. Matsunaga, S. Nakanishi, Hard carbon anode with a sodium carborane electrolyte for fast-charging all-solid-state sodium-ion batteries, ACS Energy Lett. 7 (2021) 145–149, https://doi.org/10.1021/acsenergylett.1c02307.
- [119] F. Sun, L. Duchêne, M. Osenberg, S. Risse, C. Yang, L. Chen, N. Chen, Y. Huang, A. Hilger, K. Dong, T. Arlt, C. Battaglia, A. Remhof, I. Manke, R. Chen, Na electrodeposits: a new decaying mechanism for all-solid-state Na batteries revealed by synchrotron X-ray tomography, Nano Energy 82 (2021), https:// doi.org/10.1016/j.nanoen.2021.105762.
- [120] Y. Oumellal, A. Rougier, G.A. Nazri, J.M. Tarascon, L. Aymard, Metal hydrides for lithium-ion batteries, Nat. Mater. 7 (11) (2008) 916–921, https://doi.org/ 10.1038/nmat2288.
- [121] S. Brutti, G. Mulas, E. Piciollo, S. Panero, P. Reale, Magnesium hydride as a high capacity negative electrode for lithium ion batteries, J. Mater. Chem. 22 (29) (2012) 14531, https://doi.org/10.1039/c2jm31827j.
- [122] P. Vajeeston, P. Ravindran, A. Kjekshus, H. Fjellvag, Pressure-induced structural transitions in MgH₂, Phys. Rev. Lett. 89 (17) (2002) 175506, https:// doi.org/10.1103/PhysRevLett.89.175506.
- [123] L. Zeng, K. Kawahito, T. Ichikawa, Metal hydride-based materials as negative electrode for all- solid-state lithium-ion batteries, Alkali-ion Batteries (2016), https://doi.org/10.5772/62866.
- [124] Q. Cheng, D. Sun, X. Yu, Metal hydrides for lithium-ion battery application: a review, J. Alloys Compd. 769 (2018) 167–185, https://doi.org/10.1016/ j.jallcom.2018.07.320.
- [125] L. Zeng, K. Kawahito, S. Ikeda, T. Ichikawa, H. Miyaoka, Y. Kojima, Metal hydride-based materials towards high performance negative electrodes for all-solid-state lithium-ion batteries, Chem Commun (Camb). 51 (48) (2015) 9773–9776, https://doi.org/10.1039/c5cc02614h.
- [126] L. Zeng, T. Ichikawa, K. Kawahito, H. Miyaoka, Y. Kojima, Bulk-type all-solidstate lithium-ion batteries: remarkable performances of a carbon nanofibersupported MgH₂ composite electrode, ACS Appl. Mater. Interfaces 9 (3) (2017) 2261–2266, https://doi.org/10.1021/acsami.6b11314.
- [127] A.H. Dao, N. Berti, P. López-Aranguren, J. Zhang, F. Cuevas, C. Jordy, M. Latroche, Electrochemical properties of MgH₂-TiH₂ nanocomposite as active materials for all-solid-state lithium batteries, J. Power Sources 397 (2018) 143–149, https://doi.org/10.1016/j.jpowsour.2018.07.028.
- [128] P. López-Aranguren, N. Berti, A.H. Dao, J. Zhang, F. Cuevas, M. Latroche, C. Jordy, An all-solid-state metal hydride-sulfur lithium-ion battery, J. Power Sources 357 (2017) 56-60, https://doi.org/10.1016/j.jpowsour.2017.04.088.
- [129] F. Cano-Banda, A. Gallardo-Gutierrez, L. Luviano-Ortiz, A. Hernandez-Guerrero, A. Jain, T. Ichikawa, High capacity MgH₂ composite electrodes for all-

solid-state Li-ion battery operating at ambient temperature, Int. J. Hydrogen Energy 46 (1) (2021) 1030–1037, https://doi.org/10.1016/j.ijhydene.2020.09.202.

- [130] S. Brutti, S. Panero, A. Paolone, S. Gatto, D. Meggiolaro, F. Vitucci, J. Manzi, D. Munaò, L. Silvestri, L. Farina, P. Reale, Hydrides as high capacity anodes in lithium cells: an Italian "futuro in ricerca di base firb-2010" project, Challenges 8 (1) (2017), https://doi.org/10.3390/challe8010008.
- [131] S. Sartori, F. Cuevas, M. Latroche, Metal hydrides used as negative electrode materials for Li-ion batteries, Appl. Phys. A 122 (2) (2016) 135–142, https:// doi.org/10.1007/s00339-016-9674-x.
- [132] L. Silvestri, S. Forgia, L. Farina, D. Meggiolaro, S. Panero, A. La Barbera, S. Brutti, P. Reale, Lithium alanates as negative electrodes in lithium-ion batteries, Chemelectrochem 2 (6) (2015) 877–886, https://doi.org/10.1002/ celc.201402440.
- [133] J.A. Teprovich, J. Zhang, H. Colón-Mercado, F. Cuevas, B. Peters, S. Greenway, R. Zidan, M. Latroche, Li-Driven electrochemical conversion reaction of AlH₃, LiAlH₄, and NaAlH₄, J. Phys. Chem. C 119 (9) (2015) 4666–4674, https:// doi.org/10.1021/jp5129595.
- [134] H. Oguchi, M. Matsuo, T. Sato, H. Takamura, H. Maekawa, H. Kuwano, S. Orimo, Lithium-ion conduction in complex hydrides LiAlH₄ and Li₃AlH₆, J. Appl. Phys. 107 (9) (2010), 096104, https://doi.org/10.1063/1.3356981.
 [135] L. Silvestri, M.A. Navarra, S. Brutti, P. Reale, Failure mechanism of NaAlH₄
- [135] L. Silvestri, M.A. Navarra, S. Brutti, P. Reale, Failure mechanism of NaAlH₄ negative electrodes in lithium cells, Electrochim. Acta 253 (2017) 218–226, https://doi.org/10.1016/j.electacta.2017.09.074.
- [136] L. Cirrincione, L. Silvestri, C. Mallia, P.E. Stallworth, S. Greenbaum, S. Brutti, S. Panero, P. Reale, Investigation of the effects of mechanochemical treatment on NaAlH₄ based anode materials for Li-ion batteries, J. Electrochem. Soc. 163 (13) (2016) A2628–A2635, https://doi.org/10.1149/2.0731613jes.
- [137] P. Huen, F. Peru, G. Charalambopoulou, T.A. Steriotis, T.R. Jensen, D.B. Ravnsbaek, Nanoconfined NaAlH₄ conversion electrodes for Li batteries, ACS Omega 2 (5) (2017) 1956–1967, https://doi.org/10.1021/ acsomega.7b00143.
- [138] L. Silvestri, A. Paolone, L. Cirrincione, P. Stallworth, S. Greenbaum, S. Panero, S. Brutti, P. Reale, NaAlH₄ nanoconfinement in a mesoporous carbon for application in lithium ion batteries, J. Electrochem. Soc. 164 (6) (2017) A1120–A1125, https://doi.org/10.1149/2.0761706jes.
- [139] H. Oguchi, M. Matsuo, S. Kuromoto, H. Kuwano, S. Orimo, Sodium-ion conduction in complex hydrides NaAlH₄ and Na₃AlH₆, J. Appl. Phys. 111 (3) (2012), 036102, https://doi.org/10.1063/1.3681362.
- [140] F. Mo, X. Chi, S. Yang, F. Wu, Y. Song, D. Sun, Y. Yao, F. Fang, Stable threedimensional metal hydride anodes for solid-state lithium storage, Energy Storage Mater. 18 (2019) 423–428, https://doi.org/10.1016/ j.ensm.2019.01.014.
- [141] Y. Pang, X. Wang, X. Shi, F. Xu, L. Sun, J. Yang, S. Zheng, Solid-state prelithiation enables high-performance Li-Al-H anode for solid-state batteries, Adv. Energy Mater. 10 (12) (2020) 1902795, https://doi.org/10.1002/ aenm.201902795.
- [142] S. Yang, H. Wang, H. Man, Z. Long, J. Yang, S. Sun, J. Ruan, Y. Song, F. Fang, An enhanced Li₃AlH₆ anode prepared by a solid-state ion exchange method for use in a solid-state lithium-ion battery, Int. J. Electrochem. Sci. (2020) 9487–9498, https://doi.org/10.20964/2020.08.100.