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A highly stable sodium solid-state electrolyte based on a dodeca/deca-borate equimolar mixture

Fast rotating and highly stable closo-borate anions enable fast and stable sodium cycling in Na₂(B₁₂H₁₂)₀.₅(B₁₀H₁₀)₀.₅, a new promising solid electrolyte.
A highly stable sodium solid-state electrolyte based on a dodeca/deca-borate equimolar mixture†

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All-solid-state sodium-ion batteries promise to simultaneously yield better performance and lower cost as compared to state-of-the-art lithium-ion technology using organic liquid electrolytes.1,2 To build such a competitive all-solid-state battery requires a solid-state electrolyte (SSE) with high ionic conductivity near room temperature and high thermal and electrochemical stability. Meeting these three requirements simultaneously still represents a major challenge. High ionic conductivity of or above $10^{-3}$ S cm$^{-1}$ has been reached in oxide ceramics or more recently in sulfide phases but these materials still suffer from high electrode–electrolyte interface resistance or intrinsically small electrochemical stability windows of 1 V or less, respectively.3–10 Recently, complex hydride materials and particularly metal closo-borates have emerged as promising alternative SSEx.11,12 Metal closo-borates are salts with polyhedral $B_n$H$_n$$^-$ (n = 6–12) anions, among which the salts of the $B_{10}$H$_{10}$$^-$ and $B_{12}$H$_{12}$$^-$ anions were early noted due to their high thermal and chemical stability.13 LiCB$_{12}$H$_{12}$ as a halogen free electrolyte was also predicted by theory14 and used in experiments to synthesize a Mg-electrolyte.15 closo-Borate and related carbonate salts (with monovalent $C_{n-1}B_n$$^-$ anions) also exhibit structural transitions to highly conductive phases, above room temperature.16–19 Strategies to stabilize these superionic phases at room temperature and below, including mechanical milling and cation or anion substitutions, have been implemented.20–23 Yet, studies on closo-borates have focused almost exclusively on improving conductivity, while only preliminary work has been performed on the assessment of their electrochemical stability window and of their suitability for integration into a battery. Here, we report a new sodium superionic conductor Na$_2$(B$_{12}$H$_{12}$)$_{0.5}$(B$_{10}$H$_{10}$)$_{0.5}$ with a conductivity close to $10^{-3}$ S cm$^{-1}$ at room temperature (20°C). We further demonstrate that this material is compatible with a sodium metal anode and fulfills all prerequisites to be used in a 3 V all-solid-state sodium-ion battery.

Fig. 1a shows differential scanning calorimetry (DSC) data for the individual precursors Na$_2$B$_{12}$H$_{12}$ and Na$_2$B$_{10}$H$_{10}$ and their reacted 1 : 1 equimolar mixture. Both precursors show a characteristic endothermic peak at the temperature of their respective structural phase transition, as previously described.24,25 No such event is observed for the 1 : 1 mixture indicating that Na$_2$(B$_{12}$H$_{12}$)$_{0.5}$(B$_{10}$H$_{10}$)$_{0.5}$ does not undergo a phase transition within this temperature window. Besides the first heating cycle, we also show DSC data of the third heating cycle, which almost coincides with the first cycle, and demonstrates the stability of the equimolar mixture.

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† Electronic supplementary information (ESI) available: Experimental details and supplementary figures. See DOI: 10.1039/c7cc00794a

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Fig. 1. (a) DSC data for pure Na$_2$B$_{12}$H$_{12}$, Na$_2$B$_{10}$H$_{10}$ and their equimolar 1 : 1 mixture, Na$_2$(B$_{12}$H$_{12}$)$_{0.5}$(B$_{10}$H$_{10}$)$_{0.5}$. (b) Temperature-dependent Na$^+$ conductivity for pure Na$_2$B$_{12}$H$_{12}$, Na$_2$B$_{10}$H$_{10}$,16,17 and Na$_2$(B$_{12}$H$_{12}$)$_{0.5}$(B$_{10}$H$_{10}$)$_{0.5}$. Empty circles and filled triangles shown for the 1:1 mixture are measurement points upon heating and cooling, respectively.
mixture when subjected to thermal cycling. Thermal characterization was also carried out for intermediate Na$_2$(B$_{12}$H$_{12}$)$_{0.5}$(B$_{10}$H$_{10}$)$_{0.5}$ compositions (0.1 < x < 0.6, see Fig. S1, ESI†) for which the endothermic peaks are still visible but decrease in size and ultimately vanish as the ratio approaches x = 0.5, at which the precursors fully react.

Fig. 1b presents the ionic conductivity of Na$_2$(B$_{12}$H$_{12}$)$_{0.5}$(B$_{10}$H$_{10}$)$_{0.5}$ determined by impedance spectroscopy as a function of temperature (see Experimental section and Fig. S2, ESI† for details). The conductivities of Na$_2$B$_{12}$H$_{12}$ and Na$_2$B$_{10}$H$_{10}$ obtained by Udovic et al.16,17 are also reported for comparison. The room temperature ionic conductivity for the equimolar ratio is several orders of magnitude higher than that of Na$_2$B$_{12}$H$_{12}$ and Na$_2$B$_{10}$H$_{10}$, reaching 0.9 mS cm$^{-1}$ at 20 °C. This value is comparable to typical conductivities reported for oxide and sulfide electrolytes3–8 and only slightly lower than that of a standard sodium liquid electrolyte based on 1 M NaClO$_4$ dissolved in EC:PC (3.3 mS cm$^{-1}$ at 25 °C,26 assuming a sodium transference number of 0.4). Within the family of complex hydrides, this conductivity is comparable to the recently reported Na$_2$BH$_4$B$_{12}$H$_{12}$ and highly conducting, ball-milled Na$_2$B$_{25}$H$_{32}$21,22 and is only surpassed by equimolar mixed carborane phases that can reach exceptional conductivity of 70 mS cm$^{-1}$ at room temperature25 but have yet to demonstrate their applicability as SSEs in all-solid-state batteries. Similarly to the observed thermal behavior, the equimolar mixture shows no signs of a phase transition in the temperature-dependent conductivity data, whilst the conductivity of the precursors drops sharply at the onset temperatures at which latent heat is observed in DSC. Consequently, while hysteresis in conductivity is observed for both precursors upon temperature cycling, the conductivity of the equimolar mixture shows no hysteresis between heating and cooling. Still, the activation energy for Na$^+$ diffusion in Na$_2$(B$_{12}$H$_{12}$)$_{0.5}$(B$_{10}$H$_{10}$)$_{0.5}$ decreases smoothly from 0.7 at −40 °C to 0.4 eV at 100 °C with increasing temperature. A similar behavior was observed for carbonate mixtures23 and Na$_2$BH$_4$B$_{12}$H$_{12}$21 and attributed to temperature dependent anion dynamics within the respective crystal structures. The connection between lattice parameter, anion dynamics and the evolution of cation conductivity in closo-borates was also recently discussed by Varley et al. based on ab initio molecular dynamics calculations.27

Crystal structure and lattice parameters were determined by X-ray diffraction (XRD). In Fig. 2a we compare the diffractograms of the equimolar mixture at room temperature with the ones of the precursors in their respective high temperature (HT) conductive phases, i.e. body-centered cubic (bcc) Na$_2$B$_{12}$H$_{12}$ at 300 °C and face-centered cubic (fcc) Na$_2$B$_{10}$H$_{10}$ at 180 °C. At room temperature the precursors show additional reflections which are assigned to Na$_2$B$_{12}$H$_{12}$ (300 °C) and Na$_2$B$_{10}$H$_{10}$ (180 °C) as well as a lower symmetry phase of Na$_2$B$_{12}$H$_{12}$ at 180 °C. Refinement yields a slightly larger unit cell parameter of a = 10.029 Å for Na$_2$(B$_{12}$H$_{12}$)$_{0.5}$(B$_{10}$H$_{10}$)$_{0.5}$ at room temperature vs. a = 9.854 Å for Na$_2$B$_{10}$H$_{10}$ at 180 °C (see Fig. S3b and c, ESI†). Additionally, XRD measurements of Na$_2$(B$_{12}$H$_{12}$)$_{0.5}$(B$_{10}$H$_{10}$)$_{0.5}$ at 300 °C (see Fig. S3a, ESI†) show no structural change other than an expansion of the unit cell parameters, demonstrating again the high thermal stability in agreement with DSC and conductivity measurements. Note that equimolar mixtures of Na$_2$B$_{12}$H$_{12}$ and Na$_2$B$_{10}$H$_{10}$ were recently reported by Tang et al.,22 who also used mechanical milling followed by a heat treatment at 275 °C for 16 h. However, their mixture still contained predominantly (70%) the low temperature (LT) phase of Na$_2$B$_{12}$H$_{12}$ as refined from XRD, indicating only partial conversion to the mixed phase, and no conductivity measurement was reported. Our results prove that using appropriate reaction conditions, equimolar mixtures of Na$_2$B$_{12}$H$_{12}$ and Na$_2$B$_{10}$H$_{10}$ fully react and stabilize a single mixed-anion phase.

To gain insight into the local anion configuration in the mixed-anion structure, we performed infrared (IR) spectroscopy measurements. Fig. 2b compares the IR spectra of the HT phases of both Na$_2$B$_{12}$H$_{12}$ (300 °C) and Na$_2$B$_{10}$H$_{10}$ (180 °C) with Na$_2$(B$_{12}$H$_{12}$)$_{0.5}$(B$_{10}$H$_{10}$)$_{0.5}$ at room temperature. For both precursors, B–H stretching and cage absorption modes are identified in the wavenumber ranges of 2400–2500 cm$^{-1}$ and 600–1200 cm$^{-1}$, respectively. These characteristic absorption modes correspond to those previously assigned in the IR spectra of B$_{12}$H$_{10}$–4 and B$_{12}$H$_{12}$–5 measured in solution,13,28 characteristic of the respective D$_{6d}$ and I$_{6}$ point group symmetry of these ions. Recent theoretical DFT calculations confirm these assignments.29 In the LT phases of Na$_2$B$_{12}$H$_{12}$ and Na$_2$B$_{10}$H$_{10}$ (see Fig. S4, ESI†) significant splitting of the absorption modes can be seen, indicative of a lowered symmetry of the ions, whereas the anions in the HT phases adopt a similar symmetry than in the solution. Therefore, we conclude that they sit in a very symmetric environment that is a consequence of the lower structure symmetry below the phase transition.
of the cubic symmetry of the crystal structure and of the absence of a preferred orientation of the anions, i.e. of rotational disorder. The IR spectrum of Na₂(B₁₂H₁₂)₀.₅(B₁₀H₁₀)₀.₅ at room temperature corresponds closely to the sum of the spectra of Na₂B₁₂H₁₂ and Na₂B₁₀H₁₀ in their respective HT phases and all vibration modes can be assigned to the two closo-borate anions. This shows that both B₁₀H₁₀⁻ and B₁₂H₁₂⁻ are still present in the structure and suggests either an average of rotationally disordered but static configurations, or of dynamic rotation of the anions.

To distinguish between these two cases, we recorded solid-state \(^{11}\)B, \(^{1}\)H and \(^{23}\)Na magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra of Na₂B₁₂H₁₂, Na₂B₁₀H₁₀ and their 1 : 1 mixture. All samples were measured at room temperature to compare the ion dynamics. As seen from comparison in Fig. 2c–e, the spectrum of the equimolar mixture comprises all the resonances of the constituents in the precursors. Importantly, the resonances of the equimolar mixture are all considerably narrowed compared to the signals of the pure precursors, especially in the case of boron and hydrogen (Fig. 2c–e). This narrowing is a sign of fast dynamics of the ions in the 1 : 1 mixture compared to the borate starting materials. We may thus also interpret the IR data as a result of fast anion dynamics rather than an average of frozen configurations. Additionally, since X-ray diffraction already showed that Na₂(B₁₂H₁₂)₀.₅(B₁₀H₁₀)₀.₅ has a well-defined crystal structure, we can conclude that this motion is rotational and not translational (see Fig. 3), as previously suggested based on NMR and quasi-elastic neutron scattering experiments on other closo-borates.\(^ {15}\)B NMR also confirms that the B₁₂H₁₂⁻ and B₁₀H₁₀⁻ anions remain intact in Na₂(B₁₂H₁₂)₀.₅(B₁₀H₁₀)₀.₅ with no significant \(^{11}\)B signal intensity detectable other than the ones of the closo-borate anions. The 1 : 1 B₁₂H₁₂⁻ to B₁₀H₁₀⁻ ratio was verified by \(^{11}\)B solution-state NMR by dissolving Na₂(B₁₂H₁₂)₀.₅(B₁₀H₁₀)₀.₅ in deuterated water, and it was confirmed that both anions are indeed present in a 1 : 1 molar ratio (see Fig. S5, ESI†). Finally, it can be seen in Fig. 2e that the \(^{23}\)Na NMR chemical shift and thus the sodium environment in Na₂(B₁₂H₁₂)₀.₅(B₁₀H₁₀)₀.₅ is averaged between that of Na₂B₁₀H₁₀ and Na₂B₁₂H₁₂, supporting the hypothesis of a solid solution phase, as depicted in Fig. 3.

To evaluate the suitability of Na₂(B₁₂H₁₂)₀.₅(B₁₀H₁₀)₀.₅ as SSE in an all-solid-state sodium-ion battery, we performed cyclic voltammetry tests at room temperature. Fig. 4a shows current density vs. voltage measured for a Na|Na₂(B₁₂H₁₂)₀.₅(B₁₀H₁₀)₀.₅|Pt cell cycled at voltages between −0.5 V and 6.5 V at 0.1 mV s⁻¹. Near 0 V, we observed characteristic anodic and cathodic current peaks associated with sodium stripping and plating. Towards higher voltages, the current density remains low up to 6.5 V but first oxidation currents were observed in the nA cm⁻² range. We therefore built two additional cells for a precise measure of the electrochemical stability window of Na₂(B₁₂H₁₂)₀.₅(B₁₀H₁₀)₀.₅. To determine its oxidative stability, a platinum working electrode (WE) was swept against a sodium counter electrode from the open-circuit voltage of 1.6 V up to a voltage of 5.5 V at a slow rate of 0.1 mV s⁻¹ to remain near equilibrium. Results are shown in Fig. 4b. Small currents indicative of slow electrolyte oxidation can be measured for cell voltages above 3 V but remain below 10 nA cm⁻² at higher voltages. To determine the reductive stability, an aluminum working electrode, which unlike platinum does not alloy with sodium, was preferred. Starting at the cell’s open circuit voltage of 1.6 V, the voltage was swept down to −0.5 V. On aluminium, no reduction currents are observed down to 0 V, below which the sodium plating peak appears, suggesting that the electrolyte is stable in contact with metallic sodium.

We conclude that Na₂(B₁₂H₁₂)₀.₅(B₁₀H₁₀)₀.₅ offers a practical electrochemical stability window of 3 V, most likely limited by near open-circuit voltage of 1.6 V up to a voltage of 5.5 V at a slow rate of 0.1 mV s⁻¹ to remain near equilibrium. Results are shown in Fig. 4b. Small currents indicative of slow electrolyte oxidation can be measured for cell voltages above 3 V but remain below 10 nA cm⁻² at higher voltages. To determine the reductive stability, an aluminum working electrode, which unlike platinum does not alloy with sodium, was preferred. Starting at the cell’s open circuit voltage of 1.6 V, the voltage was swept down to −0.5 V. On aluminium, no reduction currents are observed down to 0 V, below which the sodium plating peak appears, suggesting that the electrolyte is stable in contact with metallic sodium.

We conclude that Na₂(B₁₂H₁₂)₀.₅(B₁₀H₁₀)₀.₅ offers a practical electrochemical stability window of 3 V, most likely limited by
oxidation of the $\text{B}_{10}\text{H}_{10}$ anions.\textsuperscript{32} Preliminary cyclic voltammetry measurements performed on other closo-borate electrolytes suggested a much larger stability window for this class of compounds.\textsuperscript{17,21,22} However, we believe that the stability has been over-estimated due to the very small oxidation currents that may not have been detected in previous measurements. In fact, Han \textit{et al.}\textsuperscript{33} recently discussed the limitation of conventional cyclic voltammetry measurements to evaluate the true stability window of solid-state electrolytes. This limitation can be overcome only if one is able to measure very small currents (we used a low current channel with pA resolution) or by artificially increasing the contact area between the electrolyte and the working electrode.

To further confirm the compatibility with a sodium metal anode, we built a symmetric $\text{Na|Na}_2(\text{B}_{12}\text{H}_{12})_{0.5}(\text{B}_{10}\text{H}_{10})_{0.5}|\text{Na}$ cell which was galvanostatically cycled at 60 °C. Fig. 4c shows the evolution of the cell voltage over time as sodium is plated and stripped at a current of ±100 mA cm$^{-2}$ in intervals of 12 h. Our results demonstrate that sodium is plated and stripped fully reversibly with a low combined over-potential reaching a maximum of 1.2 mV, in good agreement with the measured electrochemical stability window of 3 V.

In conclusion, we demonstrated that among SSEs with comparable conductivity, $\text{Na}_2(\text{B}_{12}\text{H}_{12})_{0.5}(\text{B}_{10}\text{H}_{10})_{0.5}$ stands out as a particularly stable material, notably when compared to sulphide phases. The electrochemical stability window of 3 V is compatible with high performance sodium cathode materials such as $\text{Na}_2\text{FePO}_4\text{F}$, $\text{NaCrO}_2$. We further demonstrated that $\text{Na}_2(\text{B}_{12}\text{H}_{12})_{0.5}(\text{B}_{10}\text{H}_{10})_{0.5}$ is compatible with a sodium metal anode enabling long-term and reversible sodium plating and stripping. We also believe that further anion engineering e.g. by mixing larger halogenated closo-borates with a lower charge density, could yield even higher stability and conductivity and that this class of materials holds promise for competitive high voltage all-solid-state sodium-ion batteries.

We would like to thank the Swiss National Science Foundation for financial support within the Sinergia project ‘Novel ionic conductors’ under contract number CRSII2_160749/1. The NMR hardware was partially granted by the Swiss National Science Foundation (SNF, grant no. 206021_150638/1).

Notes and references