Mechanical Behavior and Dendrite Resistance of closo-Hydroborate Solid Electrolyte

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Stack pressure and mechanical robustness are two important parameters needed to tackle the interfacial instability of solid-state batteries. Here, the mechanical behavior of Na₄(CB₁₁H₁₂)(B₁₂H₁₂), as solid electrolyte at the interface with Na anode, is reported. The solid electrolyte is tested as function of stack pressure and different current densities, revealing a critical current density of 0.6 mA cm⁻² at room temperature and an optimal stack pressure of 1.5 MPa. These findings are achieved, thanks to the adoption of a multilayer approach, demonstrating the powerfullness of hydroborates to compensate chemical and electrochemical instability, simply employing different complex hydride polyanions that change locally the electrochemical properties while preserving structural and chemical coherence.

1. Introduction

Solid-state batteries (SSBs) are leading the competition for future post-lithium electrochemical energy storage devices. Despite this technology is theoretically very promising, allowing greater energy and larger current density, the way for application is still quite far, since all existing solid-state cells are subject to severe limitations due to the instability of the solid–solid interface between electrodes and solid electrolyte (SE). In first instance, the nature of this instability can be chemical or mechanical,[1–4] since the interface must account for deformation, ensuring no contact loss between the stacked cell components. Some approaches to mitigate these issues were proposed by means of the adoption of viscous additives (i.e., ionic liquids) at the solid–solid interface.[5]

Second, in order to realistically enhance the energy density, interfaces must be stable upon reversible electroplating on the ion source, namely Li and Na, just to mention the more likely technologies.

These arguments redefine the protagonists in the race for novel solid-state electrolytes in fulfilling requirements for a healthy evolution of SSBs. Not only ion conductivity and electrochemical stability are the essential parameters to consider for potential prototypes, but also mechanical processing, interfacial stability during cycling, and resistance to dendrite penetration are crucial aspects.

A widely known parameter to measure the attitude for a material to satisfy these requirements is the so-called critical current density (CCD). Willing to summarize many different CCD definitions in one sentence, the CCD is the maximum allowed current density above which dendrites can form.[6,7] However, CCD results from the interplay of different parameters that affect the goodness of the interface and its stability. For instance, pressure and temperature can positively influence the CCD, moving the threshold at higher values. If the pressure is sufficiently high, the alkali metal likely falls in the plastic regime, ensuring a constant deformation, preserving the contact at the electrolyte surface and avoiding void formation. The temperature gives rise to the same effect, since the homologous temperature (i.e., the ratio between room temperature and its melting temperature) is very favorable in case of sodium and lithium at ambient condition (0.80 and 0.66) and approaching the unity, ion diffusion increases. As a consequence, the plastic regime can be achieved at lower pressure, providing the abovementioned benefits.[8]

In this work, we explored the interface stability of several hydroborates, an emerging class of compounds that we previously investigated as Na-based SEs.[9] Among the possible choices of room temperature (rt) ion conductors, we focused on Na₄(CB₁₁H₁₂)(B₁₂H₁₂) (in the following NCBB) since it represents the best option in terms of Na conductivity and electrochemical stability, as recently reported,[10,11] hence being the most promising and realistic compound, among this class of materials, in a SSB.

For the present study, the pressure was considered as the only parameter affecting CCD, fixing the temperature at ambient condition (25 °C). The paper is organized in the following way: in the first part, we explore the pressure needed to minimize the interfacial resistance due to the flawed Na adhesion at the electrolyte surface. In the second part, the optimal pressure (that can provide a high current density) is investigated and, finally, at this optimum stack pressure, a CCD measurement is performed.

2. Results

2.1. Mechanical Strength of Solid Electrolyte

At the laboratory scale, processing of hydroborate-based SEs remains challenging, mainly due to the lack of knowledge to

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obtain sintering condition or surface polishing techniques relying in solvent-based methods, which would result in nonaggressive treatments for hydroborates.

Indeed, the majority of polar organic solvents, either protic (as EtOH or i-PrOH) or aprotic (CH₃COCH₃, THF, DME, or other ethers), can dissolve hydroborates and only few mixed anion-based salts, such as [CB₉H₁₀]⁻-[CB₁₁H₁₂]⁻ or [B₁₀H₁₀]²⁻-[B₁₂H₁₂]²⁻, can recrystallize as conductive compounds, due to the negligible difference in their respective solubility values. More details on this point are reported in Figure S1 (Supporting Information).

In all other mixtures, both precursors recrystallize separately as the carba-hydroborates are always more soluble compared to their hydroborate relatives.[12]

Sintering also must be rejected because hydroborates and their C-derivatives generally undergo decomposition before melting, for which different approaches, as pressure-induced melting, could be promising but remaining yet unexplored.

However, thanks to their softer lattices compared to oxide or halide electrolytes (for Na₂B₁₂H₁₂, the bulk and the shear modulus amount to \( B = 17.3 \) GPa; \( G = 3.3 \) GPa, respectively),[13] relatively low porosity (Figure S2, Supporting Information) can be achieved by cold pressing the bulky powder.

To assess this assumption, electrochemical impedance spectroscopy (EIS) spectra were collected as function of the stack pressure. The zero pressure point consisted of a hand pressed powder, just to guarantee a minimum interfacial contact. EIS data were collected in the frequency range \( 1 \text{ Hz} < f < 3 \text{ MHz} \) and the cell resistance (electrolyte) was deduced from the frequency-independent plateau in the Bode plot, after the linear dispersion contribution which comes from the electrolyte/electrode interface. This corresponds to the intercept of EIS spectra to the real axis (Nyquist plot in Figure S3 in the Supporting Information).

The resulting resistance was used to calculate the “apparent” ionic conductivity value at each pressure, adopting the die’s diameter and the thickness obtained from the theoretical crystal density \( (\rho = 1.1 \text{ g cm}^{-3}) \) as the pellet’s dimensions.[14]

This assumption is reasonable since the change in the pellet’s thickness cannot exceed 10–15% of its initial value, while the variation of intergrain contribution to the total resistance can span over several orders of magnitude (see Figure 1).

The aforementioned resistance shows a log-type variation saturating to the expected value, as reported in a previous study. This value, represented in Figure 1 by the dashed line, amounts to 4 mS cm⁻¹, which is in agreement with the rt Na-conductivity reported by Brighi et al. where the pellet was obtained by cold pressing at 550 MPa.[14]

After that, the cell was opened and sodium disks were placed on both sides. The adhesion of the soft Na on the ceramic pellet surface diminishes the interfacial resistance contribution that quickly decreases by increasing the stack pressure up to 35 MPa (Figure S4 (Supporting Information), the area specific resistance (ASR) is plotted as red circles in Figure 1 and fitted in the Nyquist plot in Figure S3 in the Supporting Information). Above 35 MPa, the total resulting conductivity increases linearly (i.e., the cell resistance decreases) as function of the applied pressure and the mechanically induced short circuit is reached at 70 MPa.

The decrease of ASR is due to the improved adhesion at the surface when the sodium is in the plastic regime, since both

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Figure 1. Pressure dependency of ionic conductivity for NCBB. Filled squares show electrolyte’s ionic conductivity evolution as function of applied axial pressure, measured with stainless-steel blocking electrodes. Filled triangles and open circles (ASR) correspond to the bulk and interface contribution, respectively, obtained using Na nonblocking electrodes. The two arrows at the bottom indicate the values at which the mechanically induced short circuit occur for NaCB₁₁H₁₂ and Na₂B₁₂H₁₂, respectively.
hydrostatic pressure and von Mises stress strongly intensify around the surface’s defects.[18] Such condition is easily satisfied for sodium, due to its low yield strain value, estimated 0.2–0.3 MPa.[8] Hence, as shown in Figure 1, at sufficiently high pressure (>35 MPa), this condition is exacerbated in correspondence of interfacial inhomogeneity and defects, allowing Na filaments to propagate through the SE eventually causing the short circuit.

Interestingly, the situation is slightly different when considering the single-anion precursors: indeed, repeating the same experiment on pure NaCB11H12 or Na2B12H12, the short circuit is obtained already at 50 and 55 MPa, respectively. Due to the low value of ionic conductivity at rt of the single anion phases (typically 10⁻⁶–10⁻⁸ S cm⁻¹)[16,17] it was not possible to appreciate any clear contributions on the EIS spectra due to the high noise. Thus, only the short circuit was determined.

However, these values are systematically lower compared to that for NCBB showed in Figure 1.

This discrepancy raises questions concerning the mechanical properties of the mixed-anion phase, since the same mechanical behavior should be expected for [B12H12]⁺, [CB11H12]⁺, or their mixture. The principal drastic difference between them is represented by the difference in ionic conductivity. In order to cross-check the dependency of the latter on the Na inclusion, NaCB11H12 and Na2B12H12 were mechanically treated, stabilizing their conductive phases at rt.[18] In this case, the resistance evolution can be clearly followed as function of the stack pressure for both compounds (Figure S5, Supporting Information). Once the Na disks have been introduced, at solely 5 MPa, the conductivity approaches the value obtained at 90 MPa with blocking electrodes. Then, while the electrolyte resistance keeps constant at this value, the ASR in NaCB11H12 progressively decreases up to 24.5 MPa (red circles in Figure S5a in the Supporting Information), where a behavior, similar to that described above, is observed and can be read as an improved contact with the Na at the SE surface. The short circuit is obtained at 54 MPa, in agreement with the crystalline NaCB11H12. Figure S5b,c (Supporting Information) shows the same measurements for Na2B12H12 with two different pellet thickness. For this sample, it was not possible to observe a clear EIS contribution coming from the interface but only the total resistance can be determined from impedance spectra. Increasing the stack pressure, the conductivity reaches the value obtained at 90 MPa faster for the thin pellet (Figure S5c, Supporting Information, thickness = 0.58 mm) and at solely 19.5 MPa, the cell resistance drops, as sign of a short circuit. This experiment was designed in order to understand if the pellet thickness plays a role in delaying the creep-induced propagation of Na through the SE. This seems the case since only for thinner Na2B12H12, the short circuit is obtained at 19.5 MPa, while for the others, the breakdown pressure falls always in the region 50–60 MPa. The different breakdown values could be associated to a kinetic aspect due to the Na diffusion on two different length scales. Notwithstanding, a common aspect is represented by the onset of what we called “sodium inclusion.” The pressure range for this effect is narrower, amounting reasonably at 20 MPa for Na2B12H12 and NaCB11H12, while rising to 30 MPa for NCBB.

Work that is more extensive must be performed in order to fully characterize the dependence of mechanical properties on chemical composition of hydroborates. Up to this pressure, the ASR is minimized, providing an optimal Na–SE contact. Beyond this critical value, mechanically induced Na propagation is not hindered and according to our findings, the resistance to penetration follows the trend Na2B12H12 < NaCB11H12 < NCBB.

### 2.2. Na Electroplating at the Interface

If a too high pressure can mechanically induce short circuits,[19] or accelerate the dendrite propagation, on the other hand a too low stack pressure cannot hinder the formation of voids during the Na stripping process.[15]

Indeed, it has been demonstrated that during this process, the Na flow at the interface must be sustained by an appropriate Na diffusion toward the bulk electrolyte. This can be easily obtained when sodium is in the plastic regime, namely for pressure higher than the yield stress, which has been recently estimated to be in the range 0.2–0.3 MPa.[8,20] When this condition is not guaranteed, once the sodium at the interface has diffused into the electrolyte, a surface void can form. Such effect can be detrimental for the cell operation, since the effective area reduces and the current density locally increases where Na is still in contact with the SE. In such condition, interfacial spots easily undergo a current density above the nominal CCD. Therefore, such condition can act as source of stress, forcing the interfacial defects to evolve in cracks and fractures of the SE body. Such cracks pave the way for Na extrusion as filaments and dendrites.

For this reason, an appropriate stack pressure is crucial to assure a healthy, long-life cycling of the battery.

To explore this aspect, the methodology used by Wang et al. was adopted in this work.[21] The voltage profile was monitored as a function of time under galvanostatic condition. To probe the effect of pressure on the stripping process, the stack pressure was gradually decreased, starting from the upper limit of 1.5 MPa. Such value was chosen to be consistent with Wang et al. who adopted for Li-based system an upper pressure of 3 MPa. In this work, the values are halved since the yield strength of sodium is, at least, 2 times lower. In order to minimize the ASR contribution, the sample was previously conditioned at higher pressure (see Figure 1 and Figure S5a in the Supporting Information).

In order to explore the limiting condition and exacerbate the interfacial stability, the current density was fixed at 1 mA cm⁻² and the length of each pressure sweep amounts to 1 h. This corresponds to a total charge of 1.8 C and it is equivalent to adopt a cathode with a specific capacity of 120 mAh g⁻¹ and a mass loading of 8 mg cm⁻² (3.5 C cm⁻²).

In Figure 2, the cell polarization matches the Ohmic resistance measured by impedance spectroscopy (38.9 Ω and corresponding to an ionic conductivity of 4 mS cm⁻¹). While the voltage is steady, or slowly increasing, a significant change is observed when the pressure drops below 1 MPa. The interfacial stripping/plating further deteriorates when the pressure reduces at 0.3 MPa, as shown by a voltage profile, which is typical of inhomogeneous stripping/plating and eventually of metallic
dendrite's evolution. In summary, a pressure higher than 1 MPa can, at this condition, likely sustain a plastic regime. However, to be more conservative, a stack pressure of 1.5 MPa was selected to perform the CCD characterization. In such condition, the exchanged charge for each cycle was fixed to be 0.5 C, equivalent to a cathode with specific capacity of 120 mAh g$^{-1}$ and a mass loading of 2.3 mg cm$^{-2}$. These values are still one order of magnitude lower with respect to the typical state-of-the-art Li-ion batteries$^{[26,27]}$ but comparable to the current liquid and solid Na-based batteries reported in literature.$^{[11,23–25]}$ Surprisingly, the first result of CCD measures on NCBB was quite disappointing since the determined current limit was rather low (0.1 mA cm$^{-2}$, see Figure S6 in the Supporting Information) but perfectly reproducible either in pristine and recycled NCBB (see the Experimental Section). For instance, Asakura et al. cycled a 4 V Na battery using the same solid electrolyte at even higher current density.$^{[11]}$ This finding then raised concerns about the anodic stability of such compound, since already during the conditioning period (consisting in ten 30-min sweeps at 10 µA cm$^{-2}$), the interfacial resistance evolved remarkably (Figure S7, Supporting Information). Anodic instability was already observed for open-cage nido-hydroborates (namely LiB$_6$H$_{14}$ and NaB$_{12}$H$_{12}$)$^{[26,27]}$ suggesting a tendency to react with lithium due to the accentuated H anisotropy on the boron cluster. The decomposition products could slightly widen the reductive limit, allowing slow-rate symmetrical cell, as was reported by Payandeh et al.$^{[25]}$ This suggests that a similar behavior can take place in NaCB$_{12}$H$_{12}$-based compound, as interfacial resistance evolution was already observed in the past on symmetric Na cells.$^{[11,14]}$ This was not the case for Na$_2$B$_{12}$H$_{12}$-based compounds, observed to be stable at low potential versus Na$_2$.$^{[28]}$

Meanwhile, as mentioned above, it was shown that mechanical treatment on Na$_3$B$_{12}$H$_{12}$ can stabilize the high conductive polymorph at rt.$^{[18]}$ We therefore realized a multilayer pellet in order to explore the interfacial stability realizing a coating of ball-milled Na$_2$B$_{12}$H$_{12}$. The thickness of such layer is about 0.142 cm), perfectly in agreement with the above result of Figure S6 in the Supporting Information but perfectly reproducible either in pristine and recycled NCBB (see the Experimental Section). For instance, Asakura et al. cycled a 4 V Na battery using the same solid electrolyte at even higher current density.$^{[11]}$ This finding then raised concerns about the anodic stability of such compound, since already during the conditioning period (consisting in ten 30-min sweeps at 10 µA cm$^{-2}$), the interfacial resistance evolved remarkably (Figure S7, Supporting Information). Anodic instability was already observed for open-cage nido-hydroborates (namely LiB$_6$H$_{14}$ and NaB$_{12}$H$_{12}$)$^{[26,27]}$ suggesting a tendency to react with lithium due to the accentuated H anisotropy on the boron cluster. The decomposition products could slightly widen the reductive limit, allowing slow-rate symmetrical cell, as was reported by Payandeh et al.$^{[25]}$ This suggests that a similar behavior can take place in NaCB$_{12}$H$_{12}$-based compound, as interfacial resistance evolution was already observed in the past on symmetric Na cells.$^{[11,14]}$ This was not the case for Na$_2$B$_{12}$H$_{12}$-based compounds, observed to be stable at low potential versus Na$_2$.$^{[28]}$

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Looking at Figure 3a, the cell polarization shows an Ohmic behavior up to 2.2C, corresponding to a current density of 0.6 mA cm$^{-2}$. Further increase of the current density modifies the voltage profile in the typical feature related to dendrite evolution, as it was recently reported by Kazyak et al.$^{[7]}$

Based on this model, the initial increase in cell polarization is likely linked to the decrease in the effective contact area ($A_{\text{eff}}$). Since ASR is directly proportional to the latter ($\text{ASR} = R_{\text{int}} \cdot A_{\text{eff}}$), inhomogeneity at the interface and surface roughness could provoke depleted Na regions, eventually reducing $A_{\text{eff}}$. Further increase of the current density (0.8 mA cm$^{-2}$) reveals a different behavior of dendrite evolution, still observed by Kazyak et al. with operando optical microscopy. The valley observed in the voltage profile results from the interplay of two effects. The first already mentioned, that increases the cell polarization by formation of voids and depleted regions at the interface. The second is related to the dendrite propagation across the SE that increases $A_{\text{eff}}$ and reduces the distance between the electrodes (i.e., the electrolyte thickness), hence decreasing the total resistance.
This behavior changes remarkably at 72°C (corresponding to a current density of 2 mA cm⁻²) where the voltage profile strongly oscillates even below its initial Ohmic value of 78 Ω. In literature, the CCD determination is sometimes related to the unambiguous short circuit of the cell, but also to the deviation of the cell polarization from its Ohmic regime.[29–31] In this case, the situation is closer to that observed by Gupta et al. for the soft polymer electrolyte PEO–LiTFSI[32] which, however, was not supported by any stack pressure, thus predominantly affected of the cell polarization from its Ohmic regime.[29–31] In this case, a nearly complete dendrite penetration, as supported by the EIS spectra of selected cycles (Figure S9, Supporting Information).

In conclusion, NCBB represents a valid competitor in the context of SEs for SSB. In addition to its mechanical resistance to compressive mechanical behavior and the interface robustness employing them as SE.

By contrast, high-rate plating preferentially accumulates cations (i.e., Na⁺) at high stress contact points, nucleates preferentially on these locations the columnar-like plating, widely known as dendrites. The cell shown in Figure 4 failed after 140 cycles, but instability in the voltage profile was present already at 50% of its operating time.

In conclusion, NCBB represents a valid competitor in the context of SEs for SSB. In addition to its mechanical resistance to compression...
Na penetration, placed between 20 and 30 MPa, the here reported CCD amounts to 0.6 mA cm$^{-2}$ and a minimal pressure of 1.5 MPa permits charge/discharge processes at acceptable rate (2.2C for the configuration of this work). While this stack pressure is sufficient for a steady stripping process, Na plating appears hitherto an unsolved problem for fast charge. However, we believe that this issue is technological rather than chemophysical limited, thus preferably addressed to engineer solutions. Related to this point, we also demonstrated the powerfulness of hydroborates in compensating chemical instability, simply by a multilayer approach employing different complex hydride polyanions, that change locally the electrochemical properties, but preserving a chemical and structural coherence.

4. Experimental Section

Materials: The hydroborate precursors, namely Na$_2$B$_{12}$H$_{12}$ and NaCB$_{11}$H$_{12}$, were purchased at Katchem and dried for 12 h at 180 °C under dynamic vacuum ($p \approx 10^{-3}$ mbar). Then, the synthesis of the mixed phase NaCB$_{11}$H$_{12}$ and Na$_2$B$_{12}$H$_{12}$ in molar ratio 2:1 was conducted as reported in a previous work.[14] Sodium was purchased at Acros Organics (>99.8%) and calendered into 1 mm thick sheet. Disks of 8 mm diameter were cut out and scraped to obtain polished surfaces. In order to obtain conductive Na$_2$B$_{12}$H$_{12}$ and NaCB$_{11}$H$_{12}$, the dry powder was mechanically treated for 45 min in stainless steel vial with a Spex 7000 (ball-to-mass ratio 200:1).

During the experiments, the used NCBB pellets were recycled. For this purpose, the Na disks were manually detached from the NCBB pellet surface, while residual Na traces, including Na dendrites were removed by soaking the pellet in i-PrOH (Fisher Chemical, >99.8%). While Na reacted immediately with the solvent, the dissolution kinetics for NCBB was relatively low, allowing the two components to be satisfactorily separated. Once all Na traces were eliminated, the NCBB pellet was removed and completely dissolved in water. After a further drying treatment on the powder at 180 °C under dynamic vacuum, NCBB was reprocessing following the same procedure described in literature.[14]

Electromechanical Characterization: Both mechanical and electrochemical characterizations were conducted in ASC-T cell (Sphere Energy SAS) with adjustable pressure, ranging from 0 to 400 MPa, and a sample holder of 8 mm diameter, placed in an Ar-containing glove box (H$_2$O and O$_2$ < 0.1 ppm). Impedance spectroscopy, CCD, and galvanostatic characterization were performed with a SP-200 potentiostat (Biologic SA) equipped with an ultralow current probe. Impedance spectroscopy was collected in a frequency range 100 mHz–3 MHz with a 10 mV voltage signal. Studying the mechanical resistance to dendrite penetration, first NCBB was consolidated by cold pressing the powder into a solid pellet. EIS was continuously collected up to 100–120 MPa, where the impedance spectra saturated to an asymptotic value. Then, 8 mm diameter Na disks were cut, scraped on both surfaces, and added on both pellet sides. EIS was, as described before, continuously recorded increasing the stack pressure until the short circuit was reached.

The protocol followed to obtain the CCD profile was reported in ref. [38] and consisted of 10 conditioning cycles of 1 h each, at low current density (10 µA cm$^{-2}$). Then, the current was progressively increased, every cycle, up to the maximum value of 8 mA cm$^{-2}$, imposing a 10 min resting time at the end of each sweep.

Structural Characterization: X-ray powder diffraction was performed on Panalytical Empyrean, in Debye–Scherrer geometry and with a Cu Kα$_{1,2}$ radiation. Samples were measured in 0.5 mm glass capillaries. Scanning electron microscopy was used to analyze the surface morphology (Zeiss LEO-1455 VP), equipped with secondary emission and backscattered electron detectors.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

The paper was written by M.B. with contributions of all authors who had given approval to the final version of the manuscript. M.B. and R.C. conceived the experiments. M.B. and F.M. performed the measurements.

Data Availability Statement

Research data are not shared.

Keywords

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