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High-Loading Low-Temperature All-Solid-State Sodium Batteries Realized by Superionic Metastable Sodium Closo-Hydroborate

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Abstract

All-solid-state batteries require a thick cathode layer, which translates to higher energy density, that can operate at subzero temperatures. A solid electrolyte with high ionic conductivity, mechanical formability, and excellent electrochemical stability is vital to enable such technology. While fast ionic diffusion is typically associated with close-packed anion frameworks, we demonstrate that a non-close-packed orthorhombic $\text{Na}_3(\text{BH}_4)(\text{B}_{12}\text{H}_{12})$ phase, which is stabilized by rapid cooling, possesses superionic conductivity and excellent reduction stability. Leveraging its high conductivity across a range of temperatures, the all-solid-state batteries with enhanced diffusion kinetics enable an ultra-thick sodium-ion cathode electrode. Moreover, the high-loading all-solid-state batteries can operate not only at room temperature but also at subzero temperatures.

Introduction

All-solid-state batteries (ASBs), with a solid electrolyte replacing the liquid electrolyte in conventional batteries, have attracted considerable attention in academia and industry due to their promising intrinsic characteristics, including enhanced safety, longer lifecycle, and high energy density. While lithium-based batteries remain the dominant technology, sodium-based ASBs are a complementary safe and cost-effective alternative chemistry due to the abundance and cost of sodium (1, 2). The general rule in the selection of optimal solid electrolyte depends on several factors; ionic conductivity, electrochemical and chemical stability, and mechanical properties (3, 4).

Due to poor sodium diffusivity and high Young's modulus of oxide cathodes, a solid electrolyte must be integrated with the active material to provide ionic percolation in the electrode layer. Thus, solid electrolytes must possess low modulus to conform effectively to the cathode while preserving the intimate contact between the materials during repeated electrochemical reactions. For the ASBs to displace conventional lithium-ion batteries, a thick and dense cathode, along with the use of a high-capacity alloy anode, is necessary to enhance the energy density at the cell level. Accordingly, a highly conductive ($> \text{mS cm}^{-1}$) solid electrolyte is highly sought after to minimize ohmic resistance and polarization in battery cells.

Sodium closo-hydroborates are promising solid electrolyte owing to their low gravimetric density ($\sim 1.2 \text{ g/cm}^3$), low toxicity, excellent reduction stability, and moderately soft mechanical properties allowing for densification at room temperature (5-7). Superionic conductivity in these materials is generally observed in the close-packed anion or body-centered cubic framework which possesses large Na^+ site vacancies, higher structural symmetry, and the propensity for anion reorientation that promotes Na^+ diffusion (7-11). However, the diffusion of the Na^+ in close-packed structures is limited to the high occupancy of the energetically favorable tetrahedral sites in the octahedral-tetrahedral-octahedral diffusion channels, which leads to a high activation energy (12-14).

In contrast, the orthorhombic sodium closo-hydroborate with $Cmc2_1$ symmetry (o-NBH, with a chemical composition of $\text{Na}_3(\text{BH}_4)(\text{B}_{12}\text{H}_{12})$) (Fig. 1A) exhibits one order of magnitude lower room temperature ionic conductivity than the close-packed phases (15). However, the unclear purity of previously synthesized o-NBH at room temperature raises the possibility of structural

instability. In this work, we combine experimental and computational approaches to demonstrate that metastable o-NBH exhibits superionic conductivity, reaching 4.6 mS cm^{-1} at 30°C , which enables an ultra-thick cathode (approximately $310 \text{ }\mu\text{m}$) ASBs.

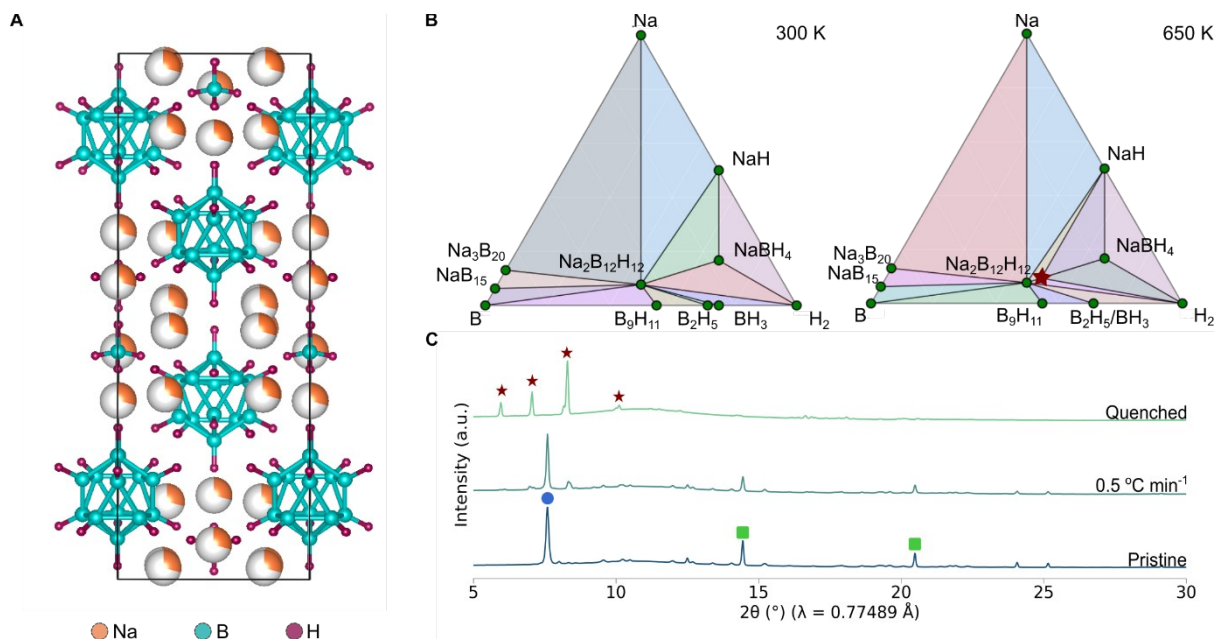


Fig. 1. Phase stability of o-NBH solid electrolyte. (A) Crystal structure of o-NBH with partial sodium occupancy. (B) Na-B-H compositional phase diagram based on the phonon thermodynamic properties. The calculated stable phases are indicated by the green dot and o-NBH is indicated by $\star$. (C) Room temperature XRD pattern of o-NBH with different cooling rates ($\star$ - o-NBH (15), $\bullet$ - $\text{Na}_2\text{B}_{12}\text{H}_{12}$ (ICSD 164649), and $\blacksquare$ - NaBH_4 (ICSD 182734))

Synthesis and Structure Analysis

The calculated phase diagram of Na-B-H in **Fig. 1B** based on density function theory (DFT) indicates that o-NBH is not thermodynamically stable with energy above hull of 16 meV atom^{-1} at room temperature. To verify the phase stability of o-NBH, differential scanning calorimetry (DSC) and synchrotron X-ray diffraction (XRD) patterns were collected to determine the phase evolution with temperature. DSC and in-situ XRD in **Fig. S3A and B**, respectively, show that the formation of the o-NBH phase begins at approximately 360°C and is fully formed at 400°C . After the formation of o-NBH, rapid cooling of the material by quenching the glass capillary in 25°C water leads to only the o-NBH phase without any observable precursor reflections (**Fig. 2A and S3C**). However, a slow cooling rate ($0.5^\circ\text{C min}^{-1}$) from 400°C to room temperature leads to a mixture of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and NaBH_4 precursors, implying that o-NBH is a metastable phase that dissociates into its enthalpy-preferred precursors if given sufficient energy and time.

The local environments of the materials prepared with different cooling rates (e.g., denoted o-NBH-2 and o-NBH-Q as with 2°C min^{-1} cooled and quenching of o-NBH, respectively) were further probed using ^{11}B , ^1H , and ^{23}Na solid-state nuclear magnetic resonance (ss-NMR) spectroscopy. The ^{11}B ss-NMR spectra of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and NaBH_4 in **Fig. 2A** indicate that $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and NaBH_4 each exhibit a single resonance with chemical shifts of -16.3 ppm and -42.1 ppm (16, 17), respectively. o-NBH-Q has two resonances centered at -15.5 ppm and

−44.3 ppm attributed to boron in $B_{12}H_{12}^{2-}$ and BH_4^- clusters, respectively. The similarity between ^{11}B spectra in the precursors and o-NBH phase suggests that the $B_{12}H_{12}$ and BH_4 clusters are maintained after thermal treatment but with somewhat different neighboring sodium distributions. The more negative chemical shift of $^{11}BH_4$ in o-NBH (−44.3 ppm) vs. in $NaBH_4$ (−42.1 ppm) is attributed to electron density donated by the additional Na^+ from the $Na_2B_{12}H_{12}$ component around the more localized (harder) BH_4 group in the o-NBH structure. Consequently, the $^{11}B_{12}H_{12}$ exhibits a more positive chemical shift from −16.3 to −15.5 ppm. This hypothesis is supported by CASTEP calculations (**Table S1**). Strong evidence that the $B_{12}H_{12}$ and BH_4 clusters are mixed into a single phase at the atomic scale comes from two-dimensional 1H - 1H dipolar-coupling-mediated spin-exchange spectra (**Fig. S4**), which shows strong correlations even at millisecond mixing times. Of great utility is that the distinct chemical shifts of $^{11}BH_4$ in o-NBH vs. $NaBH_4$ allow us to directly estimate the fraction of the o-NBH phase to be 90.4 at.% when quenched vs. 61.2 at.% when cooled at $2\text{ }^\circ\text{C min}^{-1}$.

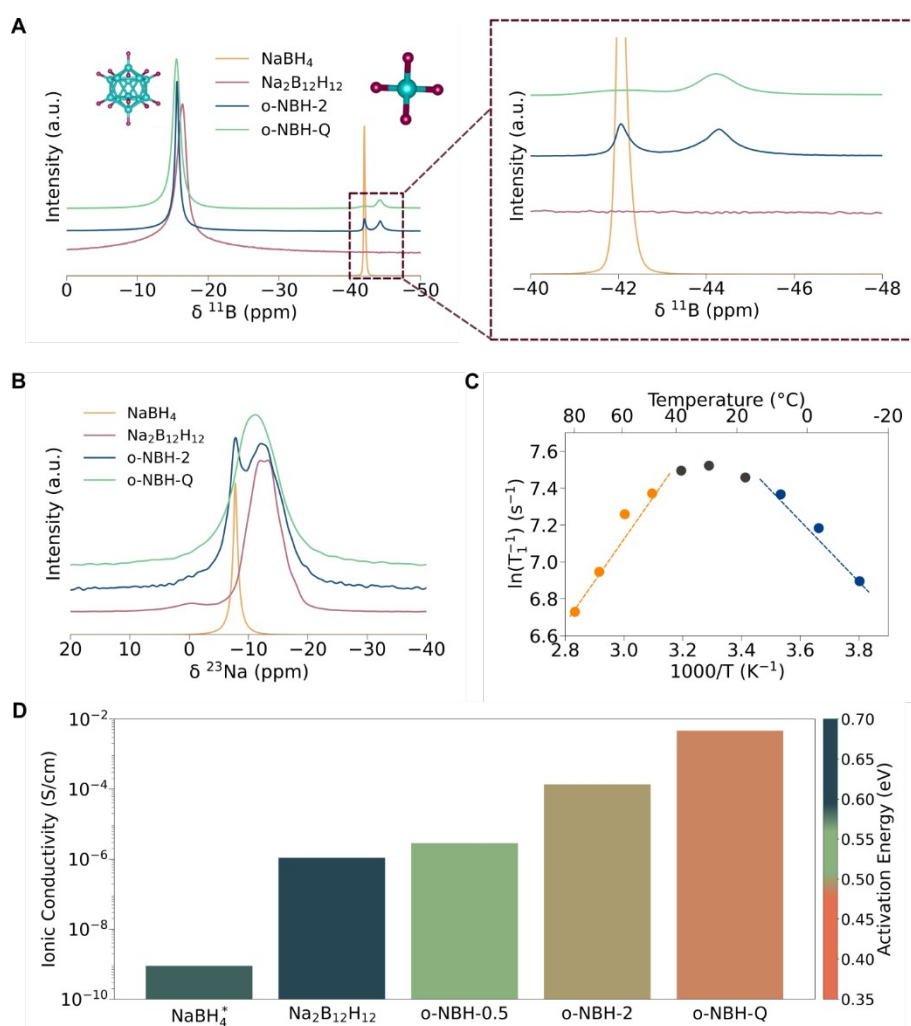


Fig. 2. Local environment and ionic conductivity of o-NBH prepared with different cooling rates. (A) ^{11}B and (B) ^{23}Na ss-NMR spectra of the precursors, o-NBH-2 and o-NBH-Q. (C) Arrhenius behavior of the ^{23}Na spin-lattice relaxation at variable temperatures. (D) Ionic conductivity at $30\text{ }^\circ\text{C}$ and activation energy of o-NBH prepared with different cooling rates (0.5, $2\text{ }^\circ\text{C min}^{-1}$, and Ar-gas quenching).

Additionally, ^{23}Na NMR spectra (**Fig. 2B**) indicate the existence of two distinct ~~averaging~~ sodium environments in o-NBH-2, which match NaBH_4 and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ at -7.8 ppm and -12.1 ppm, respectively. On the other hand, o-NBH-Q shows a single ~~averaged~~-resonance centered at -11.2 ppm, indicating that there is a chemical exchange ~~and shift averaging~~ between the two environments, which is expected in the proposed structure model featuring neighboring $\text{B}_{12}\text{H}_{12}$ and BH_4 clusters ~~with rapid Na^+ dynamics~~. ~~This-The ^{23}Na lineshapes thus~~ further supports the metastable nature of the o-NBH phase, which is stabilized at room temperature by rapid cooling. Moreover, ^{23}Na spin-lattice relaxation, which is dominated by fluctuating quadrupolar interactions stimulated by ionic motion in diamagnetic sodium closo-hydroborate, is enhanced by four orders of magnitude in o-NBH-Q ($T_1 = 0.56$ ms) relative to the precursors (**Table S2**). This magnitude of increased relaxation rate is indicative of rapid Na^+ mobility in o-NBH, as seen in other families of sodium superionic conductors (18-20).

Variable temperature spin-lattice relaxation (VT-SLR) of the ^{23}Na was measured to obtain the local activation energy of Na^+ in o-NBH-Q (**Fig. 2C**). Two activation energies can be obtained from VT-SLR; the short-range ~~relaxation-correlations~~ or localized diffusion ~~is-are~~ considered for low-temperature where $\omega_0\tau \gg 1$ holds, while longer-range ~~correlations relaxation-isare~~ considered for high-temperature where $\omega_0\tau \ll 1$ holds (21, 22). The short-range and long-range activation energies calculated from VT-SLR are 0.13 and 0.23 eV, respectively, which ~~is-are~~ lower than the close-packed $\text{Na}_4(\text{B}_{12}\text{H}_{12})(\text{B}_{10}\text{H}_{10})$ phase, exhibiting hopping barriers of 0.19 and 0.33 eV (23), respectively, indicating a lower Na^+ migration barrier in the non-close-packed o-NBH-Q phase reported here. According to the Bloembergen, Purcell, and Pound (BPP) model ($E_a^{\text{LT}} = (\beta - 1)E_a^{\text{HT}}$, β being a measure of the strength of correlation with simple BPP behavior (23-25)), a β value of 1.54 indicates uncorrelated Na^+ motion that stems from Coulomb interactions and/or structural disorder, which will be revisited computationally (*vide infra*). Furthermore, at maximum SLR (T_{max} temperature, 30°C) where $\tau\omega_0 \sim 1$ holds, a jump rate ($1/\tau$) in the order of 10^8 s^{-1} is direct evidence of ~~possibly~~-high ionic conductivity of o-NBH.

To investigate the significance of stabilizing the metastable o-NBH on bulk Na^+ diffusion, the ionic conductivity and activation energy (**Fig. S5**) of the o-NBH prepared at different cooling rates were measured. Indeed, the ionic conductivity increases while activation energy decreases with an increasing cooling rate (**Fig. 2D**). The ionic conductivity (at 30°C) reaches a maximum value of 4.6 mS cm^{-1} when the material was rapidly cooled, which is one of the highest among all sodium solid-state electrolytes reported (26, 27). Direct-current polarization experiments (**Fig. S6**) indicate that the electronic conductivity is around $10^{-5} \text{ mS cm}^{-1}$, which is five orders of magnitude lower than the ionic conductivity, indicating it is highly electronically insulating. These results support that the resultant ionic conductivity highly correlates to the purity of the o-NBH, which is a function of the cooling rate used during synthesis, ~~in-the-material~~.

Ion Diffusion Mechanism

The Na^+ diffusion mechanism in the o-NBH crystal structure was systematically investigated using molecular dynamic (MD) simulations. An accurate graph deep learning interatomic potential based on the Materials 3-body Graph Network (M3GNet) architecture was fitted from a dataset of 5595 DFT calculations (see *Methods*). The o-NBH structure has $1/3$ Na^+ occupancy among the seven sites in o-NBH (15) and the high density of accessible sites within the

structure provides multiple pathways for Na^+ hopping. Additionally, o-NBH exhibits a large variation in the instantaneous coordination number of $\text{Na-B}_{12}\text{H}_{12}$ and Na-BH_4 (**Fig. S7**) providing a flexible coordination environment and lowering the energy barrier for the fast Na^+ diffusion (8). Compared to NaBH_4 and $\text{Na}_2\text{B}_{12}\text{H}_{12}$, which have no Na^+ site vacancies for ion diffusion (**Fig. S8**), the o-NBH structure exhibits a fast macroscopic three-dimensional (3D) Na^+ ion diffusion network, as indicated by the yellow isosurfaces in the Na^+ probability density function (**Fig. 3A**). Beyond the intrinsic Na^+ site vacancies that facilitate Na^+ ion diffusion, dynamic anion motion may disrupt Na^+ site ordering, further flattening the overall energy landscape (8). While angular displacement exists in the anion clusters, the tracked hydrogen atom trajectory for a stipulated simulation duration indicates the motion is highly randomized (**Fig. S9**). Combining the high Na^+ site vacancy density, low activation energy, and anion motion, o-NBH exhibits orders of magnitude higher room temperature ionic conductivity than its precursors (monoclinic- $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and cubic- NaBH_4) (**Fig. 3B**).

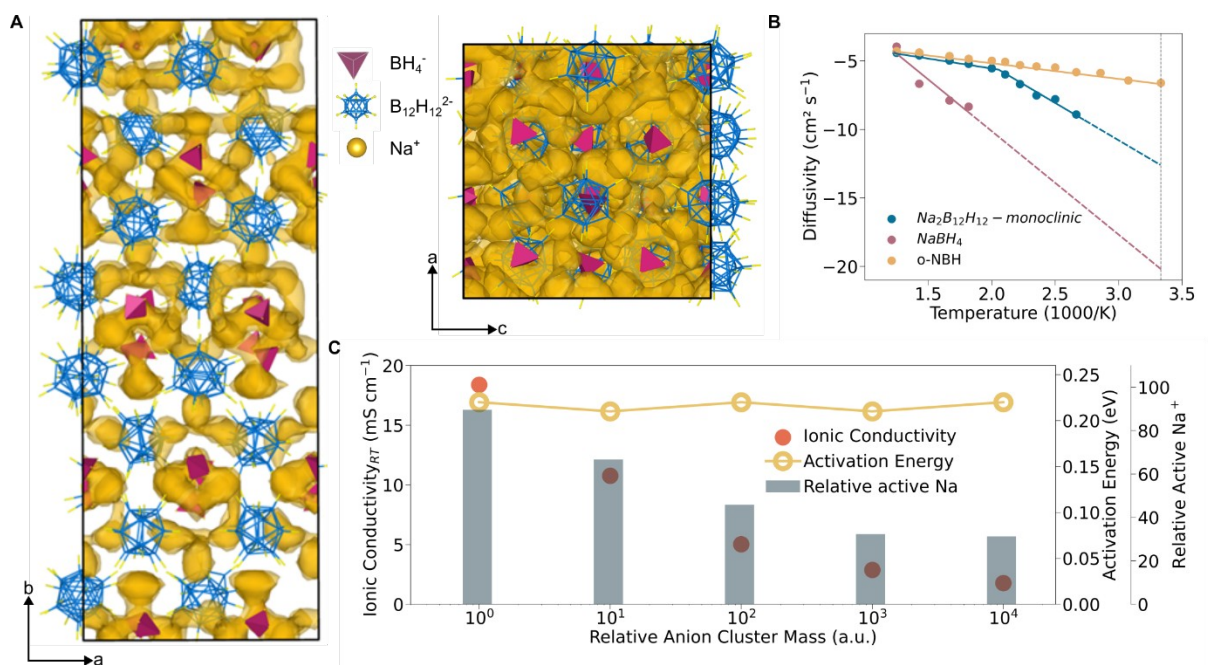


Fig. 3. o-NBH crystal structure and ionic diffusion mechanism. (A) Iso-surface of the Na^+ probability density function (threshold = $0.5 \text{ \AA}$) obtained from 2 ns MD simulation at 300 K. The BH_4^- and $\text{B}_{12}\text{H}_{12}^{2-}$ anions are shown as fixed red and blue polyhedral, respectively. (B) Arrhenius plots of diffusivity vs. temperature for NBH structures. (C) Computed room-temperature 300 K ionic conductivity, activation energy, and relative active Na^+ with higher anion cluster mass.

To better understand the influence of the two distinct polyanion polyhedrals (BH_4^- and $\text{B}_{12}\text{H}_{12}^{2-}$) in o-NBH on the Na^+ diffusion dynamics, we performed a gedankenexperiment by artificially scaling the mass of each type of polyanion in the MD simulations. Unlike previous approaches whereby anions were “frozen” in MD, this approach enables us to perform gradual adjustments to the anion rotational dynamics by modifying their moment of inertia without affecting the chemical interactions (**Fig. S10**). From **Fig. 3C**, we may observe that increasing anion mass (and decreasing anion rotation) has a small effect on the activation barrier for diffusion, even though there is a marked decrease in ionic conductivity. Instead, we find that the reduction in

ionic conductivity is highly correlated to the reduction in the number of active Na^+ with increasing anion mass. By independently modifying the BH_4 and $\text{B}_{12}\text{H}_{12}$ masses, we determined that increasing the mass of the larger $\text{B}_{12}\text{H}_{12}$ anion has a more pronounced effect on the number of inactive Na and ionic conductivity (**Figure S11**).

Electrochemical Characterization

While high ionic conductivity is a crucial intrinsic property for a practical solid electrolyte, the electrochemical stability window impacts the viability of electrodes with high and low sodium chemical potential and, therefore, the accessible battery voltage and energy density. Linear sweep voltammetry indicates that the highly ionic conductive o-NBH exhibits good reduction stability against Na_9Sn_4 but limited oxidation stability, up to 2.5 V *vs.* Na_9Sn_4 (**Fig. 4A**). The reduction stability is further demonstrated with symmetrical Na_9Sn_4 /o-NBH/ Na_9Sn_4 cell cycling that showed stable and reversible charge transfer after 100 cycles of 1 mAh cm^{-2} of (de)sodiation (**Fig. S12A**).

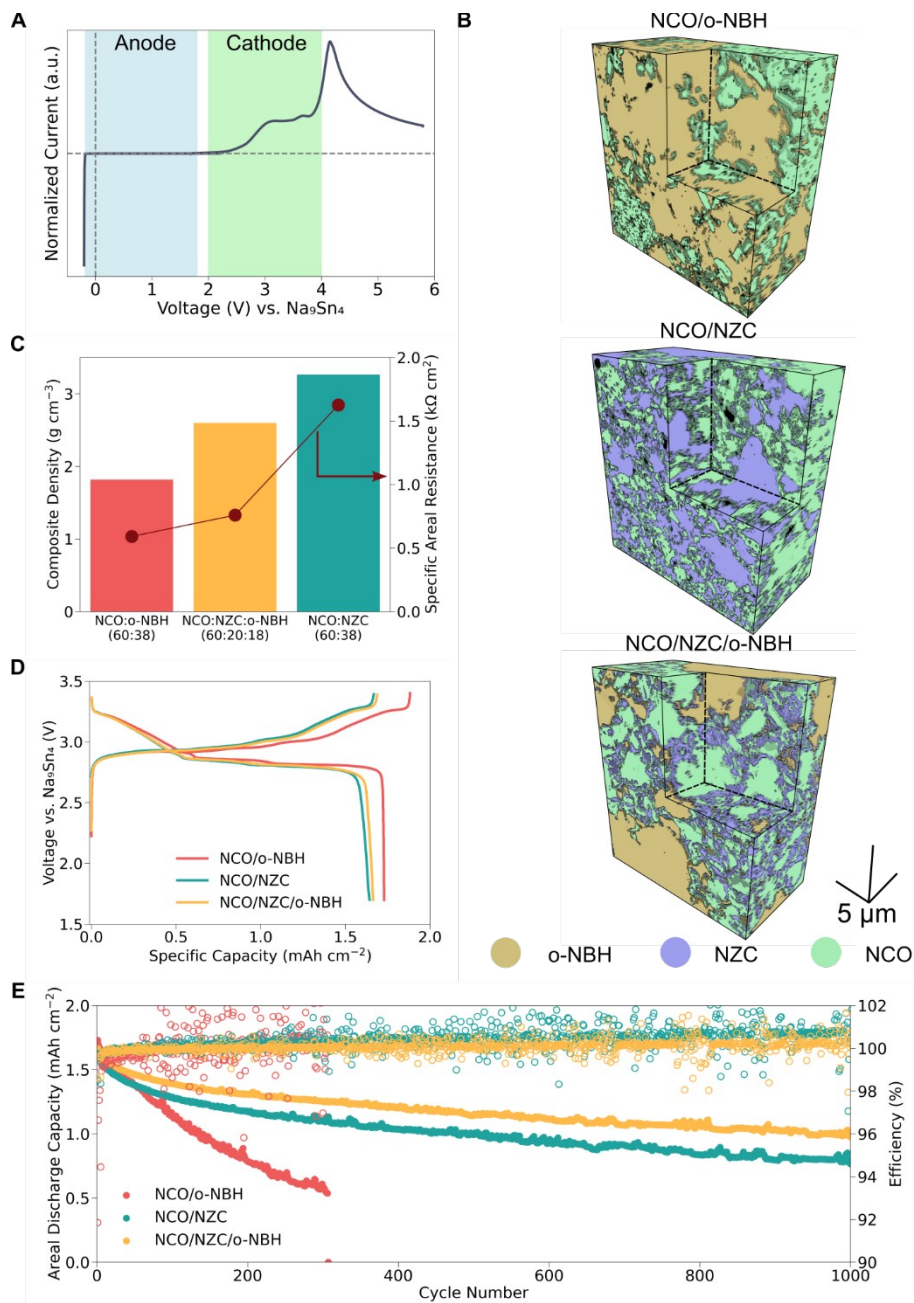


Fig. 4. Electrochemical stability of o-NBH solid electrolyte and cathode composite FIB-SEM Tomography. (A) Linear sweep voltammetry of o-NBH with typical electrode redox potentials highlighted (Table S3). (B) 3D reconstructed models of NCO/NBH, NCO/NZC, and NCO/NZC/NBH. (C) Composite density and specific areal resistance increase with increasing NZC content due to the differences in the gravimetric density and ionic conductivity. (D) Initial potential–capacity profiles of $\text{Na}_9\text{Sn}_4/\text{o-NBH/NCO}$ (E) Reversible capacity retention of the cathode composites at C/3 in Na-excess cells with Na_9Sn_4 anodes.

According to the grand potential calculation at 300 K (Figure S12B), the oxidations lower than 3.8 V vs. Na^+/Na of o-NBH are hypothesized to form a passivating $\text{Na}_2\text{B}_{12}\text{H}_{12}$. The electrochemical oxidation is further probed by galvanostatic cycling with different maximum cut-off voltages ($V_{\text{cut-off}}$) to study the implication of the various oxidation products. Initial desodiation capacities of 38 and 90 mAh g^{-1} are observed with V_{max} of 3.4 and 4.9 V vs. Na_9Sn_4 ,

respectively; negligible capacity is accessible in the subsequent cycle (**Fig. S12C**). This is further supported by the slight increase in the interfacial impedance after oxidation at 3.4 V vs. Na_9Sn_4 as $\text{Na}_2\text{B}_{12}\text{H}_{12}$ is still slightly ionically conductive (**Fig. S12D**); a large interfacial impedance was only observed after oxidizing o-NBH to 4.9 V vs. Na_9Sn_4 .

The possible passivating oxidation products of o-NBH are further investigated by assembling an all-solid-state battery using bare NaCrO_2 (NCO) and oxidation-resistant Na-Zr-Cl solid-electrolyte-coated NCO (NCO/NZC) as the cathode. The distribution of the materials and the intimate contact between them in the composite were studied by reconstructing the cross-sectional scanning electron microscopy images prepared by focused ion beam milling (**Fig. 4B**). While the gravimetric ratio of the NCO, solid electrolyte, and carbon in the composite is constant, there is more solid electrolyte volumetric content when o-NBH is added in the cathode composite stemming from the different gravimetric density of components (NZC – $\sim 2.4 \text{ g cm}^{-3}$ and o-NBH – $\sim 1.2 \text{ g cm}^{-3}$). Consequently, NCO/o-NBH, NCO/NZC, and NCO/NZC/o-NBH have a higher ionic tortuosity values of 1.53, 4.91, and 3.46, respectively. This is also reflected in the cathode composite volumetric density and impedance with NCO/o-NBH having the lowest density and areal resistivity in the series followed by NCO/NZC/o-NBH and then NCO/NZC (**Fig. 4C**). This trend is attributed to the higher ionic conductivity and high volumetric content of o-NBH compared to NZC facilitating fast ion diffusion in the cathode composite.

Sodium-Excess Cell (Half Cell)

To evaluate the oxidation stability of o-NBH, half-cell ASBs with a cathode mass loading of $15 \text{ mg}_{\text{NCO}} \text{ cm}^{-2}$ (theoretical capacity of 2.3 mAh cm^{-2}) were assembled using NCO/o-NBH, NCO/NZC, or NCO/NZC/o-NBH as the cathode and Na_9Sn_4 as the counter electrode. **Fig. 4D** shows that all the cells have good material utilization (92.5 to 104.2% of the theoretical NCO capacity) with the NCO/o-NBH cell exhibiting a slightly higher charge capacity than that of NCO/NZC and NCO/NZC/o-NBH. In the subsequent reverse cycle, the NCO/o-NBH exhibits the lowest initial coulombic efficiency (ICE) of 91.9% while NCO/NZC and NCO/NZC/o-NBH have higher ICEs of $\sim 98.2\%$. This implies the higher-than-theoretical charge capacity in NCO/o-NBH stems from the oxidation of o-NBH. The impact of ionic tortuosity and interfacial compatibility is highlighted in the subsequent C/3 cycling. The interfacial incompatibility between NCO and o-NBH leads to rapid capacity fading, the NCO/o-NBH cell retained less than 1 mAh cm^{-2} ($\sim 60\%$ of initial capacity) after 140 cycles with an average coulombic efficiency of 99.6% (**Fig. 4E**). Credited to the stable electrochemical interface, both NCO/NZC and NCO/NZC/o-NBH cells exhibited more stable cycling retaining 1.23 and 1.36 mAh cm^{-2} after 140 cycles, respectively, and 0.82 and 1.20 mAh cm^{-2} after 1000 cycles, respectively. While the first cycle differential capacity dQ/dV plot showed similar redox reactions in each cathode–solid-electrolyte composite (**Fig. S13A**), the NCO/o-NBH suffered from larger dQ/dV profiles polarization than that of the others (**Fig. S13B-D**). Furthermore, the NCO/o-NBH cell shows a faster rate of constant-voltage capacity and an increase in cell impedance with cycle number (**Fig. S13E and F**) are likely fueled by the formation of non-passivating, ionically insulating interphases due to o-NBH oxidation, increasing cell impedance with cycling.

Thick-Cathode Zero-Excess-Sodium Cell (Full Cell)

For ASBs to displace conventional Li-ion batteries, they must realize a high areal capacity using a thick cathode, minimizing inactive components at the cell level (**Fig. 5A** and **S14**), and possess the ability to operate in extreme environments. Thus, we leverage the balance of ionic conductivity and electrochemically stable interface of the NCO/NZC/o-NBH cathode composite to assemble sodium-inventory-limited ASBs with high cathode areal capacity loading (15, 30, and 45 $\text{mg}_{\text{NCO}} \text{cm}^{-2}$, corresponding to thicknesses of approximately 123 ± 0.8 , 217 ± 2.6 and 310 ± 2.0 μm , respectively, **Fig. 5B**) and tin as the anode. While material utilization is slightly affected by the increased cathode thickness due to polarization, all cells exhibit a similar ICE (70–81%) owed to sluggish Na^+ diffusion kinetics of the Sn anode at low states-of-charge (SOC), limiting the Na^+ diffusion at the 2D electrode/electrolyte interface (**Fig. 5C**, **S15** and **S16A, B**). Nevertheless, the ASBs still deliver high reversible capacities of 1.3, 2.2, and 3.5 mAh cm^{-2} at 15, 30, and 45 $\text{mg}_{\text{NCO}} \text{cm}^{-2}$ loadings, respectively. These are amongst the highest reported sodium ASB active material areal loadings (**Fig. S16D**) and feature reversible capacities that are close to or higher than conventional Li-ion batteries. Following the initial cycle, all cells have an average coulombic efficiency of 99.8–99.9% resulting in a capacity retention of >80% after 100 cycles (**Fig. 5D**).

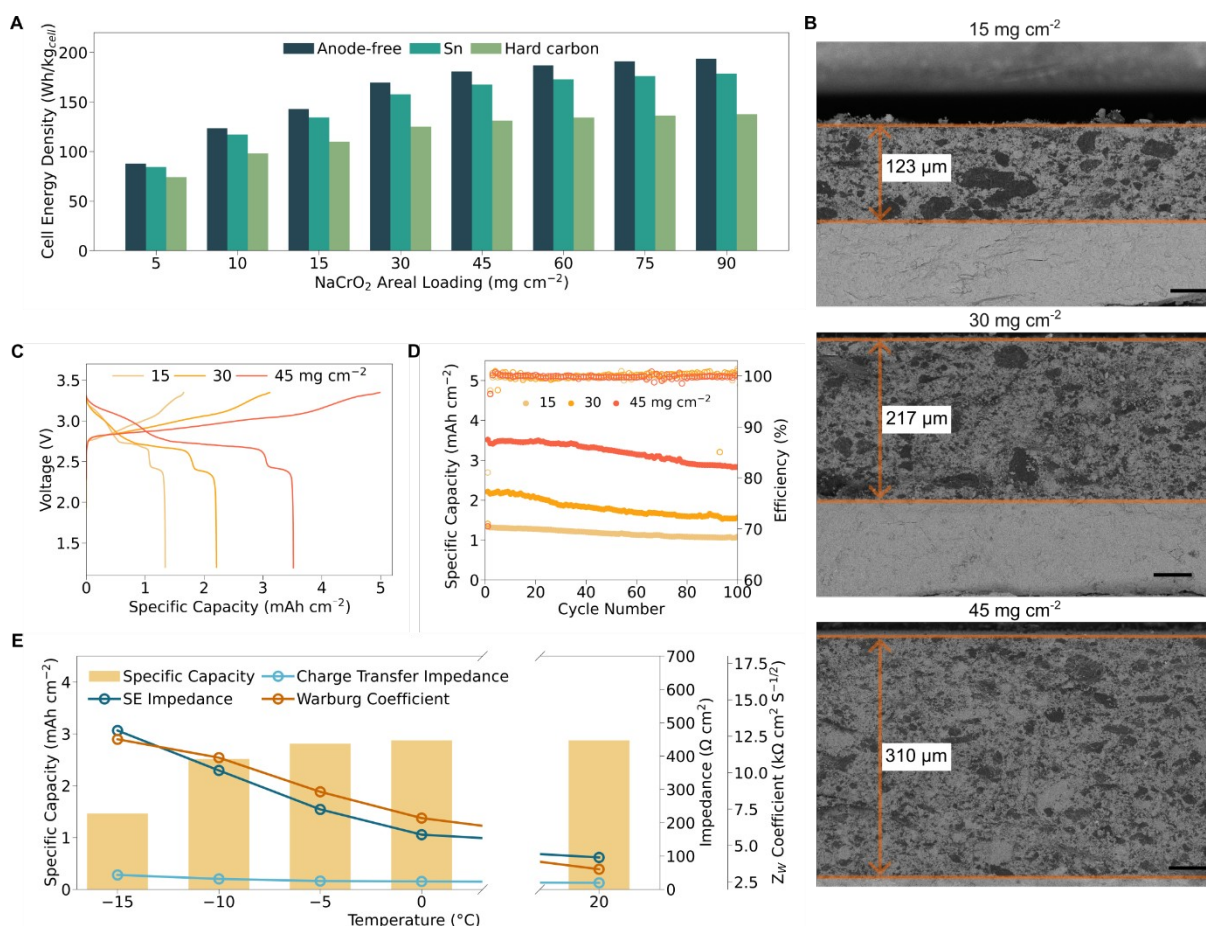


Fig. 5. Electrochemical stability of high-loading Na ASB full-cell. (A) Cell capacity increases with increasing NaCrO_2 areal loading (using 60 wt.% NaCrO_2 cathode composite). (B) Cathode thickness with various areal loadings, scale bar = 50 μm . (C) Initial potential–capacity profiles and the capacity retention with various loadings. (D) Capacity retention of the full cells at C/10. (E) Discharge capacity and cell impedance of a full cell with 45 $\text{mg}_{\text{NCO}} \text{cm}^{-2}$ at sub-ambient temperatures.

Considering the high ionic conductivity of o-NBH (0.3 mS cm^{-1} at $-10 \text{ }^{\circ}\text{C}$), we further demonstrate the capability of the high areal capacity cell configuration (45 mg cm^{-2}) at sub-ambient and sub-zero temperatures, highlighting its viability in cold climates. The cell (**Fig. 5E**) exhibits high discharge capacities of 3.1, 2.9, 2.8, 2.5, and 1.5 mAh cm^{-2} at room temperature, 0, -5 , -10 , and $-15 \text{ }^{\circ}\text{C}$, respectively. The decrease in capacity at lower temperatures is attributed to increased cell impedance (**Fig. S17**). Further examination of the EIS spectra also reveals that the Warburg diffusion coefficient in the electrodes increases by one order of magnitude at $-15 \text{ }^{\circ}\text{C}$ compared to room temperature, which is the largest among electrolyte and charge transfer impedance. This suggests that the bulk diffusion in the electrode is capacity-limiting when operating at low temperatures. Alternative electrode active materials with fast bulk diffusion at all states-of-charge or novel electrode architectures could be considered to further improve the kinetics. Nevertheless, this work highlights that high-loading all-solid-state batteries can operate in cold climates without external heating or severe discharge capacity penalty.

Conclusion

In conclusion, we demonstrate that through careful control of synthesis conditions, a metastable hydroborate structure, o-NBH, can be stabilized via quenching. The non-close-packed anion framework of o-NBH exhibits a high ionic conductivity over a wide range of temperatures, from 0.3 mS cm^{-1} at $-10 \text{ }^{\circ}\text{C}$ to 4.6 mS cm^{-1} at $30 \text{ }^{\circ}\text{C}$. A thick cathode composite can be realized by incorporating o-NBH into the NCO/NZC cathode composite, effectively balancing electrochemical stability with sodium ion kinetics. An all-solid-state sodium-ion full-cell battery with a high active material loading ($45 \text{ mg}_{\text{active material}} \text{ cm}^{-2}$, $\sim 310 \text{ }\mu\text{m}$ thick) and Sn as cathode and anode, respectively, showed a discharge capacity of 3.1 and 2.5 mAh cm^{-2} at room temperature and $-10 \text{ }^{\circ}\text{C}$, respectively. This study highlights the prospect of highly ion-conductive non-close-packed solid electrolytes, which were deemed thermodynamically unstable, yet kinetically stable to enable disruptive ASBs.

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Competing interests

One technology disclosure has been filed by University of California, San Diego Office of Innovation and Commercialization based on this work.

Authors contributions

J.A.S. Oh: Conceptualization, discovery and synthesis, analysis and investigation, and writing – initial draft; Z. Yu: computational calculation; C.-J Huang, P. Ridley, and B.J. Hwang: crystal structure characterization; C.-J Huang: tomography reconstruction and analysis; T. Zhang: DFT simulation and analysis of ss-NMR spectra. K.J. Griffith: Methodology, validation, supervision, and writing – initial draft. S.P. Ong: Methodology, validation, and supervision. S.Y. Meng: Conceptualization, fund acquisition, and supervision. All authors have approved the final version of the manuscript.

Supplementary Materials

Materials and Methods

Supplementary Text

Figs. S1 to S17

Tables S1 to S3