Fast sodium ionic conduction in $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride and application to a bulk-type all-solid-state battery

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In the present work, we developed highly sodium-ion conductive $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride via mechanically ball-milling admixtures of the pure $Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ components. Both of these components show a monoclinic phase at room temperature, but ball-milled mixtures partially stabilized highly ion-conductive, disordered cubic phases, whose fraction and favored structural symmetry (body-centered cubic or face-centered cubic) depended on the conditions of mechanical ball-milling and molar ratio of the component compounds. First-principles molecular-dynamics simulations demonstrated that the total energy of the *closo*-borane mixtures and pure materials is quite close, helping to explain the observed stabilization of the mixed compounds. The ionic conductivity of the *closo*-borane mixtures appeared to be correlated with the fraction of the body-centered-cubic phase, exhibiting a maximum at a molar ratio of $Na_2B_{10}H_{10}$:$Na_2B_{12}H_{12}$ = 1:3. A conductivity as high as $\log(\sigma/\mathrm{S\ cm^{-1}}) = -3.5$ was observed for the above ratio at 303 K, being approximately 2–3 orders of magnitude higher than that of either pure material. A bulk-type all-solid-state sodium-ion battery with a *closo*-borane-mixture electrolyte, sodium-metal negative-electrode, and TiS_2 positive-electrode demonstrated a high specific capacity, close to the theoretical value of $NaTiS_2$ formation and a stable discharge/charge cycling for at least eleven cycles, with a high discharge capacity retention ratio above 91% from the second cycle. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4977885]

Complex hydrides, which consist of metal cations (e.g., Li^+ and Na^+) and a complex anion composed of a central atom and coordinating hydrogen atoms (e.g., $[BH_4]^-$ and $[NH_2]^-$), have been historically studied as hydrogen-storage materials.[1] Moreover, these species have recently attracted particular attention as a new class of solid electrolytes due to exhibiting unique physical and chemical properties, such as high deformability, high electrochemical stability greater than 5 V vs. Li/Li^+, chemical stability with a Li metal electrode, and small weight density compared with oxide- and sulfide-type solid-electrolyte materials.[2–5] We have previously reported applications of the complex hydride solid electrolytes for all-solid-state lithium-ion rechargeable batteries that demonstrate excellent discharge/charge cycling stability and temperature durability, as well as high energy density of the batteries.[4–7] In addition to the lithium-ion-conductive materials, sodium-ion-conductive complex hydrides have been explored as well. Since sodium is more abundant than lithium, a sodium-ion rechargeable battery is advantageous with respect to a reduced device cost. Therefore, it is being more intensively studied as of late.[8] We have developed sodium-conductive complex hydrides such as the $NaBH_4$-$NaNH_2$-NaI system,[9,10] $NaAlH_4$, and Na_3AlH_6,[11] achieving high Na^+ conductivity $\log(\sigma/\mathrm{S\ cm^{-1}}) > -5.5$ at 300 K for a 1:1 molar ratio solid solution of $NaBH_4$ and $NaNH_2$.[9,10] Moreover, complex hydrides with the *closo*-borane cluster anion (e.g., $[B_{12}H_{12}]^{2-}$ and $[B_{10}H_{10}]^{2-}$) and mono-carboranes (e.g., $[CB_{11}H_{12}]^-$ and $[CB_9H_{10}]^-$) have been introduced as a novel series of complex hydride solid electrolytes with high ionic conductivity.[12–17] Solid electrolytes of these *closo*-boranes and mono-carboranes possess order/disorder phase transitions to higher-symmetry cubic or hexagonal structures above room temperature accompanied by fast reorientation of the cluster anions. These anions form ion-conduction channels with an array of low-occupancy cation sites,[16] resulting in impressively high ionic conductivity $\log(\sigma/\mathrm{S\ cm^{-1}}) > -2$.[12–15] In particular, the most recently reported 1-carba-*closo*-decaborane salt, $NaCB_9H_{10}$, shows a particularly high ionic conductivity above $\log(\sigma/\mathrm{S\ cm^{-1}}) > -1$ at 373 K,[12] exceeding the Na^+ ionic conductivity of oxide- and sulfide-based solid electrolytes such as NASICON,[18] Na_3PS_4,[19] Na_3PSe_4,[20] Na_3SbS_4,[21] and $Na_{10}SnP_2S_{12}$.[22] Furthermore, the highly conductive phases of *closo*-borane and mono-carborane salts can be stabilized near, at, or even lower than room temperature by nanosizing these materials via long-duration mechanical ball-milling[23] or by mixing of two different mono-carboranes.[24] The high ionic conductivity and thermal stability

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of these various *closo*-borane and mono-carborane salts are two important attributes for favorable all-solid-state sodium rechargeable-battery operation over a wide temperature range.

In this study, we report fast sodium ionic conduction of ball-milled compounds of $Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ admixtures and demonstrate the potential applicability of these materials as electrolytes for bulk-type all-solid-state batteries. Since *closo*-borane anions are presumed to be more chemically stable than mono-carborane anions, one might expect the former to be relatively more resistant to electrochemical degradation during battery operation. Therefore, we decided to focus our attention on evaluating an all-solid-state battery with *closo*-borane solid-electrolytes, instead of with the generally more highly conductive mono-carborane salts. We show that the phase stabilization of a highly conductive body-centered-cubic phase at room temperature, akin to that observed at higher temperatures for pure $Na_2B_{12}H_{12}$, depends on the molar ratio of the *closo*-borane mixture and results in a considerable increase in the ionic conductivity, reaching $\log(\sigma/\mathrm{S\ cm^{-1}}) = -3.5$ at 303 K for a 1:3 molar ratio of $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride. This mixed *closo*-borane electrolyte was subsequently employed in a bulk-type all-solid-state sodium rechargeable battery that demonstrates high specific capacity and stable battery operation with a sodium metal electrode for more than eleven cycles.

$Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ (Katchem Ltd.) were dried under vacuum at 448 K and 473 K, respectively, to remove residual water. Subsequently, these complex hydrides were mixed together by mechanical ball-milling (pulverisette 7, Fritsch GmbH) at 400 rpm for 5 h in an argon atmosphere. It is worth noting that for all figures, standard uncertainties are commensurate with the observed scatter in the data.

Fig. 1(a) shows powder X-ray diffraction (XRD; PANalytical X'PERT Pro diffractometer with Cu Kα radiation) patterns of ball-milled $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride compared with simulated XRD patterns of low-temperature (LT) and high-temperature (HT) phases of $Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$. The ball-milled samples show similar XRD patterns to those of the HT phases of $Na_2B_{10}H_{10}$ (face centered cubic (FCC)) and $Na_2B_{12}H_{12}$ (body centered cubic (BCC)), even at room temperature. In addition, similar XRD patterns to those of the LT phase (primitive monoclinic) of $Na_2B_{12}H_{12}$ are found for the $Na_2B_{10}H_{10}$:$Na_2B_{12}H_{12}$ = 1:3 and 1:7 compounds. From these results, the unit cell parameters are estimated assuming that the mixtures consist of two phases adopting the same Bravais lattices as those of HT and LT phases. The unit cell parameters are listed in Table S1 (supplementary material). From unit cell volume per formula unit (V/Z), by which volumes of various crystal structures can be compared,[26] the estimated unit cell parameters of the ball-milled $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride show a decreasing trend in the unit cell size with an increasing molar fraction of $Na_2B_{10}H_{10}$ in the mixed compound, consistent with the observed smaller V/Z for $Na_2B_{10}H_{10}$ than that for $Na_2B_{12}H_{12}$. These results strongly suggest that $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ anions co-exist, randomly occupying the same types of anion sites within the crystal structures. Both anions remain intact after mechanical ball-milling, as evidenced by complementary Raman spectroscopic measurements (Fig. 1(b)) in which specific Raman signals between 500 and 1100 $\mathrm{cm^{-1}}$ ascribed to the various deformation vibration modes of the $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ anions appear for all of the mixed compounds. Based on the XRD data, we note that some uncertainty does exist concerning the structural origin, HT FCC and/or LT $Na_2B_{12}H_{12}$-like monoclinic, of the lowest-angle Bragg peak appearing at $2\theta = 15.5°$ for the 1:1 compound. Nonetheless, Fig. 1(a) and Table S1 (supplementary material) indicate that the $Na_2B_{10}H_{10}$-like HT FCC phase begins to dominate for much more $Na_2B_{10}H_{10}$-rich phases, being clearly preferred at a 3:1 molar ratio. This suggests that there is a critical unit cell volume below which the $Na_2B_{10}H_{10}$-like HT FCC phase is energetically favored over the $Na_2B_{12}H_{12}$-like HT BCC phase. Compounds with 1:1 or higher $Na_2B_{12}H_{12}$ ratios are clearly observed to form stabilized $Na_2B_{12}H_{12}$-like HT BCC phases. Based on the XRD Bragg peak intensity at $2\theta = 14°$–$16°$, the $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride with a 1:3 molar ratio exhibits the highest fraction of the BCC phase among all evaluated ball-milled samples. Tang *et al.* reported similar stabilization of HT phases for *closo*-borane mixtures and mono-carborane mixtures at a 1:1 molar ratio.[23,24] In addition, we now understand that the fraction of the HT BCC phase formed is sensitive to the molar ratio of the mixture.

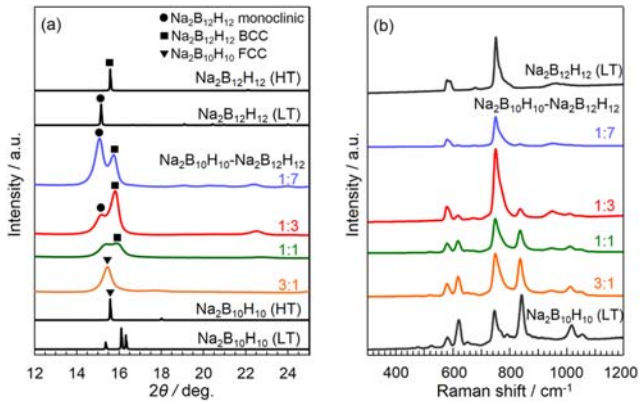

FIG. 1. (a) XRD profiles of $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride with various molar ratios prepared by mechanical ball-milling for 5 h. The profiles of the low-temperature phase and high-temperature phase of $Na_2B_{10}H_{10}$ (Refs. 14 and 25) and $Na_2B_{12}H_{12}$ (Ref. 16) simulated from their crystal structures are also shown for comparison. (b) Raman spectra of the pseudo-binary complex hydrides at 300–1200 $\mathrm{cm^{-1}}$ attributed to the different deformation vibration modes of the $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ anions. The spectra of pure $Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ without ball-milling are also shown as well for comparison. All data were obtained at room temperature using a 532 nm laser.

To thermodynamically evaluate the possible formation of $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride based on energetic arguments, we estimated the total energy change due to mixing by first-principles molecular dynamics (FPMD) simulation at 580 K. In the FPMD simulations, an electronic structure calculation code implemented in the Vienna *ab initio* simulation package (VASP) using the density functional theory (DFT) was used with plane-wave basis sets and PAW pseudo potentials under periodic boundary conditions. A Perdew-Burke-Ernzerhof (PBE) functional[27] was used for the exchange correlation with a generalized gradient approximation. The cutoff energy was 320 eV for wave

functions, and k-point sampling was $1 \times 1 \times 1$ with a $2 \times 2 \times 2$ super cell. The total number of the sites of $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$ anions is 16 in the calculation cell, and four of them are occupied by $[B_{10}H_{10}]^{2-}$ randomly in the BCC lattice. The results show that the 1:3 molar ratio mixture of $Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ is only slightly less stable than the individual pure components in their HT phases, i.e., $Na_2B_{10}H_{10}$ FCC phase and $Na_2B_{12}H_{12}$ BCC phase; the difference is 0.05 eV per $Na_2B_{10}H_{10}$ or $Na_2B_{12}H_{12}$. There is, therefore, a possibility that a small perturbation makes the mixture more stable; the perturbation may be related to nanosizing, defect formation, etc. Another reasonable explanation is that even if the mixture were more unstable than the individual pure components, any thermodynamically driven "unmixing" of the mechanical ball-milling-induced solid solution would probably be kinetically prohibited, requiring extensive translational rearrangements of anions over large diffusional barriers.

Ionic conductivities of $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride with various molar ratios are summarized in Fig. 2 together with the conductivities of both starting materials and $Na_2B_{12}H_{12}$ after long-duration mechanical ball-milling for 72 h. They were obtained from AC-impedance measurements in a frequency range of 4 Hz–1 MHz for temperatures between 303 and 353 K (HIOKI 3532–80 chemical impedance meter). Ionic conductivities of these *closo*-borane mixtures at room temperature are $\log(\sigma/\mathrm{S\ cm^{-1}}) = -4.6$ for 3:1, -3.8 for 1:1, -3.5 for 1:3, and -4.0 for 1:7 molar ratios. They are several orders of magnitude higher than those of pure $Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ and at similar levels to those of long-duration ball-milled $Na_2B_{12}H_{12}$.[23] The highest conductivity was found for the compound of the 1:3 molar ratio, in good agreement with the fraction of the $Na_2B_{12}H_{12}$-like HT BCC phase in the compound considered in Fig. 1(a). This indicates that stabilization of the BCC phase is a key reason for the observed high ionic conductivity. It is worth noting that, although the 3:1 molar ratio compound appears to be composed predominantly of the $Na_2B_{10}H_{10}$-like HT FCC phase, its conductivity is over an order of magnitude less than

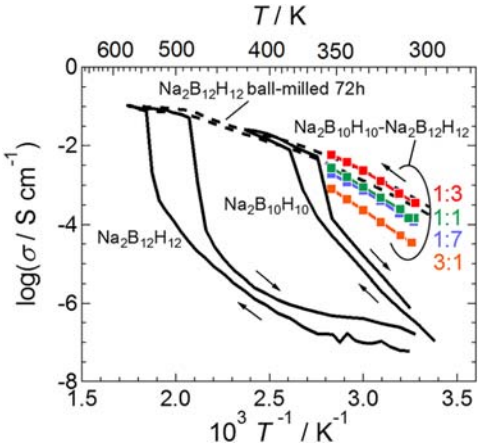

FIG. 2. Sodium-ionic conductivities for $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride with various molar ratios ball-milled for 5 h. Different symbols denote $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ molar ratios of 3:1(orange), 1:1(green), 1:3(red), and 1:7(blue). Conductivity data for pristine $Na_2B_{12}H_{12}$ (Ref. 15) and $Na_2B_{10}H_{10}$ (Ref. 14) and nanocrystalline $Na_2B_{12}H_{12}$ prepared by mechanical ball-milling for 72 h (Ref. 23) are indicated for comparison.

that for the 1:3 molar ratio compound, which is composed primarily of the HT BCC phase. Ignoring for the moment the slight differences in volumes per formula unit, this may be a hint that BCC symmetry provides a more favorable sublattice for ionic conduction than FCC symmetry, as suggested by theoretical computations.[28]

We have also evaluated the dependence of ionic conductivity on milling time (Fig. S1 of supplementary material). The compound prepared by hand-mixing using an agate mortar and pestle before mechanical ball-milling shows a low conductivity of approximately $\log(\sigma/\mathrm{S\ cm^{-1}}) = -6.7$ at room temperature, which is almost the same level as for both starting materials, whereas the ball-milled sample, even after only 1 h of mechanical ball-milling, shows that the ionic conductivity has drastically increased by several orders of magnitude. Upon further mechanical ball-milling for a total of 5 h, no further conductivity increase was observed. Yet, conductivity started gradually after 10 h and 20 h of mechanical ball-milling, yielding respective values of $\log(\sigma/\mathrm{S\ cm^{-1}}) = -3.7$ and -3.4. This behavior suggests that there are two different milling effects that account for increased ionic conductivity: one is anion mixing for short milling times (<5 h) and another is nanocrystalline formation[23] after a long time (>10 h) mechanical ball-milling that may be able to stabilize the highly conductive crystal phase near the surface. Notably, the ionic conductivity of the $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride ball-milled for 5 h is more than 20 times higher than the conductivity of either $Na_2B_{10}H_{10}$ or $Na_2B_{12}H_{12}$ after mechanical ball-milling for the same duration, which is indicative of the anion mixing effect. Although separating the relative effects of anion mixing, defect formation, and nanosizing on conductivity requires the preparation of *closo*-borane mixtures without using mechanical ball-milling (e.g., utilizing the solution process demonstrated previously[24]), this behavior nonetheless suggests that the impressively high ionic conductivity for pseudo-binary complex hydrides in Fig. 2 is more likely due to anion mixing effects that lead to the formation of a fast-ion-conducting HT phase rather than a nanocrystalline phase since the samples were ball-milled for no longer than 5 h. Activation energies for Na^+ ionic conduction calculated from the slopes of Arrhenius plots of the conductivities for these pseudo-binary complex hydride are 0.64 eV for 3:1, 0.59 eV for 1:1, 0.56 eV for 1:3, and 0.56 eV for 1:7, which are larger than those of the $Na_2B_{12}H_{12}$ HT phase (0.21 eV), possibly because the different lattice parameter may tend to increase the activation energy.

The electrochemical potential window of the $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride of a 1:3 molar ratio was examined by cyclic voltammetry (Fig. S2 of supplementary material), demonstrating no oxidative current below 5 V vs. Na/Na^+. Based on the high ionic conductivity and electrochemical stability shown herein, we expect excellent cyclability of an all-solid-state battery with this mixed *closo*-borane electrolyte.

Fig. 3 shows a discharge/charge profile of a bulk type TiS_2/Na all-solid-state battery using the $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride of a 1:3 molar ratio as an electrolyte. A TiS_2 composite positive electrode was prepared by mixing TiS_2 (99%, Sigma-Aldrich) and the *closo*-borane

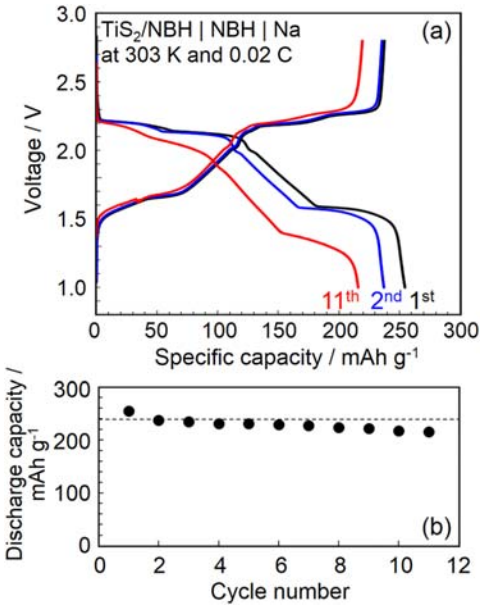

FIG. 3. (a) Typical discharge/charge profiles of a bulk-type all-solid-state TiS_2/Na battery with a $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ solid electrolyte of a 1:3 molar ratio (denote here as NBH) operated at 303 K and 0.02 C. (b) Cycle performance of the cell. The broken line indicates the theoretical capacity of the TiS_2 active material.

electrolyte in a 2:3 mass ratio. The composite positive electrode powder and the *closo*-borane mixture electrolyte were then uniaxially pressed at 240 MPa to make an electrode-electrolyte combined pellet. A Na metal film (Sigma-Aldrich) was used as a negative electrode. The battery was tested at 303 K and 0.02 C (corresponding to 11.5 μA cm^{-2}) discharge and charge rates. The obtained discharge/charge profile shows two voltage plateaus at 2.1–2.3 V and 1.2–1.7 V vs. Na/Na$^+$, explained by the known multi-step sodium intercalation into TiS_2 with respect to the sodium stoichiometry, x, in NaxTiS$_2$: (1) sodium intercalation into every second TiS_2 layer (phase II, $0.15 < x < 0.25$), (2) intercalation in each layer with trigonal prismatic configuration (phase Ib, $0.4 < x < 0.64$), and (3) phase transition to trigonal antiprismatic configuration (phase Ia, $0.75 < x < 1$).[29,30] The specific discharge and charge capacities of the first cycle are 254 mAh g^{-1} and 237 mAh g^{-1}, respectively, close to the theoretical capacity of TiS_2 (239 mAh g^{-1}). The slightly large capacity observed for the first discharge process might be due to an interfacial reaction taking place between the electrode and solid electrolyte for the formation of the interface that allows for smooth charge transfer between the TiS_2 electrode and the $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ electrolyte. The observed capacity is more than two times higher than those of other all-solid-state sodium rechargeable batteries with sulfide-type solid electrolytes reported previously, where the capacity was found to be less than 100 mAh g^{-1}[31,32] and almost comparable to that of a TiS_2/Na battery with a liquid electrolyte.[33] For the first 11 cycles, reasonable discharge cycling stability was observed, with a capacity of 216 mAh g^{-1} at the 11th cycle, which corresponds to 90% of the active-material utilization ratio and a high discharge capacity retention ratio above 91% calculated from the second discharge/charge cycle. The observed stable battery operation and high specific capacity are attributed to a sufficiently high electrochemical stability of the pseudo-binary complex hydride, uniform dispersion of the TiS_2 active material in the positive electrode layer, tight contact with a solid electrolyte, and a sufficiently high ionic conductivity even at room temperature. In addition, its compatibility with the Na metal electrode helps to increase the battery voltage.

In summary, we have demonstrated the stabilization of the $Na_2B_{12}H_{12}$-like HT BCC phase at lower temperature by mechanically ball-milling admixtures of $Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$. Powder XRD profiles demonstrate the formation of the above HT BCC phase in the $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride, at least for 1:1 molar ratios and above. The fraction of this HT BCC phase depends on the mixing ratio of *closo*-boranes and was found to be maximized for a 1:3 molar ratio. Sodium-ionic conductivities of these *closo*-borane mixtures were orders of magnitude higher than those of the pure materials, and the highest conductivity observed, occurring at a 1:3 molar ratio, agreed well with the highest observed fraction of the HT BCC phase. The battery test with TiS_2 as an active material revealed high discharge/charge capacities comparable to those of the liquid electrolyte system previously reported. Highly stable battery operation with only small capacity degradation during potential cycling indicates that the Na *closo*-borane mixture holds promise as a solid electrolyte for future all-solid-state sodium-ion batteries. In addition, we can expect that stable cycling of a battery with high current density with this type of solid-electrolyte will work over a wide temperature range, which is the focus of our next studies.

See supplementary material for unit cell parameters, sodium ionic conductivities after various ball-milling times, and cyclic voltammograms of ball-milled $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ mixtures.

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Fast sodium ionic conduction in $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ pseudo-binary complex hydride and application to a bulk-type all-solid-state battery

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Supplementary information

Table S1 Monoclinic and cubic unit cell parameters of $Na_2B_{10}H_{10}$ [1, 2], $Na_2B_{12}H_{12}$ [3] and ball-milled $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ mixtures. No monoclinic phase was observed for $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ (3:1 molar ratio). It was difficult to index Bragg peaks for $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ (1:1 molar ratio) by a monoclinic unit cell due to overlapping and broad Bragg peaks.

Compounds	Unit cell parameters	
$Na_2B_{12}H_{12}$	LT ($Na_2B_{12}H_{12}$, 293 K)	HT ($Na_2B_{12}D_{12}$, 675 K)
	Monoclinic	BCC
	a = 7.031 Å	a = 8.098 Å
	b = 10.654 Å	
	c = 7.009 Å	
	β = 94.676º	
	V = 523.28 Å^3	V = 531.0 Å^3
	V/Z = 261.64 Å^3	V/Z = 265.5 Å^3
$Na_2B_{10}H_{10}$-7$Na_2B_{12}H_{12}$	Monoclinic	BCC
(1:7 molar ratio)	a = 7.093(8) Å	a = 7.910(5) Å
	b = 10.619(8) Å	
	c = 7.017(3) Å	
	β = 94.40(7)º	
	V = 527.0(16) Å^3	V = 494.9(9) Å^3
	V/Z = 263.5(8) Å^3	V/Z = 247.5(5) Å^3
$Na_2B_{10}H_{10}$-3$Na_2B_{12}H_{12}$	Monoclinic	BCC
(1:3 molar ratio)	a = 7.063(1) Å	a = 7.872(2) Å
	b = 10.570(4) Å	
	c = 6.973(3) Å	
	β = 93.92(3)º	
	V = 519.4(6) Å^3	V = 487.8(4) Å^3
	V/Z = 259.7(3) Å^3	V/Z = 243.9(2) Å^3
$Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$		BCC
(1:1 molar ratio)		a = 7.812(4) Å
		V = 476.7(7) Å^3
		V/Z = 238.4(4) Å^3
3$Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$		FCC
(3:1 molar ratio)		a = 9.907(17) Å
		V = 972.4(50) Å^3
		V/Z = 243.1(13) Å^3
$Na_2B_{10}H_{10}$	LT ($Na_2B_{10}D_{10}$, 297 K)	HT ($Na_2B_{10}H_{10}$, 410 K)
	Monoclinic	FCC
	a = 6.714 Å	a = 9.843 Å
	b = 13.124 Å	
	c = 11.940 Å	
	β = 120.524º	
	V = 906.24 Å^3	V = 953.64 Å^3
	V/Z = 226.56 Å^3	V/Z = 238.41 Å^3

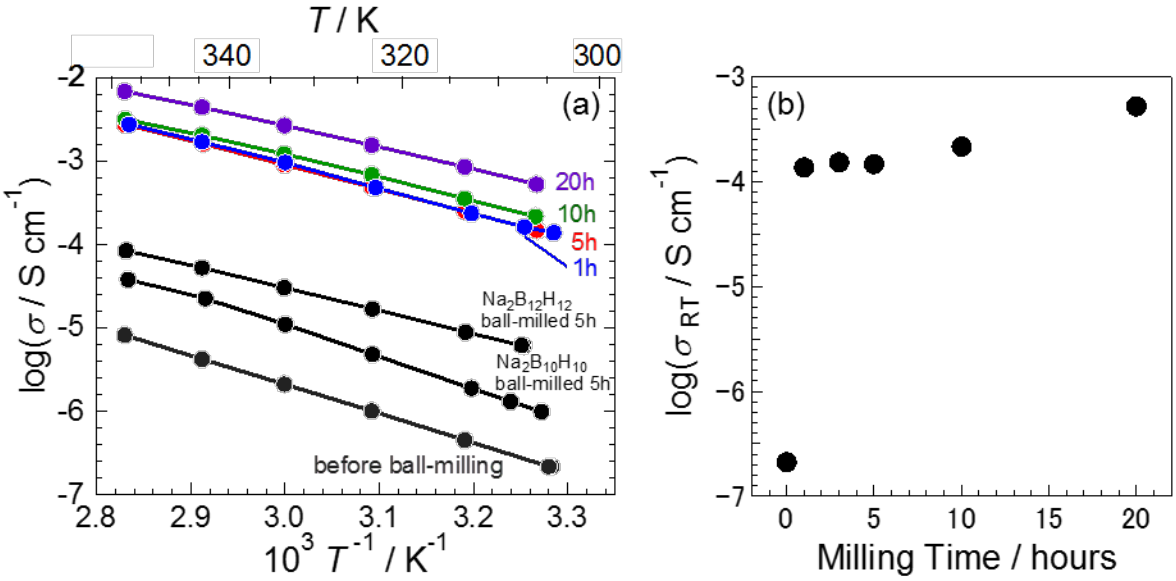

FIG. S1. (a) Sodium ionic conductivities of a $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ mixture (1:1 molar ratio) after various ball-milling times and pure $Na_2B_{10}H_{10}$ and $Na_2B_{12}H_{12}$ ball-milled for 5 h. (b) Ionic conductivity of this $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ mixture at room temperature (approximately 305 K) as a function of milling time.

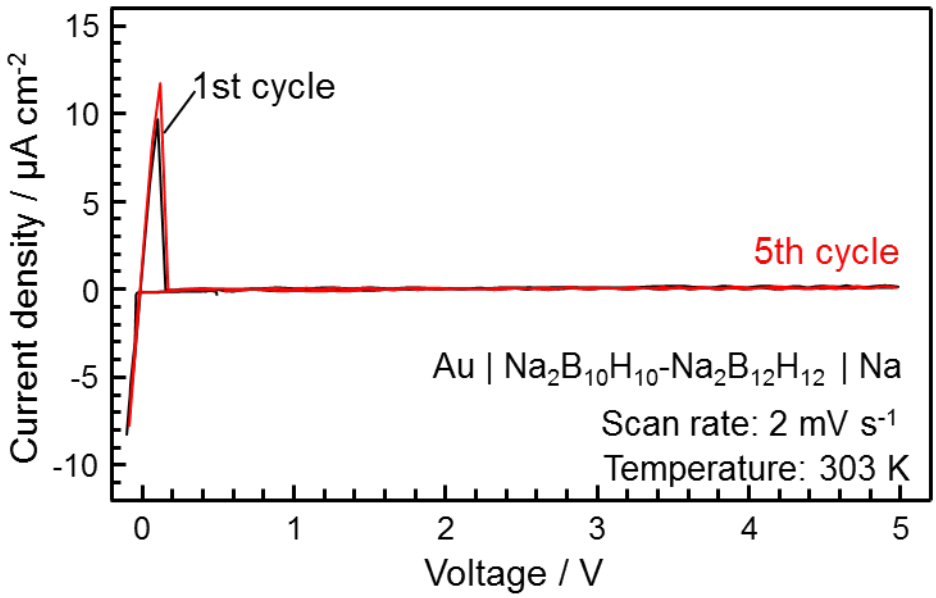

FIG. S2. Cyclic voltammogram of a ball-milled $Na_2B_{10}H_{10}$-$Na_2B_{12}H_{12}$ mixture (1:3 molar ratio) at 303 K obtained from a Princeton Versa STAT4 potentiostat/galvanostat with Na and Au electrodes at a scan rate of 2 mV s^{-1} and a voltage range of –0.1 to +5.0 V vs. Na/Na^+.

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