



A mixed anion hydroborate/carba-hydroborate as a room temperature Na-ion solid electrolyte

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HIGHLIGHTS

- $\text{Na}_{2-x}(\text{CB}_{11}\text{H}_{12})_x(\text{B}_{12}\text{H}_{12})_{1-x}$ provides high Na-conductivity at room temperature.
- Heterovalent anion mixing leads to stable and Na-conducting *bcc* structure.
- Electrochemical operating window up to 4.1 V vs. Na^+/Na .
- Reversible Na^+ shuttling for more than 700 h in symmetrical Na–Sn cell.

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ABSTRACT

The novel compound $\text{Na}_{2-x}(\text{CB}_{11}\text{H}_{12})_x(\text{B}_{12}\text{H}_{12})_{1-x}$ shows a fast ionic Na conductivity of 2 mS cm^{-1} at room temperature, reaching the superionic regime above 333 K. A low activation energy of 314 meV, in a thermodynamically and electrochemically stable structure, suggest its usage as a potential solid electrolyte in future all-solid Na-ion batteries. Density functional theory simulations indicate the heterovalent anionic mixing to be the responsible in stabilizing a *bcc* structure, which allows a facile Na^+ diffusion already at room temperature. Cyclic voltammetry measurement with a tailored setup for solid-state electrolytes reveals a wide operating window (up to 4.1 V vs. Na^+/Na). The symmetrical cell featuring Na–Sn alloy-based electrodes shows reversible Na^+ shuttling with limited polarization after more than 700 operating hours.

1. Introduction

Rechargeable batteries are of fundamental importance in the development of future hydrocarbon-free green energy grids, as they would provide a means of storing the harvested energy from intermittent renewable sources. The CO_2 level in the atmosphere is reaching primate records on a daily basis (407 ppm in December 2017) [1] and, economically, the cost-efficiency of renewable energy is actually competitive with respect to coal, oil and gas, if national subsidies and collateral damage such influencing national security, political instability and ambient disasters are taken into account [2]. The limitations of Li-ion battery-based facilities as energy leveling grids predominantly arise from safety-related issues and the actual price of their components. Furthermore, the non-homogeneous geographic distribution of lithium is prone to become a major source of political instabilities in the near

future [3]. The logical non-lithium solution for electrochemical energy storage appears to be sodium. It is inexpensive, very abundant and evenly distributed on Earth's surface. The somewhat larger mass and lower mobility of Na vs. Li has restricted Na-technologies to stationary applications, hitherto NaS or ZEBRA cells, which feature a molten negative electrode, and hence operate at several hundred °C [4]. These cells require the use of solid electrolytes (SEs) such as β -alumina or NASICON, which overcome the issues of electrolyte decomposition and dendrite formation, a potential cause of short circuit and fire. The high operating temperature, on the other hand, decreases the efficiency of the energy storage system.

Recently, the family of the complex hydrides joined the field of fast ion-conductors, flanking other commonly investigated materials, either crystalline or amorphous, such as LiPON, which is also employed in commercial batteries [5], oxide-based (LiSICON and NaSICON), sulfide

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glasses ($\text{Li}_2\text{S}-\text{Si}_2\text{S}$), thiophosphates (Li_3PS_4 , LGPS), providing conductivity values ranging from 10^{-6} to $10^{-2} \text{ S cm}^{-1}$ at room temperature (rt) [6–8]. The first complex hydride showing promising performance as SE is LiBH_4 [9,10]. It operates at a temperature above 393 K, due to a structural transformation into the superionic regime. Following the first LiBH_4 -based electrolyte, higher hydroborates of the type $[\text{B}_x\text{H}_x]^{n-}$ were found to be more stable, and thus better candidates to combine with transition metal based anodes/cathodes [11,12]. Various approaches aimed at stabilizing rt fast ion conduction in these materials were undertaken by Udovic et al. notably by means of geometrical frustration of the anion, shifting the phase transition to lower temperatures. It was shown extensively that the phase transition temperature (entropically driven by the anionic dynamics) is progressively lowered close to rt by carbon-substituted variants of *closo*-hydroborate [13–15]. Li- and $\text{NaCB}_9\text{H}_{10}$ show a two-step phase transition that is related to the anion dynamics, initially symmetrical around the C_4 axis and then disordered around the anion's geometrical center [15]. Since the re-orientation rate of this process, at high temperature, was estimated to be 2–3 times faster than the jumping rate of cations, it can be assumed that above the transition temperature the negative charge distribution is isotropically averaged and the complex anion can be considered as a sphere, which leads to the respective packed structures. Lately, a novel champion Na-conductor was reported that hosts the highest conductivity at rt , and obtained by tailoring the geometrical frustration of both $[\text{CB}_9\text{H}_{10}]^-$ and $[\text{CB}_{11}\text{H}_{12}]^-$ in the same material [16]. As both these anions are isovalent, such geometrical frustration can be only explained by a new packing type, which has already been studied for ellipsoids [17], but not for mixed spheroids. It was found by means of solid-state nuclear magnetic resonance (NMR), that sufficiently fast anion dynamics can be considered a packing-defining parameter that allows taking control over the stacking sequence in the close packed model, going from *ccp* to *hcp* simply owed to the size effect, and possible already at rt [18]. Again, very recently, the same concept was applied to form a pseudo-binary phase based on an equimolar mixture of $[\text{B}_{10}\text{H}_{10}]^{2-}$ and $[\text{B}_{12}\text{H}_{12}]^{2-}$ with exceptionally high Na-conductivity [19,20].

Our laboratory, devoted to stabilizing ionically conducting phases in the solid state, has focused on an alternative approach that exploits different combinations of cations and anions. Recently, we have published an exhaustive study on the stabilization of conducting phases regarding the packing of the anion sublattice [21].

A further important result in the progress of complex hydride Na-electrolytes was recently obtained by mixing heterovalent anions, leading to the new compound $\text{Na}_3\text{BH}_4\text{B}_{12}\text{H}_{12}$ [18]. Though highly interesting regarding its electrical properties as well as its low activation energy for Na^+ diffusion, it unfortunately lacks long-term life stability, segregating (reversibly) to the precursors after a half-year storage in inert atmosphere.

Inspired by these results we mixed the heterovalent $[\text{B}_{12}\text{H}_{12}]^{2-}$ and $[\text{CB}_{11}\text{H}_{12}]^-$ with the aim of minimizing the geometrical differences between anions: while C – B substitution does modify the negative charge, the overall shape of the molecule is left intact, avoiding any geometrical effect. Herein we will present the new material $\text{Na}_{2-x}(\text{CB}_{11}\text{H}_{12})_x(\text{B}_{12}\text{H}_{12})_{1-x}$. In the first part of this article, its experimental structure will be discussed and supported by density functional theory (DFT) calculation. The second part discusses its electrical properties as observed by electrochemical impedance spectroscopy (EIS). Lastly, promising results regarding the electrochemical stability and reversible cycling in a symmetric cell towards Na–Sn – based electrodes, point out that $\text{Na}_{2-x}(\text{CB}_{11}\text{H}_{12})_x(\text{B}_{12}\text{H}_{12})_{1-x}$ fulfills the necessary requirements of a competitive SE in Na-ion solid-state batteries (SSBs), shedding further light on the whole class of complex hydride as materials for energy storage applications.

2. Experimental section

Synthesis and structure characterization: Hydrous $\text{NaCB}_{11}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ were purchased at Katchem and dried for 12 h under dynamic vacuum at 523 K. The anhydrous compounds were ball milled in a planetary Fritsch for 1 h at 500 rpm with ball-to-mass ratio 40:1. Morphology characterization was performed by means of scanning electron microscopy (SEM) on a Leo 1450 VP (Zeiss) with an accelerating voltage of 15 kV. Synchrotron X-ray powder diffraction (S-XPD) data were collected at Swiss Norwegian Beamlines at European Synchrotron Radiation Facility (ESRF) on Dectris Pilatus M2 detector at a wavelength 0.7143 Å and at the Material Science Beamline Swiss Light Source at Paul Scherrer Institute (PSI) at a wavelength 0.7098 Å. The proposed structure was solved *ab initio* using the software FOX [22] and refined with the Rietveld method with the software TOPAS [23]. To obtain Na_xSn , Na (99.95%) and Sn (99.8%) were purchased from Sigma-Aldrich and Across International respectively, the alloy of selected composition $x = 2.25$ was prepared following the same synthetic approach reported elsewhere [24].

Ionic conductivity characterization: Ionic conductivity was measured with an HP 4192 FL impedance analyzer, in a frequency range 5 Hz–2 MHz with an amplitude signal of 10 mV. A BDS 1200 Novocontrol sample holder was placed under a nitrogen stream for variation temperature measures. An axial hydraulic press was used to pelletize the samples (diameter $\frac{1}{4}$ "") in two steps (100 and 550 MPa). Between the two compaction a mixture 1:1 wt ratio of the examined compound and carbon black was applied on both sides. The final pellet thickness was 0.7 mm. Impedance data were validated according to the procedure in ref. [25] and analyzed with the software EqC [26] using an equivalent (R)Q circuit (R stands for resistor and Q for constant phase element).

Electrochemical characterizations: for CV measurements, $\text{Na}_{2-x}(\text{CB}_{11}\text{H}_{12})_x(\text{B}_{12}\text{H}_{12})_{1-x}$ and carbon black (CB, Ketjenblack EC600JD, Akzo Nobel Chemicals) were mixed together into an agate mortar (20:1 wt ratio). Then a two layer pellet was created with 8 mg of such mix and 20 mg of $\text{Na}_{2-x}(\text{CB}_{11}\text{H}_{12})_x(\text{B}_{12}\text{H}_{12})_{1-x}$, using the above-mentioned setup with a pressure of 240 MPa. The obtained pellet was therefore tested in a 2-electrode $\frac{3}{4}$ " PTFE Swagelok-type cell, with a sodium disk as counter and reference electrode and a gold disk as current collector, in contact with the $\text{Na}_{4/3}(\text{CB}_{11}\text{H}_{12})_{2/3}(\text{B}_{12}\text{H}_{12})_{1/3}$ + CB side of the pellet. For Na–Sn – based symmetric-cell galvanostatic cycling, a similar protocol was adopted: Na–Sn alloy was mixed in an agate mortar with $\text{Na}_{4/3}(\text{CB}_{11}\text{H}_{12})_{2/3}(\text{B}_{12}\text{H}_{12})_{1/3}$ and vapor ground carbon fibers (VGCF, Showa Denko K.K., VGCF-H) (10:10:1 wt ratios) in order to increase the electrode-electrolyte interface. It is worth mentioning that VGCFs were preferred to the CB as carbonaceous additive for electrodes undergoing long-lasting electrochemical characterizations (galvanostatic cycling) since they provide mechanical strength to the electrode mixture, whereas CB was employed for relatively short test such as CVs.

The so-obtained electrodic mixture was then separated by a $\text{Na}_{4/3}(\text{CB}_{11}\text{H}_{12})_{2/3}(\text{B}_{12}\text{H}_{12})_{1/3}$ layer (20 mg), therefore pelletized and put in electrochemical cell as described before. For $\text{Na}|\text{Na}_{4/3}(\text{CB}_{11}\text{H}_{12})_{2/3}(\text{B}_{12}\text{H}_{12})_{1/3}|\text{Na}$ cell, only 20 mg of $\text{Na}_{4/3}(\text{CB}_{11}\text{H}_{12})_{2/3}(\text{B}_{12}\text{H}_{12})_{1/3}$ were pelletized and subsequently put in contact with two freshly polished sodium disks (Aldrich). All these operations were carried out in an Ar-filled glove box. Electrochemical tests were performed by using a MPG (BioLogic) research-grade battery tester, at the temperature of 333 K. CVs were done with a scan rate of 0.5 mV s^{-1} in the voltage range $-0.1-5 \text{ V}$. Galvanostatic tests were performed applying alternatively a current density of $25 \mu\text{A cm}^{-2}$ with 30-min lasting sweeps.

Ab initio DFT calculations were set for five different compositions: pure $\text{Na}_2\text{B}_{12}\text{H}_{12}$, pure $\text{NaCB}_{11}\text{H}_{12}$, and $x = 1/4$; $1/2$; $3/4$ mixture. The plane-wave basis set was used together with the gradient corrected exchange correlation functional [27]. The valence configurations $1s^1$ for H; $2s^22p^1$ for B; $2s^22p^2$ for C were represented by projector-

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