



Na₃NH₂B₁₂H₁₂ as high performance solid electrolyte for all-solid-state Na-ion batteries



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HIGHLIGHTS

- Na₃NH₂B₁₂H₁₂ with *Pna*2₁ space group is prepared for the first time.
- Outstanding electrochemical and thermal stabilities up to 10 V and 593 K.
- A high Na⁺ conductivity of 1.0 × 10⁻⁴ S cm⁻¹ at 372 K.
- All-solid-state Na-ion battery repeatedly works over 200 cycles.

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ABSTRACT

Solid electrolyte with stable and fast Na⁺ ionic conductivity is of central importance in the development of all-solid-state sodium batteries. Here we present a novel Na⁺ conductor based on complex hydrides with composition of Na₃NH₂B₁₂H₁₂. It exhibits remarkable thermal stability up to 593 K and excellent electrochemical stable window up to 10 V (vs. Na⁺/Na). It demonstrates a high Na⁺ conductivity of 1.0 × 10⁻⁴ S cm⁻¹ at a temperature of 372 K, which is much higher than those of its precursors NaNH₂ and Na₂B₁₂H₁₂. All-solid-state Na-ion batteries were constructed by employing the obtained Na₃NH₂B₁₂H₁₂ as electrolyte, TiS₂ as cathode and sodium foil as anode, which can reversibly discharge/charge for over 200 cycles with more than 50% capacity retention at temperature of 353 K and a rate of 0.1 C. This work opens the gate to develop advanced solid electrolytes via combination of metal amides with closo borates.

1. Introduction

The tough issues of Li-ion batteries such as high cost and low security seem hardly to be overcome for the case of low abundance of metal Li in the earth's crust and the adoption of flammable liquid organic electrolytes. For the realization of low-carbon society in the future, development of inexpensive and safe next generation battery is urgently in great necessity. All-solid-state Na-ion battery is then proposed as one of the most competitive alternatives to Li-ion battery for: on one hand, the weight abundance of Na in the earth's crust is over 400

times more than that of Li which results in much lower cost of Na than that of Li [1,2]; on the other hand, substituting inflammable solid electrolytes for flammable liquid electrolytes remarkably increases the security of batteries during practical operation [3]. Additionally, Na is the second lightest metal element (Be is not considered for its toxicity) with similar chemical properties to Li which facilitates to high energy capacity and good compatibility to Li-ion battery devices [2].

To develop all-solid-state Na-ion battery with high performance, long cycle life and high security for commercial application, solid electrolyte materials are essential and worthy of careful study. Na-ion

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battery solid electrolyte materials can be easily divided into polymer electrolytes and inorganic electrolytes. Polymer electrolytes such as poly (ethylene oxide) (PEO) is also commonly used in Li-ion batteries, their good ductility offers the probability to make advanced super-thin battery. Nevertheless, the solid Na-ion batteries using polymer electrolytes often exhibit serious capacity fading ($< 1/3$ of first discharge) even only after ten discharge/charge cycles which severely hampers the practical application [4,5]. Among inorganic electrolytes, β -alumina as the first super ionic conductor material used in Na-S batteries exhibits high conductivity of more than 0.2 S cm^{-1} at 573 K [6]. However, the hygroscopicity and fragility of β -alumina as well as its demand of high operating temperature confine its application as solid electrolyte only to stationary energy storage. In NASICON structure, compounds $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($0 < x < 3$) were firstly proposed as solid electrolyte materials for Na-ion battery, and a highest conductivity value of $2.7 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature has been achieved [2,7]. High temperature of sintering is indispensable for preparing them which increases the cost and hampers their practical application. Glass-ceramic electrolytes such as cubic Na_3PS_4 and $\text{Na}_{10}\text{SnP}_2\text{S}_{12}$ have recently been reported for Na-ion battery, both of which have room temperature conductivity of over $10^{-4} \text{ S cm}^{-1}$. The disadvantages of sulfides are their poor stabilities in air or during discharge/charge cycling [8,9].

In recent years, metal complex hydrides with light weight, high electrochemical stability and excellent deformation properties [10] have attracted more and more attentions to be potential solid electrolyte materials since the first superionic conduction in LiBH_4 was reported [11]. Subsequently, the research of superionic conductivity was extended to $[\text{B}_{10}\text{H}_{10}]^{2-}$ and $[\text{B}_{12}\text{H}_{12}]^{2-}$ compounds which are thought to be dehydrogenation intermediate of $[\text{BH}_4]^-$ compounds and more stable [12–14]. Such complex hydrides usually exhibit a typical first-order phase transition from low-temperature phase to high-temperature phase at a certain temperature accompanying with several orders of magnitude improvement in conductivity [11–14]. Nevertheless, the phase transition temperature is usually much higher than 373 K and hardly meets the practical utilization. In order to lower phase transition temperature and increase conductivity, many new electrolytes via ionic doping or modification have been reported, such as $\text{Li}_x\text{Na}_{1-x}\text{B}_{12}\text{H}_{12}$, $\text{NaCB}_{11}\text{H}_{12}$, $\text{Na}_3\text{BH}_4\text{B}_{12}\text{H}_{12}$, $\text{NaCB}_9\text{H}_{10}$ and $\text{Na}_2\text{B}_{10}\text{H}_{10}\text{-Na}_2\text{B}_{12}\text{H}_{12}$ [15–20]. Though the conductivities have been much improved in optimized Na-ion complex hydride electrolytes, all-solid-state Na-ion batteries using complex hydrides as electrolytes have been rarely reported for many possible factors such as large interface resistance and poor cyclability and so on [20,21]. Poor cyclability and quick capacity fading remain the main issues for all-solid-state Na-ion batteries, and the reported reversible discharge/charge cycles in all-solid-state Na-ion batteries are usually less than 200 [8,20,22,23]. Herein, NaNH_2 with relatively high stability and low cost is reacted with $\text{Na}_2\text{B}_{12}\text{H}_{12}$ with high stability [24] in order to synthesize a kind of new composite electrolyte material $\text{Na}_3\text{NH}_2\text{B}_{12}\text{H}_{12}$ via simple calcination at appropriate conditions. $\text{Na}_3\text{NH}_2\text{B}_{12}\text{H}_{12}$ exhibits much higher ionic conductivity than both of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and NaNH_2 . All-solid-state $\text{TiS}_2/\text{Na}_3\text{NH}_2\text{B}_{12}\text{H}_{12} | \text{Na}_3\text{NH}_2\text{B}_{12}\text{H}_{12} | \text{Na}$ battery operated at 353 K reversibly discharges/charges for over 200 cycles and keeps more than 50% of capacity retention.

2. Experimental

Commercial $\text{B}_{10}\text{H}_{14}$ (99%, Wako), NaBH_4 (99.99%, Aldrich) and NaNH_2 (99%, ThermoFisher) were all stored in glove box and used without further purification. $\text{Na}_2\text{B}_{12}\text{H}_{12}$ was synthesized according to the reported method [25]. The reactants NaNH_2 and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ with stoichiometric molar ratio of 1:1 were firstly hand milled for 30 min in glove box with < 0.1 ppm of $\text{H}_2\text{O}/\text{O}_2$ concentration. Subsequently, the hand milled reactants were sealed into ($\sim 0.7 \text{ cm}^3$) stainless steel crucibles for calcination at 523 K for 3 h. All the operation procedures were

completed in glove box protect by pure Ar.

Powder X-ray diffraction (XRD) experiments were performed by a Rigaku Smartlab X-ray diffractometer with Cu-K radiation using 45 kV/200 mA as accelerating voltage/tube current. In order to avoid air exposure during the measurement, all the sample powders were firstly placed in a quartz glass plate and then sealed by Scotch tape in glove box. Raman spectra were recorded by Horiba LabRAM HR Evolution using a green laser with a wavelength of 532 nm. The thermal stability is investigated using Thermogravimetric-Differential Thermal Analysis (TG-DTA) using 100 ml/min Ar as carrier gas.

Ionic conductivities were measured with electrochemical impedance spectroscopy for the sample pressed into a pellet with a diameter of 8 mm and a thickness of approximately 1 mm. Cu foils with a thickness of $9 \mu\text{m}$ were used as electrodes, which were mechanically fixed on both sides of the pellet sample in an air-tight 2025 coin cell. Impedance plots were measured using IM6ex electrochemistry workstation (Zahner-Elektrick, German) with a frequency range from 1 MHz to 1 Hz.

Cyclic voltammetry (CV) measurements were conducted using an IM6ex electrochemistry workstation (Zahner-Elektrick, German) with a scanning rate of 10 mV/s and voltage range from -0.5 V to 10 V. The $\text{Na}_3\text{NH}_2\text{B}_{12}\text{H}_{12}$ powder was placed in an 8-mm-diameter die and uniaxially pressed at 40 MPa and then kept for 12 h. The resultant compact electrolyte pellet was sandwiched by Na and Pt electrodes and then sealed in an air-tight 2025 coin cell for CV measurement.

The battery performance was evaluated by galvanostatic discharge/charge measurements using Neware battery test system (Shengzhen, China) at 353 K with a potential range from 1.0 to 2.4 V (vs. Na^+/Na). 50 wt% of $\text{TiS}_2/\text{Na}_3\text{NH}_2\text{B}_{12}\text{H}_{12}$ powder was used as cathode ($\text{TiS}_2 = 0.3 \text{ mg}$) and pressed together with electrolyte $\text{Na}_3\text{NH}_2\text{B}_{12}\text{H}_{12}$ powder under 40 MPa for 12 h in order to make a combined pellet with both cathode and electrolyte layers. The produced pellet with 8 mm diameter is then attached to Na foil and sealed into an air-tight 2025 coin cell to assemble $\text{TiS}_2/\text{Na}_3\text{NH}_2\text{B}_{12}\text{H}_{12} | \text{Na}_3\text{NH}_2\text{B}_{12}\text{H}_{12} | \text{Na}$ battery for battery performance evaluations.

3. Results and discussion

3.1. Material synthesis

$\text{Na}_2\text{B}_{12}\text{H}_{12}$ is obtained via our previously reported method [25], $\text{Na}_3\text{NH}_2\text{B}_{12}\text{H}_{12}$ is then synthesized by simple calcination of commercial NaNH_2 with $\text{Na}_2\text{B}_{12}\text{H}_{12}$ at different conditions (below the decomposition temperatures of both reactants). The optimal reaction condition is determined as 523 K for 3 h, the XRD pattern and Raman spectrum of thus synthesized sample are shown in Fig. 1. The XRD pattern indicates the main formation of new phase different from both NaNH_2 and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ though with small amount of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ retention ($2\theta = 15.0^\circ$) as impurity. In Raman spectrum, only vibration signals of $[\text{B}_{12}\text{H}_{12}]^{2-}$ and $[\text{NH}_2]^-$ from $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and NaNH_2 are obviously observed which clearly proves no decomposition of reactants but the formation of new compound $\text{Na}_3\text{NH}_2\text{B}_{12}\text{H}_{12}$.

3.2. Structural analysis

Room temperature X-ray powder diffraction was measured at constant wavelength $\lambda = 1.54184 \text{ \AA}$ with a 2θ step size 0.013° . The data was refined with the FULLPROF suite [26] using the Rietveld method as shown in Fig. 2(a). An initial approximate structural model, as a starting point, was taken from the isostructural $\text{Na}_3\text{BH}_4\text{B}_{12}\text{H}_{12}$ [18]. The Pseudo-Voigt function was chosen to model the peak profile shape; the background contribution was determined using a linear interpolation between automatically selected data points; the scale factor, zero shift, lattice parameters, peak shape parameters, overall thermal parameters, preferred orientation as well as atomic positions were refined [27]. In the final analysis, all these parameters were refined

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