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COMMUNICATION

Synthesis, Stability and Li-ion Mobility of Nanoconfined $\text{Li}_2\text{B}_{12}\text{H}_{12}$

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This communication presents the first synthesis of nanoconfined Lithium *closo*-borate, $\text{Li}_2\text{B}_{12}\text{H}_{12}$, using nanoporous SiO_2 as scaffold. The yield of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ is up to 94 mol%. The as-synthesized nanoconfined $\text{Li}_2\text{B}_{12}\text{H}_{12}$ exhibits a structural transition around 380 °C and conversion to H-deficiency $\text{Li}_2\text{B}_{12}\text{H}_{12-x}$ at 580 °C.

Complex hydrides, based on complex anions such as $[\text{BH}_4]^-$, $[\text{NH}_2]^-$ and $[\text{B}_{12}\text{H}_{12}]^{2-}$, have been attracting great attention as energy-storage materials.¹⁻⁵ Lithium *closo*-borate, $\text{Li}_2\text{B}_{12}\text{H}_{12}$, has been extensively discussed as a reaction intermediate in the hydrogen sorption process of bulk LiBH_4 .⁶⁻¹⁰ Due to its high thermal stability and low chemical reactivity, it has been considered as a boron sink hindering the rehydrogenation of LiBH_4 .

Recently, fast ion conduction has been discovered in *closo*-borate anion based complex hydrides.¹¹⁻²⁰ Their high thermal stability and low chemical reactivity are obviously big advantages regarding potential application as Li solid-state electrolytes. $\text{Li}_2\text{B}_{12}\text{H}_{12}$ crystallizes in two polymorphs, the low conducting α -phase at room temperature and the highly conducting, disordered β -phase above 355 °C²¹ showing Li-ion conductivity of around 0.1 S·cm⁻¹.¹⁵ Much lower Li-ion conductivities at room temperature, in the order of 10⁻⁷ S·cm⁻¹ or 10⁻⁴ S·cm⁻¹, respectively, were reported by different groups.¹³⁻¹⁶ Li-ion conductivity of 10⁻⁶ S·cm⁻¹ at room temperature was achieved in nanocrystalline $\text{Li}_2\text{B}_{12}\text{H}_{12}$,¹⁵ which, however, is not sufficient for the utilization for solid-state electrolyte applications in batteries.

Nanoconfinement has been reported as an effective approach to tune the thermodynamic and kinetic properties of material.²² For example, nanoconfined LiBH_4 using nonporous carbon or zeolite scaffolds shows faster desorption kinetics with initial desorption temperature down to below 200 °C and more importantly, improved rehydrogenation properties under moderate conditions (e.g. 260 °C to 300 °C and 5 to 10 Mbar H_2 , respectively).²³⁻²⁵ However, it is still unclear whether $\text{Li}_2\text{B}_{12}\text{H}_{12}$ is circumvented in the

hydrogen sorption cycle of nanoconfined LiBH_4 or whether it is destabilized owing to a nanoconfinement effect. On the other hand, nanoconfinement enhances the cation mobility of hydrides, e.g. nano- LiBH_4 shows improved ionic conductivity of 10⁻⁴ S·cm⁻¹ at room temperature.^{26, 27} Therefore, it is of great interest to investigate the nanoconfinement effect on $\text{Li}_2\text{B}_{12}\text{H}_{12}$. In the present study, we report the first synthesis of nanoconfined $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and evaluate its thermal stability and Li-ion mobility.

Nano-porous SiO_2 , SBA15, is used as scaffold. N_2 physisorption (Fig. 1a) yields a surface area (S_{BET}) of 487.3 m²/g, a total pore volume (V_p) of 0.765 cm³/g and an average pore diameter of 5.9 nm. The pore length of as-purchased SBA15 is around 1 ~ 2 μm .²⁸ The synthesis of nanoconfined $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (denoted by NC- $\text{Li}_2\text{B}_{12}\text{H}_{12}$) is described in Fig.1 and carried out in two steps. First, nanoconfined LiBH_4 (denoted as NC-20 LiBH_4) using SBA15 as a scaffold, with a loading ratio of 20 wt% is prepared at 300 °C and 100 bar H_2 . Loading of 20 wt% LiBH_4 (density: 0.666 g/cm³) corresponds to the filling of half pore volume of SBA15. Subsequently, the as-synthesized NC-20 LiBH_4 is treated in a $\text{H}_2/\text{B}_2\text{H}_6$ atmosphere at 150 °C to form $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (density: 1.18 g/cm³), following the reaction pathway:

Figure 1. Illustration of synthesis of nanoconfined $\text{Li}_2\text{B}_{12}\text{H}_{12}$ (NC- $\text{Li}_2\text{B}_{12}\text{H}_{12}$).

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Figure 2. (a) N₂ isotherms of SBA15, NC-20LiBH₄ and NC-Li₂B₁₂H₁₂. Open and closed circles represent adsorption and desorption isotherms, respectively. (b) XRD patterns of physical mixture of SBA15 and LiBH₄ before melt infiltration, NC-20LiBH₄ and NC-Li₂B₁₂H₁₂. (c) Rietveld refinement of NC-Li₂B₁₂H₁₂. The experimental data are shown as solid line, best fit as open circles and the difference plot is shown at bottom. The peak positions are referred to α-Li₂B₁₂H₁₂ (ICSD#249756). (d) ¹¹B MAS NMR of NC-Li₂B₁₂H₁₂. The spectrum is deconvoluted into individual Li₂B₁₂H₁₂ and Li₂B₁₀H₁₀ components.

Figure 3. (a) *in situ* XRD patterns of NC-Li₂B₁₂H₁₂ and (b) ¹¹B MAS NMR and ¹H-¹¹B cross polarization MAS NMR spectra of NC-Li₂B₁₂H₁₂ decomposed at 580 °C. Dashed lines represent two individual components of the ¹¹B MAS NMR spectrum.

The full conversion of NC-20LiBH₄ will generate a nanoconfined Li₂B₁₂H₁₂ with loading ratio of 47.4 wt%, approximately corresponding to complete filling of the pore volume. Nanoconfined LiBH₄ with a 34 wt% loading (denoted as NC-34LiBH₄), corresponding to complete filling of the pore volume of SBA15, was also prepared for evaluation of the Li-ion conductivity of nanoconfined LiBH₄ as compared to the complete filling by Li₂B₁₂H₁₂.

Figure 4. (a) Static ⁷Li NMR of NC-Li₂B₁₂H₁₂ in the temperature range of 25 to 105 °C. The spectrum at 25 °C is deconvoluted into a narrow Lorentzian component and a broad Gaussian component. (b) Temperature-dependent full widths at a half maximum (FWHM) of Static ⁷Li NMR signal of NC-Li₂B₁₂H₁₂. (c) ⁷Li MAS NMR (ω=12kHz) of NC-LiBH₄ and NC-Li₂B₁₂H₁₂ at 25 °C. (d) Arrhenius plots of Li-ion conductivity of NC-Li₂B₁₂H₁₂ and NC-34LiBH₄, compared to bulk LiBH₄,²⁹ and bulk Li₂B₁₂H₁₂.¹⁵

The change of surface area of SBA15 within the two-step process was documented by N₂ sorption as shown in Fig. 2a. After loading of 20 wt% LiBH₄, *S*_{BET} and *V*_p are reduced to 182.3 m²/g and 0.405 cm³/g, respectively. All the X-ray reflections originating from crystalline LiBH₄ precursor disappear in the X-ray diffraction (XRD) pattern of NC-20LiBH₄ (Fig. 2b), indicating the loss of long-range ordering and confirming the successful confinement in the pores of scaffold. *S*_{BET} and *V*_p further decrease to 27 m²/g and 0.04 cm³/g after B₂H₆ treatment, respectively, and new X-ray reflections appear indicating the formation of Li₂B₁₂H₁₂ (Fig. 2b). Rietveld refinement (Fig. 2c) was performed for the as-synthesized nanoconfined Li₂B₁₂H₁₂, further indicating that all the new X-ray reflections are attributed to α-Li₂B₁₂H₁₂. However, the asymmetric feature of (111) reflection implies that coexistence of a small portion of high-temperature β-Li₂B₁₂H₁₂ (space group *Fm-3m*) at room temperature could not ruled out.²¹ NC-Li₂B₁₂H₁₂ shows broad reflections, e.g. the dominant reflection (111) at 2θ=15.98 displays a large FWHM of 0.34 degree, in agreement with its nanoconfined structure suppressing long-range order.

The formation of Li₂B₁₂H₁₂ is confirmed by ¹¹B magic angle spinning nuclear magnetic resonance (MAS NMR) (Fig. 2d), where a narrow and a broad resonance at -15.0 ppm assigned to Li₂B₁₂H₁₂ are observed. Two shoulders at -0.4 and -29.6 ppm, respectively, can be assigned to Li₂B₁₀H₁₀. By deconvoluting the ¹¹B MAS NMR spectrum, it is found that the product contains 94 mol% Li₂B₁₂H₁₂ and 6 mol% Li₂B₁₀H₁₀. No residual resonance of LiBH₄ is detected.

Fig. 3a shows the temperature evolution of the XRD pattern of NC-Li₂B₁₂H₁₂ from 30 to 580 °C. The transition of low-temperature α-Li₂B₁₂H₁₂ to high-temperature β-Li₂B₁₂H₁₂, characterized by an abrupt shift in the reflections (111) and (200), is observed at 380 °C. At higher temperatures, the reflections of the β phase decrease and fully disappear at 580 °C, indicating the occurrence of decomposition. In the ¹¹B MAS NMR spectrum of the decomposed NC-Li₂B₁₂H₁₂ (sample heated to 580 °C) in Fig. 3b, the resonance shifting to -12.6 ppm is assigned to H-deficient Li₂B₁₂H_{12-x} and a shoulder at 6 ppm possibly originating from elemental boron is observed.³⁰ The formation of H-deficient Li₂B₁₂H_{12-x} is confirmed by ¹H-¹¹B cross polarization MAS NMR (Fig. 3b).

The Li dynamics of NC-Li₂B₁₂H₁₂ was investigated by ⁷Li static NMR in a temperature range from 25 to 105 °C, as shown in Fig. 4a.

At 25 °C, the spectrum of NC-Li₂B₁₂H₁₂ contains a relatively narrow Lorentzian component (1.1 kHz) and a broader Gaussian component (6.5 kHz). With increasing temperature, no significant line narrowing in the spectra and no decrease in full width at half maximum (FWHM) are observed (Fig. 4b). Fig. 4c compares the ⁷Li MAS NMR spectra of NC-Li₂B₁₂H₁₂ and NC-20LiBH₄ at 25 °C. The NC-Li₂B₁₂H₁₂ shows a FWHM of 0.52 kHz, which is larger than that of NC-20LiBH₄ (0.23 kHz). This line narrowing implies a slight decrease of Li⁺ mobility after the B₂H₆ treatment of NC-20LiBH₄.

Fig. 4d compares the Li-ion conductivity of nanoconfined LiBH₄ with nanoconfined Li₂B₁₂H₁₂. The nanoconfined LiBH₄, NC-34LiBH₄, shows Li-ion conductivity of 8.0×10^{-6} S·cm⁻¹ at 25 °C. Overloading will increase the fraction of LiBH₄ with high mobility. The as-synthesized NC-Li₂B₁₂H₁₂ in SiO₂ scaffold exhibits a lower Li-ion conductivity around 1.0×10^{-7} S·cm⁻¹ at 25 °C, similar to the value obtained for bulk Li₂B₁₂H₁₂ which is synthesized from the wet-chemistry.¹⁵

Above all, we demonstrate the synthesis of nanoconfined Li₂B₁₂H₁₂ using nanoporous SiO₂ as scaffold. The yield of Li₂B₁₂H₁₂ is up to 94 mol% with 6 mol% Li₂B₁₀H₁₀ formed as a byproduct determined by ¹¹B MAS NMR measurement, where no residual of LiBH₄ precursor remains. Such a high yield is much superior to that (26 mol%) of the synthesis *via* the reaction of bulk LiBH₄ and B₂H₆ at 200 °C.³¹ This improvement is owing to the utilization of nanoconfined LiBH₄ that overcomes the limitation resulted from the formation of a passivation layer, which was observed in the reaction between bulk LiBH₄ and B₂H₆. Thus high-purity and anhydrous Li₂B₁₂H₁₂ is provided in present study, which will be used as a precursor for the synthesis of mixed-anion systems that can reach high ionic conductivity at ambient temperature.¹⁷⁻¹⁹

The nanocrystalline Li₂B₁₂H₁₂ exhibits a structural transition to the high-temperature β phase around 380 °C. The β phase decomposes around 580 °C leading to the conversion of the material into H-deficient Li₂B₁₂H_{12-x}. Similar observations were found for bulk Li₂B₁₂H₁₂,²¹ indicating that no obvious destabilization effect is achieved in the as-synthesized nanoconfined Li₂B₁₂H₁₂. The destabilization effect of nanoconfinement owes in a great extent to the interaction between scaffold and the active material.²² Such interactions have been observed in the case of other complex hydrides such as LiBH₄ and NaAlH₄, which is evidenced by considerable changes of ¹¹B (or ²⁷Al) NMR chemical shifts.^{32,33} In the recently reported nanoconfined LiBH₄, this interaction enables the formation of an active LiBH₄-SiO₂ interface resulting in fast Li-ion conduction at room temperature.^{26,27} The ¹¹B NMR shift of as-synthesized Li₂B₁₂H₁₂, i.e. -15 ppm, is in line with the reported value of bulk Li₂B₁₂H₁₂,³¹ implying only weak interaction between Li₂B₁₂H₁₂ and SBA15. As a result, we do not observe an increase of Li-ion conduction in the as-synthesized nanoconfined Li₂B₁₂H₁₂.

The Li-ion conductivity of 8.3×10^{-6} S·cm⁻¹ at 25 °C observed for NC-34LiBH₄ is two orders of magnitude higher than that of bulk LiBH₄ (Fig. 3d), supporting the presence of highly conductive interface due to the interaction between LiBH₄ and SBA15. However, this value is lower than the reported conductivity ($\sim 10^{-4}$ S·cm⁻¹ at 40 °C) for nanoconfined LiBH₄ with an overloading of 20 to 30%,²⁶ suggesting that overloading will improve the conductivity. In future work, we expect higher conductivity in nanoconfined Li₂B₁₂H₁₂ due to overloading and nanoconfinement effects in scaffold with smaller pore sizes due to larger surface/bulk ratio.

In summary, nanoconfined Li₂B₁₂H₁₂ using nanoporous SiO₂ as scaffold with a high yield of Li₂B₁₂H₁₂ of 94 mol% is synthesized *via* the reaction between nanoconfined Li₂B₁₂H₁₂ and B₂H₆. The nanocrystalline Li₂B₁₂H₁₂ exhibits a structural transition to the high-

temperature β phase around 380 °C. The β phase decomposes around 580 °C leading to the conversion of the material into H-deficient Li₂B₁₂H_{12-x}. The Li-ion conductivity of nanoconfined Li₂B₁₂H₁₂ is measured to be 1.0×10^{-7} S·cm⁻¹ at 25 °C.

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Graphical abstract

We demonstrate the first synthesis of nanoconfined $\text{Li}_2\text{B}_{12}\text{H}_{12}$ using nano-porous SiO_2 scaffold and evaluate the thermal stability and Li-ion mobility.