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Electronic supplementary information

Developing high voltage electrolyte based on *conjuncto*-hydroborate for solid-state sodium battery

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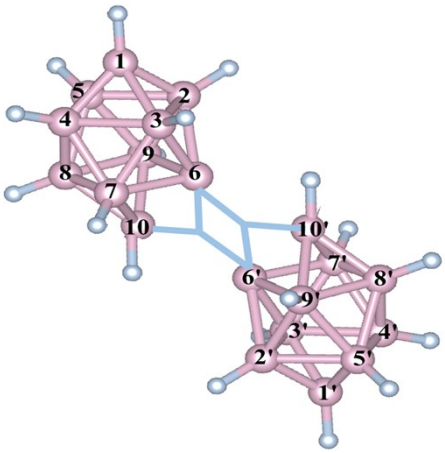

Table S1. ^{11}B nuclei chemical shifts (ppm) for $[B_{20}H_{18}]^{2-}$

^{11}B Nuclei	$\delta(^{11}B)$ (ppm)
B (1) = B (1')	31.07
B (6) = B (6')	16.03
B (8) = B (8')	-6.75
B (7) = B (9) = B (7') = B (9')	-12.46
B (2) = B (3) = B (2') = B (3')	-15.81
B (4) = B (5) = B (4') = B (5')	-19.25
B (10) = B (10')	-25.49

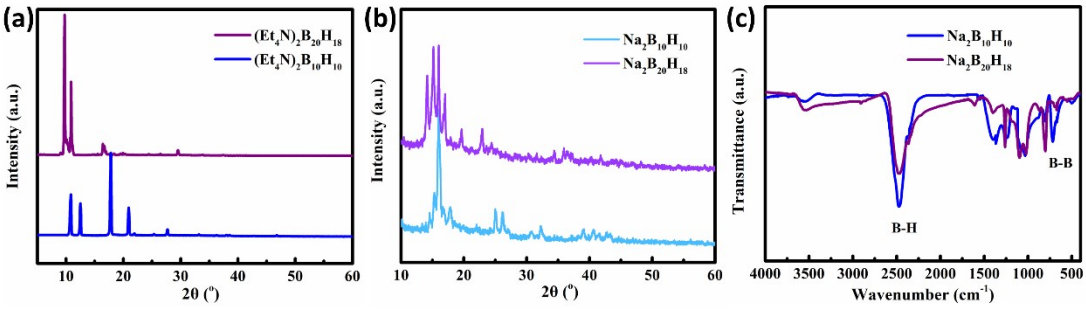

Fig. S1 XRD patterns of (a) $(Et_4N)_2B_{20}H_{18}$ and $(Et_4N)_2B_{10}H_{10}$. (b) anhydrous $Na_2B_{20}H_{18}$ and $Na_2B_{10}H_{10}$. (c) FTIR spectra of $Na_2B_{20}H_{18}$ and $Na_2B_{10}H_{10}$.

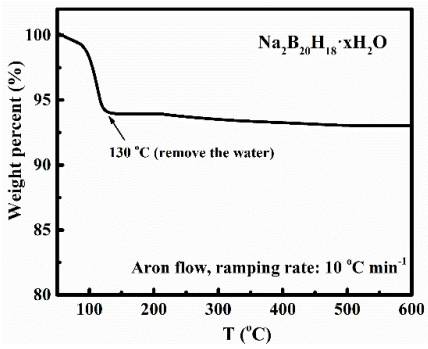

Fig. S2 TGA result of $Na_2B_{20}H_{18}.xH_2O$ (Argon flow， $\Delta T/\Delta t$=10 °C min^{-1}).

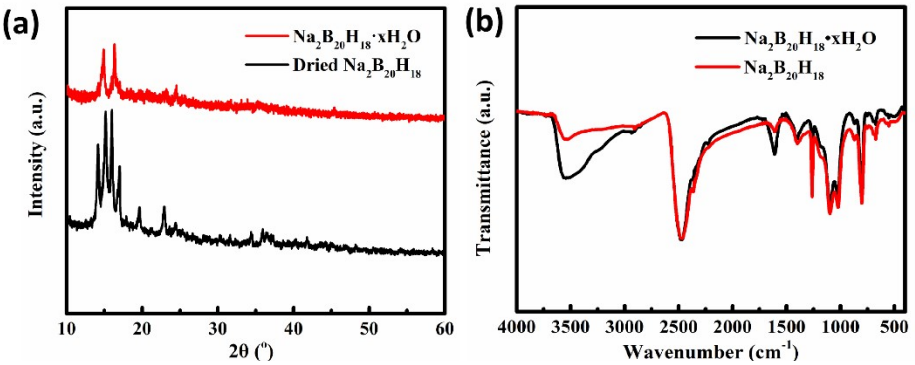

Fig. S3 (a) XRD patterns of dried $Na_2B_{20}H_{18}$ and $Na_2B_{20}H_{18}{\cdot}xH_2O$. (b) FTIR spectra of dried $Na_2B_{20}H_{18}$ and $Na_2B_{20}H_{18}{\cdot}xH_2O$.

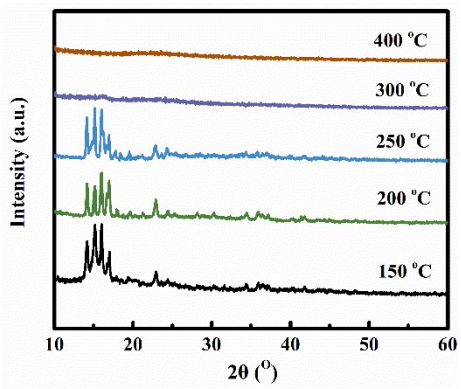

Fig. S4 *Ex-situ*-temperature-dependent XRD patterns of $Na_2B_{20}H_{18}$

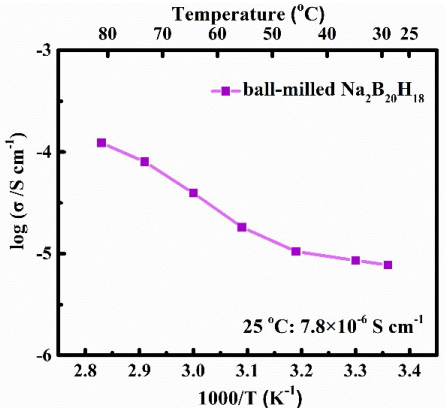

Fig. S5 Arrhenius plot (log (σ) vs 1/T) of ball-milled $Na_2B_{20}H_{18}$.

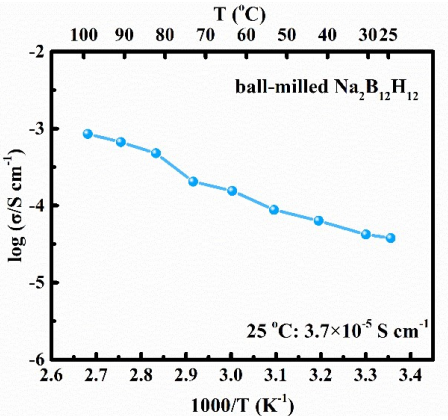

Fig. S6 Arrhenius plot (log (σ) vs 1/T) of ball-milled $Na_2B_{12}H_{12}$.

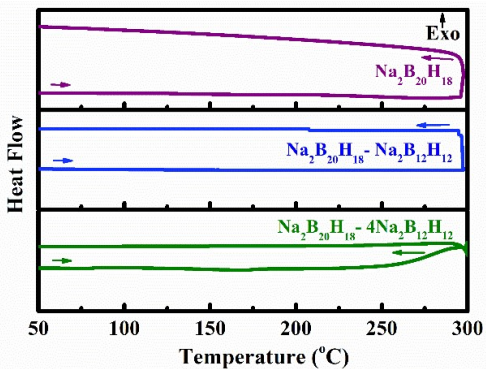

Fig. S7 Differential scanning calorimetry of the samples (ΔT/ Δt =5 °C min^{-1}).

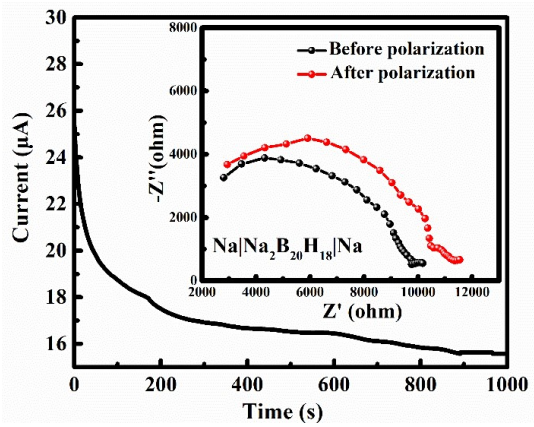

Fig. S8 The chrono current curve of a symmetrical battery Na|$Na_2B_{20}H_{18}$|Na at a polarization

voltage of 10 mV. The inset is the impedance spectrum before and after polarization

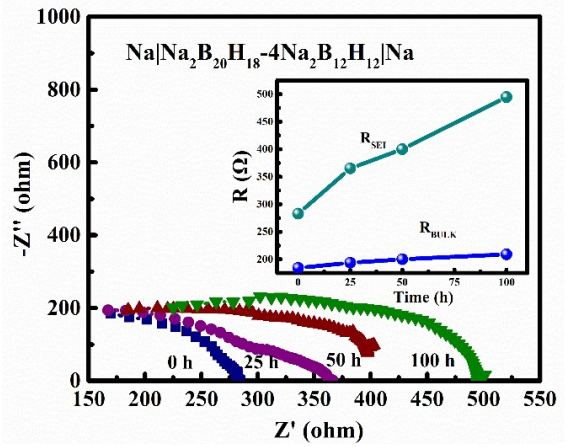

Fig. S9 Nyquist plots measured after 0-100 h of contacting the $Na_2B_{20}H_{18}$-$4Na_2B_{12}H_{12}$ SE with Na metal. The inset shows solid electrolyte interface (SEI) and bulk resistances plotted versus time.