Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Hemi-Methylamine Lithium Borohydride as Electrolyte for All-Solid-State Batteries

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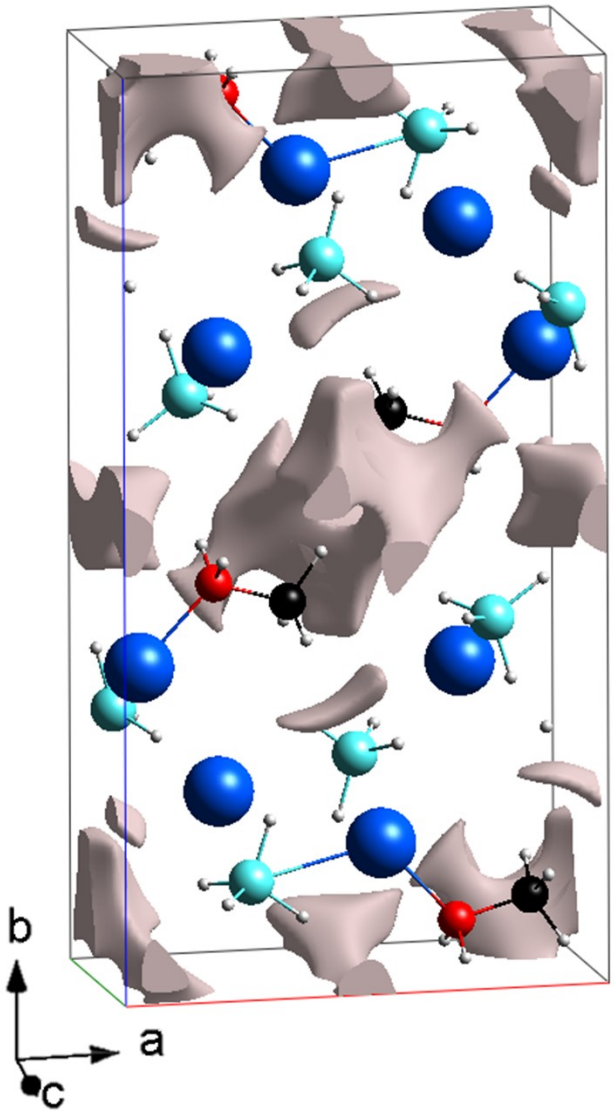

Figure S1. Crystal voids analysis of $LiBH_4 \cdot ½CH_3NH_2$ using Crystal explorer and the standard isovalue of 0.002 $e \cdot au^{-3}$. Color scheme: Li (blue), B (light blue), N (red), C (black), H (grey). The light purple ribbons illustrate voids.

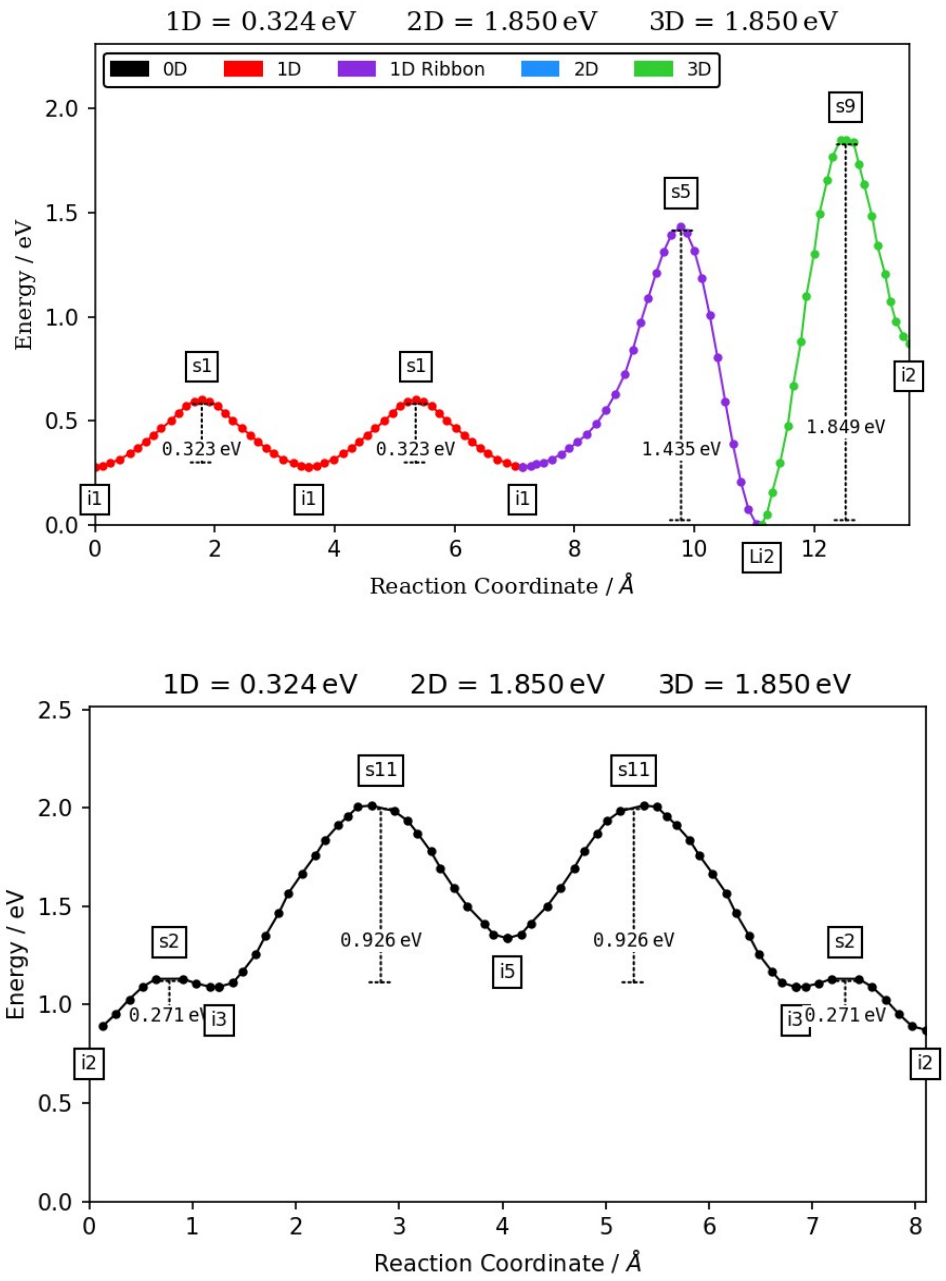

Figure S2. Energy barriers of the Li^+ ion migration pathway in the $LiBH_4 \cdot ½CH_3NH_2$ unit cell as calculated by the software SoftBV using the Bond-Valence approach. a) shows the energy profile for conduction pathway A (1D) and the complete energy landscape for a three-dimensional conduction pathway, which also include a framework Li^+. b) shows the energy profile for conduction pathway B. Note that SoftBV calculates for a static structure.

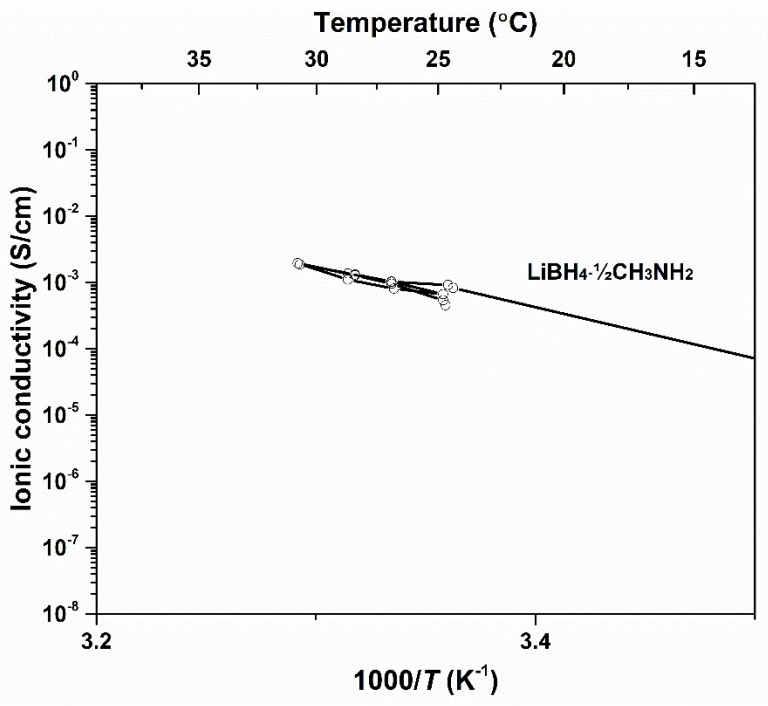

Figure S3. Temperature-dependent ionic conductivity of $LiBH_4 \cdot ½CH_3NH_2$ upon cycling.

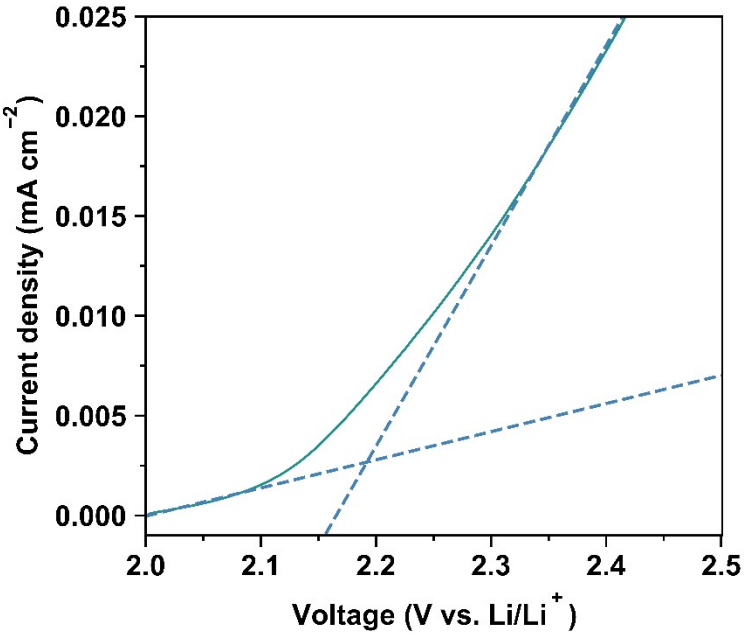

Figure S4. Linear sweep voltammetry of $LiBH_4 \cdot ½CH_3NH_2$ in a two electrode setup with Li as counter/reference electrode and Mo as working electrode recorded at $T = 30$ °C with a scan rate $\upsilon = 1$ mV s^{-1} in the potential range from OCV to 2.4 V to evaluate the oxidative stability.

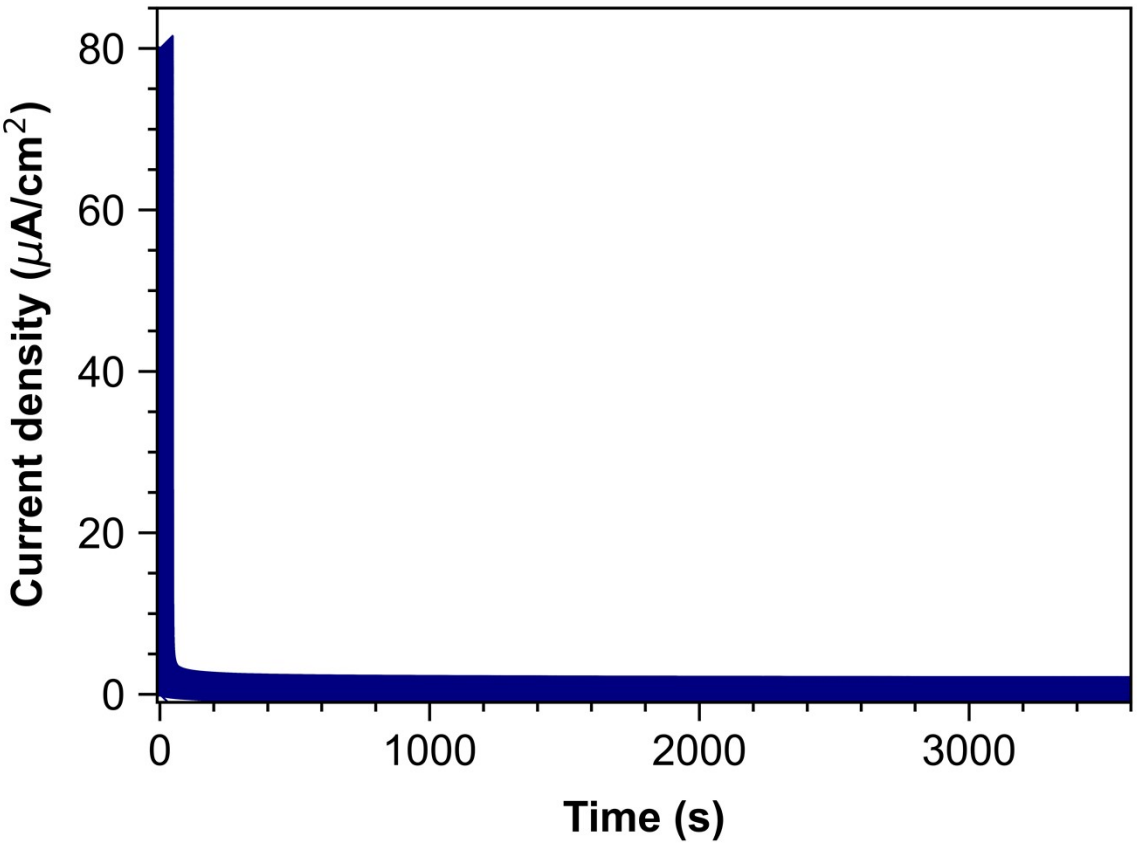

Figure S5. Chronoamperometry in a symmetric Mo|LiBH4·½CH_3NH_2|Mo cell at 30 °C by applying 0.5 V for 1 h

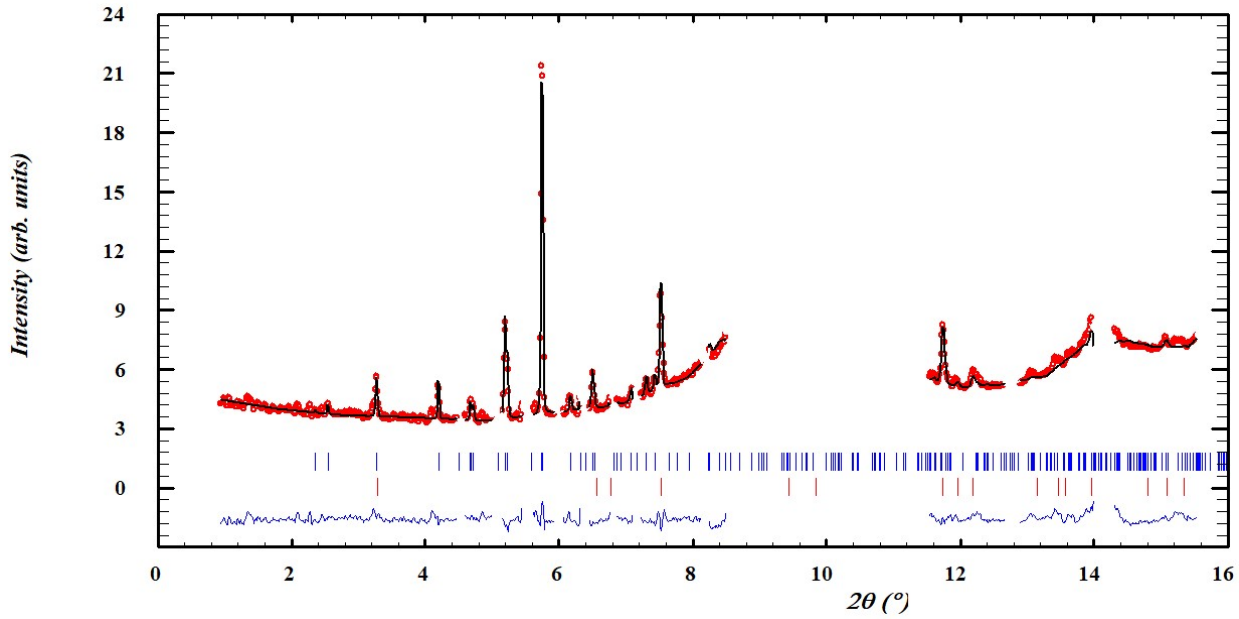

Figure S6. Rietveld refinement of the *in operando* data collected for Li|$LiBH_4 \cdot ½CH_3NH_2$|TiS_2 from SR PXD data measured at room temperature, λ = 0.3542 Å, showing experimental (red circles) and calculated (black line) PXD patterns, and a difference plot below (blue line). Blue tick marks: $LiBH_4 \cdot ½CH_3NH_2$, red tick marks: TiS_2. Final discrepancy factors: R_p = 2.65 %, R_{wp} = 3.40 % (not corrected for background), R_p = 45.6 %, R_{wp} = 23.2 % (conventional Rietveld R-factors). The ranges containing scattering from the Al-windows and Li-metal has been excluded in the refinement.