Electronic Supplementary Material (ESI) for

Inorganic Chemistry Frontiers.

In-situ interfacial reactions in hydride–oxide composite electrolytes for stable all-solid-state Li-metal batteries

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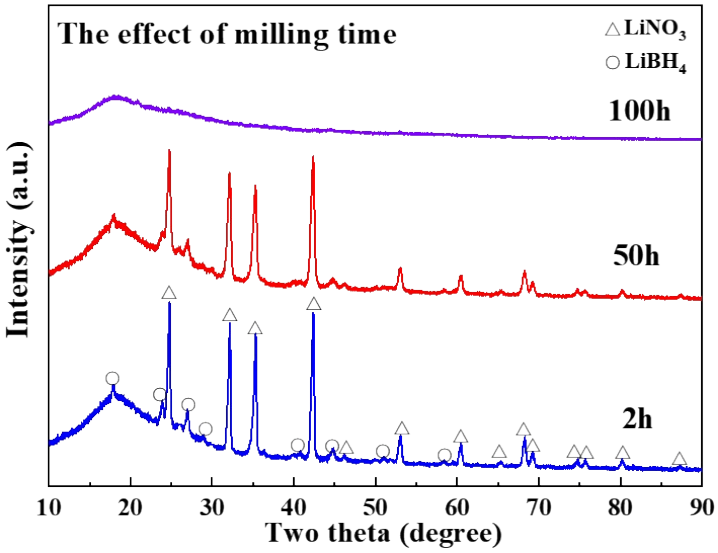

Fig. S1. X-ray diffraction patterns of 50 wt% $LiBH_4/LiNO_3$

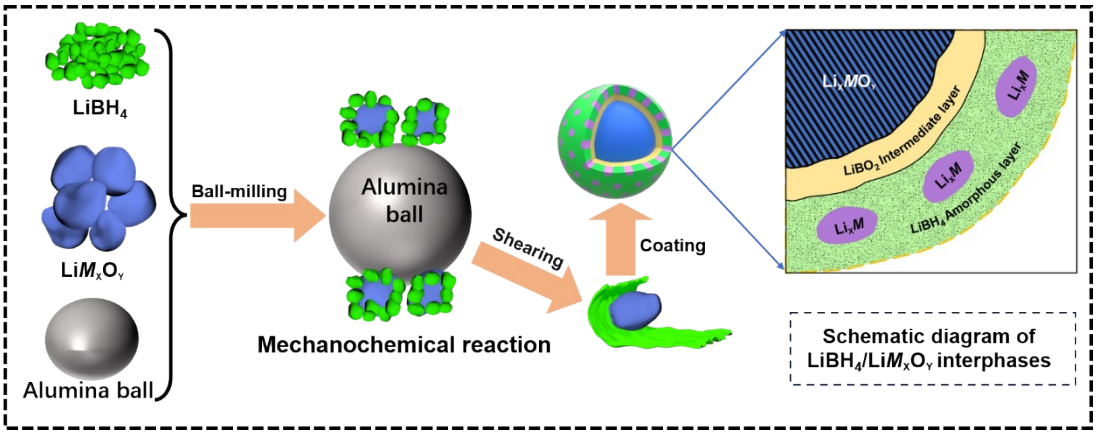

Fig. S2. Mechanism diagram of mechanochemical reaction formation of hydride-oxide dual core-shell

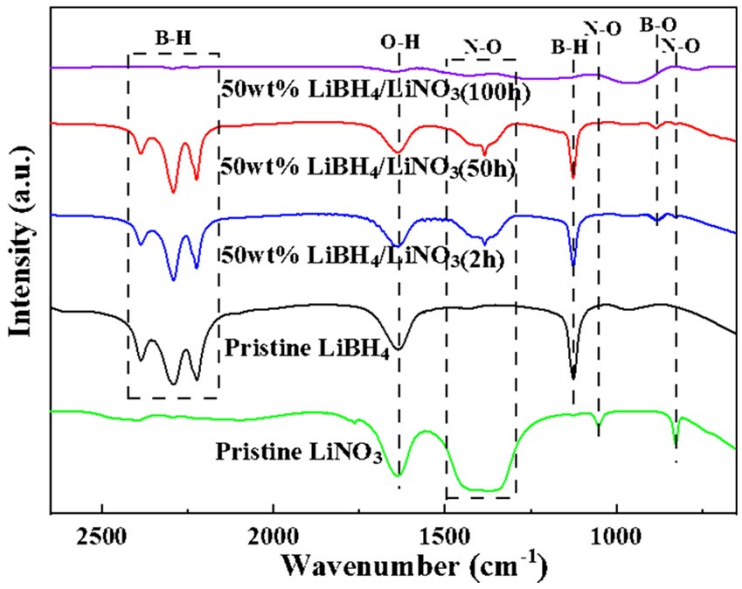

Fig. S3. FT-IR spectra of 50 wt% $LiBH_4/LiNO_3$ with different milling time.

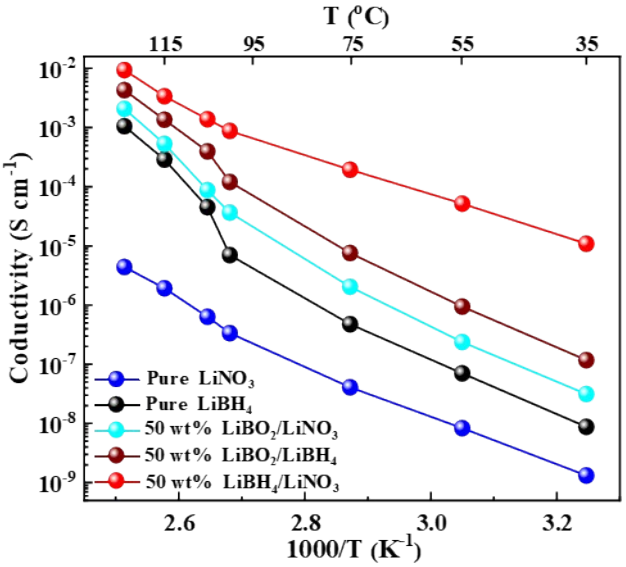

Fig. S4. Temperature-dependent ionic conductivities of composites SSEs.

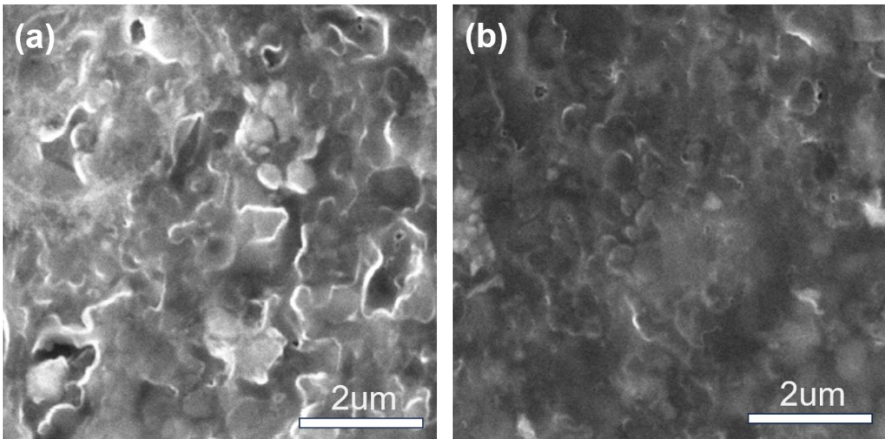

Fig. S5. SEM images of pellets for (a) pristine $LiNO_3$ and (b) 50 wt% $LiBH_4/LiNO_3$.

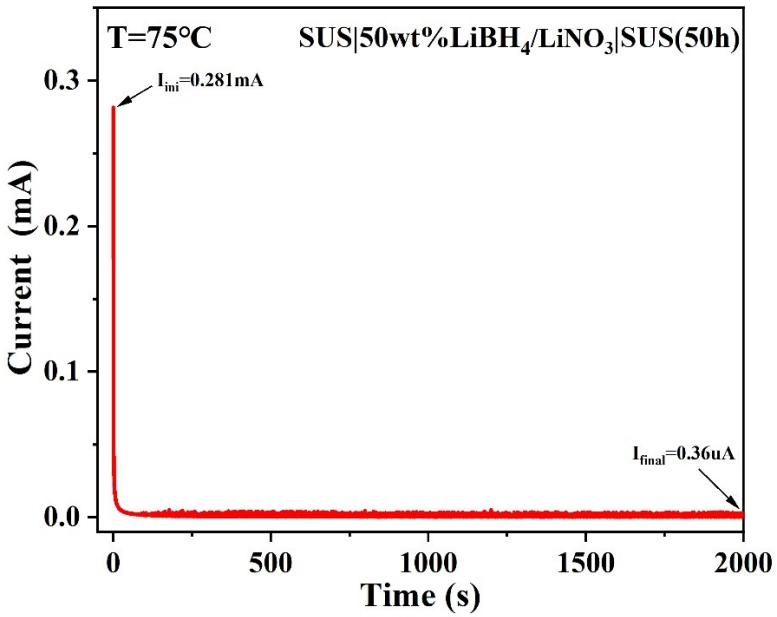

Fig. S6. Direct current (DC) polarization of 50 wt% $LiBH_4/LiNO_3$

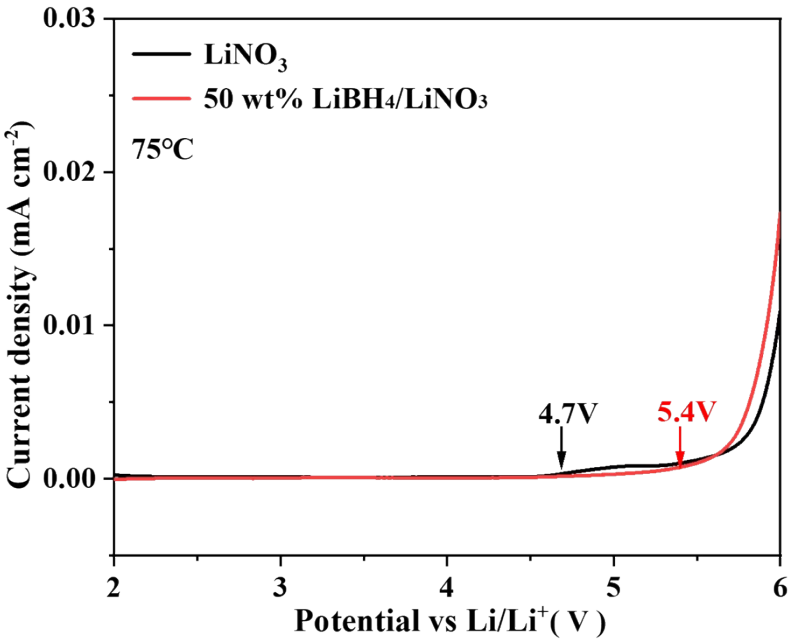

Fig. S7. LSV curves of $LiNO_3$ and 50 wt% $LiBH_4/LiNO_3$ at a scanning rate of 0.5 mV S^{-1} at 75 ℃

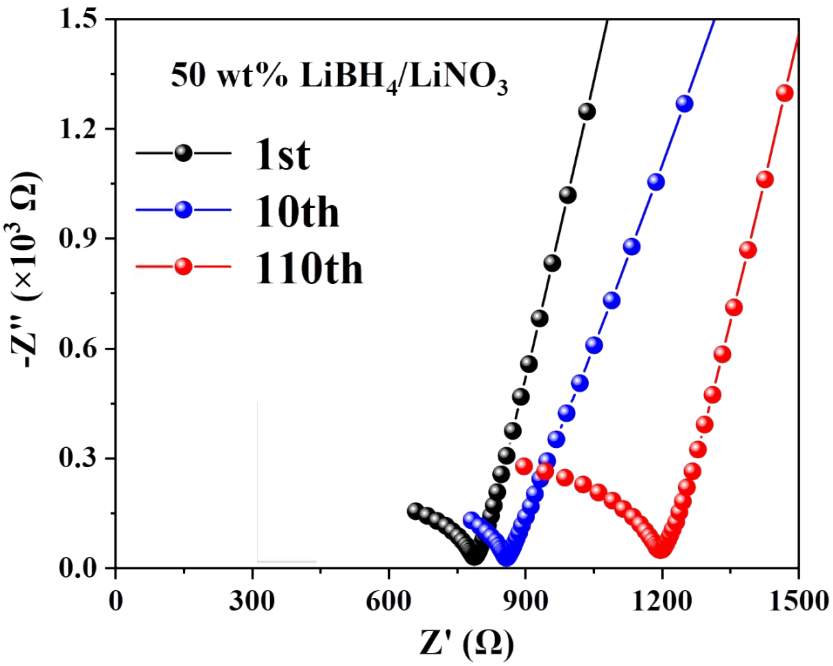

Fig. S8. Electrochemical impedance spectroscopy of cells after galvanostatic charge/discharge curves of 50 wt% $LiBH_4/LiNO_3$ solid electrolytes measurements at 75 °C.

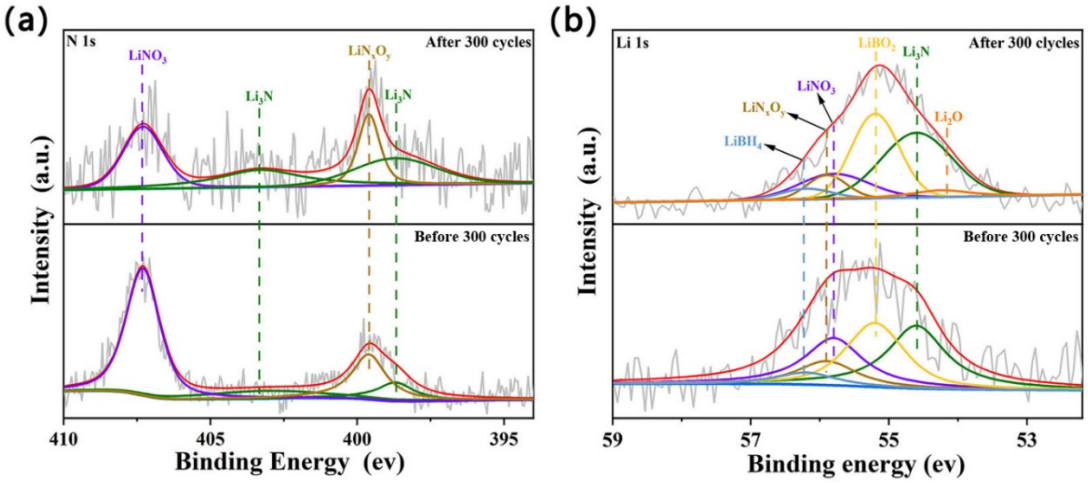

Fig. S9. XPS spectra of N ^{1s} and Li ^{1s} for $LiBH_4/LiNO_3$ surface layer before and after 300 cycles.

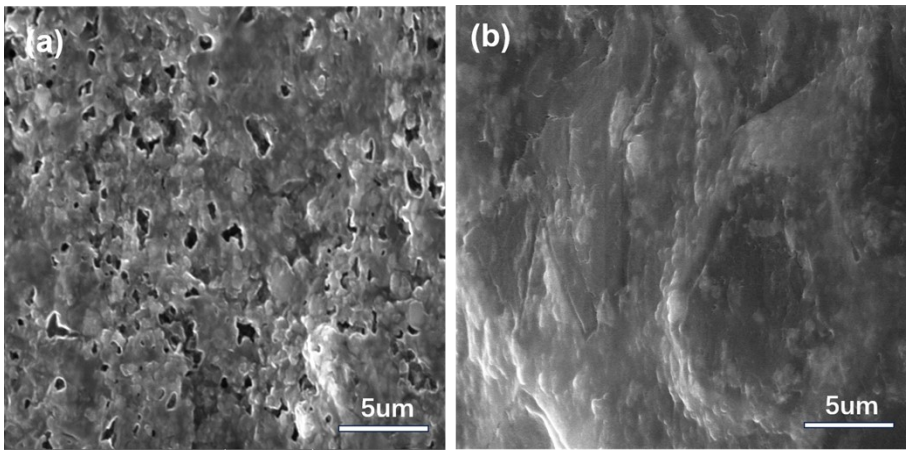

Fig. S10. SEM images of Li surface of (a) $LiNO_3$ and (b) 50 wt% $LiBH_4/LiNO_3$ in Li||Li cell after 110 cycles.

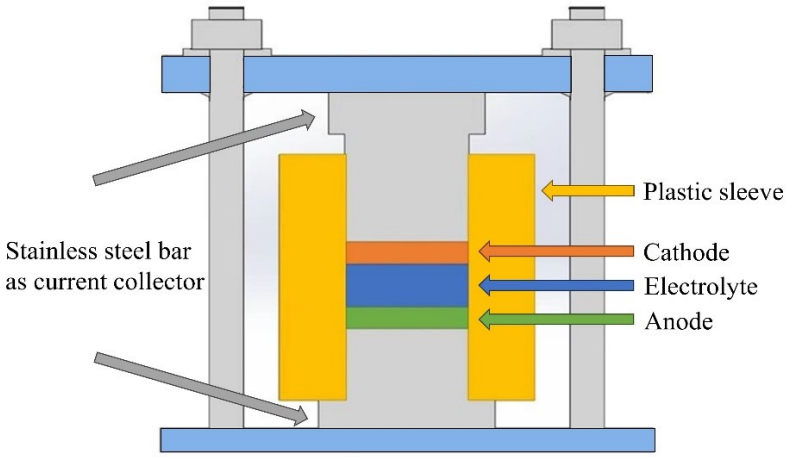

Fig. S11. Schematic illustration of the homemade Swagelok-type full cell.

Supplementary Table 1. The electrochemical properties of reported solid electrolytes and this work were compared.

Solid electrolytes	**Electrochemical window**	**Critical current density**	**Li||Li cycling stability**	**Ref.**
$LiBH_4 \cdot xNH_3$-Li_2O	0.5~3.8V	N. A	0.1mA cm^{-2} for 30 h at 30 °C	1
$Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$-$Li_3PO_4$	-1~5V	1.2mA·cm^{-2}	0.2mA cm^{-2} for 500 h at 30 °C	2
$Li_7La_3Zr_2O_{12}$-$LiBH_4$	0~5V	0.5mA·cm^{-2}	N. A	3
$Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$–$LiBH_4$	-1~6V	0.7mA·cm^{-2}	0.15mA cm^{-2} for 1000 h at 60 °C	4
$LiBH_4 \cdot 1/2NH_3$-MgO	-0.5~4V	N. A	0.1mA cm^{-2} for 40 h at 30 °C	5
$LiBH_4 1/2NH_3$	0.2–1.8 V	N. A	N. A	6
$LiBH_4/LiNO_3$	-0.5~6V	2.3mA · cm^{-2}	0.2mA cm^{-2} for 650 h at 75 °C	This work

Supplementary References

1. Zhao, W. *et al.* Li-Ion conductivity enhancement of $LiBH_4 \cdot xNH_3$ with *in-situ* formed Li_2O nanoparticles. *ACS Appl. Mater. Interfaces* **13,** 31635–31641 (2021).
2. Bi, Z. *et al.* Molten salt driven conversion reaction enabling lithiophilic and air-stable garnet surface for solid-state lithium batteries. *Adv. Funct. Mater.* **32,** 2208751 (2022).
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4. Gao, Y. *et al.* Amorphous dual-layer coating: enabling high Li-ion conductivity of non-sintered garnet-type solid electrolyte. *Adv. Funct. Mater.* **39,** 2009692 (2021).
5. Zhang, R. *et al.* Size effect of MgO on the ionic conduction properties of a $LiBH_4 \cdot 1/2NH_3$–MgO nanocomposite. *ACS Appl. Mater. Interfaces* **14,** 8947–8954 (2022).
6 Y. G. Yan, J. B. Grinderslev, Y. S. Lee, M. Jørgensen, Y. W. Cho, and T. R. Jensen, Ammonia-assisted fast Li-ion conductivity in a new hemiammine lithium borohydride, $LiBH_4 1/2NH_3$, *Chem. Commun.*, 2020, **56**, 3971