## Improving the Interfacial Stability of Ultrahigh-Nickel Cathode with PEO-based Electrolyte by Targeted Chemical Reactions

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Fig. S1. SEM images of (a) LBO2-NCM and (b) LBO3-NCM.



Fig. S2. XRD patterns of LBO0-NCM and LBO1-NCM.



Fig. S3. Electrometric titration curve of LBO0-NCM and LBO1-NCM.



Fig. S4. XRD patterns of samples sintered with different mole ratio of  $H_3BO_3$  and LiOH  $\bullet$   $H_2O$ .



Fig. S5. The voltage curve of the three-electrode PEO-based SLMB during the measuring procedure of this study.



Fig. S6. The Nyquist plots of the three-electrode (a) Li|PEO|LBO0-NCM and (b) Li|PEO|LBO1-NCM.



Fig. S7. CV curves of the pristine (a) LBO0-NCM and (b) LBO1-NCM in the first three consecutive cycles between 2.8-4.3 V with a scanning rate of 0.05 mV s<sup>-1</sup>.



Fig. S8. Corresponding charge/discharge curves of Li|PEO|LBO1-NCM pouch cell at different electrochemical cycles.



Fig. S9. Cycling performance and the corresponding Coulombic efficiency at 0.5C of Li|PEO|LFP.



Fig. S10. The SEM images of the disassembled-lithium metal after 100 cycles in Li|PEO|LFP.