

## Supporting Information

# Synergistic Regulation of Bulk and Interfacial Properties in PEO Electrolyte by CaF<sub>2</sub> for Stable Lithium Metal Batteries

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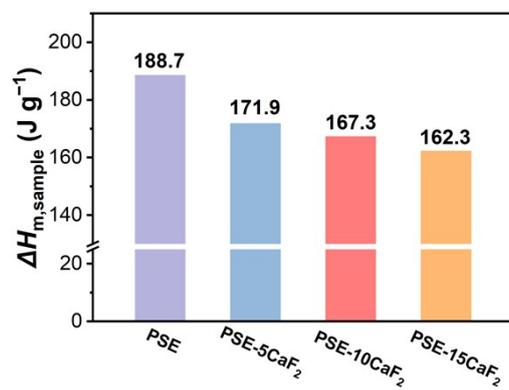
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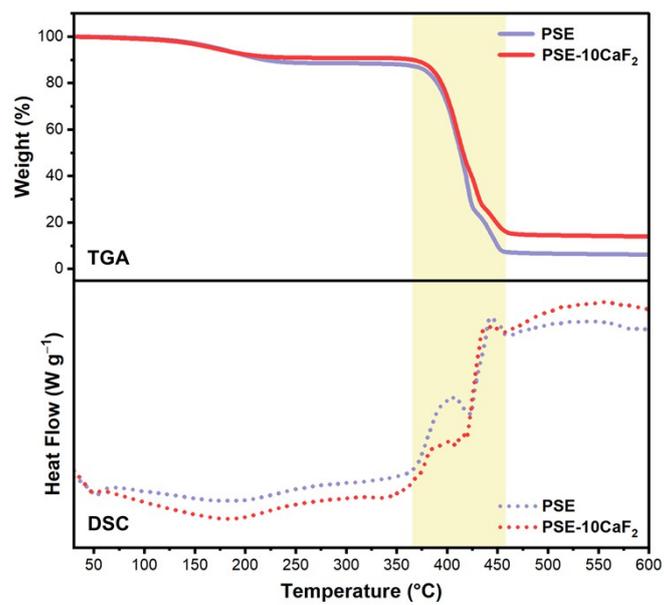
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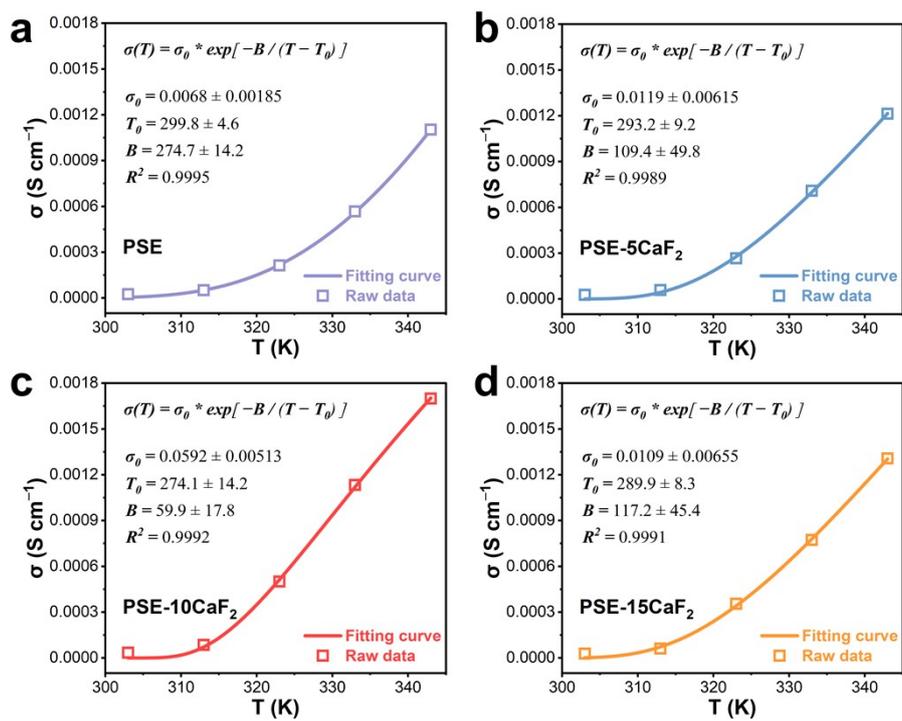
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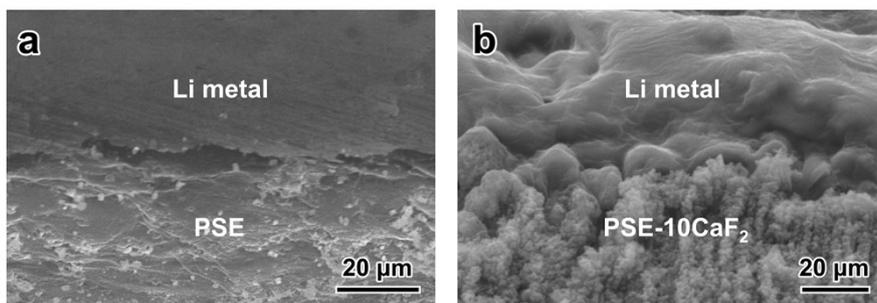
**Fig. S1.** Melting enthalpy of the PSE and composite electrolytes.



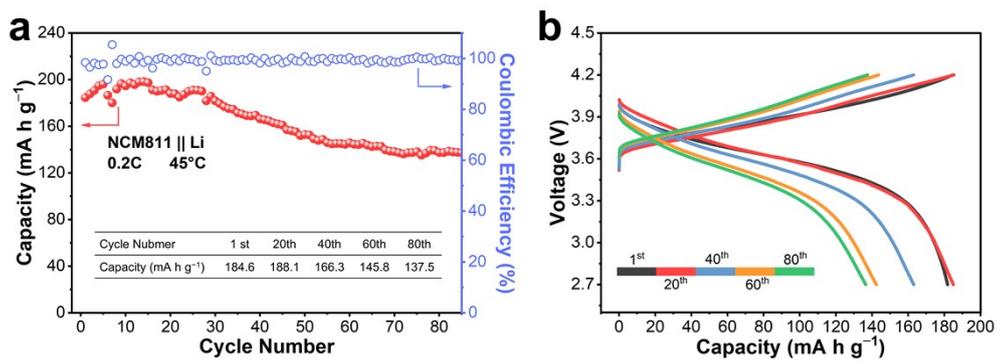
**Fig. S2.** Synchronous thermal analysis curves of PSE and PSE-10CaF<sub>2</sub> electrolytes.



**Fig. S3.** Temperature-dependent ionic conductivity fitting curve based on the Vogel–Fulcher–Tammann (VFT) model.



**Fig. S4.** Cross-sectional SEM images of the electrolyte/Li interface.



**Fig. S5.** (a) Long-term cycling performance of of NCM811||Li cell at 45 °C and 0.2 C rate. (b) Typical charge-discharge curves of NCM811||Li cell at different cycles.

**Table S1.** Comparison of the electrochemical performance of the full cell.

<b>Ref.</b>	<b>Temperature</b>	<b>Capacity retention (Rate)</b>	<b>Cycle number (Cathode)</b>	<b>Doi</b>
[S1]	60 °C	82.5% (0.5 C)	400 (LiFePO <sub>4</sub> )	10.1016/j.jcis.2025.01.270
[S2]	60 °C	84.7% (0.1C)	300 (LiFePO <sub>4</sub> )	10.1016/j.jcis.2024.12.236
[S3]	30 °C	95.0% (1.0 C)	160 (LiFePO <sub>4</sub> )	10.1021/acsaem.3c00371
[S4]	60 °C	94.9% (0.2 C)	200 (LiFePO <sub>4</sub> )	10.1016/j.nanoms.2023.01.001
[S5]	55 °C	85.7% (0.5 C)	600 (LiFePO <sub>4</sub> )	10.1002/advs.202404307
[S6]	40 °C	75.0% (0.2 C)	300 (LiFePO <sub>4</sub> )	10.1002/eem2.12580
[S7]	30 °C	92.5% (0.3 C)	300 (LiFePO <sub>4</sub> )	10.1021/acsami.4c22242
[S8]	25 °C	89.7% (0.3 C)	400 (LiFePO <sub>4</sub> )	10.1021/acsami.4c18304
[S9]	27 °C	80% (0.2 C)	228 (LiFePO <sub>4</sub> )	10.1016/j.jpowsour.2025.236249
[S10]	60 °C	78% (0.2 C)	200 (LiFePO <sub>4</sub> )	10.1016/j.ces.2023.118705
[S11]	60 °C	88% (0.5 C)	200 (LiFePO <sub>4</sub> )	10.1016/j.est.2024.114619
[S12]	60 °C	61% (0.5 C)	480 (LiFePO <sub>4</sub> )	10.1016/j.compscitech.2025.111432
[S13]	25 °C	77% (0.2 C)	300 (LiFePO <sub>4</sub> )	10.1016/j.cej.2025.169042
<b>This work</b>	<b>40 °C</b>	<b>98.1% (0.5 C)</b>	<b>300 (LiFePO<sub>4</sub>)</b>	

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