Electronic Supplementary Information

Ammonium fluoride induced barrier-free and oxygen vacancies enhanced LLZO powder for fast interfacial lithium-ion transport in composite solid electrolytes

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Additional Figures

Figure S1. Particle size distribution curve of pristine LLZO powder

Figure S2. Nyquist plot of Li$_{6.4}$Ga$_{0.2}$La$_{3}$Z$_{2}$O$_{12}$ pellet
Figure S3. TG curve of NH$_4$F powder

Figure S4. (a) XPS spectra of pristine LLZO powder. Surface elements contents (b); La 3d spectra (c); Zr 3d spectra (d) of LLZO, Ar environment annealed LLZO and NH$_4$F etched LLZO powder that detected by XPS.
Figure S5. Optical photograph of PVDF-LiTFSI-NH$_4$F etched LLZO, PVDF-LiTFSI-LLZO.

Figure S6. Morphologies of PEO-LiTFSI-LLZO membrane (a) were captured by SEM. The distribution of O, F and Zr respectively on surface of PEO-LiTFSI-LLZO membrane (b)-(d) were detected by EDX mapping.
Figure S7. Nyquist plots of PEO-LiTFSI-NH$_4$F etched LLZO (a); PEO-LiTFSI-LLZO (b); PEO-LiTFSI (c) membranes.

Figure S8. Detailed lithium-ion transference number data of PEO-LiTFSI-NH$_4$F etched LLZO membrane
Figure S9. LSV curves of PVDF-LiTFSI-NH₄F etched LLZO and PVDF-LiTFSI-LLZO

Figure S10. Arrhenius plots of PVDF-LiTFSI-NH₄F etched LLZO, PVDF-LiTFSI-LLZO and PVDF-LiTFSI.
Figure S11. EIS spectra of Li symmetric cells with PEO-LiTFSI, PEO-LiTFSI-LLZO, and PEO-LiTFSI-NH$_4$F etched LLZO membranes.

Figure S12. a) Cycling performance of different electrolytes coupled with NCM811 cathode and lithium metal anode at 0.2 C and b) corresponding voltage curves at first cycle.
**Additional Table**

**Table S1.** Ionic conductivity of PEO-LiTFSI, PEO-LiTFSI-LLZO and PEO-LiTFSI-NH₄F etched LLZO membranes under different temperatures.

<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>Ionic conductivity (10⁻⁴ S cm⁻¹) at different temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
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<tr>
<td>PEO-LiTFSI-NH₄F etched LLZO</td>
<td>1.93</td>
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<tr>
<td>PEO-LiTFSI-LLZO</td>
<td>0.279</td>
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<tr>
<td>PEO-LiTFSI</td>
<td>0.335</td>
</tr>
</tbody>
</table>

**Additional Experiment section**

*Preparation of PVDF matrix composite solid electrolytes:*

LiTFSI (Aladdin, 99.95%), and PVDF (Arkema, Kynar 761) were dried under vacuum at 80 °C for 24 h before use. PVDF solid electrolyte membranes were prepared via solution-casting method. PVDF and LiTFSI were dissolved in N, N-dimethylformamide (DMF) with weight ratio of 2:1 followed by ball-milling at 200 rpm for 3 h. After that, PVDF solid electrolytes solution was cast onto a Teflon mold (4 × 4 cm²) and then dried at 60°C for 24-36 h to evaporate solvent. PVDF-LLZO and PVDF-NH₄F etched LLZO composite electrolytes were prepared by adding different amounts of inorganic electrolytes into PVDF solid electrolytes solution. Then the suspension was ball-milled at 200 rpm for 12 h to ensure the fine dispersion before casting.