Supporting Information

High cathode utilization efficiency through interface engineering in all-solid-state lithium metal battery

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**Fig. S1 a,** Contour plot of 2D covariance analysis of HTXRD patterns. **b,** The corresponding *in-situ* XRD patterns with the appearance of new phase from 550 to 1000 °C and cooling down to 25°C.

**Fig. S2 a,** The typical particle of NCM622 MCG material. **b,** The corresponding high-resolution transmission electron microscopy (HRTEM) with the d spacing of 0.242 nm and **c,** selected area electron diffraction (SAED) pattern for the (101) plane of the red marked area of **a.**
Fig. S3 a, The SEM image and b, XRD pattern of the commercial LLZTO powder.

Fig. S4 The elemental mappings of La and Ni in the NCM622 MCG based composite cathode after co-sintering.

Fig. S5 a, The XRD pattern and b, SEM image of as-prepared LBO.
Fig. S6  

(a) Morphology of NCM622 spherical agglomerates.  
(b) The cross-sectional SEM images of the composite cathode with agglomerates and LLZTO particles after co-sintering.  
(c-d) The elemental mappings of Ni and La in the composite cathode after co-sintering.  
(e-f) The SEM images of the top surface of composite cathode before (insert) and after co-sintering.  
(g) The XRD patterns of composite cathode with LBO additive before and after co-sintering.
Fig. S7. The charge-discharge curves of NCM622 cathode material with a, MCG and b, agglomerates in the liquid electrolyte based batteries at the same current densities.

Table S1 The comparisons of electrochemical performces with LLZO supporting bulk-type ASSLMBs with NCM or LCO cathode material.

<table>
<thead>
<tr>
<th>Configuration of the solid state battery</th>
<th>Cathode</th>
<th>Temperature</th>
<th>Current density</th>
<th>Voltage Range (V)</th>
<th>Initial Capacity (mAh/g)</th>
<th>Cycles</th>
<th>Final Capacity (mAh/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCM623+LBO+ITO/LZTO/Li</td>
<td>agglomerates</td>
<td>80 °C</td>
<td>5 µA/cm²</td>
<td>3.0-4.6</td>
<td>123.3</td>
<td>5</td>
<td>76.6</td>
<td>[45]</td>
</tr>
<tr>
<td>NCM622+LBO+LLZTO/LLZTO/Gel/Li</td>
<td>agglomerates</td>
<td>RT</td>
<td>0.05 C (1C=115mA/g)</td>
<td>3.0-4.2</td>
<td>106</td>
<td>30</td>
<td>74.2</td>
<td>[46]</td>
</tr>
<tr>
<td>LCO+LLZTO+LCBO/LZTO/Li</td>
<td>micro-sized particles</td>
<td>100°C</td>
<td>0.05 C (1C=115mA/g)</td>
<td>3.0-4.05</td>
<td>106</td>
<td>40</td>
<td>67</td>
<td>[47]</td>
</tr>
<tr>
<td>LCO+LBO+ITO/LLZTO/O/Li</td>
<td>micro-sized particles</td>
<td>80°C</td>
<td>5 µA/cm²</td>
<td>2.8-4.3</td>
<td>69.6</td>
<td>1</td>
<td>69.6</td>
<td>[59]</td>
</tr>
<tr>
<td>NCM622+LBO+LLZTO/O/LLZO/Li</td>
<td>MCG</td>
<td>80°C</td>
<td>0.05 C (1C=180mA/g)</td>
<td>2.8-4.3</td>
<td>138.8</td>
<td>50</td>
<td>79 This work</td>
<td></td>
</tr>
</tbody>
</table>
**Fig. S8.** *a, c,* The cross-sectional SEM images after co-sintering and *b, d,* the corresponding charge-discharge curves of the composite cathode by co-sintering the mixture of NCM622 MCG, LLZTO particles and LBO powder with a weight ratio of 43:35:22 and 45:40:15 at 700 °C for 1h, respectively.
Fig. S9. **a**, The comparisons of EIS spectra of ASSLMBs constructed with NCM622 MCG material at the initial state and after 50 cycles. **b-d**, Cracking occurs in the composite cathode after 50 cycles.