Electrochemical Performance of Garnet based Lithium Metal Battery with Interface Modification.

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Supporting Information:
Figure S1: XRD pattern of pristine NMC (red). Li$_2$SiO$_3$ (blue) and composite cathode (black)
Figure S2: XRD pattern of pristine LLZA (red), Li$_2$SiO$_3$ (blue) and LS-LLZA (black)
Figure S3: Raman Spectrum of LLZA (blue) and LS-LLZA (red)
Table 1: Equivalent circuit and parameter of NMC||LS-LLZA-LS||NMC

<table>
<thead>
<tr>
<th>Component</th>
<th>Equivalent circuit parts</th>
<th>Capacitance</th>
<th>Resistance (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLZA</td>
<td>R1, R2, Q2</td>
<td>~10⁻¹² F</td>
<td>114</td>
</tr>
<tr>
<td>LS-LLZA</td>
<td>R3, Q3</td>
<td>~10⁻⁵ F</td>
<td>1308</td>
</tr>
<tr>
<td>NMC-LS</td>
<td>R4, Q4</td>
<td>~10⁻⁵ F</td>
<td>42.6</td>
</tr>
<tr>
<td>NMC</td>
<td>W5, Q5</td>
<td>~10⁻⁵ F</td>
<td></td>
</tr>
</tbody>
</table>

Figure S4:
Figure S5: Cole-Cole plot of LS-LLZA-LS. The impedance data’s were fitted with the equivalent circuit shown as inset in which $R_1$ corresponds to bulk resistance, $R_2$ corresponds to grain boundary impedance and $Q_2$ corresponds to constant phase element of LLZA,$R_3$ and $Q_3$ corresponds to charge transfer resistance and double layer capacitance on LS$||$LLZA interface.
Figure S6: Cole-Cole plot of Li||Au||LLZA||Au||Li symmetric cell after heat-treatment at 180 °C
Figure S7: $R_1$ corresponds to bulk resistance, $R_2$ grain boundary impedance and $Q_2$ corresponds to constant phase element of LLZA, $R_3$ and $Q_3$ corresponds to charge transfer resistance and constant phase element of LS||LLZA and Au||LLZA interface, $R_4$ and $Q_4$ corresponds to charge transfer resistance and constant phase element of LS||NMC and Au||Li interface and $W_5$ and $Q_5$ corresponds to diffusion impedance inside of cathode.
Figure S8: Charge-Discharge capacity of NMC||LLZA||Li all-solid-state cell without any interface modification.
Figure S9a:

Figure S9a: Cole-Cole plot of Li||GPE||LLZA||GPE||Li symmetric cell measured at 25 °C.
Figure S9b: Galvanostatic cycling performance of Li||GPE||LLZA||GPE||Li symmetric cell at a current density of 0.4 mA cm\(^{-2}\). The inset shows the zoom-in figure with a stable voltage response.
Figure S9c:

Figure S9c: Galvanostatic cycling of Li||LLZA||Li symmetric cell without any interface modification. Spike like structure are observed because of large polarization between LLZA membrane and Li metal resulting in poor contact.