Supporting Information

**Long Cycling Life Solid-State Li Metal Batteries with Stress Self-Adapted Li/Garnet Interface**

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Experimental Section

Materials

The used Ta-doped Garnet Li$_{6.5}$La$_3$Zr$_{1.5}$Ta$_{0.5}$O$_{12}$ (LLZTO) pellets with the diameter of 10 mm and the thickness of 1 mm were provided by Jining CreaTech Energy Technology Co. Ltd, Shandong, China. Compressible PDMS (polydimethylsiloxane) film with the thickness of 500 $\mu$m were acquired from Bald Advanced Materials Corporation, Zhejiang, China. Li foil with the thickness of 50 $\mu$m was used for PDMS/Li anode and Li foil with the thickness of 500 $\mu$m was used as the control without any compressibility.

Structural and morphology characterizations

X-ray diffraction (XRD) patterns of LLZTO pellets and compressible conductive foam were conducted by using Rigaku D/max-2500B2+/PCX system with CuK$_\alpha$ X-ray radiation. Surface morphology and cross-sectional analysis on the interface were performed on Hitachi S4800 field emission scanning electron microscopy (SEM) coupled with an energy dispersive X-Ray (EDX) spectrometer. Finite element simulation (COMSOL Multiphysics, COMSOL Inc.) was used to simulate the contact between Li anode and Garnet electrolyte with and without the assistance of compressible PDMS substrate.

Symmetric cell fabrication and measurements

To measure the ionic conductivity of Garnet LLZTO electrolyte, a thin
layer of Au was deposited on both side of LLZTO pellet to fabricate the
Au/LLZTO/Au Li-ion blocking cell. Electrochemical Impedance Spectra
(EIS) were recorded with an AC amplitude of 10 mV and a frequency
range from 1 MHz to 0.1 Hz. The symmetric cell was assembled into a
Swagelok cell. Both LLZTO pellets and the surface of Li electrode were
polished to remove the oxide layer and both sides of the pellets were
sputtered with Au then sandwiched with two compressible PDMS/Li
anodes or Li foil without any compressibility. The symmetric cells were
thermal treated at 180 °C for 20 min and naturally cooled down to room
temperature to assure Li fully alloyed with Au before testing.

**Full cell fabrication and measurements**

To fabricate the full cells, PDMS/Li anode was first integrated with
LLZTO electrolyte sputtered with Au. LiCoO$_2$ cathodes were prepared by
mixing LiCoO$_2$, Super P and polyvinylidene fluoride (PVDF) in the ratio
of 8:1:1 with N-methyl-2-pyrrolidone (NMP) as the solvent. The slurries
were then coated on Al foils and dried at 80 °C in vacuum overnight. Few
drops of 1.0 mol/L LiPF$_6$ in a mixture of ethylene carbonate (EC) and
diethyl carbonate (DEC) (v/v=1:1) as electrolyte was used to wet the
cathode/Garnet interface. NCM111 cathodes were prepared as the same
procedure by replacing LiCoO$_2$ into ternary NCM111. All the cells were
assembled in an Ar-filled glovebox with O$_2$ and moisture content below
0.1 ppm. The galvanostatic charge and discharge test was measured using
a cut-off voltage window of 3 to 4.2 V.

**ABAQUS simulation method**

The interface stability between PDMS/Li anode and Garnet electrolyte was simulated using the finite element method (FEM) in ABAQUS/Explicit module. Parameters are carefully chosen to make the model as close as possible to the actual experiments and simplify the simulation process at the same time. Following steps are taken to build the model to verify the experiment result. First, the experimental condition can be considered as a two-dimensional problem because of the periodicity of the load and geometry. Geometric model in the thickness direction was built according to the actual experimental situation (Figure S15). Material properties of Li metal used here is the perfect plasticity with the Young's modulus of 4 GPa and the yield strength of 0.5 MPa. Correspondingly, PDMS and Garnet electrolyte use linear elasticity with the Young's modulus of 8 MPa and 189.3 GPa, respectively (Figure S16). Second, the deformation caused by electrochemical plating and stripping can be considered as the mechanical deformation caused by stress or displacement when do not focus on the chemical reaction itself but the mechanical stability of the interface. According to the current density and capacity of the electrochemical reaction, we can calculate the displacement that should be applied.

\[ h = \int \frac{jV_{Li}}{F} dt \]
Here $j$ is the current density, $V_{Li}$ is the molar volume of Li and $F$ is Faraday's constant. The interaction property of the interface has been set as the ‘hard’ contact in the normal direction and contact with a coefficient of friction of 0.1 in the tangential direction. We counted the total contact area in real time during the simulation, which can be defined as the sum of all the facets where there is contact force. Finally, boundary value problem is solved by finite element method (FEM) using ABAQUS/Explicit module.
Table S1. Current density and cycling life of Li-Li symmetric cells modified with various strategies for negating anode/Garnet electrolyte interfacial impedance.

<table>
<thead>
<tr>
<th>Method</th>
<th>Current density/mA cm$^{-2}$</th>
<th>Cycling life/hour</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D Li-ion host</td>
<td>0.5</td>
<td>300</td>
<td>1</td>
</tr>
<tr>
<td>Li-Sn alloy anode</td>
<td>0.05</td>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td>Li-C composite anode</td>
<td>0.3</td>
<td>250</td>
<td>3</td>
</tr>
<tr>
<td>Nano-Si polished Garnet</td>
<td>0.1</td>
<td>220</td>
<td>4</td>
</tr>
<tr>
<td>Acid-treated Garnet</td>
<td>0.2 (30 °C)</td>
<td>700</td>
<td>5</td>
</tr>
<tr>
<td>Carbon-treated Garnet</td>
<td>0.3</td>
<td>450</td>
<td>6</td>
</tr>
<tr>
<td>Bilayer Garnet electrolyte</td>
<td>0.3</td>
<td>170</td>
<td>7</td>
</tr>
<tr>
<td>SPE interface layer</td>
<td>0.2 (90 °C)</td>
<td>700</td>
<td>8</td>
</tr>
<tr>
<td>Cu$_6$Sn$_5$ interlayer</td>
<td>0.25</td>
<td>300</td>
<td>9</td>
</tr>
<tr>
<td>Graphite soft interface</td>
<td>0.3</td>
<td>1000</td>
<td>10</td>
</tr>
</tbody>
</table>

Reference:
(5) Huo, H.; Chen, Y.; Zhao, N.; Lin, X.; Luo, J.; Yang, X.; Liu, Y.; Guo, X.; Sun, X. In-situ formed Li$_2$CO$_3$-free garnet/Li interface by rapid acid treatment for dendrite-free solid-state batteries. *Nano Energy* 2019, 61, 119-125.
2018, 17, 309-316.


Figure S1. Characterization of the LLZTO Garnet electrolyte. (a) SEM and digital images of LLZTO Garnet pellet; (b) XRD pattern and (c) EDS Mapping characterization of LLZTO Garnet pellet; (d) Ionic conductivity and physical parameters of the used LLZTO electrolyte at room temperature.
**Figure S2.** Optical illustration of the compressible PDMS/Li soft anode.

**Figure S3.** Cross-sectional SEM images for (a) Li|Garnet and (b) PDMS/Li|Garnet interface after 1000 cycles. Loose deposited Li layer and obvious microscopic voids were generated on Li|Garnet interface after cycling, while intimate contact for PDMS/Li|Garnet interface which is ascribed to the consecutive and moderate applied compressive stress.
**Figure S4.** Electrolyte crack in Li||Garnet||Li symmetric cells due to the unreleased localized stress during Li plating/stripping.

**Figure S5.** Surface morphology of Garnet electrolyte with dendrite propagation after cycling in Li||Garnet||Li symmetric cells in different resolution.
Figure S6. Electrochemical impedance of Li||bare Garnet||Li and PDMS/Li||bare Garnet||PDMS/Li batteries with bare Garnet electrolyte without any modification before melting into molten Li.
**Figure S7.** Critical current density of Li||Garnet||Li symmetric cells with the current density step increased from 20 to 500 μA cm⁻².

**Figure S8.** Typical charge/discharge curves of PDMS/Li||Garnet||PDMS/Li batteries at current density of 0.2 mA cm⁻² over long-term cycles.
Figure S9. Electrochemical impedance comparison of Li||Garnet||Li batteries before and after different cycles.

Figure S10. Long-term cycling performance of PDMS/Li||Garnet||PDMS/Li symmetric cells at high current density of 0.3 mA cm$^{-2}$ at room temperature.
**Figure S11.** Hysteresis comparison of PDMS/Li||Garnet||PDMS/Li symmetric cells at different current densities of 0.1 mA cm$^{-2}$, 0.2 mA cm$^{-2}$ and 0.3 mA cm$^{-2}$.

**Figure S12.** SEM images of the conductive compressible foam under different resolution.
Figure S13. EDS mapping of the conductive compressible foam.

Figure S14. XRD characterization of the conductive compressible foam.
**Figure S15.** Schematic illustration of compressible CF scaffold in stabilizing the Li/Garnet interface.

**Figure S16.** Electrochemical impedance spectra comparison of CF/Li||bare Garnet||Li and Li||bare Garnet||Li symmetric batteries.
**Figure S17.** Cycling performance of CF/Li||Garnet||Li symmetric cell at the current density of 0.01 mA cm$^{-2}$ with 0.2 mAh cm$^{-2}$ Li pre-deposited onto the conductive compressible foam current collector.

**Figure S18.** Hysteresis comparison of Li||Garnet||Li and CF/Li||Garnet||Li symmetric cells at 0.01 mA cm$^{-2}$. 
Figure S19. Schematic showing the modeling of stress self-adapted interface between PDMS/Li anode and Garnet electrolyte.

Figure S20. Cross-sectional SEM image of Li/Garnet interface after 0.2 mAh cm$^{-2}$ Li stripping.
Figure S21. Full cell performance of Li||bare Garnet||LiCoO$_2$ and Li||bare Garnet||NCM111 cells at 1C rate.