# Supporting Information

## Engineering Lithiophilic Ni-Al@LDH Interlayers on Garnet-type Electrolyte for Solid-State Lithium Metal Batteries

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**Experimental Section**

**Preparation of garnet SSE.** The cubic $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) SSE pellets were synthesized via traditional solid-phase sintering (Ramakumar et al., 2017 , Thangadurai et al., 2003). Afterwards, the LLZTO pellets were sanded and polished by sandpaper and stored in an Ar-filled glovebox to avoid the formation of contaminant layers.

**Preparation of Ni-Al@LDHs.** The Ni-Al@LDHs were synthesized via a typical wet-chemical method(Wang et al., 2017). Briefly, $Ni(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and urea with an appropriate molar ratio were dissolved in 500 mL of deionized water. The resulting solution was transferred into a three-necked flask, refluxed at 95 °C for 12 hours and then cooled down to room temperature. The as-synthesized products were collected by centrifugation. Finally, a homogeneous colloid solution (1.0 wt.%) was obtained by dispersing the Ni-Al@LDHs into anhydrous ethanol via ultrasonication.

**Interfacial modification of SSE.** At first, a dense Ni-Al@LDH layer was deposited onto the surface of LLZTO pellets via spray deposition, and dried at 60 °C for 24 h in a vacuum oven. Afterwards, the modified LLZTO pellets were transferred into an Ar-filled glovebox and heated to 300 °C on a heating plate for 30 min. Following this step, the Ni-Al@LDHs modified LLZTO (NA-LLZTO) SSEs were put into molten lithium under mechanical stirring. Finally, the lithium-plated LLZTO pellets were used as the anode and SSE for further electrochemical tests.

**Materials characterization.** X-ray diffraction (XRD) measurement was carried out on a X-ray diffractometer (Rigaku D/max 2500 PC, Cu Kα radiation (λ = 1.5406 Å )). The morphology was investigated using a scanning electron microscope (SEM) (ZEISS AURIGA FIB/SEM) with an accelerating voltage of 5 kV. The energy dispersive spectrometer (EDS) was used to characterize the elemental distributions of the materials with an accelerating voltage of 20 kV. Thermogravimetry (TG) (TG, 209, F3 Tarsus) was used to test the thermal stability of materials.

**Electrochemical measurements.** Electrochemical impedance spectroscopy (EIS) was collected by an Autolab PGSTAT302N Analyzer with a frequency range from 1 MHz to 0.1 Hz by applying an AC voltage with amplitude of 10 mV. The Li//Li symmetric batteries and full cells with LFP or Li-rich cathodes were evaluated using a Neware battery tester (Shenzhen Neware Electronics Co., China) at 25 °C. The cutoff voltage is 2.5-4.0 V for LFP cathodes and 2.0-4.6 V for Li-rich cathodes.

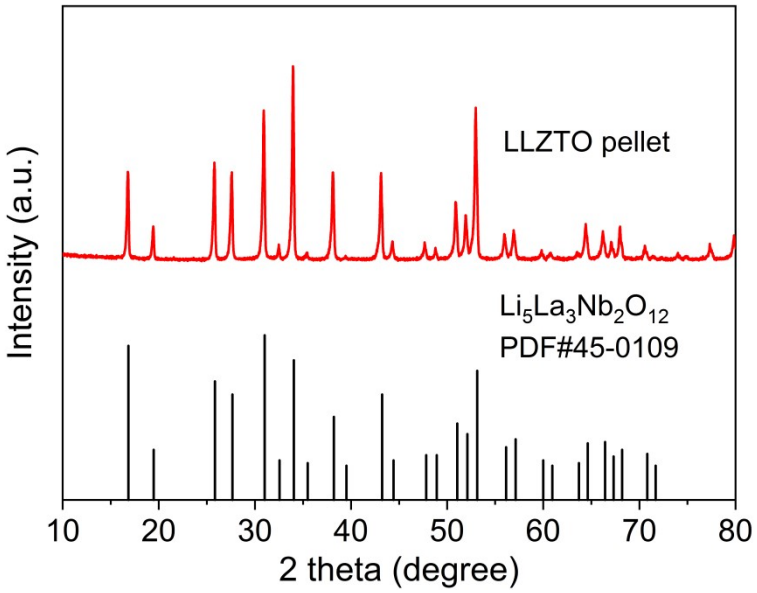


**Fig. S1**. XRD pattern of LLZTO pellet.

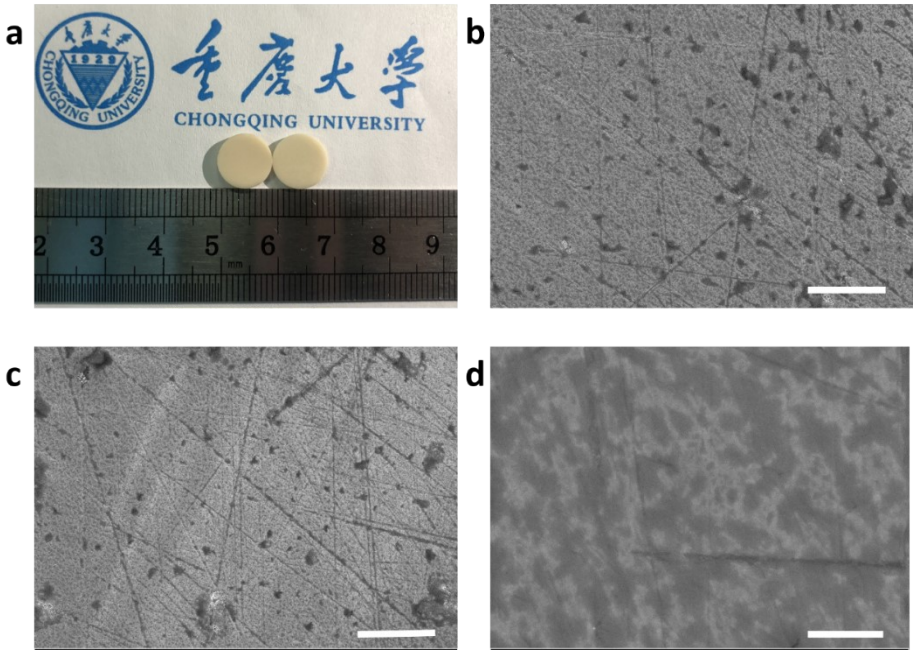


**Fig. S2**. (a) LLZTO optical photo. (b, c, d) LLZTO surface under different magnification. (b, c) Scale bar: 20 μm; (d) Scale bar: 2 μm.

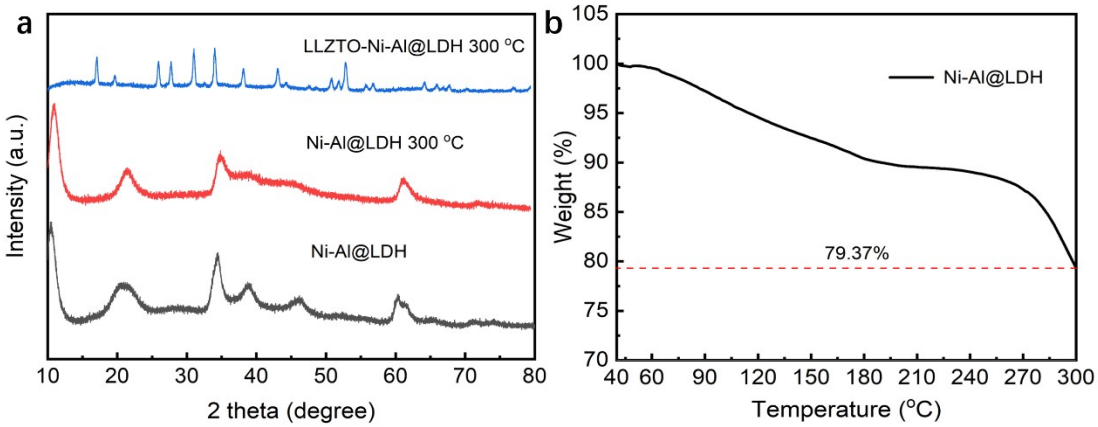


**Fig. S3**. (a) XRD of LDHs, LDHs after 300 °C heating, LDHs in LLZTO. (b) TG curve of LDHs.

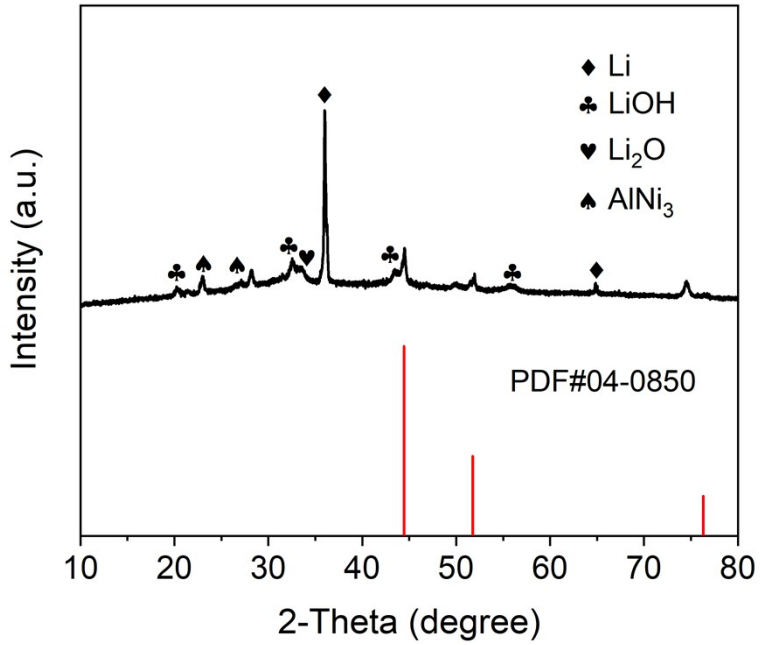


**Fig. S4**. The XRD phase of the reaction product of LDH and lithium at 300 °C.

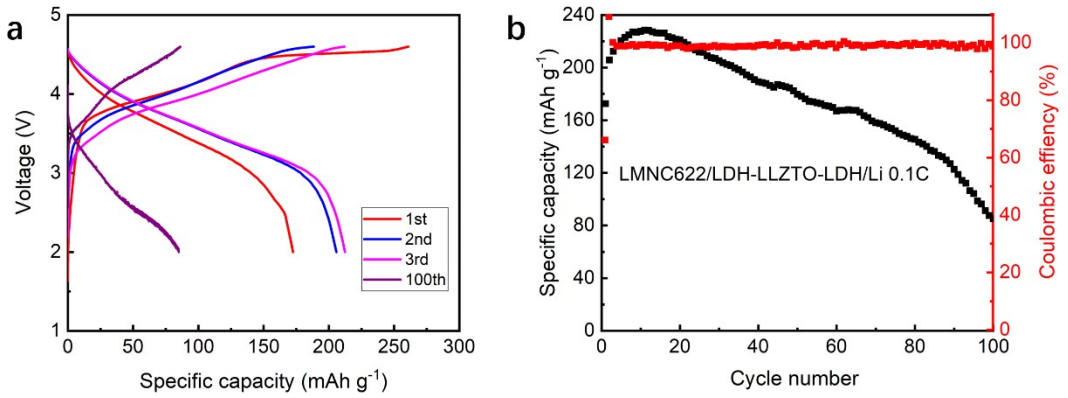


**Fig. S5**. The cyclic performance of the LMNC622/LDH-LLZTO-LDH/Li battery at 0.1C.

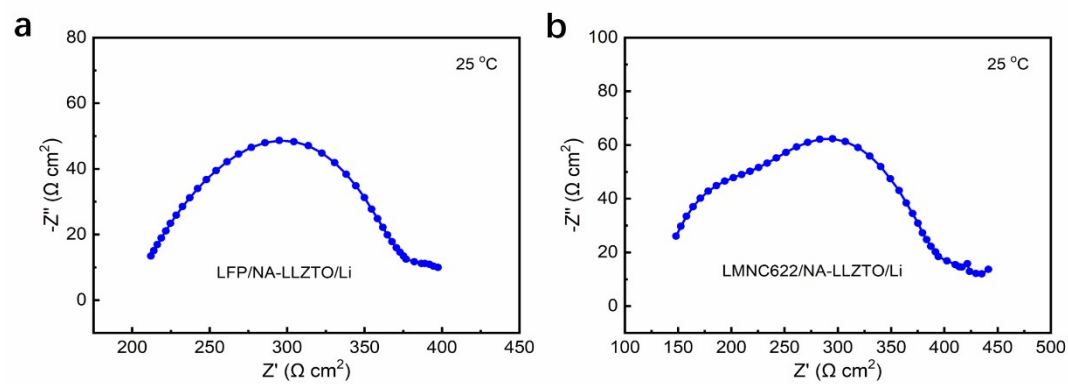


**Fig. S6**. The EIS of full battery. (a) LFP/NA-LLZTO/Li. (b) LMNC622/NA-LLZTO/Li .

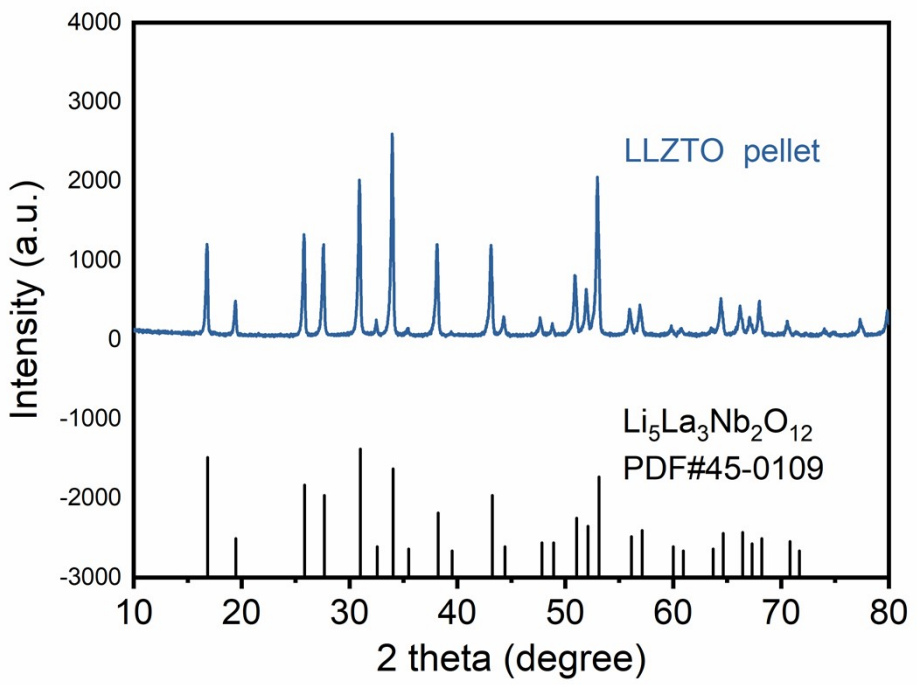


**Fig. S7**. The XRD of LLZTO after the alcohol.

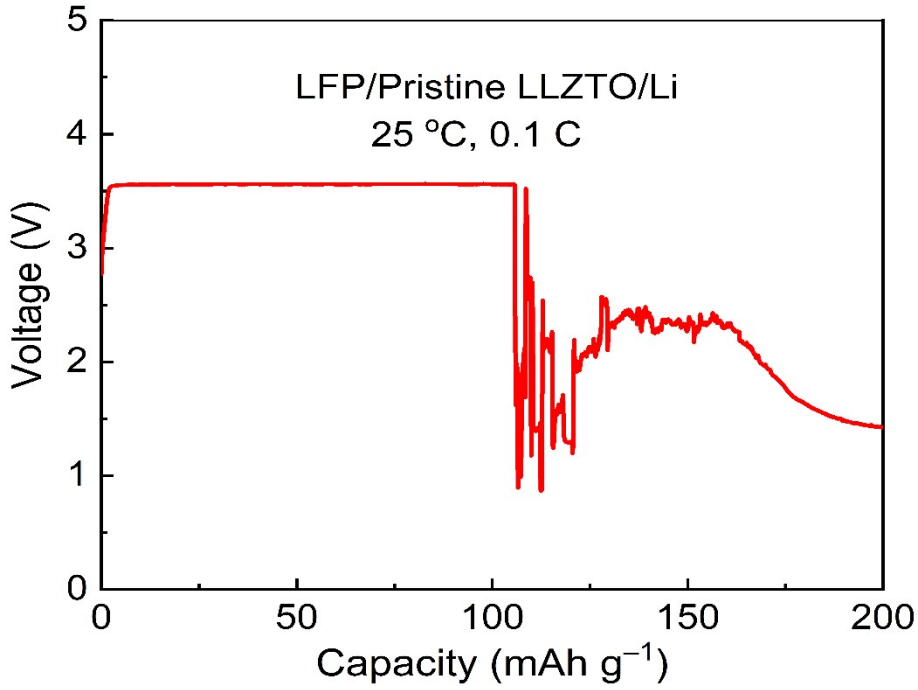


Fig. S8. The full battery of Pristine LLZTO.

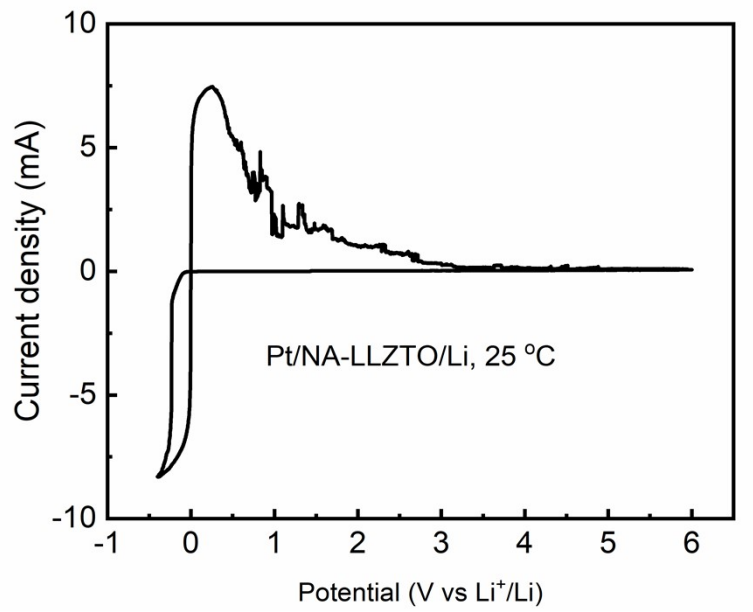


Fig S9. CV of Pt/NA-LLZTO/Li at 25 °C.

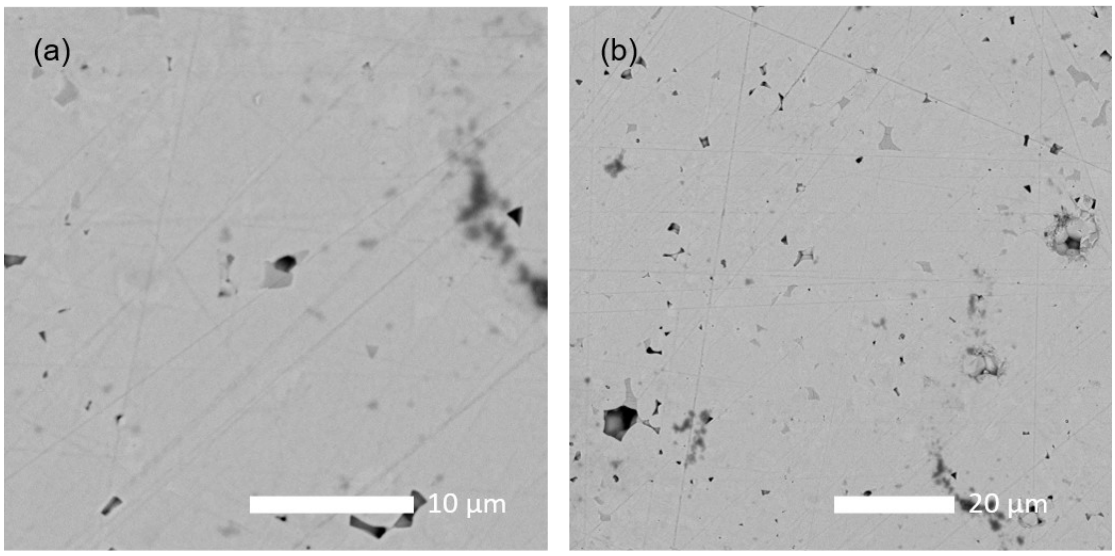


Fig S10. The surface morphology images of NA-LLZTO electrolyte membrane before the cycles.

**References**:

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