

Supporting Information

Conversion Inorganic Interlayer of LiF/Graphene Composite in All-Solid-State Lithium Batteries

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Abstract: The issues at the interface between solid-state electrolyte (SSE) and electrodes limit the development of all-solid-state lithium batteries (ASSLBs). Herein, we report a LiF/graphene inorganic composite interlayer (ICI) which is in situ constructed at cathode/garnet interface by electrochemical pre-lithiation of fluorinated graphene (GF). The ICI with flexibility and ion-conductivity can improve the contact between cathode and garnet electrolyte, and thus enables the ASSLB stably operating for 60 cycles without any liquid conditions .

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Experimental Section

Preparation of solid electrolyte

The dense and highly conducting garnet electrolytes of $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (LLZTO) was prepared by the previous methods^{1, 2}. Specifically, stoichiometric amounts of $\text{LiOH}\cdot\text{H}_2\text{O}$ (Aladdin Reagent, 99.99%), $\text{La}(\text{OH})_3$ (Aladdin Reagent, 99.95%), ZrO_2 (Aladdin Reagent, 99.99%), Ta_2O_5 (Aladdin Reagent, 99.95%) and 15 wt.% excess of LiOH were mixed and ball milled in isopropanol for 12 h. They were dried and calcined in air at 900°C for 12h to form the cubic LLZTO phase. These powders underwent hot-press sintering in a carbon die at 1150°C and 20 MPa for 1h under Ar atmosphere. The obtained LLZTO ceramics were processed into lamellar disks with the diameter of 1.2 cm and the thickness of 0.1 cm for battery testing. Optical photo of LLZTO disk is shown in the inset of figure S1a.

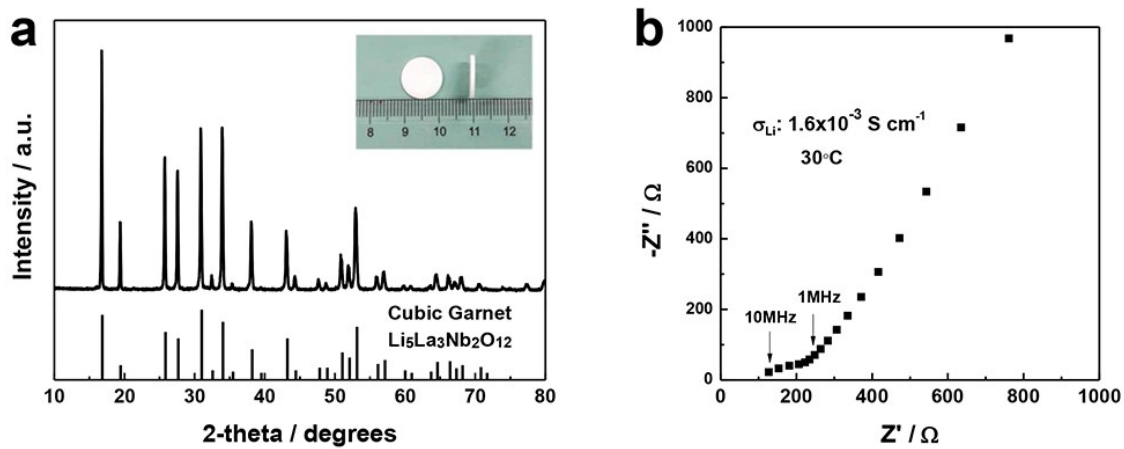
Interface layer construction and Battery assembly.

The 2 mg/ml fluorinated graphene (GF) suspension was obtained by sonicating ~10 mg GF powder (Zhongshan Ptoelectric Material Co.Ltd) in 5 ml N-Methyl-2-pyrrolidone (NMP) using the pulse mode (1s on, 1s off, 20% amplitude) of a probe sonicator (Ultrasonic Homogenizer, model: JY92) for 20 minutes. The composite cathodes slurry was prepared by stirring carbon-coated LiFePO_4 (LFP), ketjen black (KB), $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ (LiTFSI) (Aladdin Reagent, 99.9%), poly(vinylidene fluoride) (PVDF) (Sigma-Aldrich) at a mass ratio of 6:1.5:1.5:1 for 12 hours. The slurry concentration was controlled at 60 mg/ml by adding an appropriate amount of NMP. The two suspensions prepared were coated on one side of the fresh-polished LLZTO ceramic disks in turn, and each layer was dried under vacuum at 60°C for 3 hours and then dried at 80°C for 12 hours to remove NMP. Finally, the load of fluorinated graphene on the LLZTO is around 0.05 mg cm^{-2} and the load of the composite cathode is around 0.6 mg cm^{-2} . In order to assemble the all-solid-state battery, the other side of the ceramic disks was sputtered with a layer of SnO_2 in advance and coated with Li-metal anode by heat treatment, as mentioned in the prior literature³. Finally, the laminated all-solid-state lithium batteries were vacuum encapsulated in the aluminum-plastic composite membrane with stainless steel as a current collector. The assembled ASSLB (Li- SnO_2 /LLZTO/GF/LFP) was placed in a 60°C oven for 6 hours, and then discharged at a constant current of $5\text{ }\mu\text{A cm}^{-2}$ to 2 V by the Land battery tester to achieve the pre-lithiation. The pre-lithiated ASSLB (Li-

SnO₂/LLZTO/Gr-LiF/LFP) was used for electrochemical performance testing. For comparison, we assembled Li-SnO₂/LLZTO/LFP ASSLB and Li-SnO₂/LLZTO/Gr/LFP ASSLB. The 2 mg/ml graphene (Gr) (ACS MATERIAL, LLC) suspension was prepared in the same method as GF.

Material characterization and Electrochemical analysis

The crystal structure of LLZTO disk was measured by X-ray diffraction (XRD, Bruker D2 Phaser), using the Cu K α radiation with 2θ at a scan rate of 4° min⁻¹. Scanning electron microscopy (SEM, SU8220) was used to observe the surface and cross-section morphology of the interlayer before and after pre-lithiation and it was also used for EDS mapping analysis. X-ray photoelectron spectroscopy (XPS, ESACLAB-250) was performed in order to investigate the composition of the interface layer before and after pre-lithiation, and the microscopic morphology and electron diffraction pattern were collected through a transmission electron microscope (TEM, JEM-2010F). Samples of the interface layer were scraped from the LLZTO ceramic disks and then stored in an argon-filled aluminum plastic bag before testing. Electrochemical impedance spectroscopy (EIS) measurements were recorded by an Autolab instrument in a frequency range of 1MHz to 0.1Hz with an amplitude of 10 mV. Galvanostatic charge-discharge performances of the all-solid-state batteries were investigated using a Land battery tester (LAND, CT2001) with the potential range from 2.8V to 3.8V at 60 °C. Prior to testing, the batteries were rested in a thermostatic oven for 6h to reach the set temperature.



Figures

Figure S1. (a)The XRD pattern of the LLZTO ceramic disk and the diffraction pattern of cubic garnet $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$ (PDF#45-0109) is labelled as a reference; The inset is the optical photo of LLZTO. **(b)** The impedance spectra of LLZTO ceramic pellet measured at 30 °C with Au blocking electrodes.

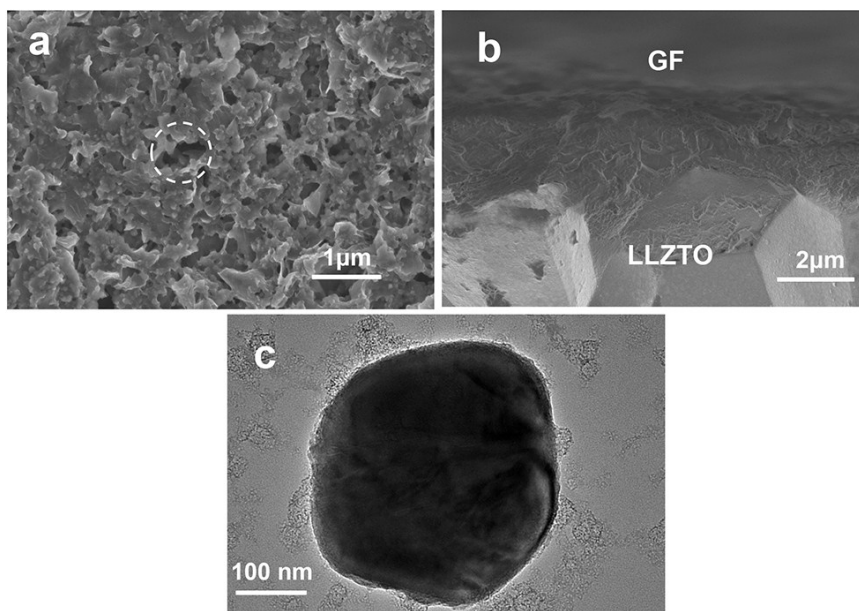


Figure S2. (a) Surface morphology and (b) Cross-section SEM image of the LLZTO pellets coated with GF. (c) TEM image of LiFePO₄.

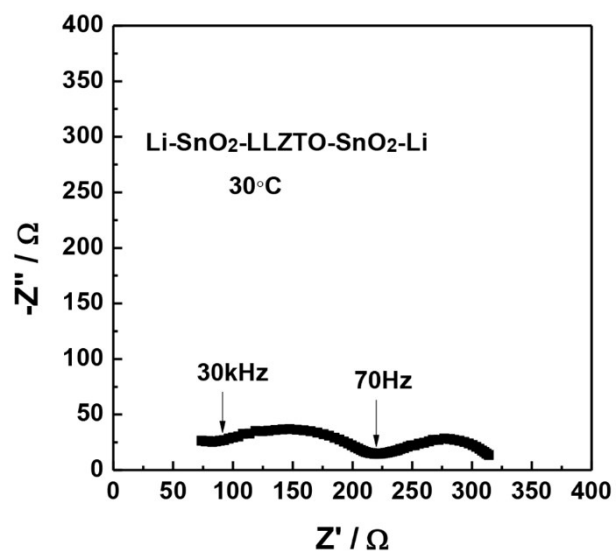


Figure S3. The impedance spectra of symmetric garnet cells with Li electrodes.

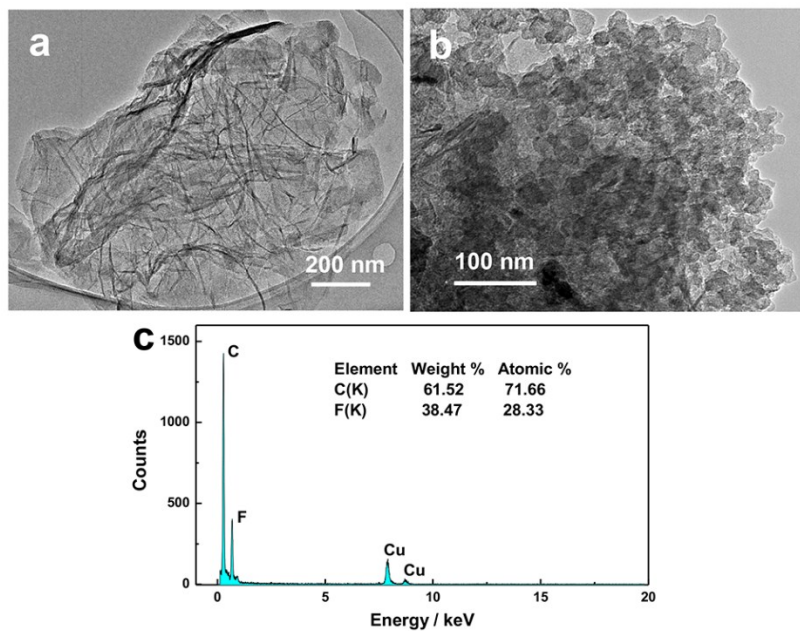


Figure S4. (a) TEM image of the GF, (b) TEM image of the Gr-LiF converted by the GF. (c) Energy dispersive X-ray (EDX) analysis of GF.

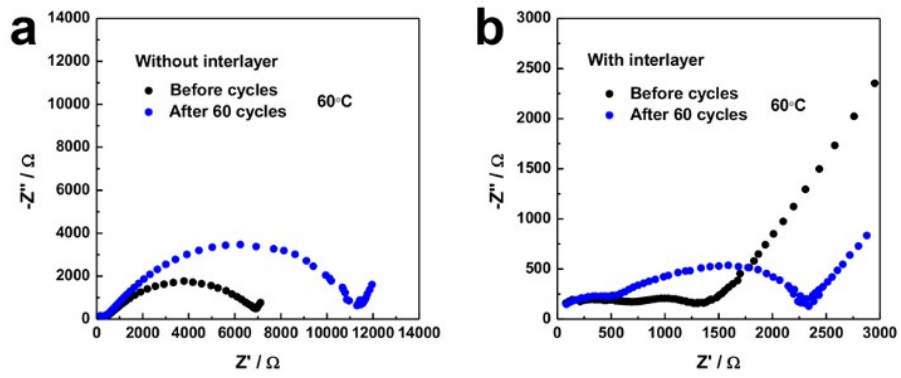


Figure S5. The impedance of ASSLB (a) without and (b) with ICI before and after cycling.

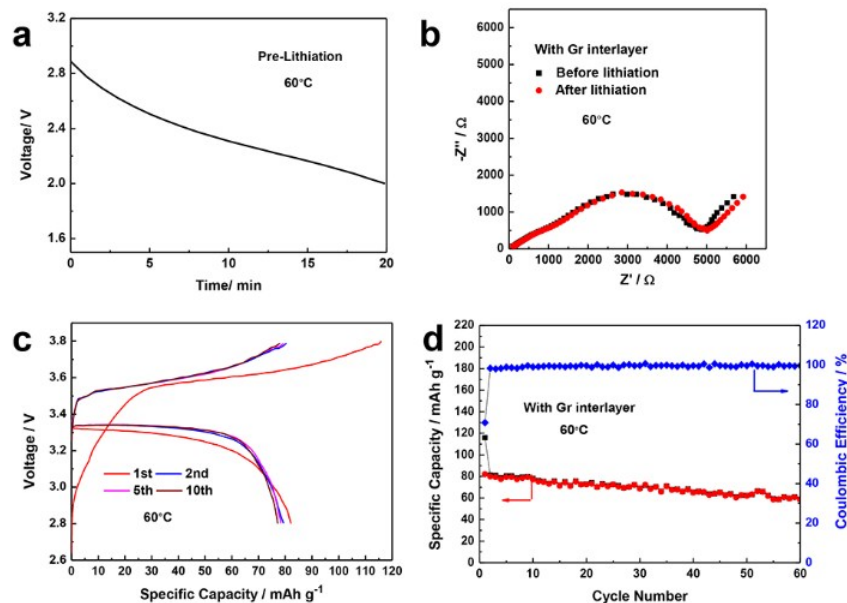


Figure S6. (a) Discharge curve of the pre-lithiation process at 60 °C. (b) The EIS profiles of ASSLB with Gr interlayer before and after pre-lithiation at 60 °C. (c) Galvanostatic discharge and charge curves and cycling performance of the ASSLB with Gr interlayer, measured at 0.05C and 60 °C.

As shown in the Fig. a-b, The ASSLB with Gr interlayer does not have a discharge platform during the pre-lithiation process. The impedance of ASSLB is $5472 \Omega \text{ cm}^2$, and there is no significant change before and after pre-lithiation, which indicates that no conversion reaction occurred between 2.88 V to 2 V. The constant current charge-discharge test is shown in Fig. c-d. We can find that the polarization voltage is 0.23V, the discharge capacity in the first cycle is 82.1 mA h g^{-1} , and the capacity retention rate is 71% after 60 cycles.

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