Design of a mixed conductive garnet/Li interface for dendrite-free

solid lithium metal batteries

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Experimental

Fabrication of LLZTO-Cu₃N

Ta-doped garnet Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ (LLZTO) powders and dense pellets were prepared as reported in our previous work ¹. The Cu₃N layer was deposited on the polished LLZTO pellets by magnetron sputtering (JGP-450A) with the mode of direct current at room temperature. The target was Cu (99.999%). And a mixture of Ar/N₂ = 1:1 (v/v) was used as the working gas. The base pressure in the sputtering chamber was approximately 3×10^{-4} Pa. The power and the working pressure of deposition were 30 W and 0.25 Pa, respectively.

Materials characterizations

Crystal structures of samples were examined by X-ray diffraction (XRD, Bruker D2 Phaser), using Cu K α radiation with 2 θ in the range of 10°~80° and a step size of 0.02°. Surface and cross-section morphologies of the LLZTO pellets were investigated by scanning electron microscopy (SEM, S3400). The TOF-SIMS test was conducted using TOF-SIMS IV (ION-TOF GmbH, Germany) with a 25 keV bismuth liquid metal ion source and a base pressure at ~10⁻⁸ mbar in the analysis chamber. The negative secondary ions were induced by the primary ion beam bombardment on the surface of LLZTO. The analysis area was 334 µm × 334 µm. Depth profiles were obtained by sputtering ion beams of Cs⁺ (3 keV) on a 100 µm × 100 µm square. The sputtering rate was obtained on a Si wafer as 0.96 nm s⁻¹ with a sputtered area of 100 µm × 100 µm. X-ray photoelectron spectroscopy (XPS, ESCALAB-250) and TEM (JEOL, JEM-ARM 200F) analyses were performed to characterize the composition and

microstructure of the MCL.

In order to investigate the interface between LLZTO ceramic pellets and Li metal, the detailed procedures for SEM samples preparation are shown as follows: The Li metal on the LLZTO pellets was melted at 200 °C for 30 min and then cooled down to room temperature. The LLZTO pellets with Li metal were fractured using a thin-tipped tweezer. The cross-sectional samples, which showed the same heights of LLZTO and Li metal, were chosen for SEM investigation. Note that a thin Li metal is good for sample preparation considering its high toughness compared with LLZTO pellets.

To investigate the Li dendrite growing along the grain boundary of LLZTO ceramic pellets, the detailed procedures for SEM samples preparation are shown as follows: The short-circuited cells were disassembled in the Ar-filled glovebox. After completely removing the attached Li metal on the LLZTO pellets by sanding, "dark spots" were observed on the white LLZTO surface, indicating the endpoints Li dendrites penetration. The LLZTO pellets were fractured at a "dark spot" position using a thin-tipped tweezer. The cross-sectional sample with a "black line" along the grain boundary was chosen for SEM investigation.

Simulation method

The simulation was performed using the finite element method implemented in the commercial software Ansys (Ansys Workbench 2019 R2). The dendrite was modeled by an axisymmetric section of a cone with 10 degrees opening angle. A voltage of 5V was applied to the top nodes of the lithium electrode, and the lower nodes of the electrolyte were grounded (0 V). We considered two systems: an Li dendrite immersed

in i) an LLZTO electrolyte and ii) a Li_3N/Cu interlayer. The interface between the interlayer and electrolyte was assumed to be flat. Table S2 lists the resistivities of various components that were used for our simulation. The resistivity of Li_3N/Cu interlayer was estimated by applying the parallel equivalent of the law of mixtures²:

$$\frac{1}{\sigma_i} = \frac{\nu_{Cu}}{\sigma_{Cu}} + \frac{\nu_{Li_3N}}{\sigma_{Li_3N}} \tag{1}$$

where ν and σ are the volume fraction and conductivity of each component of the interlayer, respectively. The parallel approximation was chosen since the proportion of Cu in the interlayer was estimated to be 43.7 vol.%, which is higher than the percolation threshold. The interlayer resistivity was calculated to be $3.9 \cdot 10^{-6} \Omega$ cm.

Electrochemical performance tests

Ionic conductivities of the LLZTO samples were measured by an impedance analyzer (Novocontrol Beta High Performance Impedance Analyzer) with an AC of 10 mV from 0.1 to 20 M Hz in frequency. Thin gold layers on both surfaces of ceramic pellets were performed by magnetic sputtering as electrodes before the conductivity test. The LLZTO-Cu₃N pellets were sandwiched between two pieces of Li metal to construct the symmetric cells. Li metal electrodes were melted onto the two sides of the LLZTO-Cu₃N pellets at 200 °C for 30 min in an Ar-filled glovebox before sealing in Swagelok-type cell mold. A pressure of approximately 10 N cm⁻² was exerted on the ceramic plates via springs to keep close contact. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 1 MHz to 0.1 Hz with an amplitude of 10 mV by an Autolab instrument. Galvanostatic cycling tests were conducted using an Arbin battery cycler under different current densities at 25 °C. Li/LLZTO/Li symmetric cells were also fabricated and cycled under the same procedure as a comparison.

The composite cathode was prepared as follows: firstly, 0.3 M Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma-Aldrich) was dissolved in ionic liquid (IL) (PY14TFSI, Sigma-Aldrich) to obtain a homogeneous IL-0.3M solution. Then, The LiCoO₂ (LCO), super P conductive additive (SP), Polyvinylidene Fluoride (PVDF) and IL-0.3M with the weight ratio of LCO: SP: PVDF: IL-0.3M = 8: 1: 1: 6 were ground thoroughly in the mortar. Finally, the toothpaste-like slurry was coated on Al foils to form the composite cathode with the active materials of approximately 2 mg cm⁻².



Fig. S1 a) EIS spectrum of the unmodified LLZTO pellet at 25 °C. b) Cross-sectional SEM image of the LLZTO pellet.



Fig. S2 EIS spectra of Li/LLZTO-Cu₃N/Li with different deposition times (10 s, 30 s, 1 min, 2 min).



Fig. S3 Cross-sectional view of the sputtered volume of LLZTO-Cu₃N.



Fig. S4 XRD pattern of MCL by Cu₃N reacting with molten Li on a glass plate.



Fig. S5 EIS spectra of a) LLZTO-MCL/Li interface and b) LLZTO/Li interface in a temperature range from 25 to 75 °C.



Fig. S6 a) Optical image and b-c) SEM images of the LLZTO pellet after short circuit. The Li metal electrodes were removed by sanding.



Fig. S7 a) EIS spectrum, b) cross-sectional SEM image of the LLZTO-MCL/Li interface after 1000 h cycling under 0.1 mA cm⁻² at 25 °C. c) Optical image of cycled LLZTO after sanding.



Fig. S8 Galvanostatic cycling performance of Li/LLZTO-MCL/Li cells under different current densities at 25 °C.



Fig. S9 Schematic construction of SSBs with a Li metal anode, an LLZTO-MCL electrolyte, and an LCO cathode.



Fig. S10 EIS spectra of the LCO/LLZTO-MCL/Li and the LCO/LLZTO/Li cells at 25 °C.



Fig. S11 Charge/discharge curves of the LCO/LLZTO-MCL/Li and the LCO/LLZTO/Li cells at various current rates.

Interfacial modification	Interfacial resistance $(\Omega \text{ cm}^2)$	CCD (mA cm ⁻²)	Stability (RT) (mA cm ⁻² /lifetime in h)	Ref
Bare LLZTO	1138.5	0.1	0.1/8	
Sputtering Au	101.6/167.8	0.5	0.08/150	3
ALD Al ₂ O ₃	34	N/A	0.2/90	4
PECVD Si	127	0.2	0.1/225	5
ALD Al	75	0.2	0.2/42	6
Drawing Soft graphite	105	N/A	0.3/1000	7
Co-sputtering Cu ₆ Sn ₅	236	N/A	0.25/300	8
Polishing MoS ₂	14@100 °C	2.2@100 °C	0.8/240@100 °C	9
PECVD Li ₃ N	175	N/A	0.1/210	10
Sputtering Cu ₃ N	83.4	1.2	0.5/400	This work

Table. S1 Comparison on critical current densities (CCD) and cycling stabilities between our work and recent publications.

Table. S2 Considered resistivities of various components for modeling current densities in LLZTO/Li dendrite and LLZTO-MCL/Li dendrite.

Material	Resistivity (Ω cm)	Ref
Li	9.28×10 ⁻⁸	11
Cu	1.68×10 ⁻⁸	12
Li ₃ N	109	13
LLZTO	109	14

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