Electronic Supplementary Information for

Surface Coating of $LiMn_2O_4$ Cathodes by Garnet Electrolytes for Improving Cycle Stability of Solid Lithium Batteries

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Experimental Section

Materials synthesis

The cubic garnet $Li_{6.375}La_3Zr_{1.375}Nb_{0.625}O_{12}$ electrolyte coated $LiMn_2O_4$ (LMO@LLZNO) cathode was synthesized by a facile one-step sol-gel process. Stoichiometric $LiNO_3$ (10% excess was added to compensate for Li loss), $La(NO_3)_3{\cdot}6H_2O$, $ZrOCl_2{\cdot}8H_2O$, and $NbCl_5$ were completely dissolved in deionized water through vigorous stirring. Citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$) was added to the precursor solution, the amount of which was twice the total moles of cations. Magnetic stirring was then carried out at 50 °C for 4 h until a transparent sol was formed. $LiMn_2O_4$ powder was further added into a certain amount of sol (2 wt%) followed by fully stirring at 50 °C. Afterwards, the solvent was evaporated at 80 °C until a quite viscous wet gel was obtained. The wet gel was then completely dried at 100 °C for 4 h in an oven. Finally, the dried powder was sintered at 850 °C for 6 h at a muffle furnace, followed by naturally cooling to room temperature to obtain the final LMO@LLZNO.

The garnet $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) pellet was prepared by solid-state reaction and hot-pressing sintering as described in our previous reports.[S1] Briefly, stoichiometric $LiOH{\cdot}H_2O$ (15% excess), $La(OH)_3$, ZrO_2, and Ta_2O_5 were uniformly mixed and ball-milled followed by sintered at air atmosphere at 950 °C for 12 hours to form cubic LLZTO powder. The powder was then hot-pressing sintered in a carbon die at 1150 °C for 1 h at 20 MPa under Ar atmosphere to obtain LLZTO pellets with 1 mm in thickness and 12 mm in diameter.

Materials characterization

The X-ray diffraction (XRD) patterns were obtained using a high-resolution Bruker D8 discover diffractometer equipped with Cu $K_{\alpha 1}$ radiation (λ = 1.5406 Å). The morphologies and compositions were detected by a JEM-2100F transmission electron microscopy (TEM), and a Hitachi S-4800 scanning electron microscope (SEM) equipped with a scanning transmission electron microscopy (STEM) and an energy dispersive spectrometer (EDS).

Electrochemical measurements and batteries assembly

The Li^+ conductivity of the LLZTO pellet was measured by a Princeton electrochemical workstation at frequency ranging from 7 MHz to 0.01 Hz between 30 °C to 80 °C with Ag symmetric blocking electrodes. Linear sweep voltammetry (LSV) from 2.8 to 8.0 V at a scan rate of 10 mV s^{-1} was also recorded by a Princeton electrochemical workstation with the cell configuration of Ag/LLZTO/Li. The mixed cathode slurry was consisted of 90 wt% active cathode material, 5 wt% Super P and 5 wt% polyvinylidene fluoride (PVDF) binder in N-methylpyrrolidone (NMP) solvent. The slurry was then uniformly casted onto Al foil. The working electrode was completely dried at 100 °C in a vacuum oven for 12 h. The active cathode mass loading was ~ 2 mg cm^{-2}. Finally, the Swagelok-type cell comprised of a LMO@LLZNO cathode, a LLZTO pellet and a Li foil anode was packaged in an Ar-filled glove box with both H_2O and O_2 contents below 0.1 ppm. Merely 1.0 μL cm^{-2} N-Methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13-TFSI) ionic liquid was used to wet the interface between cathodes and solid electrolytes. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were recorded via a Princeton electrochemical workstation. Galvanostatic charge-discharge tests were carried out using a Land CT2001A cycler at the potential range of 3.0-4.3 V vs Li^+/Li at 45 °C and 55 °C.

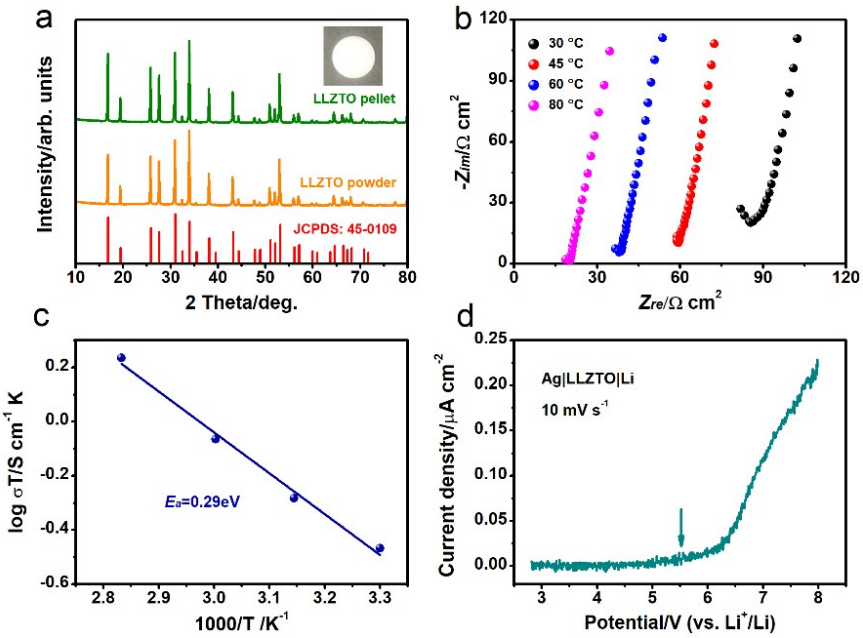

Figure S1. (a) XRD patterns of the as-prepared LLZTO powder and pellet. The inset is the photograph of LLZTO pellet. (b) EIS spectra of the LLZTO pellet tested at different temperatures. (c) Arrhenius plot of the LLZTO pellet. (d) LSV curve of LLZTO pellet at a scanning rate of 10 mV s^{-1}.

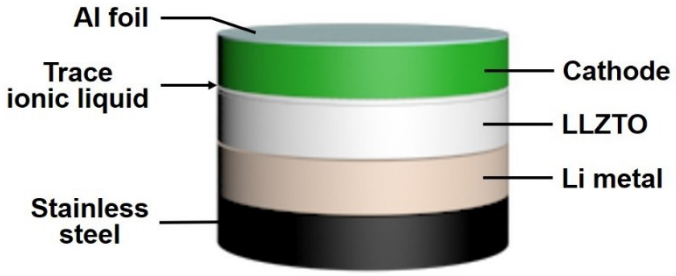

Figure S2. Schematic of the configuration of solid batteries with LMO or LMO@LLZNO cathode, LLZTO electrolyte and Li anode.

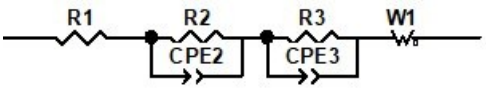

Figure S3. Equivalent circuit of the solid-state batteries.

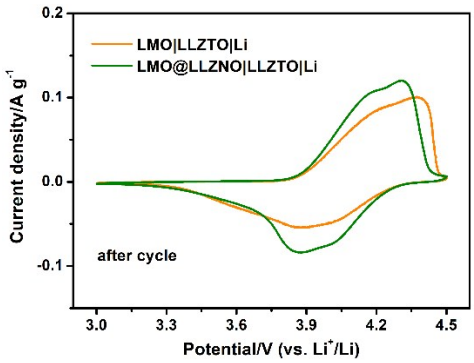

Figure S4. CV curves for LMO and LMO@LLZNO based batteries at 0.1 mV s^{-1} after cycling.

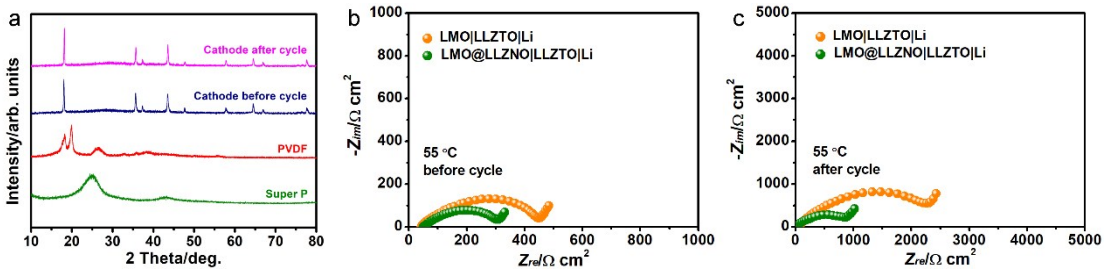

Figure S5. (a) XRD patterns of the Super P and PVDF which are added in the composite cathodes, and the LMO@LLZNO composite cathodes before and after cycling. EIS of the solid batteries with different cathodes (b) before and (c) after cycling at 55 °C.

Table S1. Cycle Performance of Liquid Lithium Ion Batteries Based on $LiMn_2O_4$ Cathodes at Elevated Temperature in the Literatures

Cathodes	Electrolytes	*T*/°C	Rate/C	Cycle number	Capacity retention/%	Ref.
TiO_2-LMO	$LiPF_6$:EC:DEC	55	0.5	250	62	S2
Al_2O_3-LMO	$LiPF_6$:EC:EMC	50	0.1	50	69.8	S3
nano TiO_2-LMO	$LiPF_6$:EC:DEC	55	0.5	300	69.5	S4
Al_2O_3-LMO	$LiPF_6$:EC:DMC	50	1	100	~70	S5
TiO_2-LMO	$LiPF_6$:EC:DEC	55	0.5	150	62.4	S6
YPO_4-LMO	$LiPF_6$:EC:DMC	55	0.2	100	75.8	S7
LMO@LLZNO	LLZTO	55	0.2	100	81.3	This work

References

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