Supplementary Information

A Thin Free-standing Composite Solid Electrolyte Film for Solid-State Lithium Metal Battery

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Experimental section

Nano powder Materials Preparation: The Ca and W doped $Li_7La_3Zr_2O_{12}$ (LLZO) solid electrolyte was prepared by conventional solid-state reaction. The starting materials, Li_2O (99.99%, Aladdin,), La_2O_3 (99.99%, Aladdin), ZrO_2 (99.99%, Aladdin), WO_3 (99%, Aladdin), CaO (99.9%, Aladdin) were mixed with a certain ratio by ball-milling in ethyl alcohol for 8 h as precursors. 10% excess Li_2O was added to compensate the loss of lithium in sintering process. The precursors were dried in the oven at 80 °C for 24 h, and then calcinated in air at 900°C for 6 h. After cooling down, the powders were Attrition -milling for 20 min again in N-Methyl-2-pyrrolidone (NMP, 99%, Aladdin) medium. Nano powder LLZO was obtained after drying.

Preparation of PVDF-LLZO (PL) film: Firstly, 1 g Poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP, Sigma-Aldrich) was dissolved in 5 g NMP solution with strong stirring for 12 h at room temperature. Subsequently, 1 g nano LLZO powder was added into the solution. And the mixed slurry was strongly stirred for 12 h and ultrasonic dispersion for 2 h. The slurry was poured on a thin glass plate and tape casting by automatic coating machine. Finally, a free-standing and flexible PL film was obtained after drying at 40 °C. The PL film was then soaked in precursor solution (lithium bistrifluoromethanesulfonimide (LiTFSI) (0.3 g), liquid VEC monomer (1 g) and trace the 2,20-Azobis(2-methylpropionitrile) (AIBN) as the catalyst). The PLP film was obtained after thoroughly vacuum-dried and polymerized in a vacuum oven at 80 °C for 12 h.

By comparison, the PVDF-HFP-LLZO-LiTFSI (PLL) film was prepared. 1 g PVDF-HFP and 0.3g LiTFSI dissolved in 5 g NMP solution with strong stirring at room temperature. Subsequently, 1g nano LLZO powder was added into the solution and stirred for 12 h. Finally, a free-standing and flexible PLL film was obtained by tape casting.

Characterization

The Fourier Transform Infrared Spectroscopy (FT-IR) was carried out using Bruker Alpha FT-IR spectrometer instrument to distinguish the structures of membrane. The crystal structure of membrane was characterized via XRD with a range of 10°-80°. The morphology and thickness of the membrane was characterized by a field emission scanning electron microscope (SEM, Hitachi S-4800). TG (Netzsch 449F3) was carried out to measure the thermal property of membrane from 25 to 600 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

Electrochemical measurement

The ionic conductivity of the samples was tested by Electrochemical Impedance Spectroscopy (EIS) using V Solartron 1470E cell test system at varied temperatures ranging from conductivity was calculated from equation (1): $\sigma = L / R_b S$, where R_b is the bulk resistance, L and S are the thickness and area of the composite solid electrolyte, respectively. The membranes were sandwiched between two stainless-steel (SS) plate electrodes and the spectra were recorded in the frequency range of 10^6 to 0.1 Hz with an AC amplitude of 10 mV. The electrochemical window was investigated by linear sweep voltammetry (LSV) performed on a working electrode of SS, Li metal as the counter and reference electrode at a scan rate of 1.0 mV/s between 2.5 and 5.5 V (vs. Li^+/Li). The lithium-ion transference number (t_{Li^+}) was calculated by the Chronoamperometry test on the Li/PH-BCPE/Li battery with an applied voltage of 0.01 V, and was determined by equation (2): $t_{Li^+} = \frac{I_{ss}(V - I_0 R_0)}{I_0(V - I_{ss} R_{ss})}$ where I_0 and I_{ss} are the initial and steady-state currents, and R_0 and R_{ss} are the first and last resistances, respectively. The tests were completed by EIS measurements that taken before and after the polarization scans over a frequency range of 10^6 to 0.1 Hz with a 10 mV amplitude at 25 °C.

Battery test

The $LiCoO_2$ (LCO) cathode was prepared by pasting the mixture of 80 wt% LCO, 10 wt% carbon black, and 10 wt% binder (PVDF) on the Al current collector. The loading mass of active materials was controlled with areal density of 1.5–2.5 mg/cm^2. The solid lithium metal batteries composed of LCO cathode that assembled via in-situ process were charged and discharged between 3 and 4.6 V/4.5 V at varied current densities. The C rates are defined based on 1 C = 160 mA/g. The galvanostatic charge/discharge tests of coin-type batteries (CR2032) were conducted on LAND testing system (Wuhan LAND Electronics Co., Ltd.) at 25 °C.

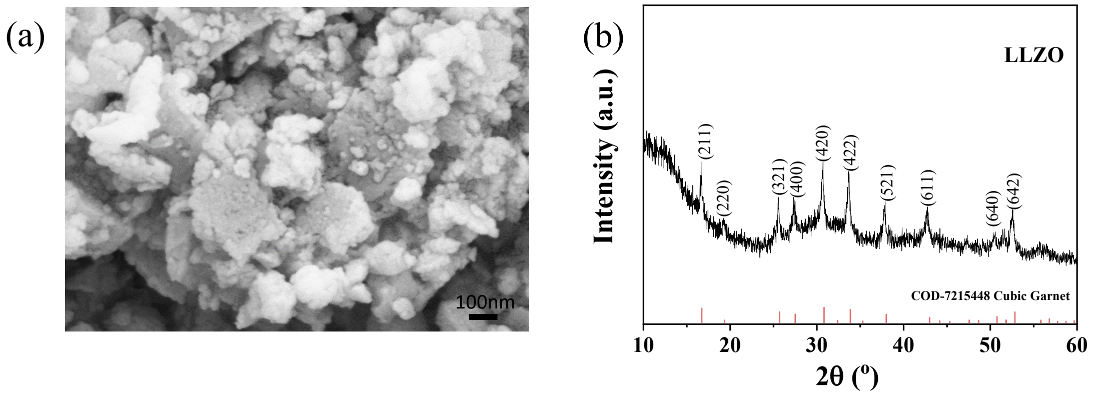

Fig. S1 The characterization of the LLZO after Attrition-milling: (a) SEM image and (b) XRD pattern.

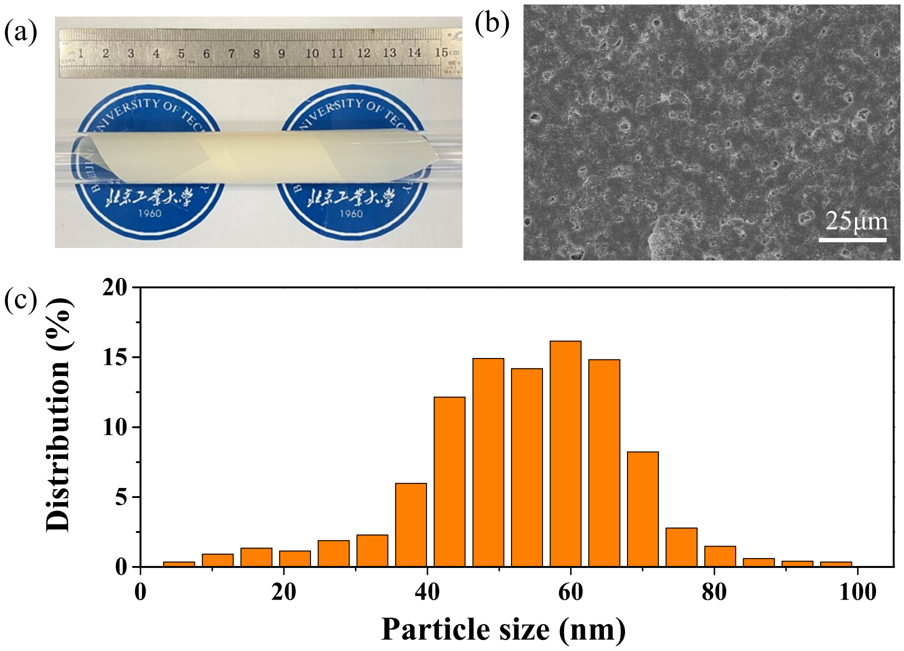

Fig.S2 (a)The optical image, (b)SEM image of the surface and (c) the particle size distribution of the PL film.

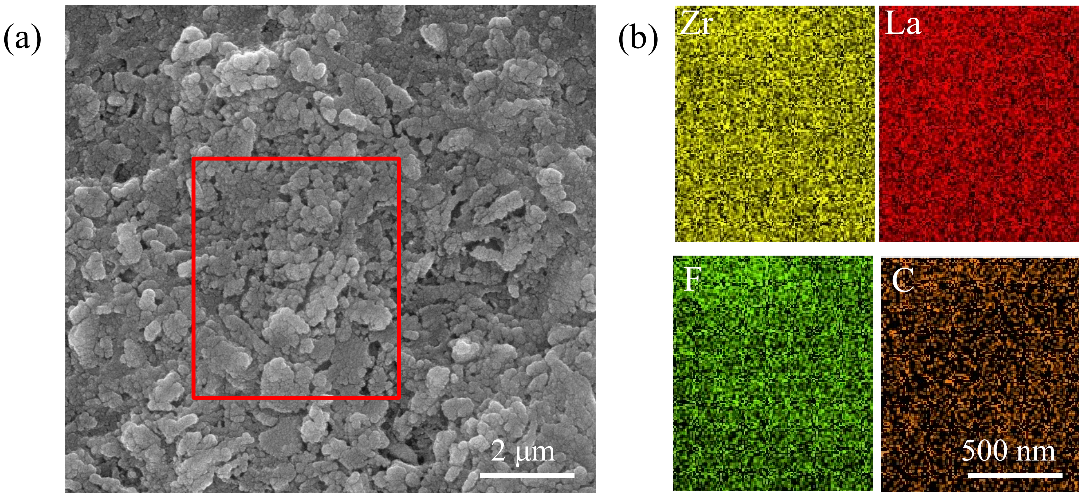

Fig. S3 (a)The SEM and (b) the element distribution of the cross-section of PL thin film.

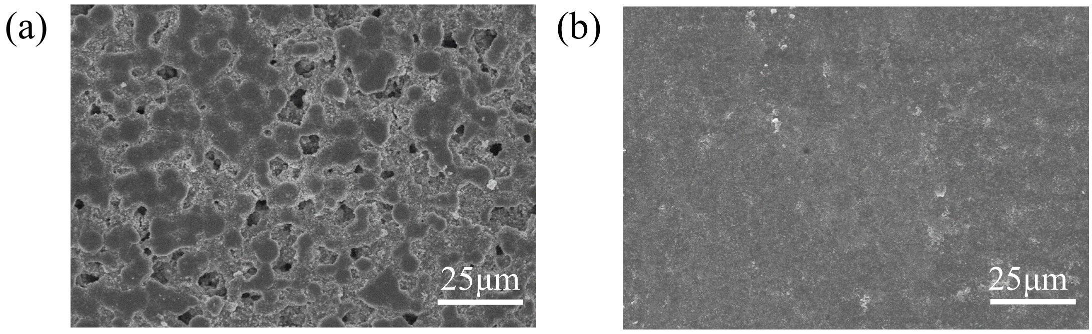

Fig. S4 The surface morphology of the (a) PLL and (b) PLP thin film.

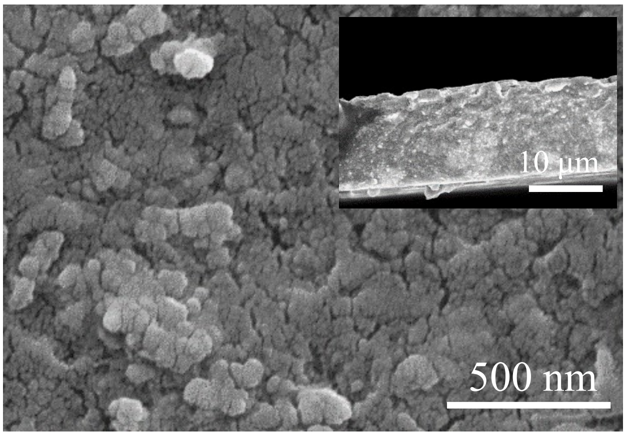

Fig. S5 The cross-section of the PLL thin film.

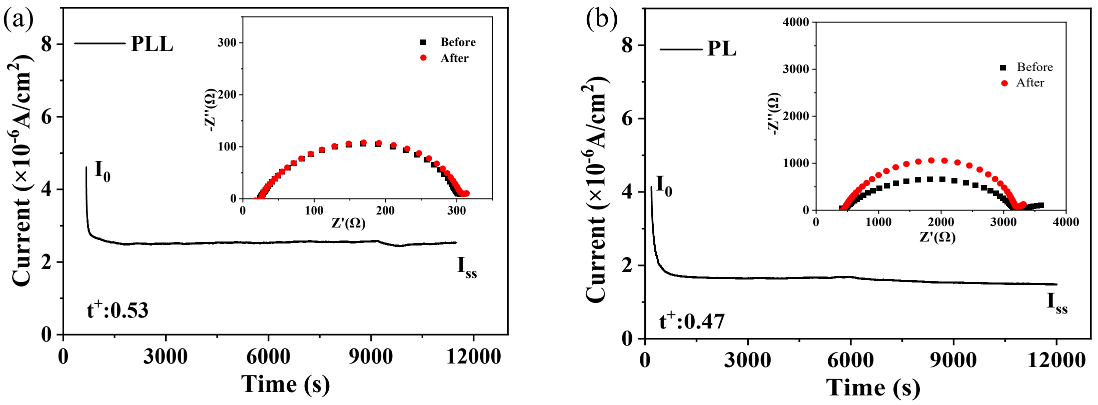

Fig. S6 AC impedance spectra and polarization current-time curves of (a) PLL and (b) PL thin film.

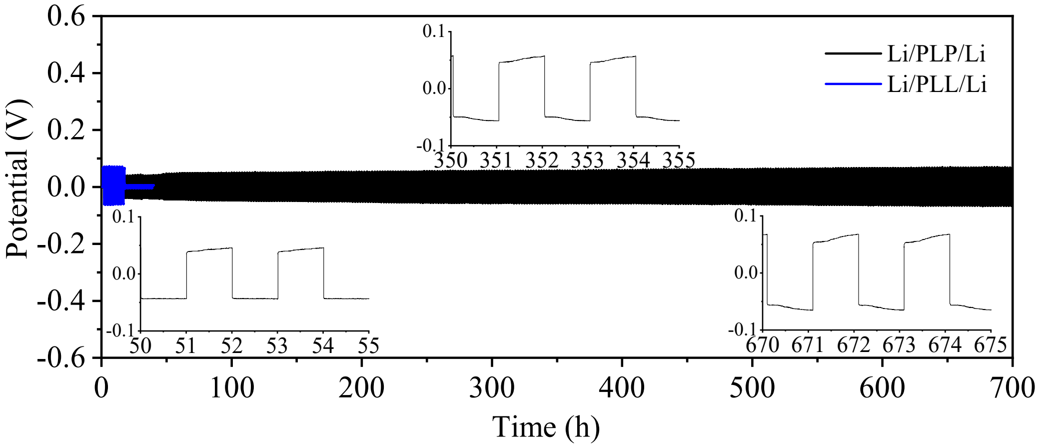

Fig.S7 The potential profiles of repeated Li plating/striping in Li/PLP/Li and Li/PLL/Li symmetric battery by in-situ method with current density of 0.1 mA/cm^2.

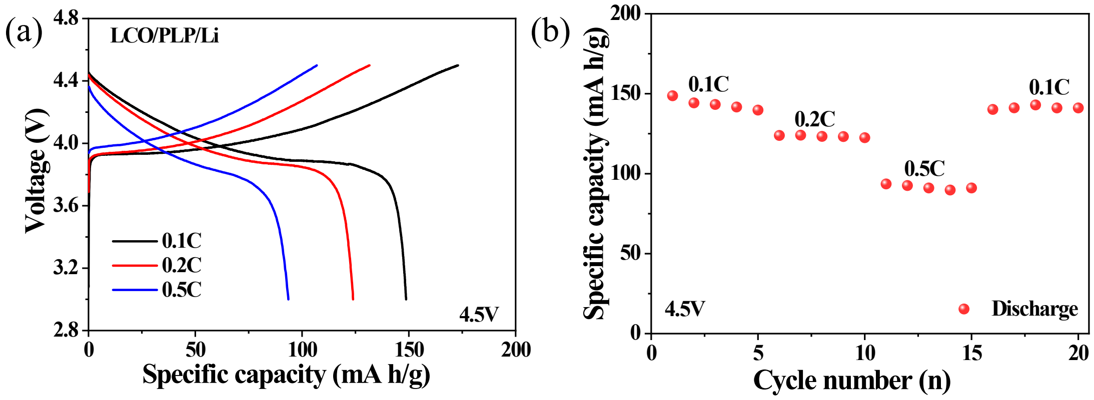

Fig. S8 The typical charge/discharge curves (a) and rate performances (b) of LCO/PLP/Li battery with different current density