

Supporting Information for
Interfacial Functionalized Porous $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ Enabling Fast
Lithium-ion Transport in Solid Polymer Electrolytes

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Experiment

Materials

Lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), tetrabutyl titanate ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$) Lithium nitrate (LiNO_3) and citric acid were sourced from Aladdin reagent. Lithium trifluoromethanesulfonamide (LITFSI) and F127 reagents were supplied by Sigma-Aldrich. 3-glycidyloxypropyltrimethoxysilane (KH560) was sourced from Picasso. The commercial LLTO is presented by Ningbo Institute of Materials, Chinese Academy of Sciences. LiFePO_4 , polyvinylidene fluoride (PVDF), and Super-P are supplied by Duoduo Reagent.

Preparation of the PLLTO, Si-PLLTO, and SPE

As shown in Scheme **Figure 1a**, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ were selected as metal precursors, while citric acid (30.0 mmol) was employed as a coordinating agent. These reagents were dissolved in ethanol (35.0 mL) and stirred at 60 °C for 2 h to form a precursor solution with a stoichiometric composition corresponding to 10.0 mmol

LLTO. Then, LiNO₃ (38.5 mmol) together with an F127 solution (5.0 g dissolved in 10.0 mL deionized water and 15.0 mL ethanol) was introduced into the mixture, followed by stirring at 60 °C for an additional 2 h. The formed sol was maintained at 60 °C for 4 h. After solvent removal by drying at 120 °C for 10 h, the obtained intermediate was sintered at 700 °C under an argon atmosphere for 2 h. Further calcinations at 700 °C, 800 °C, and 900 °C were conducted in an air atmosphere over a period of 2 h to obtain PLLTO.

Add 2 g of PLLTO to a mixture of methanol and silane coupling agent (weight ratio 9:1, 10.0 g), stir for 24 h, centrifuge three times, and freeze for 12 h and dry for 6 h to obtain Si-PLLTO.

PVDF and LITFSI with a weight ratio of 2:1 was added to N-Methylpyrrolidone (8.0 g) and dispersed by magnetic stirring for 2 h. LLTO was then introduced into the solution at a content of 5%-20% based on the total solid content, followed by further stirring for 10 h. The resulting slurry was coated onto a Teflon plate, and SPEs were obtained after drying in a vacuum oven at 60 °C for 10 h.

Characterization of the electrolytes

The morphologies, elemental composition, and structural features of LLTO and SPEs were characterized using a field emission scanning electron microscope (SEM, FESU8100, Hitachi, Japan) and a transmission scanning electron microscope (TEM, HT7700, Hitachi, Japan). The crystal structure of LLTO was identified by X-ray diffraction (XRD) analysis conducted on an Xtalab Synergy diffractometer (Rigaku, Netherland). The alternating current (AC) impedance of the SPEs and the assembled batteries was measured with an electrochemical workstation (Chenhua, CHI 760-e, China) over a frequency window ranging from 100 kHz to 1 Hz. The distribution of relaxation time (DRT) analysis was performed based on methodologies reported in previous studies. Linear sweep voltammetry (LSV) tests for the SPEs were carried out within a potential range of 2-6 V at a scan rate of 0.1 mV s⁻¹. The redox stability of different composite solid electrolytes and the reversibility of LFP/Li cells were determined by cyclic voltammetry (CV) at a scanning rate of 0.1 mV s⁻¹ and the voltage step was 1 mV in the voltage range of 3V-4V. X-ray photoelectron spectroscopy (XPS)

measurements were conducted using an ESCALAB250 electron spectrometer (Thermo Fisher Scientific, USA), while Fourier transform infrared spectroscopy (FTIR) analysis was performed on a Nicolet iS5 Fourier transform infrared spectrometer (Thermo Fisher Scientific, USA).

LiFePO₄, super-P, PVDF, and succinonitrile (SCN) were combined at a mass ratio of 7:1:1:1 to prepare the cathode mixture, while lithium metal was employed as the anode. The Li|Li symmetric cells and LiFePO₄|Li cells were subjected to charged/discharged tests at 60 °C using a Neware battery testing system (China) to evaluate their cyclic and rate capability.

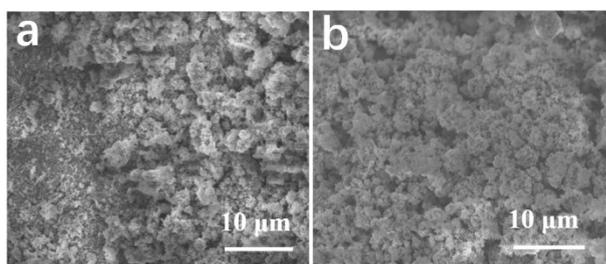


Figure S1 SEM morphology of PLLTO sintered at (a) 700 °C and (b) 800 °C.

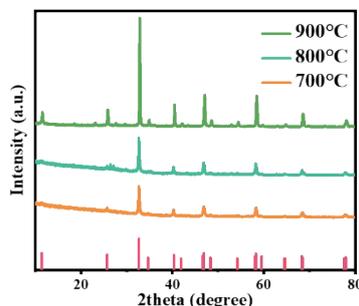


Figure S2 The XRD patterns of PLLTO with different sintering temperatures.

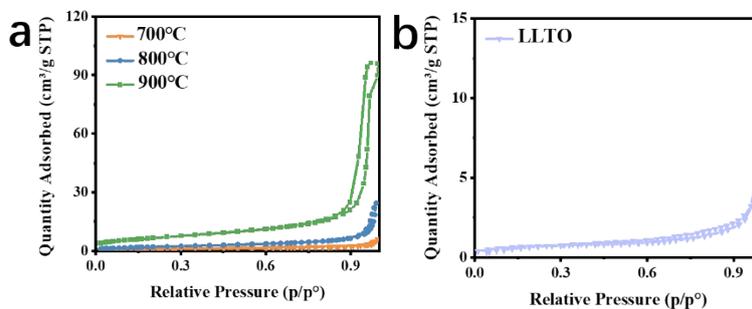


Figure S3 (a) Nitrogen gas sorption isotherms of PLLTO (700-900 °C). (b) Nitrogen gas sorption isotherms of commercial LLTO.

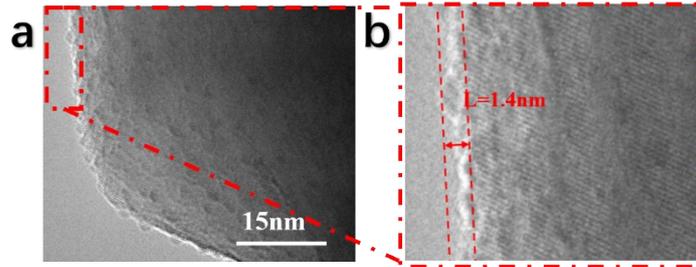


Figure S4 (a) High-resolution TEM images of Si-PLLTO surfaces. (b) The thickness of the KH560 coupling agent layer is 1.40 nm.

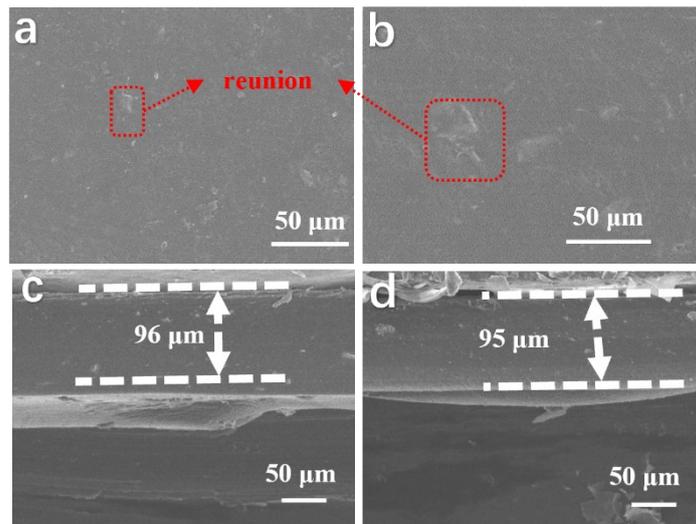


Figure S5 Surface SEM morphology of (a) SPE-PL and (b) SPE-CL. The cross-section SEM morphology of (c) SPE-PL and (d) SPE-CL.

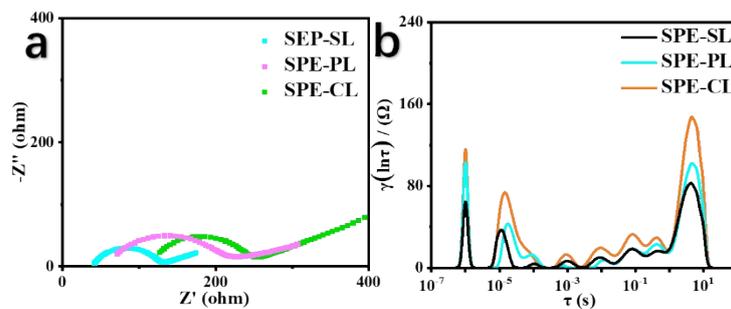


Figure S6 (a) The Nyquist plots of DRT batteries assembled with SPE-CL, SPE-PL, and SPE-SL.

(b) The DRT curves SPE-CL, SPE-PL, and SPE-SL.

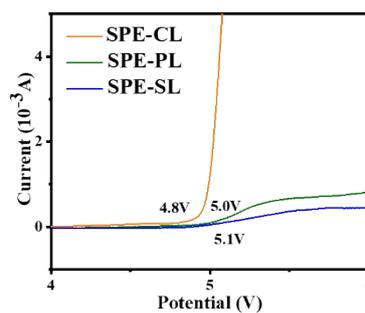


Figure S7 The LSV curves of SPE-CL, SPE-PL, and SPE-SL.

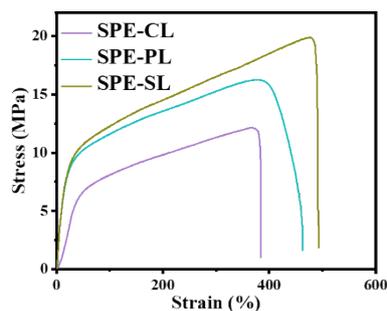


Figure S8 Stress-strain plots of SPE-CL, SPE-PL, and SPE-SL.

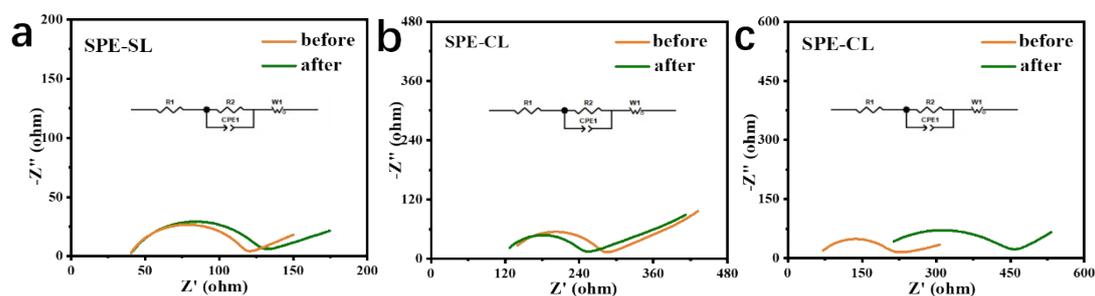


Figure S9 The Nyquist plots of Li symmetric batteries assembled with (a) SPE-SL, (b) SPE-PL, and (c) SPE-CL.

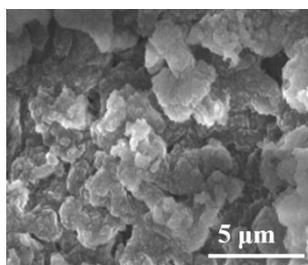


Figure S10 Surface morphology of Li anodes observed via top-view SEM in batteries constructed with SPE-CL after 50 cycles.

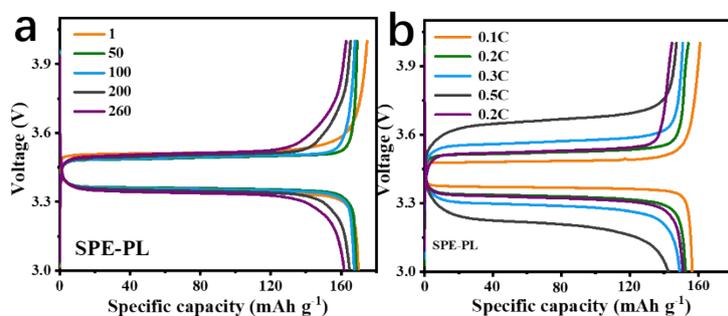


Figure S11 (a) Cycle charge/discharge curves of LiFePO₄/Li batteries with SPE-PL at a current rate of 0.2C and an operating temperature of 60 °C. (b) Rate charge/discharge curves of LiFePO₄/Li batteries with SPE-PL.

