

Flexible self-supporting inorganic nanofiber membranes reinforced solid-state electrolyte for dendrite-free lithium metal batteries

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1. Experimental Section

1.1 Preparation of Al₂O₃ nanofibrous membranes

The preparation of Al sol for the experiments has been reported in detail in our previous work. Next, spinning solution was prepared by dissolving Al sol and polyvinylpyrrolidone (PVP, $M_w = 1,300,000$) in distilled water in the weight ratio of 10:0.5, 10:1 and 10:1.5 in this work. It was then transferred to an electro-blown spinning (EBS) equipment, where the solution was drawn and received to obtain pristine nanofibers under the combined effect of gas pressure at 0.1 MPa and high voltage at 40 kV. The obtained fibers were then placed in a muffle furnace and calcined in air to 1100 °C for 2 h with a heat-up rate of 5 °C min⁻¹ to form Al₂O₃ nanofibers. The 0.04 g of Al₂O₃ nanofibers were dispersed into a certain amount of distilled water, the nanofibers were dissociated to form a homogeneous dispersion by a high-speed disperser, and the dispersion was vacuum pumped and filtered on a filter membrane to obtain Al₂O₃ nanofibrous membranes with a gram weight of 20 g cm⁻².

1.2 Fabrication of composite solid-state electrolytes

The PEO ($M_w = 600000$) and lithium bis (tri fluoromethanesulfonyl) imide (LiTFSI, 99.99%) were bought from Aladdin commercially and were not further processed prior to use. Then, they were dissolved in anhydrous acetonitrile (CH₃CN) in a molar ratio of 11:1 for [EO] and [Li] and stirred for 6 h. Firstly, the PEO-LiTFSI solution was cast in the interstices of the Al₂O₃ nanofibrous membranes to form a dense composite solid-state electrolyte denoted as AOM-PEO-LiTFSI. In addition, the prepared Al₂O₃ nanofibers were dispersed in the PEO-LiTFSI solution and cast in the grooves of a Teflon plate

to prepare a composite solid-state electrolyte named AOF-PEO-LiTFSI as a comparative sample. Then, the purchased Al₂O₃ nanoparticles were also dispersed into the PEO-LiTFSI solution to prepare the composite solid-state electrolyte (AOP-PEO-LiTFSI) for comparison. All of the above electrolytes were dried in a vacuum oven at 60 °C for 24 h to evaporate the solvent cleanly, and then placed in an argon-filled glove box (O₂ < 0.1 ppm, H₂O < 0.1 ppm) for cells assembly.

1.3 Preparation of cathodes

The applied LFP, PEO, conductive carbon black and LiTFSI by the weight ratio of 6:2:1:1 was dissolved into CH₃CN after 12 h of mechanical stirring to make a homogeneous mixture. Subsequently, the mixture was scraped onto an Al foil and placed in an oven at 60 °C for 24 h to ensure complete solvent evaporation. They were then cut into cathode discs of 7 mm radius and kept in an argon-filled glove box for use. Similarly, LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811), conductive carbon black and polyvinylidene fluoride (PVDF) were mixed in a weight ratio of 8:1:1, and added to the *N*-methyl-2-pyrrolidone (NMP, 99.5%) solvent and mixed well with constant stirring to obtain the NMC811 high-voltage cathode. The loadings of both LFP and NMC811 active materials were approximately 1.5 mg cm⁻².

1.4 Physical and chemical structure characterization of composite solid-state electrolytes

Microstructure and morphology of prepared nanofibers and composite solid-state electrolytes were characterized using field emission scanning electron microscopy (SEM, Crossbeam 550, ZEISS, Germany) at an accelerating voltage of 10 kV. Also, the elemental distribution in the composite solid-state electrolytes were analyzed using an energy dispersive spectrometer (EDS). The glass transition temperatures (T_g) of different composite solid-state electrolytes were described by differential scanning calorimetry (DSC, DSC204F1, Germany) in the range of -80 °C to -20 °C with a temperature rise rate of 10 °C min⁻¹. The crystal structure of Al₂O₃ nanofibers and composite solid-state electrolytes were tested and described by X-ray diffraction (XRD, D8 ADV ANCE, Germany) with Cu K_α radiation in the range from 10° to 70° of 2θ . The stress-strain curves of the composite solid-state electrolyte can be obtained by a YG005 electronic single fiber strength tester at a stretching speed of 10 mm min⁻¹.

1.5 Electrochemical measurements of composite solid-state electrolytes

Various electrolytes were put into the CR2032-type coin cell through different assembly forms in an argon-filled glovebox (O₂ < 0.1 ppm, H₂O < 0.1 ppm) to test their electrochemical properties. The ionic conductivity (σ) of the stainless steel (SS)/electrolyte/SS cells from 30 °C to 70 °C was calculated by the electrochemical impedance spectra (EIS) in the frequency range of 0.01–10⁶ Hz measured on an electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China). The calculation formula is as follows: $\sigma = D/RS$, where D (cm) is the thickness of the electrolytes, R (Ω) and S (cm²) represent the bulk resistance and the effective contact area between the SS and the electrolyte, respectively. The Li⁺ transference number (t_{Li^+}) was derived from the AC impedance and DC polarization of the Li/electrolyte/Li cells on an electrochemical workstation at 50 °C. The t_{Li^+} was calculated by the formula: $t_{Li^+} = I_{SS}(\Delta V - I_0 R_0)/I_0(\Delta V - I_{SS} R_{SS})$, where the ΔV is the polarization voltage with a voltage of

10 mV. I_0 and I_{SS} are the initial and steady state currents, respectively. R_0 and R_{SS} are the resistance before and after polarization, respectively. Linear sweep voltammetry (LSV) was used to test the electrochemical stability window of the electrolytes in the range of 2.5–6.0 V with a scan rate of 1 mV s⁻¹ at 50 °C. In addition, the LAND multichannel battery-testing systems (Wuhan LAND Electronics Co., Ltd., China, CT2001A) were used to test the Li dendrite suppression ability of Li/electrolyte/Li symmetric cells and also monitored the cycling ability of the assembled LFP/electrolyte/Li cells and NMC811/electrolyte/Li cells under 50 °C.

2. Supporting Table

Table S1 Performance of different PEO-based composite solid-state electrolytes containing Al₂O₃.

Additive	Tensile strength (MPa)	Ionic conductive (S cm ⁻¹)	Refs.
Al ₂ O ₃ nanoparticle	3.24	9.39×10 ⁻⁷ at RT	[21]
Atomic-scale Al ₂ O ₃	–	5.4×10 ⁻⁴ at 60 °C	[22]
Al ₂ O ₃ nanofiller	0.18	1.25×10 ⁻⁴ at RT	[23]
γ-Al ₂ O ₃ nanosheets	0.12	2.02×10 ⁻⁴ at 25 °C	[24]
Al ₂ O ₃ nanorods	–	~1.7×10 ⁻⁶ at RT	[25]
Al ₂ O ₃ nanoparticles	–	~10 ⁻⁵ at 30 °C	[26]
Al ₂ O ₃ nanoparticle	–	1.4×10 ⁻⁷ at 20 °C	[27]
Al ₂ O ₃ nanofibrous membrane	3	1.36×10 ⁻⁴ at 30 °C	This work

3. Supporting Figures

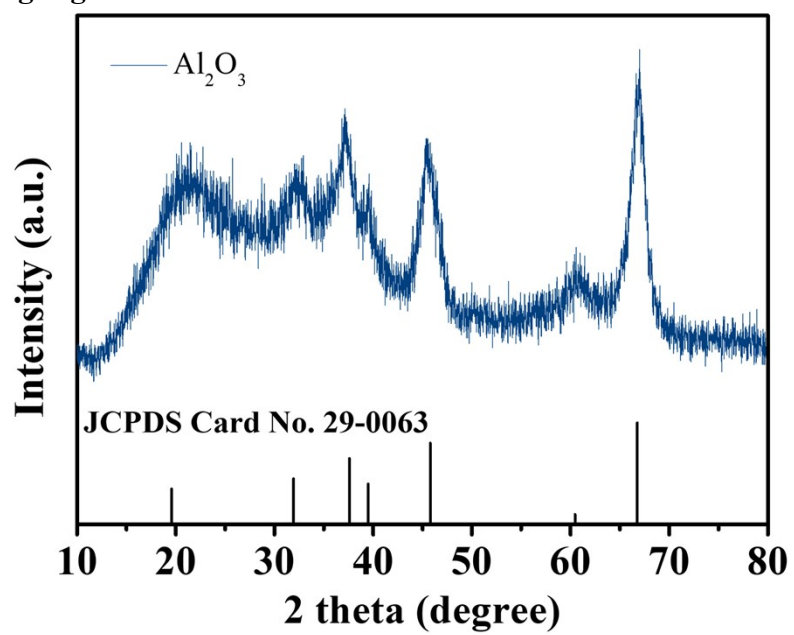


Fig. S1 The XRD spectra of the Al₂O₃ nanofiber.

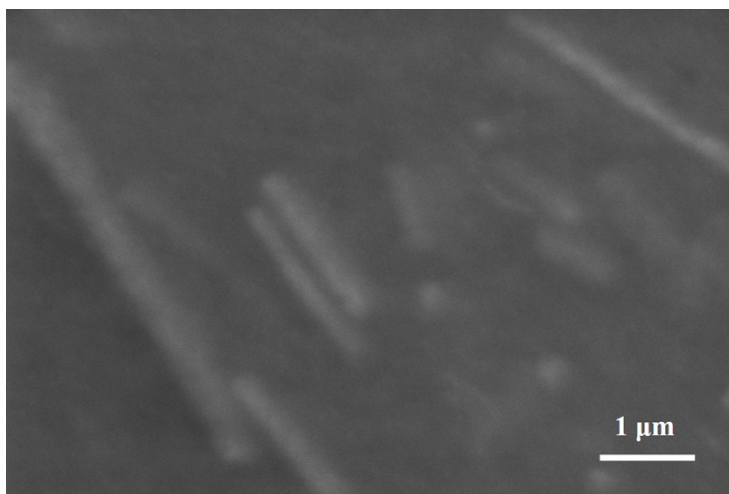


Fig. S2 The top-view morphology image of AOF-PEO-LiTFSI composite solid-state electrolyte.

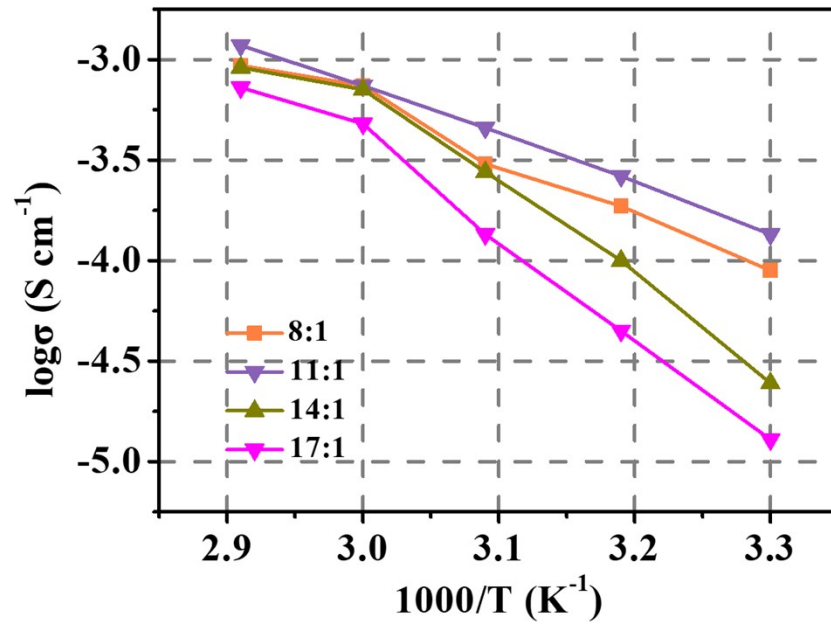


Fig. S3 The Arrhenius ionic conductivities diagram of the AOM-PEO-LiTFSI electrolytes with different [EO]:[Li] ratios.

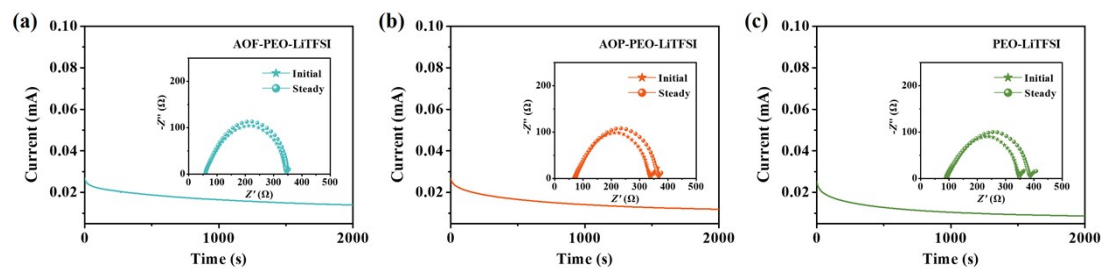


Fig. S4 The chronoamperometry curves of the Li/Li battery under 10 mV at 50 °C and corresponding EIS curves of this battery before and after polarization (inset): (a) Li/AOF-PEO-LiTFSI/Li battery; (b) Li/AOP-PEO-LiTFSI/Li battery; (c) Li/PEO-LiTFSI/Li battery.

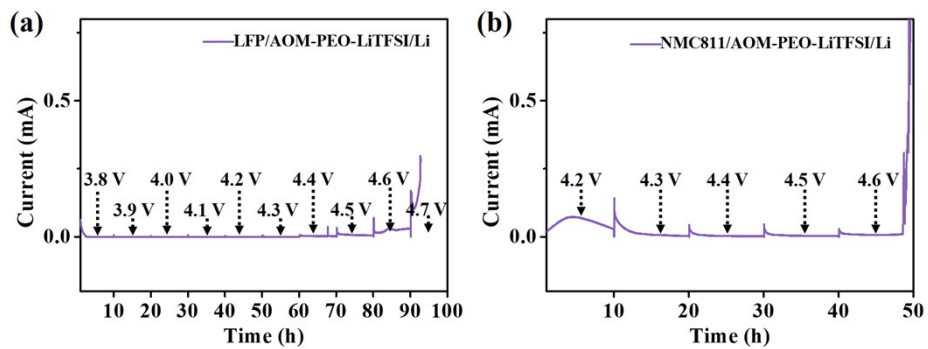


Fig. S5 Electrochemical floating analysis of LFP/AOM-PEO- LiTFSI/Li and NMC811/AOM-PEO-LiTFSI/Li cells at 50 °C.

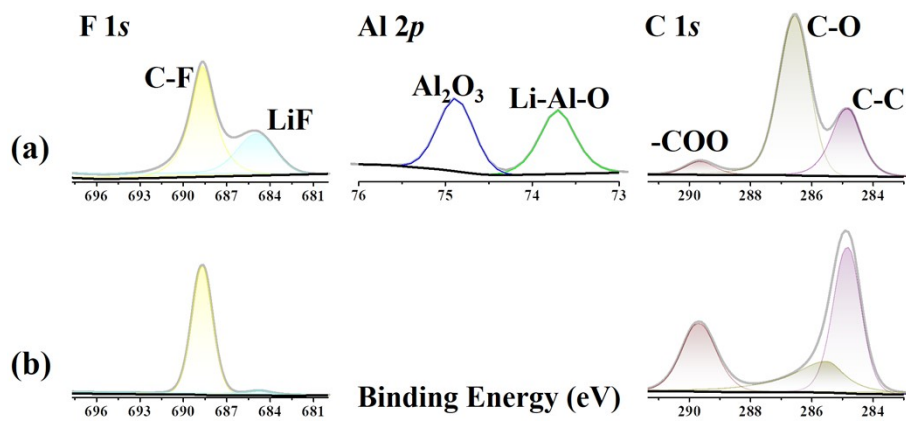


Fig. S6 The XPS of lithium anode of (a) Li/AOM-PEO-LiTFSI/Li battery and (b) Li/PEO-LiTFSI/Li battery after cycling.

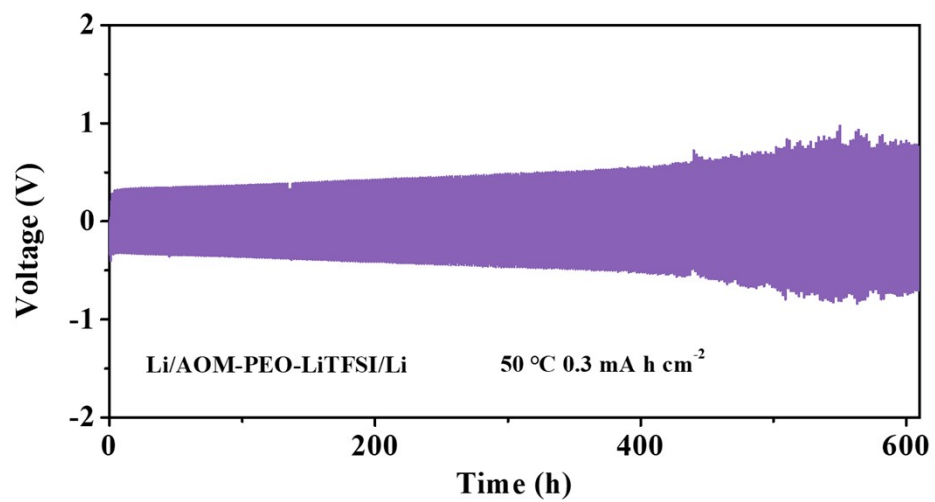


Fig. S7 Voltage–time profiles for Li/AOM-PEO-LiTFSI/Li symmetric cells at current densities of 0.3 mA cm^{-2} for 0.3 mA h cm^{-2} under $50 \text{ }^\circ\text{C}$.