Supporting Information

A Ternary Composite Nanofiber-Derived Thin Membrane Electrolyte for Solid-State Li Metal Batteries

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Experimental section

Preparation of h-BN fillers

In typical, 1 g of h-BN was dispersed in 200 mL of N, N-dimethylformamide (DMF) and sonicated for 8 h to obtain the dispersed solution. Subsequently, the supernatant was carefully poured into a separate beaker, leaving behind the bulk h-BN at the bottom. The resulting supernatant was centrifuged at 5000 rpm to collect the white detached h-BN nanosheets. Finally, the h-BN products were washed with deionized water and dried overnight at 80°C.

Preparation of solid-state electrolytes

The electrospinning technique was employed for the fabrication of Poly(vinylidene fluoride-co-hexafluoropropylene) (PVH) skeleton. The electrospinning process entailed the preparation of a solution, in which 1.5 grams of PVH nanoparticles were dissolved in 10 g of DMF/acetone (7:3, v: v) and stirred for a period of 2 h at 60°C. The electrospinning solution was extruded and drawn through a syringe under high-voltage static electricity with a speed of 1 mL h^{-1} and a voltage of 24 kV. The resulting PVH membrane was subjected to vacuum drying at 60°C for 4 h to remove the residual solvent, which was then stored for later use. A specific mass of polyethylene oxide (PEO) and LiTFSI (with a molar ratio of EO: Li$^+$ of 18:1) was added to anhydrous acetonitrile, which was then stirred at 55°C for 6 h to achieve a uniform dispersion. Subsequently, h-BN with varying mass fractions were added to the mixture, which was then subjected to continuous stirring for a further two hours. The prepared solution was poured onto the PVH substrate and vacuum dried at 55°C for 36 h to completely remove the acetonitrile solvent. The solid-state electrolytes with varying h-BN contents are designated as PEO, PEO/PVH, 0.2%h-BN@PEO/PVH, 0.4%h-BN@PEO/PVH, and 0.8%h-BN@PEO/PVH electrolytes, respectively.

Materials Characterizations

Fourier transform infrared (FTIR) spectra were recorded via a FT-IR spectrometer (Thermo Nicolet Nexus 670). The crystalline structure of samples was investigated on X-

ray diffraction analysis (XRD, Rigaku Ultima IV) with Cu Kα radiation (40 kV / 30 mA, λ = 0.154 nm). The morphologies were characterized by Scanning electron microscopy (SEM, Hitachi S-4800) and Transmission electron microscopy (TEM, JEM-2010 HR). The X-ray photoelectron spectra (XPS) of samples were performed on a ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific).The atomic force microscopy (AFM) examinations were conducted on Bruker Anasys nanoIR2-fs instrument. Nanoindentation technique (Fischer Scope, ST200) was applied to mimic the punctuation of Li dendrites at nanoscale. The tensile strength of the solid-state electrolytes was inspected using the universal testing machine (CMT6103, SANS).

Electrochemical tests

An electrochemical test was conducted at 60 °C utilizing a coin cell comprising a Li-metal anode, the solid-state electrolyte and $LiFePO_4$ cathode. The high-loading LFP/LCO/NCM523 cathodes were fabricated by casting the slurry containing active material (80 mg), carbon black (10 mg), and PVDF (10 mg) with a high areal-loading of ~ 2 mg cm^{-2} on the Al foil. After drying at 60°C overnight, the electrode was cut into round discs with a diameter of 12 mm prior to use.

The ionic conductivity of the prepared solid-state electrolytes was determined by EIS technique using a symmetric coin cell with two stainless steel electrodes. The cells were performed with the frequency range from 10^{-2} to 10^5 Hz and a voltage amplitude of 10 mV. The ionic conductivity (σ) of the electrolyte was calculated using below equation, where R_b is the resistance (Ω), L represents the thickness (cm), and S stands for the area of the solid electrolyte (cm^2):

$$\sigma = \frac{L}{R_b S}$$

The Li-ion transference number (t_{Li}^+) of the solid-state electrolytes was measured in a symmetrical Li//Li cell. A voltage of 10 mV (ΔV) was applied and EIS spectra of the cell before and after polarization were obtained from 10^{-2} to 10^5 Hz. The Li-ion transference number was determined based on the following equation:

$$t_{Li^+} = \frac{I_s(\Delta V - I_i R_i)}{I_i(\Delta V - I_s R_s)}$$

Where t_{Li}^+, I_s, I_0, R_s and R_0 are the Li-ion transference number, the current and the resistance at the final state and initial state, respectively.
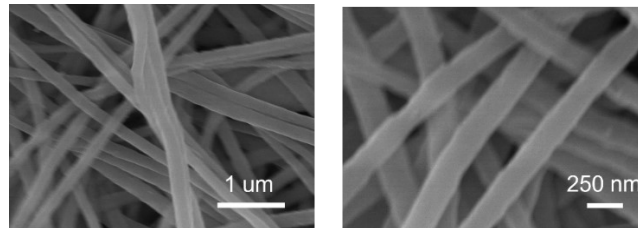

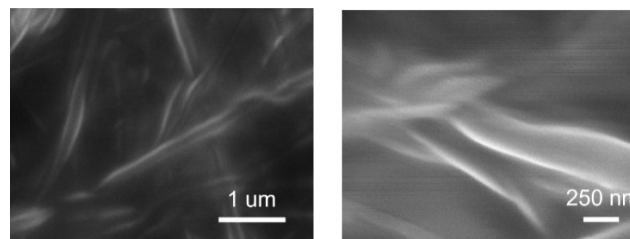**Fig. S1** SEM images of PVH membrane of different sizes.

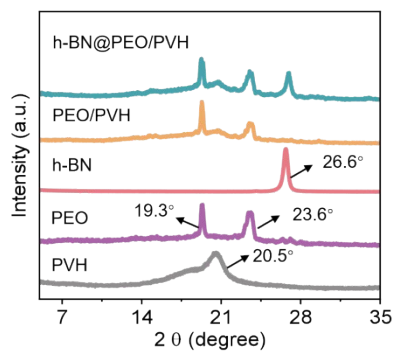**Fig. S2** SEM images of the h-BN@PEO/PVH electrolyte of different sizes.

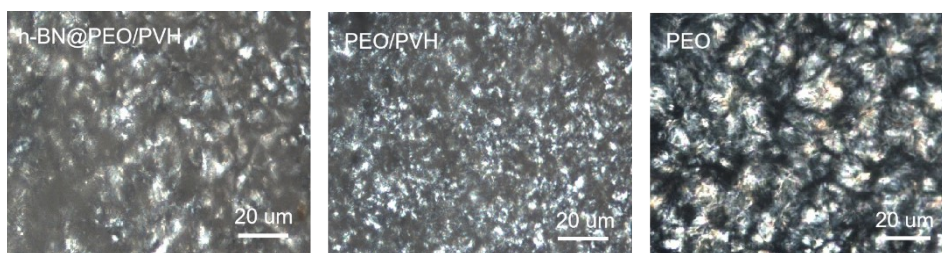**Fig. S3** XRD patterns of h-BN fillers, PVH substrate, PEO, PEO/PVH and h-BN@PEO/PVH electrolytes.

Fig. S3 Polarization microscopies of h-BN@PEO/PVH, PEO/PVH and PEO electrolytes.
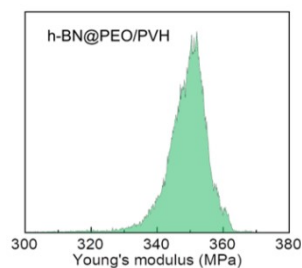

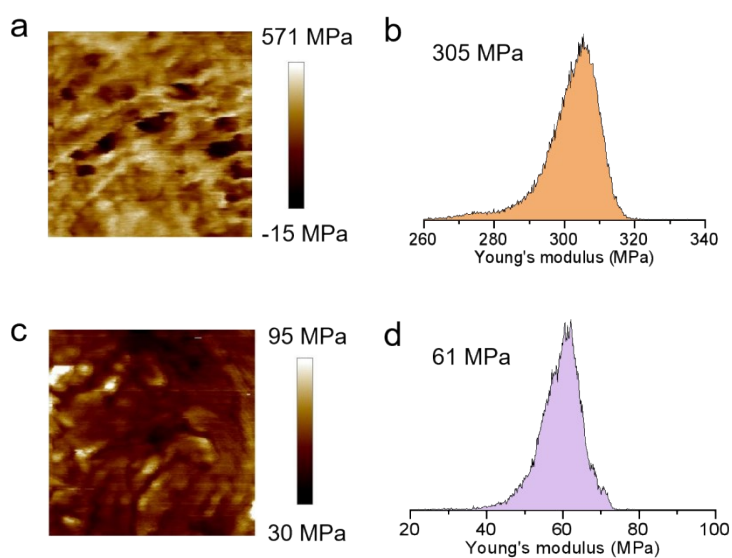**Fig. S4** The distribution curve of Young's modulus collected from AFM image of h-BN@PEO/PVH electrolyte.

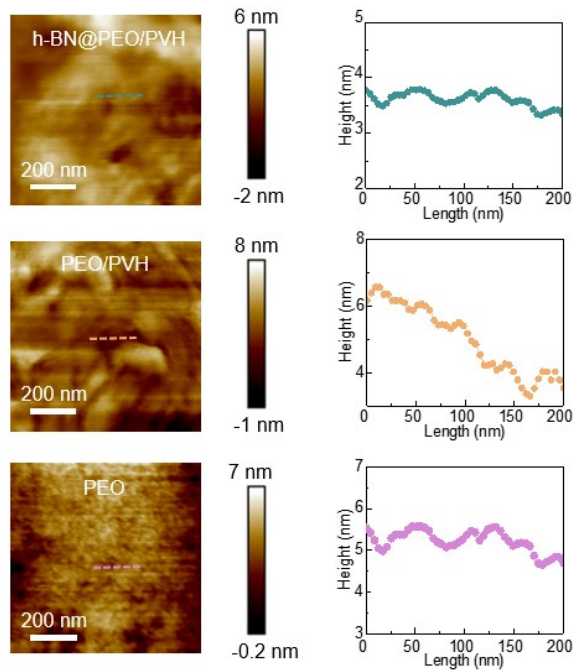**Fig. S5** AFM images of Young's modulus and their distribution curves of (a, b) PEO/PVH and (c, d) PEO electrolytes.

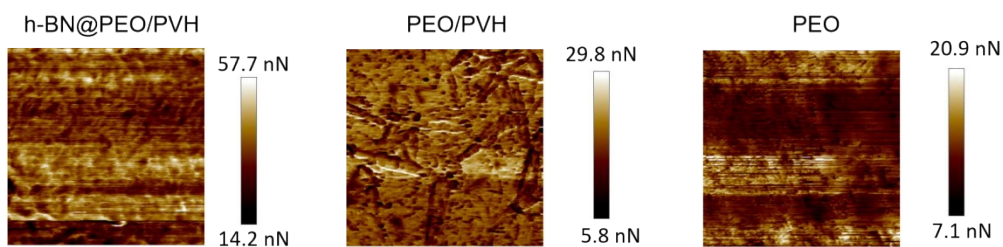**Fig. S6** AFM images of the surface roughness on different electrolytes.

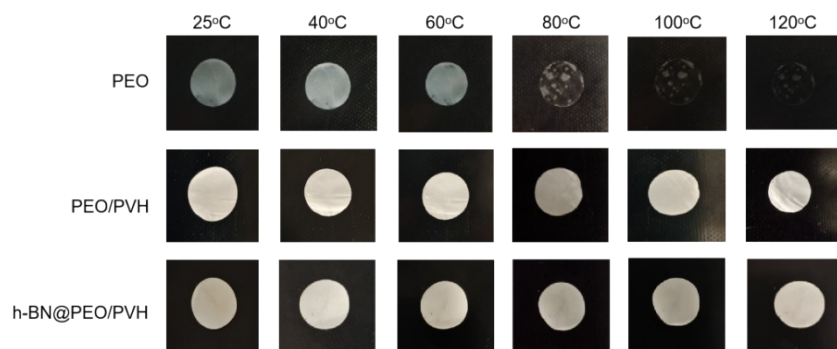**Fig. S7** AFM images of the adhesion force on different electrolytes.

Fig. S8 The thermal stability of PEO, PEO/PVH and h-BN@PEO/PVH electrolytes at different temperatures.
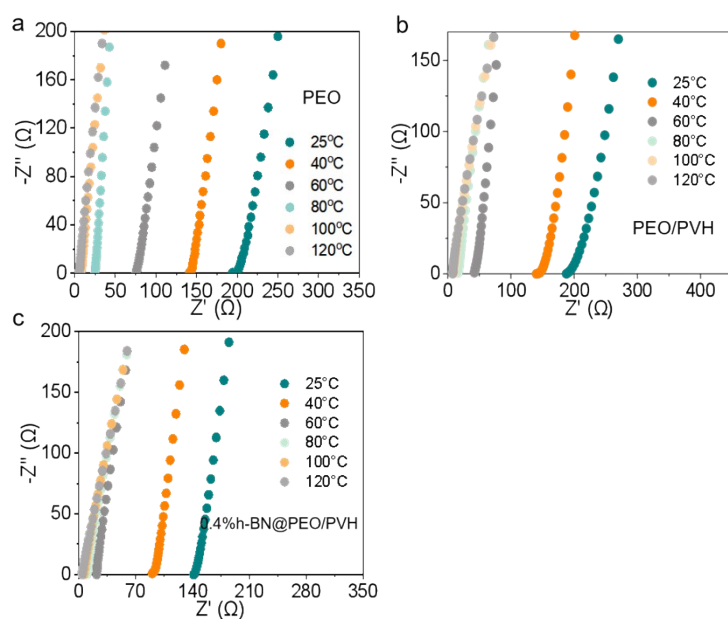
Fig. S9 EIS curves of (a) PEO, (b) PEO/PVH and (c) 0.4%h-BN@PEO/PVH electrolytes. (d) The ionic conductivity at 60 °C of PEO, PEO/PVH and 0.4%h-BN@PEO/PVH electrolytes.
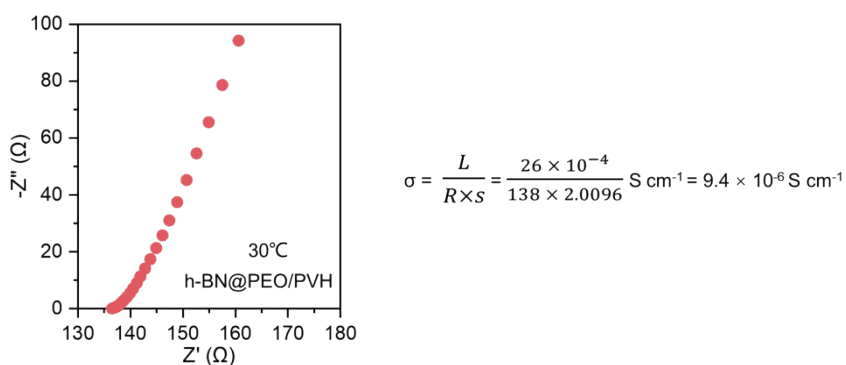

$$\sigma = \frac{L}{R \times s} = \frac{26 \times 10^{-4}}{138 \times 2.0096} \text{ S cm}^{-1} = 9.4 \times 10^{-6} \text{ S cm}^{-1}$$

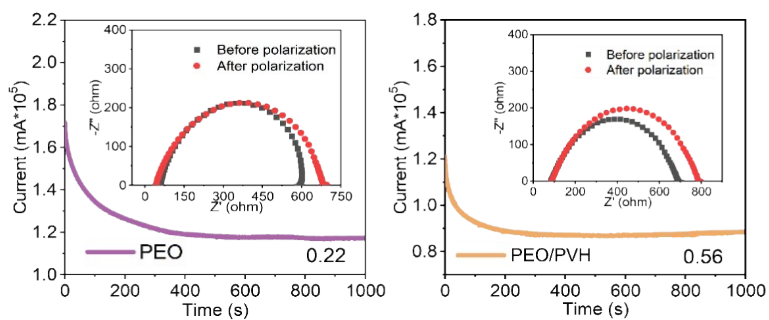**Fig. S10** The ionic conductivity of h-BN@PEO/PVH electrolytes at 30 °C.

Fig. S11 Li-ion transference number of PEO and PEO/PVH electrolytes at 60 °C.
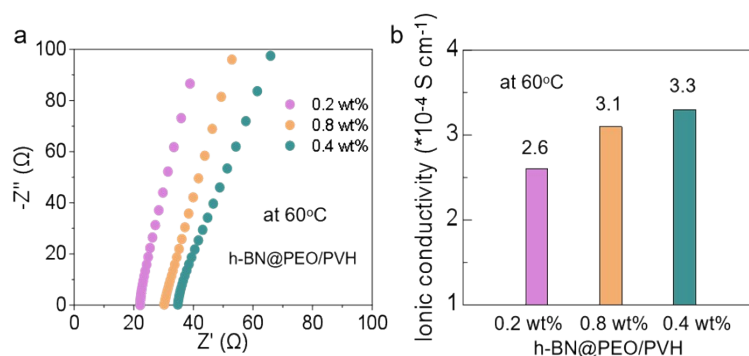
Fig. S12 (a) EIS curves and (b) the ionic conductivities at 60 °C of h-BN@PEO/PVH electrolytes with different h-BN contents.

Tab. S1 The comparison of the h-BN@PEO/PVH electrolyte with previously reported PEO-based electrolytes.

Solid electrolyte	Li-ion transference number	Filler content (wt%)	Thickness (μm)	Voltage window (V)	Ref.
h-BN@PEO/PVH	0.74 (60°C)	h-BN (0.4%)	~ 26	5.0	This work
PEO-ZCNF	0.62 (60°C)	ZCNF (10%)	~ 150	4.51	Angew. Chem. 2024, 136, e202400477.
LAZP/PEO	0.43 (60°C)	LAZP (20%)	~ 150	4.6	Inorg. Chem. Front., 2024, 11, 1289.
VCOF-PEO	0.38 (60°C)	VCOF-1 (4%)	~ 618	4.0	J. Mater. Chem. A 2024, 12, 1694.
PEO-5%C4P	0.70 (60°C)	C4P (5%)	~ 110	2.8	Adv. Mater. 2023, 2308507.
PEO/MOFs-NH$_2$	0.64 (60°C)	MOFs-NH$_2$ (10%)	~ 100	4.5	Adv. Mater. 2023, 2303193.
PEO-BIT-BOB HNFs	0.54 (50°C)	BIT-BOB HNFs (10 %)	~ 120	4.75	Adv. Funct. Mater. 2023, 33, 2307263.
PEO-LLZO	0.41 (60°C)	LLZO (7.5%)	~ 100	5.3	ACS Appl. Mater. Interfaces 2023, 15, 38759.
PEO-SCP	0.42 (60°C)	SCP (5%)	~ 100	4.8	J. Mater. Chem. A 2022, 10, 14849.
SiO$_2$-PEO	0.42 (60°C)	SiO$_2$ (10%)	~ 200	5.3	J. Mater. Chem. A 2022, 10, 3400.