Supporting Information

Materials and experimental methods

Materials.

Poly(ethylene oxide) (PEO) (average M_w. 300 000), Poly(vinylidene fluoride) (PVDF) (average M_w. 500 000), bis(trifluoromethane) sulfonimide lithium (LiTFSI, 99.95%), $LiClO_4$ (99.5%), lithium iron phosphate ($LiFePO_4$, LFP), acetylene black (AB), N,N-dimethylformamide (DMF) and acetonitrile (ACN) (anhydrous, 99.8%) were purchased from Sigma-Aldrich. $La(NO_3)_3 \cdot 6H_2O$ (99.99%), $LiNO_3$ (99.99%), $Ti(OC_4H_9)_4$ (99.0%), citric acid (99.5%), N-methyl-2-pyrrolidone (NMP) and ethylene glycol (99.5%) were purchased from Aladdin. Absolute ethanol (anhydrous, 99.7%) was purchased from Sinopharm. Nanoporous polycarbonate membranes (PC membranes) were purchased from GVS Corp. (pore size ~ 100 nm, 200 nm, 450 nm, and 1 μm). PEO, PVDF, LiTFSI, and $LiClO_4$ were dried at 60 °C under vacuum for 24 hours and subsequently stored in an argon-filled glove box overnight before use. PC membranes were carefully cleaned with pure water and absolute ethanol to remove possible surface contaminations before use.

Synthesis of VLSPE (VLNA), Particle-CPE (LLTO particles), and Electrospun-CPE (LLTO nanowires).

In the fabrication process of the VLSPE, the PC membranes were soaked into LLTO precursor solution and then attached to supporting silicon substrates. Saturated

PC membranes were further kept at a temperature gradually increased from 70 to 120 °C and kept at 120 °C for 12 hours to evaporate the solvent, and then the samples were calcined under 800 °C for 3 hours to allow the LLTO precursor inside the PC template to form a self-supported nano-bundle array on the substrate. Lastly, PEO solution containing LiTFSI was cast onto the vertical LLTO nano-array structure, and after drying in a thermostatic oven and vacuum oven at 60°C for 48 hours, the VLSPE was then obtained.

First, the vertically $Li_{0.5}La_{0.5}TiO_3$ (LLTO) nano-array was prepared by infiltration of LLTO precursor solution and by the following calcined process. For the preparation of the vertically LLTO nano-array, $La(NO_3)_3 \cdot 6H_2O$, $LiNO_3$, and $Ti(OC_4H_9)_4$ of various corresponding molar masses were dissolved in absolute ethanol with 15 wt. % citric acid and 8 vol.% ethylene glycol to form a transparent solution by vigorous stirring. Subsequently, the solvent was evaporated at 70°C for a certain time in the oil bath to form a homogeneous LLTO precursor solution. The porous PC membranes were placed into LLTO precursor solution and sealed in the container then put into a thermostatic oven at 60°C for 24 hours to make sure that the LLTO precursor solution fully infiltrated the PC membranes. For the evaporation and calcination procedure, the obtained porous PC membranes were applied on polished platinum sheets and use a scraper to remove excess solution from the surface of PC membranes. They were then transferred into a thermostatic oven at 70°C for 3 hours, 90°C for 3 hours, and 120°C for 12 hours to remove the solvent. The prepared LLTO gel was subsequently placed in a muffle furnace and calcined on the silicon substrates. The LLTO particles were prepared by the same sol-gel method and the other procedures followed the same drying temperature and time. For the synthesis of electrospun LLTO nanowires, lithium nitrate, lanthanum nitrate hydrate, and tetrabutyl titanate with a molar ratio of 0.3:0.57:1 was dissolved in a mixed solution of acetic acid and DMF with a volume ratio of 2:8 and stirred until transparent. Then, 1.2 g of PVP was dissolved in 8.8 g of DMF and stirred until transparent. Next, the two solutions were mixed and stirred overnight to obtain a 6 wt.% PVP, 0.5 mol L^{-1} LLTO precursor solution. The solution was then drawn into a syringe for electrospinning. A positive voltage of 12 kV was applied to the needle, maintaining a distance of 10 cm between the needle tip and the collector, with a feeding rate of 0.04 mm min^{-1}. The collected LLTO/PVP composite fibers were sintered at 800 °C with a ramp rate of 1 °C min^{-1} and held for 3 hours to obtain electrospun LLTO nanowires.

For the synthesis of composite polymer electrolyte with VLNA (VLSPE), LLTO particles (Particle-CPE), and LLTO nanowires (Electrospun-CPE), LiTFSI and PEO ([EO]: [Li] = 16: 1) were first dissolved in ACN. The mixture was vigorously stirred at room temperature for 5 hours and then cast in a polytetrafluoroethylene (PTFE) petri dish on the obtained materials (VLNA, and LLTO nanowires). For the synthesis of Particle-CPE, LLTO particles with 30 wt. % (total weight of PEO and LiTFSI) were added in the ACN solution and then cast on the PTFE petri dish to get the homogeneous electrolyte film. The filler-free electrolyte was prepared by the same method without adding LLTO particles.

Finally, all the as-obtained films were further dried in a thermostatic oven at 60°C for 12 hours. They were then transferred into a vacuum oven at 60°C for at least 48 hours before measurement to completely remove the solvent. All the CPEs were prepared following the same procedures and drying temperature and time.

We also prepared PVDF-VLSPE and PVDF-Particle-CPE to verify the universality of this structure. For the preparation of PVDF-based electrolytes, $LiClO_4$ and PVDF (2: 1 weight ratio) were dissolved in DMF with a concentration of 10 wt. % of PVDF to form a homogeneous solution. The other procedure to prepare the electrolytes remained the same.

Electrochemical analysis

Electrochemical impedance spectroscopy (EIS) measurements were used to evaluate the ionic conductivity of samples. In the measurements, VLSPE and stainless-steel sheets were assembled into a coin cell with a platinum sheet and a stainless-steel barrier electrode in an argon-filled glove box. Electrochemical impedance spectroscopy (EIS) was carried out at various temperatures of 25 °C and 80 °C in the frequency range of 1 MHz to 1 Hz. For electrochemical stability testing, VLSPE was assembled into a coin cell with a metallic platinum barrier electrode and lithium metal electrode. Linear sweep voltammetry (LSV) was performed at 40 °C, -1 V to 6 V, with a scan rate of 0.2 mV s^{-1}. The interfacial stability between Li metal and SPEs was measured at 60 °C by galvanostatic cycling process of Li//Li cell. The Li//Li symmetric cell was at current densities of 0.10 mA cm^{-2}. During each cycle, Li//Li symmetric cell was charged for 1 hour and discharged for 1 hour. The mixture of LFP, PVDF and AB (8 : 1 : 1, weight ratio) in NMP was mechanically stirred to get homogenous slurry. Then, the slurry was coated on the aluminium foil collector, and the collector was dried under vacuum at 80 °C for 24 h to remove NMP. The loading of active materials in cathode were 1~2 mg cm^{-2}. The electrochemical performances of LMBs were investigated by the battery apparatus (LANHE CT2001 A) at 60 °C using a CR2032 LFP/SPEs/Li coin cell in the voltage range of 2.5 to 4.2 V.

Characterization

X-ray diffraction (XRD) was conducted by the Rigaku Ultima IV system with Cu Kα radiation. The morphology and microstructure of these samples were characterized by field-emission scanning electron microscopy (SEM, ZEISS SIGMA 500) and transmission electron microscopy (TEM, FEI Tecnai G20). The crystallinity of different samples was observed by polarized light microscopy (Axio Scope A1). Thermogravimetric analysis measurements were conducted using Netzsch STA 449 F3. Samples (~10 mg) placed in alumina pans with lids and an empty reference pan were heated from RT to 800 °C at the rate of 10 K min^{-1} to measure the weight. % of LLTO and the thermal stability while under flowing N_2 gas (50 ml min^{-1}). Stress-strain of SPEs were tested using electronic universal testing machine (CMT4104, Shenzhen San Testing Machine Co.).

Definitions:

Vertical LLTO Nano-bundle Array: VLNA

Vertical LLTO nano-array Strengthened Polymer Electrolyte: VLSPE

Templates: PC-0.1, PC-0.22, PC-1, PC-2.5

VNLAs: VLNA-0.1, VLNA-0.22, VLNA-1, VLNA-2.5,

CPEs: VLSPE-0.1, VLSPE-0.22, VLSPE-1, VLSPE-2.5

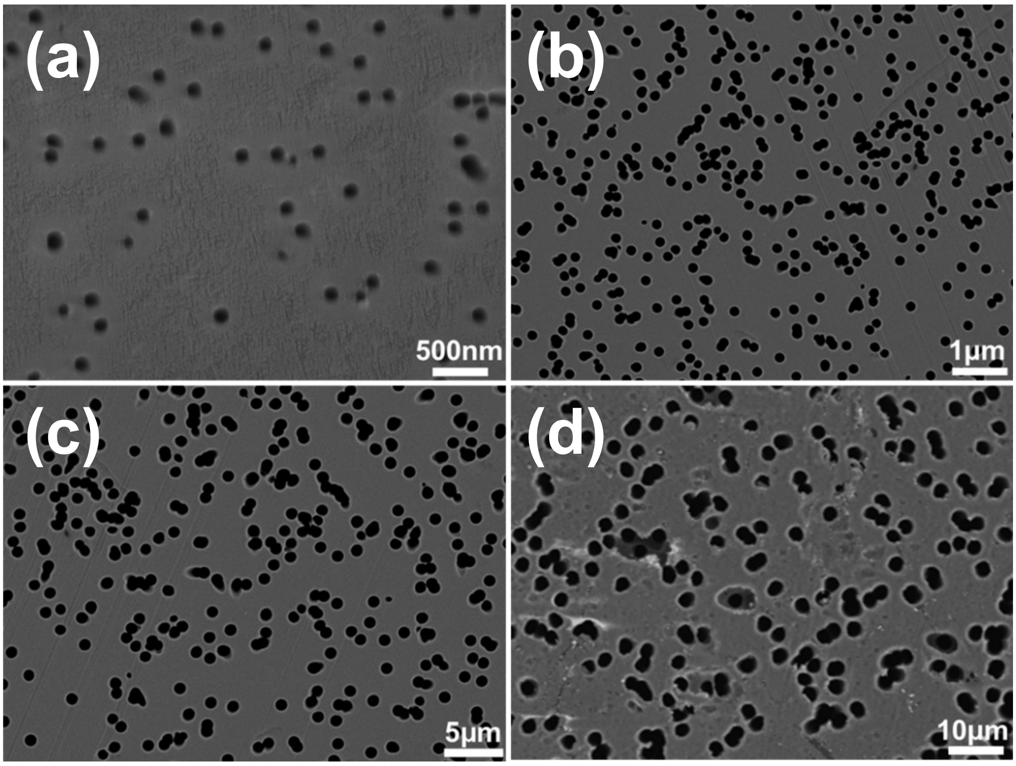

Figure S1. SEM images of flexible polycarbonate (PC) template: (a) PC-0.1, (b) PC-0.22, (c) PC-1, and (d) PC-2.5.

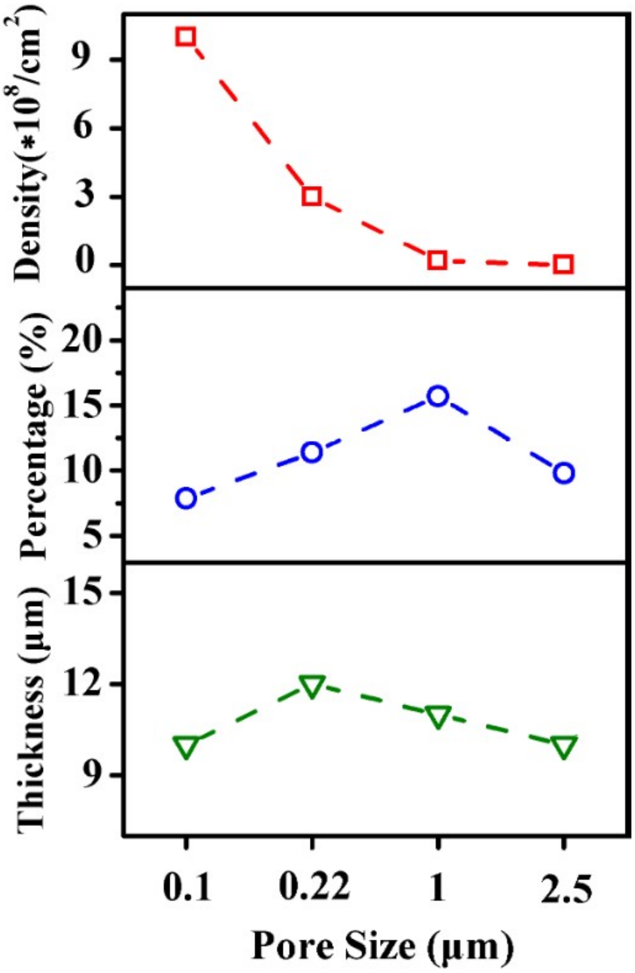

Figure S2. PC membranes' relationships of Pore Size *vs* Parameter: Diameter *vs* Thickness (PC membranes' thicknesses), Diameter *vs* Percentage (total pore area as a percentage of total membrane area) and Diameter *vs* Density (number of micro holes per square centimeter), respectively.

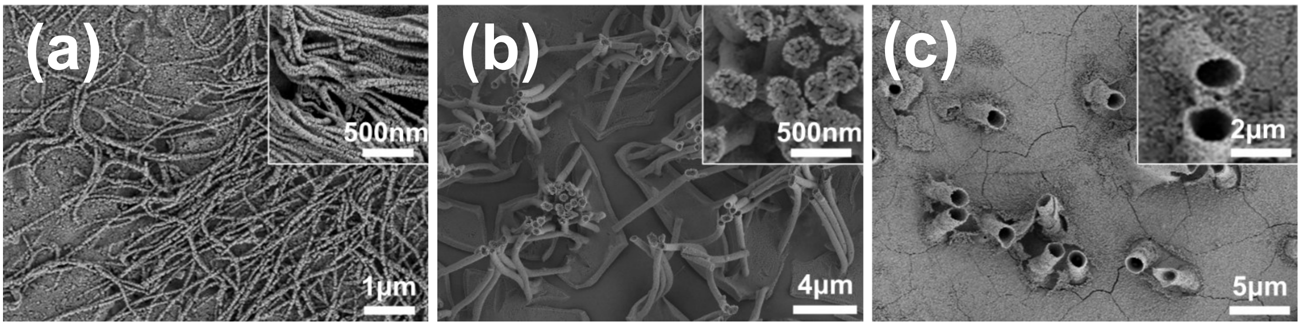

Figure S3. SEM images of VLNAs with different nano-array diameters: (a) 0.1 μm, (b) 1 μm and (c) 2.5 μm, respectively.

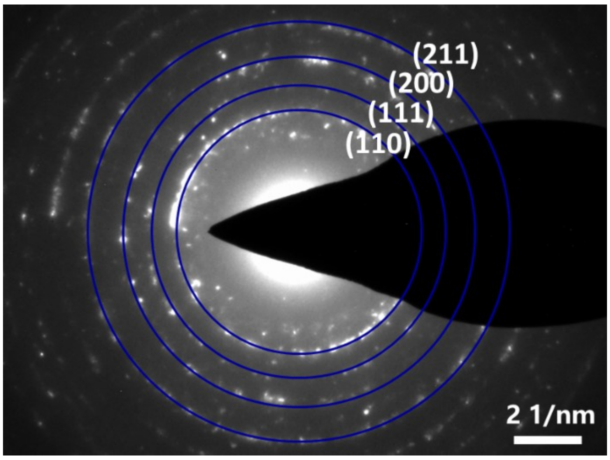

Figure S4. Selected area electron diffraction (SAED) pattern of a single LLTO nanowire.

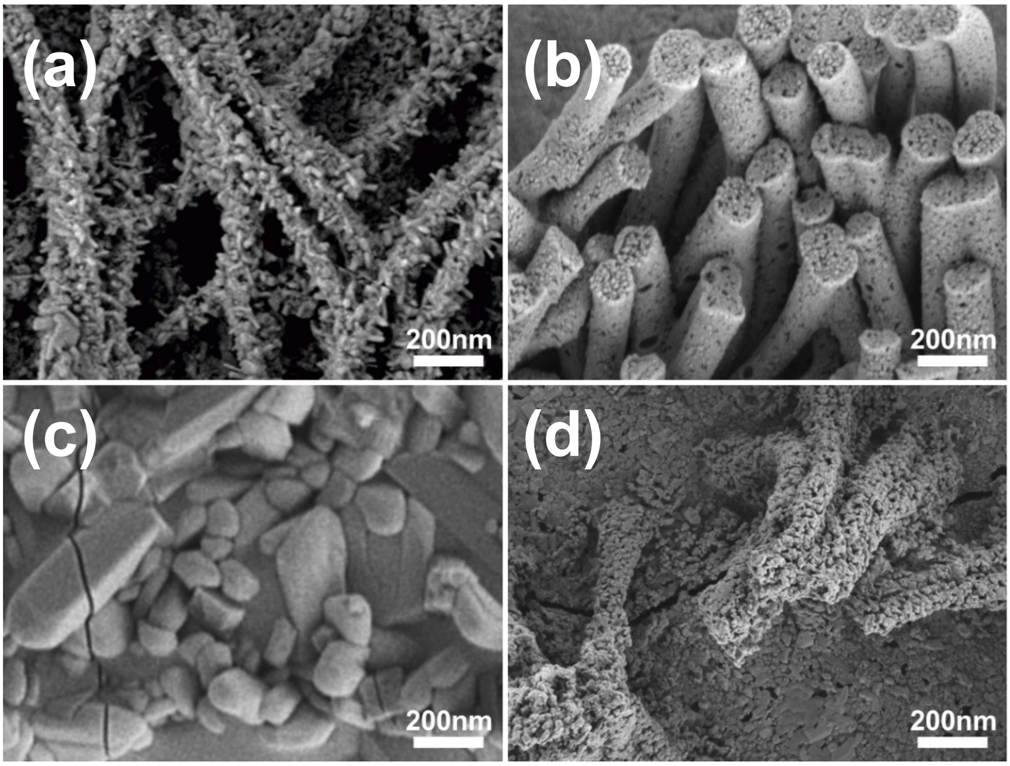

Figure S5. SEM images of VLSPE-0.22 at different heat treatment process: (a) 700 °C for 3 hours, (b) 800 °C for 3 hours, (c) 900 °C for 3 hours, and (d) 800 °C for 1 hour.

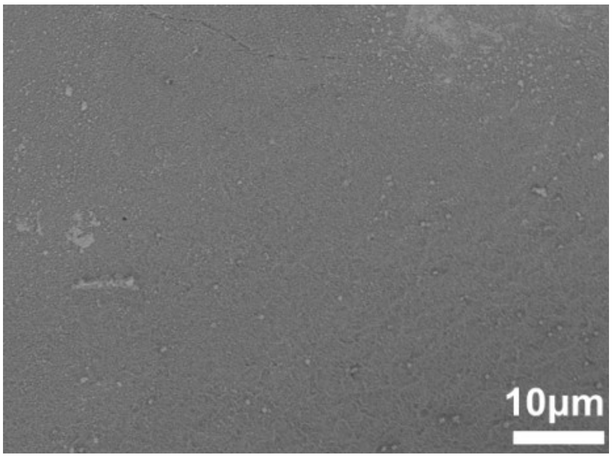

Figure S6. SEM image for the VLSPE-0.22 sample top surface.

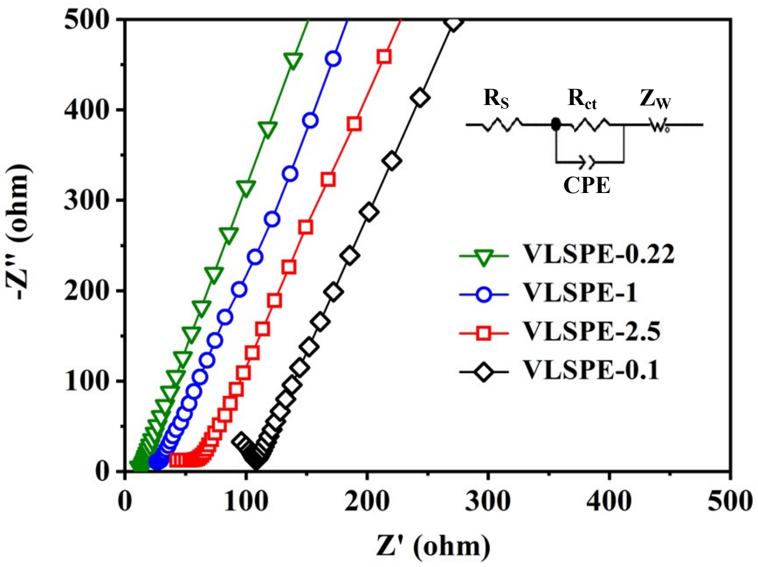

Figure S7. EIS curves for VLSPE with different pore dimeters under 25 °C.

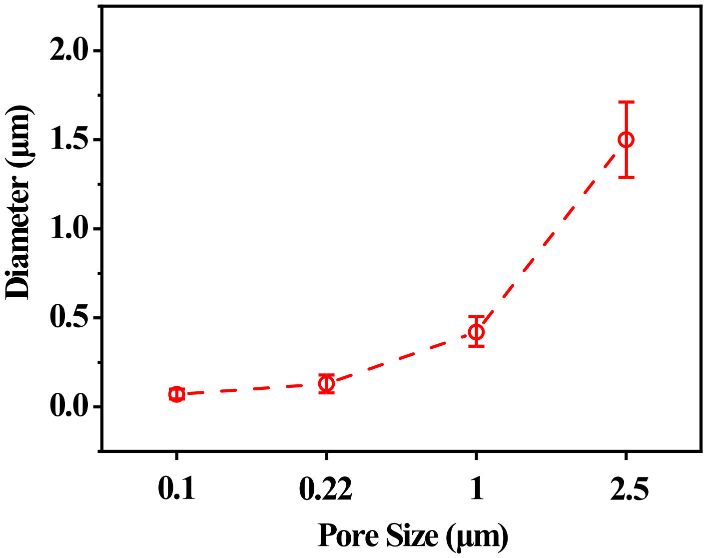

Figure S8. Diameter distribution of VLNA corresponding to PC templates with different pore sizes.

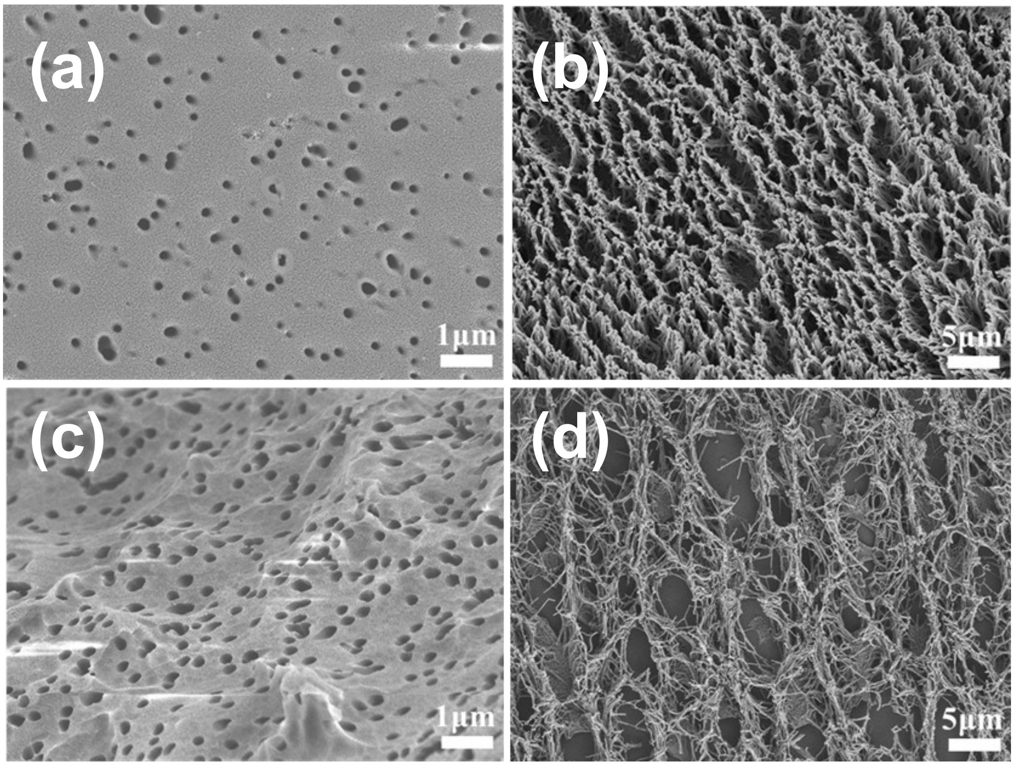

Figure S9. SEM images of flat and rough surfaces of PC templates and their corresponding VLNAs. (a) SEM image of PC-0.22 flat surface and corresponding (b) prepared VLNA, (c) SEM image of PC-0.22 rough surface and corresponding (d) prepared VLNA.

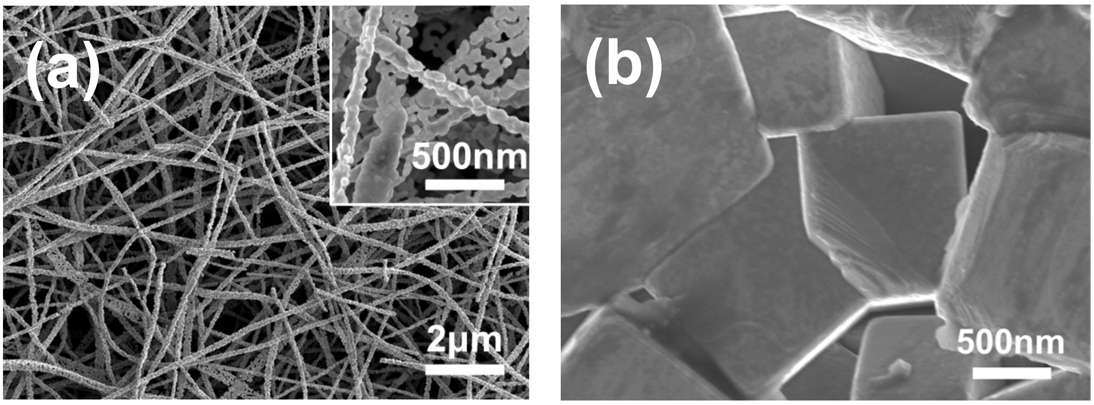

Figure S10. SEM images of (a) electrospun LLTO nanowires, (b) particle LLTO.

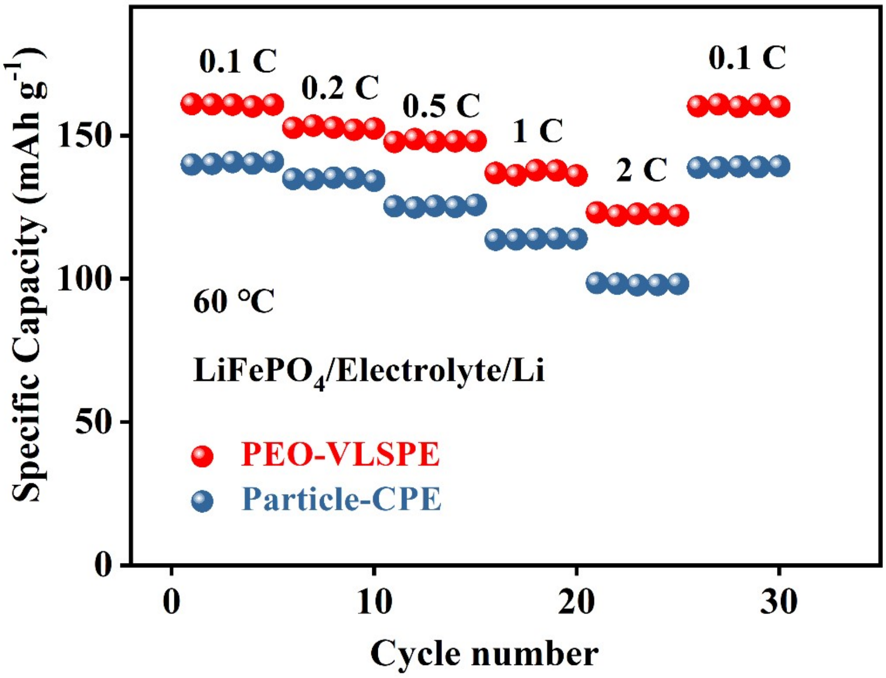

Figure S11. The rate performance curves between PEO-VLSPE and Particle-CPE.

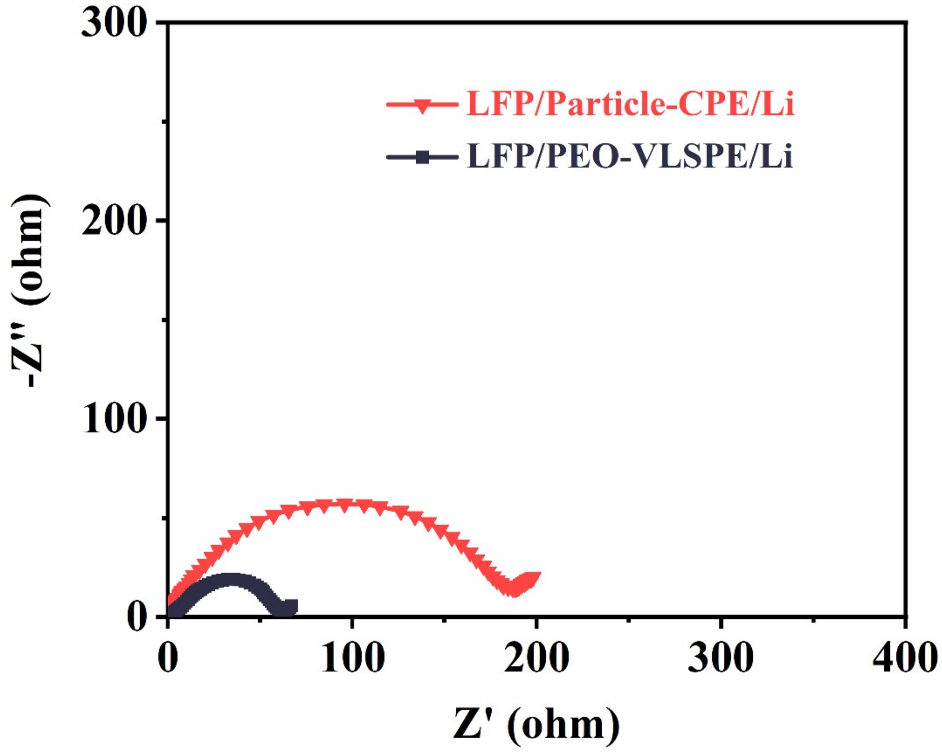

Figure S12. EIS of LFP/Particle-CPE/Li battery and LFP/PEO-VLSPE/Li battery.

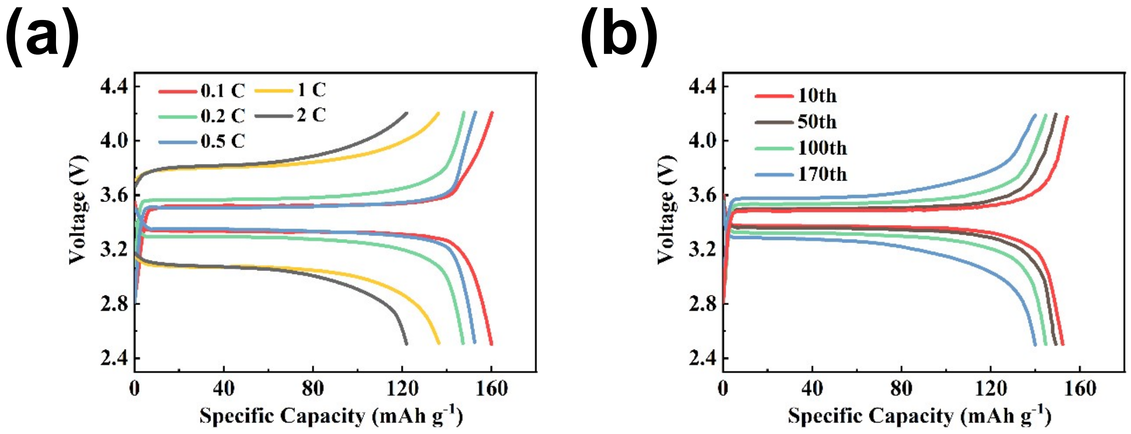

Figure S13. Charge/discharge curves of Li/PEO-VLSPE/LFP cell of (a) rate performances at 60 °C and (b) different cycles at 0.2 C and 60 °C.

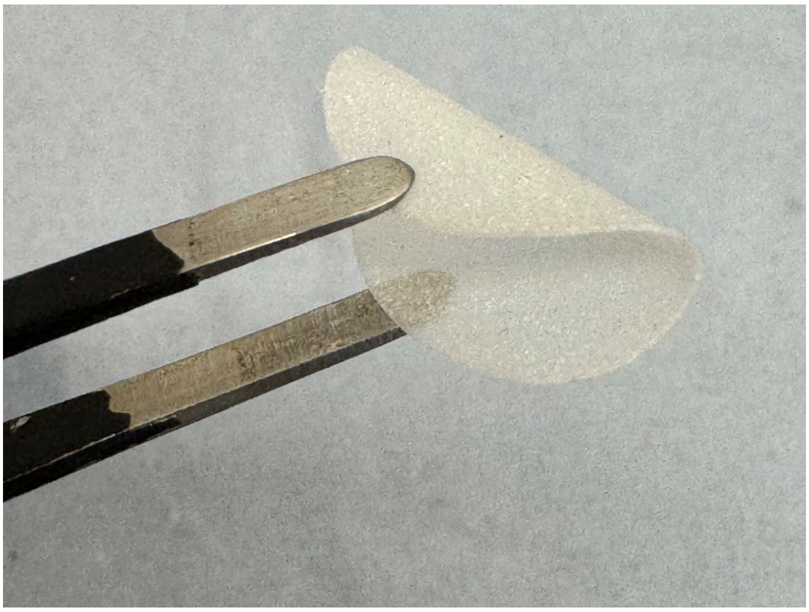

Figure S14. Digital photographs of VLSPE under mechanical bending.

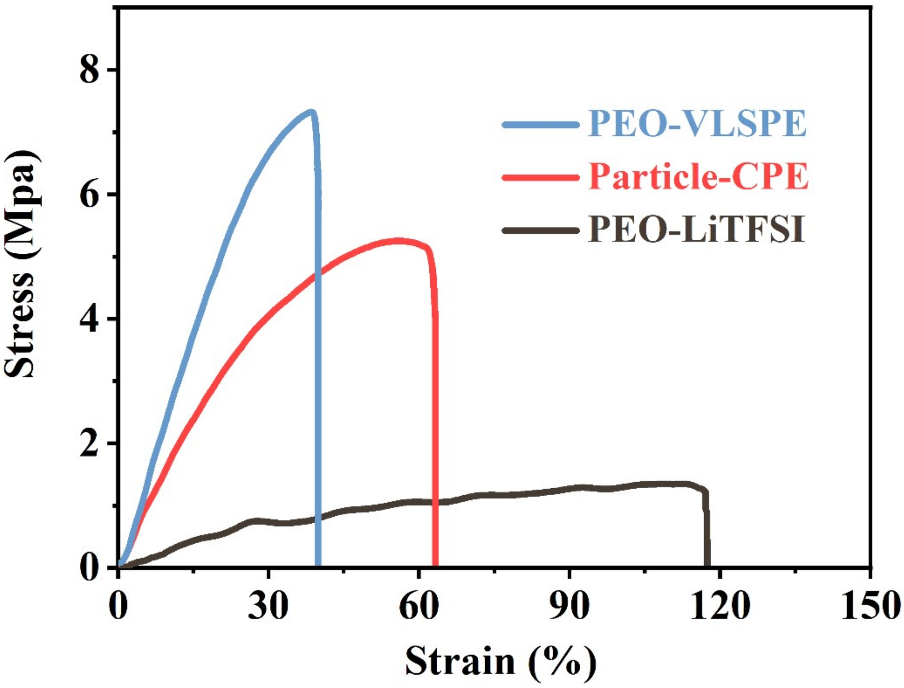

Figure S15. Stress-strain curves of composite electrolytes.

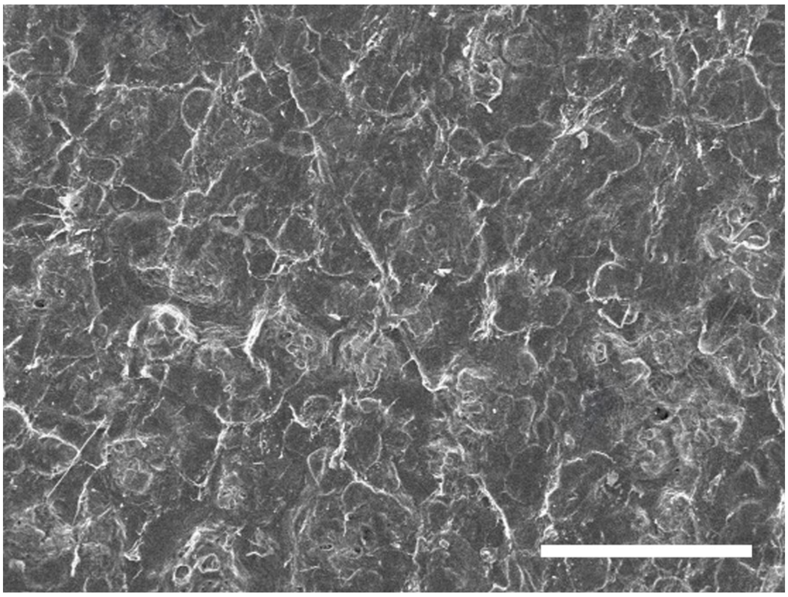

Figure S16. PEO-VLSPE after cycling. Scale bar, 10μm.

Table S1. Ionic conductivities of CPEs under different temperatures.

Temperature (°C)	30	40	50	60	70	80
PEO-VLSPE-0.22	8.47×10^{-5}	1.95×10^{-4}	3.71×10^{-4}	6.44×10^{-4}	1.05×10^{-3}	1.41×10^{-3}
PVDF-VLSPE-0.22	4.25×10^{-5}	8.79×10^{-5}	1.60×10^{-4}	2.70×10^{-4}	3.83×10^{-4}	4.66×10^{-4}
Electrospun-CPE	2.75×10^{-5}	8.91×10^{-4}	2.01×10^{-4}	3.89×10^{-4}	6.17×10^{-4}	8.91×10^{-4}
Particle-CPE	7.08×10^{-6}	2.52×10^{-5}	8.82×10^{-5}	2.06×10^{-4}	3.11×10^{-4}	5.24×10^{-4}

Table S2 Comparison of ionic conductivities between VLSPE and CPEs from published research.

Composite methods	**Fillers**	**Polymers**	**Salt**	**Temperatures**	**Ionic conductivity**
VLSPE-PEO-0.22	LLTO	PEO	LiTFSI	30 °C	8.47×10^{-5}
VLSPE-PVDF-0.22	LLTO	PVDF	$LiClO_4$	30 °C	4.25×10^{-5}
LLZO electrospun fibers[1]	$Li_{6.4}La_3Zr_2Al_{0.2}O_{12}$	PVDF	$LiClO_4$	30 °C	1.16×10^{-4}
Random aligned LLTO[2]	$L_{0.33}L_{0.557}TiO_3$	PAN	$LiClO_4$	30 °C	2.4×10^{-4}
Parallel aligned LLTO[3]	$L_{0.33}L_{0.557}TiO_3$	PAN	$LiClO_4$	30 °C	6.05×10^{-5}
Vertical LATP by ice-templates[4]	$Li_{1+x}Al_xTi_{2-x}(PO_4)_3$	PEO+PEG	$LiClO_4$	25 °C	5.2×10^{-5}
Vertical Al_2O_3 by AAO templates[5]	Al_2O_3	PEO	LiTFSI	25 °C	5.82×10^{-4}
PI membrane templates[6]	PI	PEO	LiTFSI	30 °C	2.3×10^{-4}

References

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