

1D Nanorod-oriented Composite Polymer Electrolytes Fabricated by Electric-field-induced Alignment

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Electronic Supplementary Information

Abstract High-performance solid-state electrolytes (SSEs) are essential for safe and high-energy-density lithium metal batteries. Polymer electrolytes are promising candidates owing to their flexibility and favorable interfacial contact; however, they inherently suffer from insufficient ionic conductivity, which severely limits their practical application. Constructing continuous ion transport pathways within the polymer matrix has proven effective in enhancing ionic conductivity, yet achieving controllable and uniform construction of these pathways remains a significant challenge. Herein, we report a universally applicable and facile electric-field-induced alignment strategy to fabricate a composite solid polymer electrolyte with vertically oriented Al_2O_3 nanorods. The oriented nanorods establish continuous filler-polymer interfaces that function as rapid Li^+ transport pathways, simultaneously enhancing ionic conductivity (75% reduction in full-cell impedance) and mechanical robustness. Furthermore, the oriented structure promotes stable solid electrolyte interphase formation, improving interfacial stability. The oriented electrolyte delivers a reversible capacity of $142.7 \text{ mAh}\cdot\text{g}^{-1}$ after 220 cycles at 60°C and 0.1 C , surpassing the non-oriented counterpart ($133.4 \text{ mAh}\cdot\text{g}^{-1}$).

Keywords Solid-state electrolyte; Electric-field-induced orientation; Lithium batteries; Al_2O_3 nanorods

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INTRODUCTION

Solid-state lithium metal batteries are widely regarded as the most promising next-generation rechargeable energy storage devices, owing to the combined merits of intrinsic safety and the exceptional electrochemical properties of metallic lithium, which exhibits the most negative redox potential (-3.04 V versus standard hydrogen electrode) and an ultrahigh theoretical capacity of $3860 \text{ mAh}\cdot\text{g}^{-1}$.^[1–3] To fully realize these advantages in practical devices, the development of high-performance solid-state electrolytes (SSEs) is highly desirable. Among various candidates, polymer electrolytes have attracted considerable attention due to their excellent flexibility, favorable interfacial contact, and scalable processability.^[4,5] However, they inherently suffer from insufficient ionic conductivity at room temperature and inadequate mechanical strength to effectively suppress lithium dendrite growth.^[6,7]

To address these shortcomings, inorganic fillers have been extensively integrated into polymer electrolytes.^[8–10] Among these, 1D nanofillers (nanowires and nanorods) offer distinct advantages because they not only possess a continuous structure exceeding the traditional percolation threshold to

form long-range ionic percolation networks significantly enhancing ion transport,^[11] but also are more conveniently dispersed and prepared than their 2D and 3D counterparts.^[12,13] Mainly composed of oxides, 1D nanomaterials feature abundant oxygen vacancies or hydroxyl ($-\text{OH}$) groups on their surfaces that interact with the polymer host and Li salt, thereby reducing crystallinity,^[14,15] promoting Li salt dissociation, and enhancing Li^+ mobility.^[11] Consequently, the nanowire–polymer interface is widely considered to serve as a fast ion transport pathway.^[11,16] To construct a continuous nanowire–polymer interface functioning as this efficient ion transport pathway, orienting nanorods perpendicular to the membrane plane represents an effective strategy.^[17] Various strategies have been successfully developed to oriented nanowires in polymer matrices, including directional freeze casting,^[18] mechanical stretching,^[19] magnetic alignment,^[19] and bar coating,^[20] electrospinning,^[21] each yielding well-oriented nanowire architectures in their respective systems. Nevertheless, these approaches suffer from several limitations, including specific material requirements, structural porosity requiring post-infiltration, and complex fabrication steps. Therefore a more universally applicable and facile orientation strategy—one that is compatible with diverse 1D filler compositions—remains highly desirable.

Herein, we report an electric-field-induced orientation strategy for fabricating a vertically oriented composite solid polymer electrolyte with Al_2O_3 nanorods (Figs. 1a and 1b). The continuous interfaces formed between the Al_2O_3

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nanorods and the polymer serve as rapid Li^+ transport pathways, (Fig. 1c) achieving a 75% reduction in full-cell impedance relative to the non-oriented counterpart (Fig. S3 in the electronic supplementary information, ESI). Meanwhile, this oriented architecture promotes the formation of beneficial SEI components such as nitrides and fluorides, improving interfacial stability. Consequently, the oriented composite electrolyte retains a specific capacity of $142.7 \text{ mAh}\cdot\text{g}^{-1}$ after 220 cycles at 60°C and 0.1 C , outperforming the non-oriented counterpart ($133.4 \text{ mAh}\cdot\text{g}^{-1}$).

EXPERIMENTAL

Materials

Polytetrahydrofuran (PTHF, $M_n \approx 2000 \text{ g}\cdot\text{mol}^{-1}$, Shanghai Aladdin

Biochemical Technology Co., Ltd., China), 2-isocyanatoethyl methacrylate (98%, Macklin Inc., China), 1-hydroxycyclohexyl phenyl ketone (Photoinitiator 184, 98%, Shanghai Aladdin Biochemical Technology Co., Ltd., China), dichloromethane (CH_2Cl_2 , 99.9%, extra dry, with molecular sieves, Energy Chemical, China), dibutyltin dilaurate (95%, Shanghai Aladdin Biochemical Technology Co., Ltd., China), (3-aminopropyl)triethoxysilane (KH550, 99%, Energy Chemical, China), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, 99.0%, Shanghai Meryer Biochemical Technology Co., Ltd., China), poly(ethylene glycol) (PEG, $M_n \approx 2000 \text{ g}\cdot\text{mol}^{-1}$, Shanghai Aladdin Biochemical Technology Co., Ltd., China), urea (98%, Shanghai Aladdin Biochemical Technology Co., Ltd., China), *N*-methyl-2-pyrrolidone (NMP, 99.8%, Shanghai Aladdin Biochemical Technology Co., Ltd., China), and anhydrous acetonitrile (ACN, 99.8%, Shanghai Aladdin Biochemical Technology Co., Ltd., China).

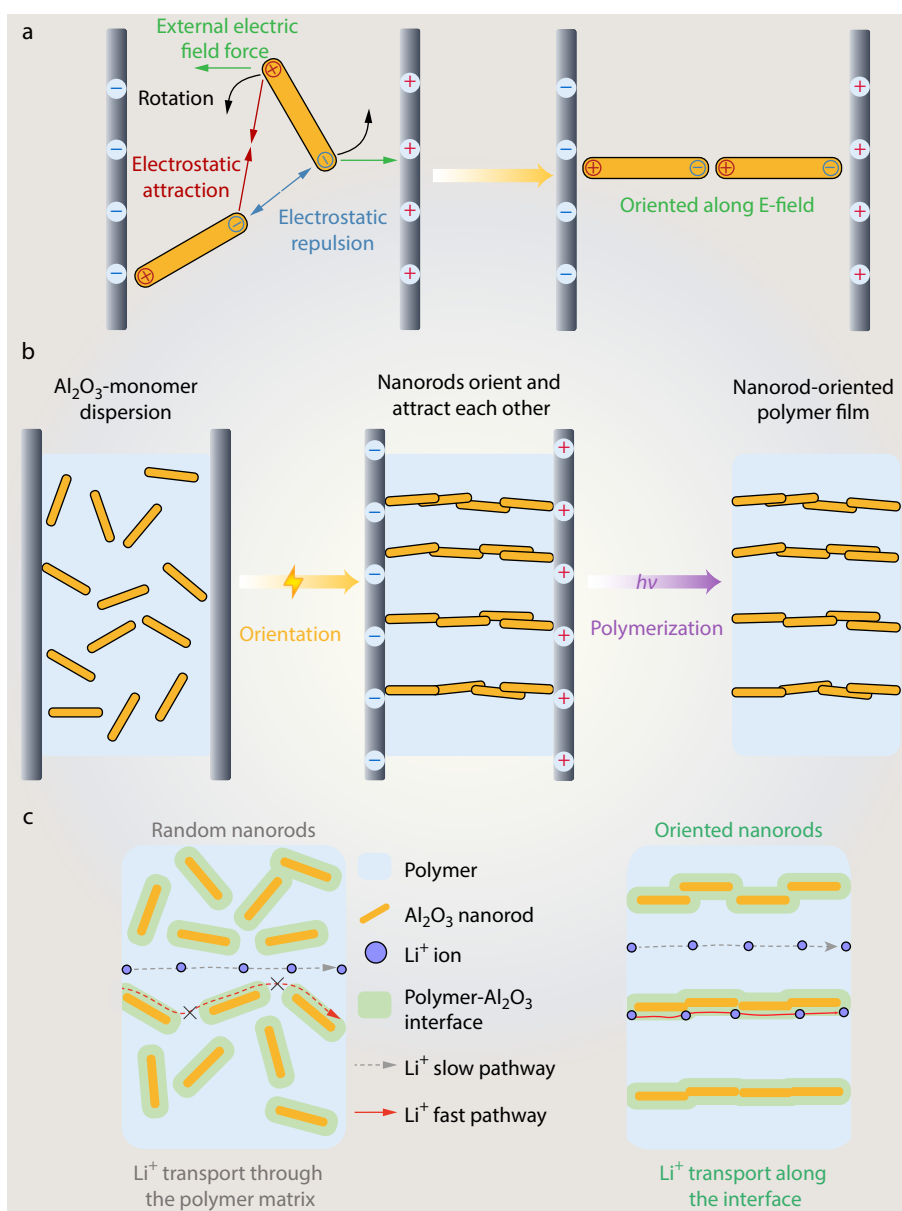


Fig. 1 (a) Schematic of nanorod orientation and interaction under an electric field; (b) Schematic of the electric field-induced orientation process; (c) Schematic illustration showing the construction of Li^+ transport pathways by oriented Al_2O_3 nanorods for enhanced ionic conductivity.

gy Co., Ltd., China) were used as received.

Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99%, Shanghai Aladdin Biochemical Technology Co., Ltd., China) was stored in an argon-filled glovebox ($\text{H}_2\text{O} < 0.1 \mu\text{mol}\cdot\text{mol}^{-1}$, $\text{O}_2 < 0.1 \text{ mL}\cdot\text{m}^{-3}$) after purchase. A customized liquid electrolyte ($1 \text{ mol}\cdot\text{L}^{-1} \text{LiNO}_3 + 0.2 \text{ mol}\cdot\text{L}^{-1} \text{LiDFOB} + 0.05 \text{ mol}\cdot\text{L}^{-1} \text{LiPF}_6$ in diethylene glycol dimethyl ether) was obtained from Suzhou Duoduo Chemical Technology Co., Ltd., China. Poly(vinylidene fluoride) (PVDF), conductive carbon black (Super P), and lithium iron phosphate (LiFePO_4) were purchased from Guangdong Kanai New Energy Technology Co., Ltd. Copper conductive tape, indium tin oxide (ITO) conductive glass, and electrical tape were obtained from 3M Company. All chemicals were used without further purification unless otherwise noted.

Fabrication of Electrolyte Membranes

Synthesis of photopolymerizable monomer

Polytetrahydrofuran (PTHF, $M_n \approx 2000 \text{ g}\cdot\text{mol}^{-1}$, 8.5 g) was placed in a flask and heated at 115°C under vacuum with stirring for 30 min to remove residual moisture. After cooling to room temperature, 2-isocyanatoethyl methacrylate (1.195 mL) was added *via* pipette, followed by anhydrous CH_2Cl_2 (17.0 mL) *via* syringe and one drop of dibutyltin dilaurate as catalyst. The mixture was stirred at 30°C under nitrogen atmosphere for 15 h (Fig. 2a). The disappearance of the isocyanate absorption peak (about 2250 cm^{-1}) of 2-isocyanatoethyl methacrylate confirms that the reaction has reached completion (Fig. 2b and Fig. S1 in ESI).

Synthesis of Al_2O_3 nanorods

8.0 g of aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$), 8.0 g of urea, and 20.0 g of poly(ethylene glycol) (PEG, $M_n = 2000 \text{ g}\cdot\text{mol}^{-1}$) were dissolved in 42.0 mL of deionized (DI) water under magnetic stirring. The resulting homogeneous solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 120°C for 24 h. After cooling naturally to room temperature, the white precipitate was collected by filtration, washed with DI water and ethanol, and dried at 60°C overnight to obtain the alumina nanorod precursor. Subsequently, the dried powder was placed in an alumina crucible and calcined in a muffle furnace at 600°C for 3 h (heating rate: $10^\circ\text{C}\cdot\text{min}^{-1}$) in air to yield aluminum oxide (Al_2O_3) nanorods.

1.0 g of Al_2O_3 nanorods was dispersed in ethanol (30.0 g) in

a flask. Magnetic stirring and ultrasonication were alternated for 1 h to achieve uniform dispersion. (3-Aminopropyl)triethoxysilane (KH550, 4.0 mL) was added, and the mixture was heated at 70°C with stirring for 15 h. The product was collected by centrifugation at $9000 \text{ r}\cdot\text{min}^{-1}$ for 5 min, washed with ethanol for three times, and dried under vacuum at 60°C for 12 h to obtain surface-modified Al_2O_3 nanorod (supporting note 1 in ESI).

Preparation of precursor dispersion

Modified Al_2O_3 nanorod were dispersed in the as-synthesized monomer solution (3.00 mL) in a 5 mL vial. Magnetic stirring and sonication were used for 2 h to obtain a stable dispersion that remained homogeneous without visible sedimentation for over 5 min.

A series of dispersions containing varying mass fractions of nanorods were prepared. Through conductivity measurements of the resulting electrolyte membranes (Figs. 3a and 3b), a loading of 2 wt% was identified as the optimal ratio, corresponding to 60 mg of nanorods dispersed in 3.00 mL of monomer solution.

Fabrication of oriented and non-oriented polymer membranes

10 mg of Photoinitiator 184 was added to the precursor dispersion and dissolved *via* brief ultrasonication (about 5 min). The dispersion was injected into a custom mold assembled from two parallel ITO-coated conductive glass slides separated by a silicone spacer of defined thickness (about $300 \mu\text{m}$).

For oriented membranes: an alternating current electric field (500–2.0 kV, 1 kHz) was applied across the dispersion for 5 min using a Trek 610E high-voltage amplifier (Trek, Inc., USA) connected to a Keysight 33500B waveform generator (Keysight Technologies). Photopolymerization was subsequently initiated by UV irradiation (365 nm , $10 \text{ mW}\cdot\text{cm}^{-2}$) for 200 s.

For non-oriented membranes: the dispersion was injected into an identical mold assembled from glass slides and photopolymerized under identical UV conditions without electric field application.

The resulting polymer membranes were removed from the mold and dried in air for 30 min.

Fabrication of solid-state electrolyte membranes

A solution of LiTFSI in acetonitrile was prepared at a mass ratio

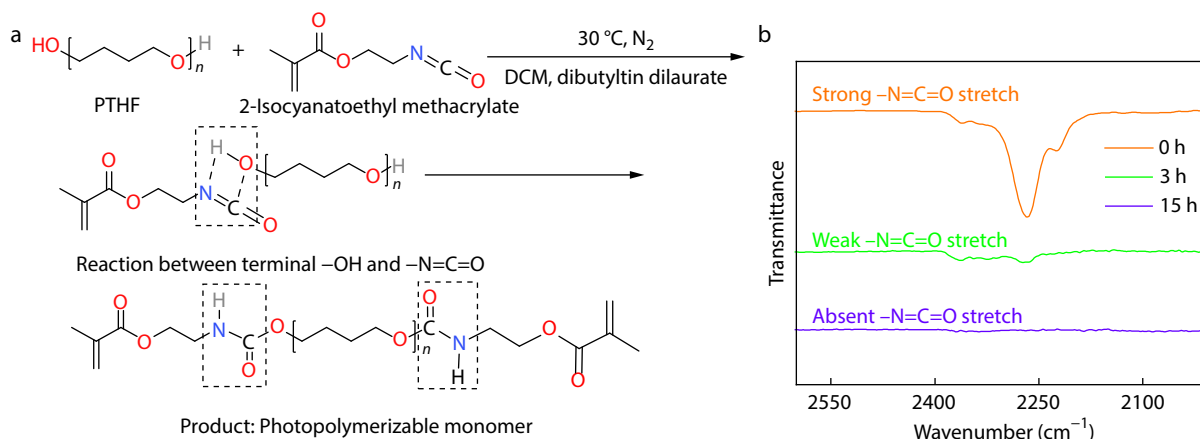


Fig. 2 (a) Synthesis of photopolymerizable monomers; (b) FTIR spectra of the reaction mixture: initial (0 h), 3 h, and 15 h.

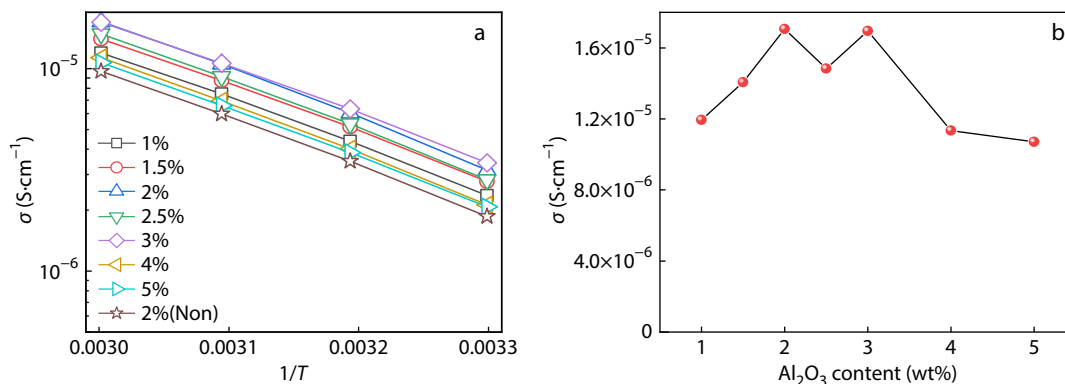


Fig. 3 (a) Temperature-dependent ionic conductivity of electrolyte membranes with varying nanorods contents (30–60 °C); (b) Ionic conductivity at 60 °C as a function of nanorods content.

of 0.273 g : 1.00 mL. The polymer membrane was immersed in this solution for 30 min until saturated (no further mass increase observed upon extended immersion). The membrane was then dried at 60 °C for 12 h, followed by vacuum drying at 60 °C for 24 h. The resulting solid-state electrolyte membrane was transferred to an argon-filled glovebox ($\text{H}_2\text{O} < 0.1 \mu\text{mol}\cdot\text{mol}^{-1}$, $\text{O}_2 < 0.1 \text{ mL}\cdot\text{m}^{-3}$) for storage and subsequent characterization.

Sample nomenclature: samples prepared with electric-field-induced orientation are denoted as Oriented; those prepared without electric field treatment are denoted as Non-oriented; samples prepared without nanorods and without electric field treatment are denoted as Pure polymer.

Characterization

Scanning electron microscopy (SEM) images were acquired using a Zeiss Gemini 500 microscope at an accelerating voltage of 10 kV. Confocal Raman spectroscopy was performed on a LabRAM Soleil spectrometer (Horiba) equipped with a 785 nm laser. ^7Li solid-state nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 600 MHz spectrometer at a spinning rate of 10 kHz. Differential scanning calorimetry (DSC) measurements were conducted on a TA Instruments Discovery DSC 250 under nitrogen atmosphere ($50 \text{ mL}\cdot\text{min}^{-1}$). Samples were subjected to a thermal program consisting of: (i) cooling from room temperature to -150°C at $10^\circ\text{C}\cdot\text{min}^{-1}$, (ii) heating to 100°C at $10^\circ\text{C}\cdot\text{min}^{-1}$, and (iii) cooling to 0°C at $10^\circ\text{C}\cdot\text{min}^{-1}$. Glass transition temperatures (T_g) were determined from the second heating curve using the inflection point method.

Tensile testing was performed using a CMT1503 universal testing machine (SUST, China) at room temperature. All samples were punched into dumbbell-shaped specimens (overall dimensions: $50 \text{ mm} \times 8.5 \text{ mm}$; gauge section: $20 \text{ mm} \times 4 \text{ mm}$; thickness: about $190 \mu\text{m}$). Tests were conducted at a crosshead speed of $3 \text{ mm}\cdot\text{min}^{-1}$ using a 50 N load cell. At least five specimens were tested for each sample, and average values with standard deviations are reported.

X-ray photoelectron spectroscopy (XPS) depth profiling was performed on a PHI GENESIS 500 spectrometer (ULVAC-PHI, Japan) using monochromated Al K α radiation ($h\nu = 1486.6 \text{ eV}$, 48.1 W). Lithium metal anodes retrieved from symmetric cells after 50 cycles were rinsed with anhydrous 1,3-dioxolane (DOL) to remove residual surface species and transferred to the spectrometer *via* an argon-filled transfer vessel to prevent air exposure. Ar^+ etching was performed at 2 kV

for 30 s and 60 s (cumulative etching time), with high-resolution spectra of C 1s, O 1s, N 1s, Li 1s, F 1s and S 2p acquired sequentially after each etching cycle. Binding energies were calibrated to the C 1s peak at 284.8 eV.

Cell Assembly and Electrochemical Measurements

LiFePO_4 , Super P and PVDF were mixed in a mass ratio of 8:1:1 and ground with *N*-methyl-2-pyrrolidone (NMP) to form a homogeneous slurry. The slurry was coated onto carbon-coated aluminum foil using a doctor blade and vacuum-dried at 100°C for 24 h. The resulting cathode film was punched into 12 mm diameter discs with an areal mass loading of $1.5\text{--}2.0 \text{ mg}\cdot\text{cm}^{-2}$ (active material).

Ionic conductivity (σ) was determined by electrochemical impedance spectroscopy (EIS) using stainless steel|solid polymer electrolyte|stainless steel (SS|SPE|SS) symmetric cells. The polymer membrane was sandwiched between two stainless steel blocking electrodes (diameter: 16 mm) in 2025-type coin cells. EIS measurements were performed on a PARSTAT MC electrochemical workstation (Princeton Applied Research) over a frequency range of 1 MHz to 1 Hz with an AC amplitude of 10 mV. The ionic conductivity (σ) was calculated according to:

$$\sigma = \frac{L}{A \times R_b} \quad (1)$$

where L (cm) is the thickness of the electrolyte membrane measured by micrometer, A (cm^2) is the geometric contact area, and R_b (Ω) is the bulk resistance determined from the high-frequency intercept of the Nyquist plot with the real axis.

Symmetric cells: Li|SPE|Li cells were assembled using pristine lithium discs (diameter: 14 mm, thickness: about $450 \mu\text{m}$) as both electrodes.

Full cells: Li|SPE|LiFePO $_4$ cells were assembled with lithium metal as the anode and LiFePO $_4$ as the cathode. To ensure sufficient ionic contact within the composite cathode, $2.5 \mu\text{L}$ of customized liquid electrolyte was drop-cast onto the cathode surface prior to assembly.

All cells were assembled in 2025-type coin cells (stainless steel, Canrd) in an argon-filled glovebox ($\text{O}_2 < 0.1 \text{ mL}\cdot\text{m}^{-3}$, $\text{H}_2\text{O} < 0.1 \mu\text{mol}\cdot\text{mol}^{-1}$) in the following order (from positive to negative): cathode, solid polymer electrolyte, lithium anode, spacer, spring, and negative case.

Cells were rested at 60°C for 8 h prior to electrochemical testing. All measurements were performed at 60°C . Galvanos-

tatic cycling of symmetric cells was conducted at a current density of $0.05 \text{ mA}\cdot\text{cm}^{-2}$ with a plating/stripping capacity of $0.05 \text{ mAh}\cdot\text{cm}^{-2}$ per half-cycle. Full cell cycling tests were performed at 0.1 C ($1 \text{ C}=170 \text{ mA}\cdot\text{g}^{-1}$) within a voltage window of $2.8\text{--}4.0 \text{ V}$ versus Li/Li^+ using a Neware battery testing system (CT-4008-5V50mA-164, Shenzhen, China).

RESULTS AND DISCUSSION

To establish the generality of electric-field-induced alignment for one-dimensional ceramic fillers in solid-state electrolytes, a model system with well-defined and reproducible properties is required. In this work, Al_2O_3 nanorods were employed as the platform material. As a wide-bandgap insulator, Al_2O_3 is electrochemically inert toward lithium metal and has been widely adopted as a passive filler in polymer electrolytes.^[15] The dielectric permittivity of Al_2O_3 ($\epsilon_r \approx 9\text{--}10$) is typical of common inorganic oxide fillers, and successful alignment of such nanorods indicates that the electric-field-induced strategy is not restricted to high-permittivity materials, but is applicable to a wide variety of ceramic fillers.^[22] Additionally, Al_2O_3 nanorods can be synthesized *via* established hydrothermal routes with precisely controlled aspect ratios and surface chemistry, enabling uniform morphology and facile silane modification for stable dispersion. With this model system, we investigated the electric-

field-driven alignment behavior and its impact on the ionic transport properties of the resulting composite electrolytes.

The Al_2O_3 nanorod-monomer dispersion was injected into a custom orientation mold and subjected to an electric field. As shown in Fig. 1(a), the suspended nanorods become polarized under the field, with opposite charges accumulating at their two ends, thereby forming positive and negative poles (induced dipoles). The nanorods are subjected to two distinct forces: (1) an orienting force from the external field that exerts a torque on each nanorod, causing it to rotate until it points parallel to the field direction; and (2) electrostatic interactions between neighboring nanorods, where opposite poles attract and same poles repel, pulling adjacent nanorods into close contact. Ultimately, the nanorods assemble into linear chains oriented along the electric field.

Through varying the applied voltage, electrolyte membranes exhibiting different orientations were prepared (supporting note 2 in ESI). As shown in Fig. 4(a), the nanorods had diameters below 500 nm and lengths of approximately $20 \mu\text{m}$. Cross-sectional SEM images (Figs. 4b–4d) reveal that the degree of nanorod orientation increased with the applied voltage: the nanorods were randomly distributed at 500 V (Fig. 4b), partially oriented and non-uniform at 1000 V (Fig. 4c), and preferentially oriented perpendicular to the membrane plane with a uniform distribution at 2000 V (Fig. 4d)

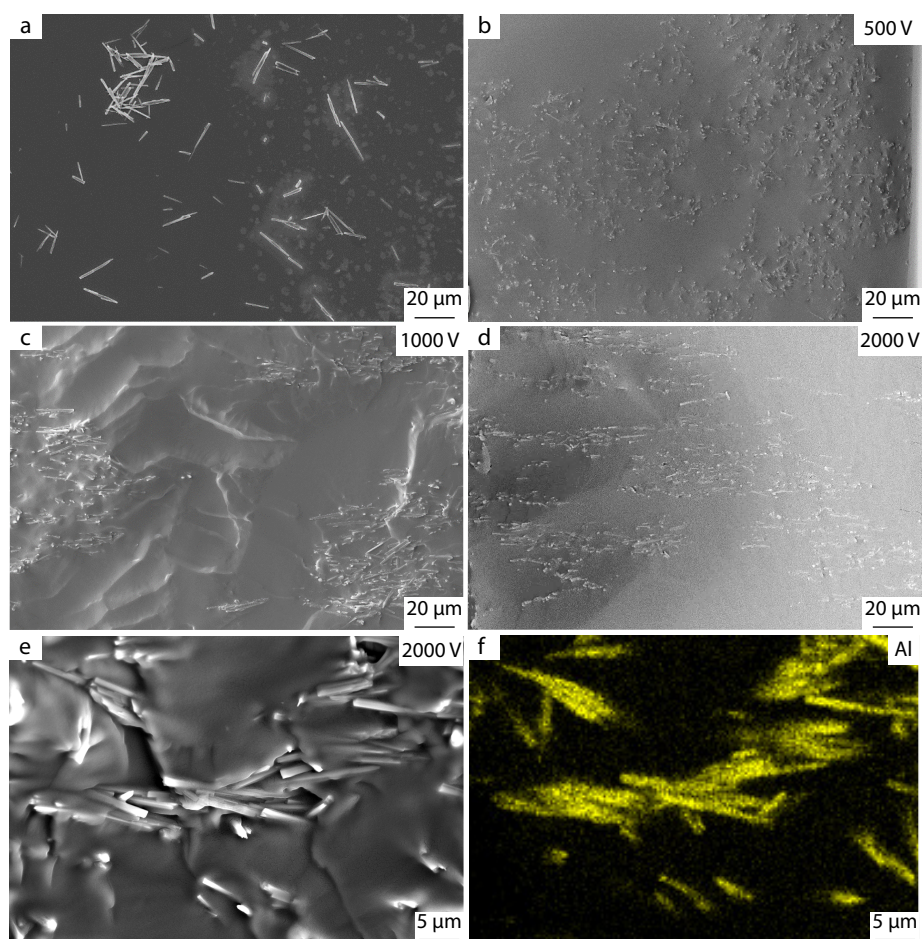


Fig. 4 (a) Al_2O_3 nanorods SEM image, and cross-sectional SEM images of membranes prepared under various electric fields (1 kHz): (b) 500 V , (c) 1000 V , (d, e) 2000 V ; (f) The Al elemental mapping of (e).

(The orientation distribution histograms are shown in Fig. S6 in ESI). Fig. 4(e) presents a higher-magnification cross-sectional SEM image revealing individual Al_2O_3 nanorods aligned perpendicular to the membrane surface. Fig. 4(f) shows the corresponding EDS mapping of Al, confirming that the rod-like features are indeed Al_2O_3 nanorods. Based on these results, all subsequent samples were fabricated under an electric field of 2000 V. In this work, samples prepared with electric-field-induced orientation are designated as oriented samples; those prepared without electric field treatment are designated as non-oriented samples; and samples prepared without nanorods and without electric field treatment are designated as pure polymer samples.

To investigate the effect of orientation on the thermal and mechanical properties of the samples, differential scanning calorimetry (DSC) and tensile tests were conducted. As shown in Fig. 5(a), the glass transition temperatures (T_g) for the oriented, non-oriented, and pure polymer samples are -63.0 , -61.5 and -63.4 °C, respectively. The incorporation of Al_2O_3 nanorods results in a pronounced elevation of T_g , which can be ascribed to the restricted segmental mobility arising from the adsorption interactions between randomly dispersed nanorods and polymer chains. By contrast, the oriented sample exhibits a T_g comparable to that of the pure polymer, indicating that regularly oriented nanorods do not significantly hinder polymer segmental motion.^[23,24] These findings are further substantiated by tensile testing (Fig. 5b). Compared to

the pure polymer, the non-oriented sample shows a marked decrease in elongation at break. This arises from the adsorption of polymer chains onto the nanorod surface, which restricts segmental mobility and suppresses molecular sliding. Furthermore, the random distribution of nanorods creates localized stress concentration points, leading to premature matrix fracture.^[25,26] In contrast, the oriented sample exhibits increased elongation at break relative to the pure polymer sample. The oriented nanorod architecture exhibits minimal constraints on chain motion, while favorable interfacial interactions overall enhance the mechanical properties compared to the non-oriented state.

Raman spectroscopy was performed to investigate the influence of oriented nanorods on the solvation structure of the polymer electrolyte. The corresponding spectra are presented in Fig. 5(c). The peaks in the $739\text{--}745\text{ cm}^{-1}$ region are generally assigned to the S—N—S stretching vibration of TFSI⁻.^[27–29] The non-oriented sample exhibits the similar peak positions to the pure polymer electrolyte, at 739.5 and 743.0 cm^{-1} , while the oriented sample shows peaks shifted to 741.3 and 744.8 cm^{-1} . The higher S—N—S stretching vibration frequency of TFSI⁻ observed in the oriented sample is attributed to stronger interactions between TFSI⁻ and the Lewis acidic Al sites on the surface of the aligned nanorods.^[30,31] NMR results further confirmed this observation. As shown in Fig. 5(d), the ^7Li -NMR peaks for the pure polymer, and oriented samples appeared at -0.23 , and -0.12 ppm , respectively. A down-

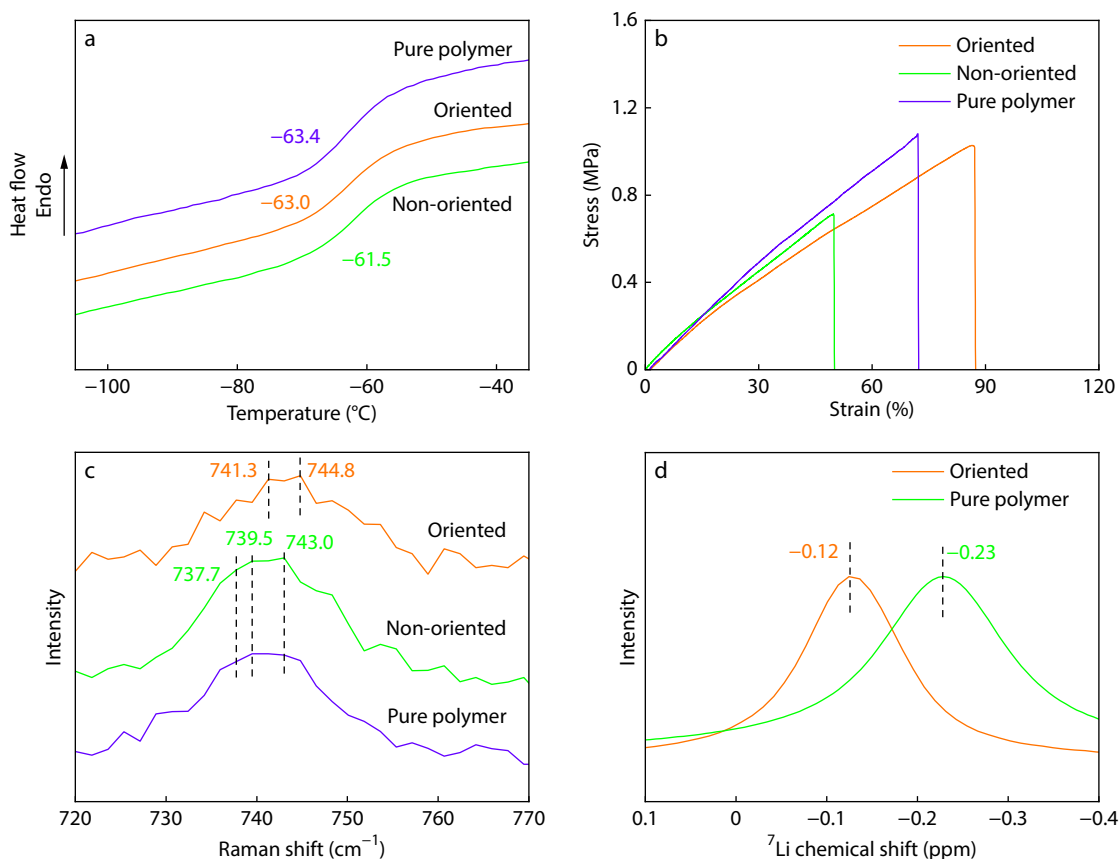


Fig. 5 Thermal, mechanical, and spectroscopic characterization of the oriented, non-oriented, and pure polymer electrolytes: (a) DSC curves; (b) tensile properties; (c) Raman spectra in the $720\text{--}770\text{ cm}^{-1}$ region; (d) ^7Li solid-state NMR spectra.

field shift of 0.11 ppm (from -0.23 ppm to -0.12 ppm), suggesting an increased deshielding effect and decreased electron cloud density around Li^+ .^[32,33] This indicates enhanced Li^+ dissociation and increased free Li^+ concentration. This is consistent with the anion-immobilization mechanism: as TFSI^- is anchored to the Al_2O_3 surface, Li^+ is released from Li^+TFSI^- ion pairs and becomes available for transport.

The combined evidence supports a mechanism where aligned Al_2O_3 nanorods create continuous interfacial regions with (1) anion-acceptor sites that immobilize TFSI^- and promote salt dissociation, and (2) fast Li^+ conduction pathways along the nanorod-polymer interface where freed Li^+ cations migrate with lower activation energy. This anion-immobilization-induced cation-release mechanism is well-documented in composite solid electrolytes.

To evaluate the interfacial stability and elucidate the SEI evolution under electrochemical cycling, Ar^+ etching and XPS analysis were conducted on the Li metal anodes of symmetric cells after 50 cycles. The SEI layer formed on the oriented sample was abundant in fluorinated compounds after cycling (Figs. 6a–6c and Fig. S4 in ESI), whereas the non-oriented and pure polymer samples exhibited lower fluoride contents.^[34] The formation of the LiF-rich SEI layer is widely rec-

ognized for its high mechanical modulus, low electronic conductivity, and chemical inertness, which is favourable for stabilizing the Li interface, demonstrating that the oriented nanorods promote the formation of fluorinated species in the SEI.^[35–37] The oriented sample showed a strong C–F peak at the surface; however, the C–F signal decreased while the LiF signal increased after etching (Fig. 6a), suggesting a bilayer SEI structure composed of a flexible organic exterior and a rigid inorganic interior. This structure enhances both interfacial contact and ion transport. The distinct SEI composition originates from the stronger interaction between aligned Al_2O_3 nanorods and TFSI^- anions, as established in our Raman and ^7Li -NMR analysis. In the oriented electrolyte, the aligned nanorods present a continuous, high-density interface with surface-exposed Al^{3+} Lewis acid sites that effectively immobilize and catalytically activate TFSI^- anions. This promotes the reductive decomposition of TFSI^- at the electrode interface, generating: LiF (from C–F bond cleavage in TFSI^-); Li_3N (from S–N bond cleavage in TFSI^-); organic fluorides (residual C–F containing fragments, evidenced by C–F bonds in the outer SEI layer).^[38,39]

In the N 1s XPS spectra (Figs. 6d–6f), the nitrogen peak of the pure polymer sample was barely detectable. In contrast,

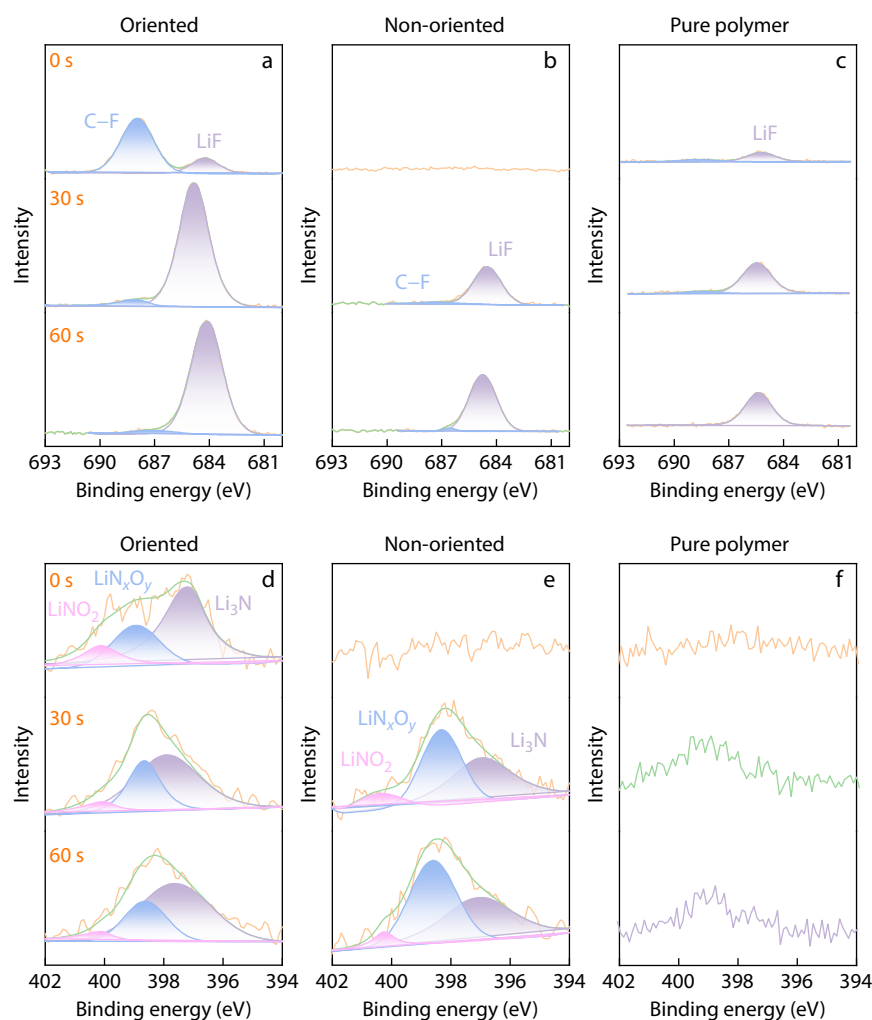


Fig. 6 XPS depth profiles of the SEI layer of three samples after 50 cycles at different etching times (0, 30, 60 s): (a, b, c) F 1s, and (d, e, f) N 1s.

both the oriented and non-oriented samples exhibited distinct nitrogen signals, whereas the oriented sample displayed a significantly higher nitrogen content. These results indicate that the oriented Al_2O_3 nanorods facilitate the formation of nitrogen- and fluorine-containing compounds in the SEI layer on the Li metal anode.

Li symmetric cells were assembled with the three samples, and electrochemical impedance spectroscopy (EIS) was performed after 1, 5, 10, 20, and 50 cycles to investigate the interfacial behavior between the Li metal anode and the electrolyte. The interfacial layer resistance (R_{SEI}) and charge transfer resistance (R_{ct}) were extracted by fitting the Nyquist plots (Figs. 7a–7c). The impedance values of both the oriented and non-oriented samples were substantially lower than that of the pure polymer sample, indicating that the incorporation of Al_2O_3 nanorods addition significantly reduced both R_{SEI} and R_{ct} . The impedance values of both the oriented and non-oriented samples were comparable after cycling and decreased progressively with increasing cycle number. Notably, the two samples differed markedly in their initial impedance: the oriented sample initially exhibited a substantially larger R_{ct} (about 1100 Ω), which gradually decreased to about 550 Ω after 50 cycles (Fig. 7a). In contrast, the non-oriented sample remained relatively stable within the range of 500–600 Ω with little change throughout cycling (Fig. 7b). This initial difference originated from interfacial contact issues; although the

oriented nanorods enhanced the mechanical properties of the membrane, they compromised the physical contact with the Li metal anode, resulting in inferior initial interfacial contact compared to the non-oriented sample (Fig. 5b). Nevertheless, the oriented sample rapidly developed a high-quality SEI layer during cycling, which substantially reduced the interfacial impedance and thereby improved long-term performance. Consequently, the oriented sample achieved superior long-term cycling stability in symmetric cells relative to its non-oriented counterpart (Fig. 7d). Pure polymer sample exhibited poorer initial contact and inferior SEI formation (Fig. 7c), resulting in the worst cycling performance, as confirmed by XPS analysis.

The full-cell cycling results are presented in Figs. 8(a)–8(d). The oriented sample exhibited slight initial capacity fading that rapidly stabilized, delivering 142.7 $\text{mAh}\cdot\text{g}^{-1}$ after 220 cycles. In contrast, the non-oriented sample showed more capacity fading within the first 10 cycles, with a final capacity of 133.4 $\text{mAh}\cdot\text{g}^{-1}$. The Pure polymer was highly unstable, exhibiting rapid capacity decay during the initial 10 cycles and retaining only 123.7 $\text{mAh}\cdot\text{g}^{-1}$ after 220 cycles. The superior performance of the oriented composite is attributed to a stable SEI layer, uniform Li deposition, and enhanced ionic conductivity. Notably, the full-cell impedance decreased by 75% (from 1170 Ω to 288 Ω) for the oriented sample compared to the non-oriented counterpart (Figs. S3 and S5 in ESI), further

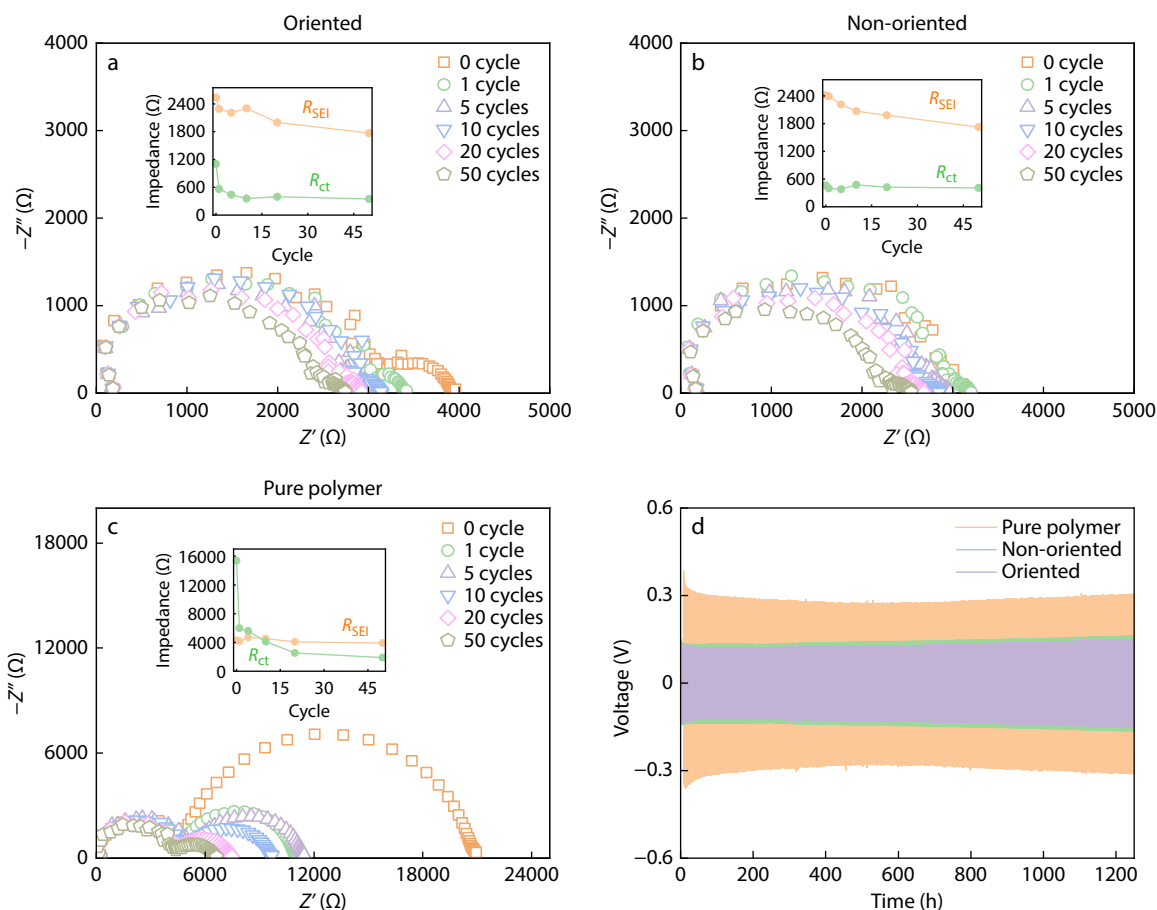


Fig. 7 Electrochemical impedance spectra of Li symmetric cells after 1, 5, 10, 20, and 50 cycles: (a) oriented, (b) non-oriented, and (c) pure polymer samples; insets show the evolution of R_{SEI} and R_{ct} as a function of cycle number. (d) Galvanostatic cycling of symmetric cells at 0.05 mA and 60 °C.

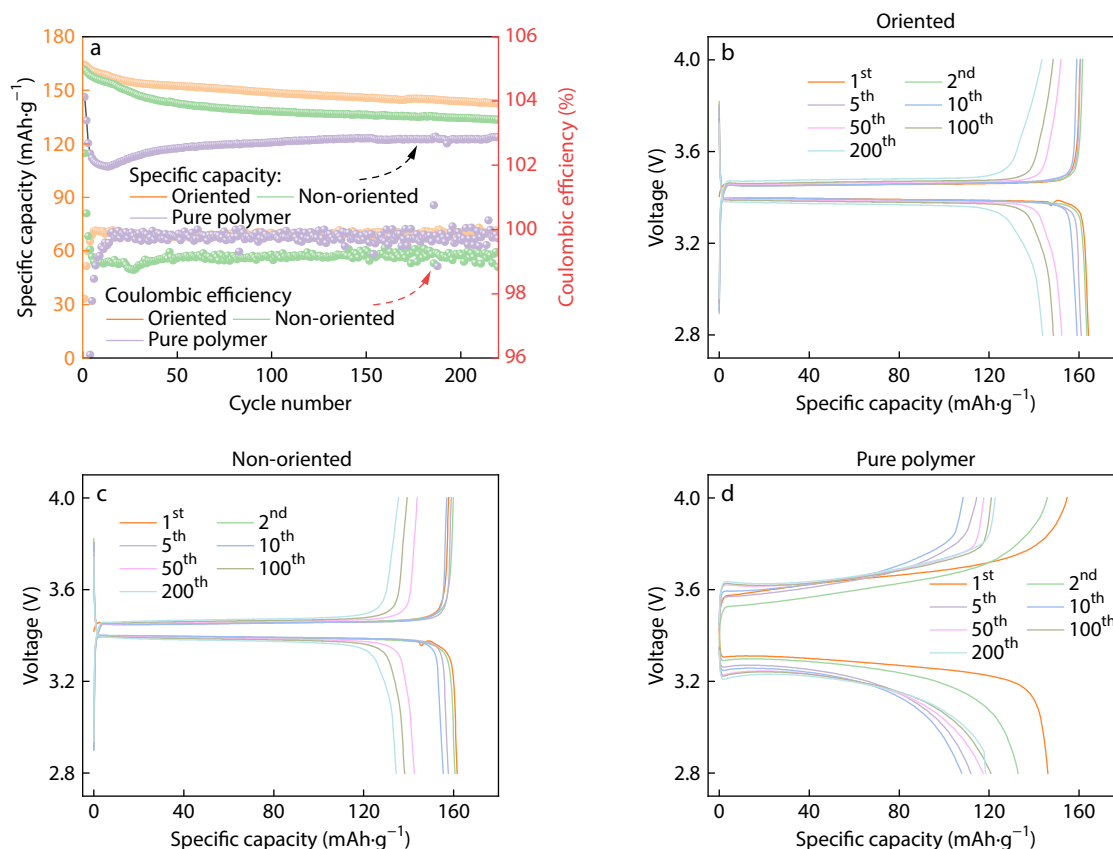


Fig. 8 (a) Full-cell cycling performance at 0.1 C and 60 °C; (b–d) Representative galvanostatic charge-discharge profiles at selected cycles from the long-term cycling test in (a) for (b) oriented, (c) non-oriented, and (d) pure polymer samples.

confirming the formation of efficient Li⁺ transport pathways.

Finally, we note that the electric-field-induced alignment strategy demonstrated here is not limited to the Al₂O₃/PTHF system. The dielectrophoretic mechanism is material-agnostic and applicable to various ceramic fillers (SiO₂, TiO₂, LLZO, LATP, etc.), polymer matrices (PEO, PEGMA, etc.), and potentially other battery systems (Na-ion, solid-state Li-S, etc.), provided that the dielectric properties and precursor viscosity are compatible with the alignment process. Detailed discussion of these extensions is provided in the Supporting Information.

CONCLUSIONS

In this work, an electric-field-induced orientation strategy was employed to prepare a composite solid-state electrolyte with vertically oriented Al₂O₃ nanorods. These oriented nanorods establish stable filler-polymer interfaces that function as rapid Li⁺ transport pathways, significantly enhancing ionic conductivity and reducing full-cell impedance by 75%. Furthermore, the oriented structure promotes the formation of nitrogen- and fluorine-containing species in the SEI layer, improving cycling stability. Consequently, the oriented sample delivers a reversible capacity of 142.7 mAh·g⁻¹ after 220 cycles at 60 °C and 0.1 C, outperforming the non-oriented sample (133.4 mAh·g⁻¹).

More broadly, this work establishes a facile orientation strategy with minimal material constraints. Using readily available Al₂O₃ nanorods and photopolymerizable monomers

as model materials, oriented architectures are readily achieved *via* straightforward electric-field induction. This universally applicable approach is thus extendable to diverse 1D fillers within various polymer matrices (supporting note 3 in ESI).

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-026-3812-5>.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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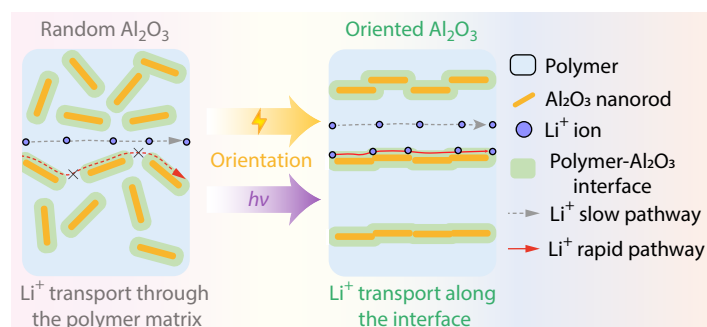
Graphical Abstract

1D Nanorod-oriented Composite Polymer Electrolytes Fabricated by Electric-field-induced Alignment

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An electric-field-induced alignment strategy is demonstrated for composite solid polymer electrolytes. Oriented nanorods create continuous Li^+ transport pathways, enhancing ionic conductivity, battery performance, and cycling stability *via* a stable solid electrolyte interface (SEI).



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