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# Thin Polymer Electrolytes with 3D Nanofiber Skeletons Enabling High-Performance Solid-State Lithium Metal Batteries

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**ABSTRACT:** Polymer electrolytes are extensively utilized in solid-state batteries due to their high flexibility, excellent interfacial contact with the electrodes, and low cost. However, they suffer from issues such as large thickness, low room-temperature ionic conductivity, and poor mechanical properties. In this study, we employ an environmentally friendly and straightforward vacuum filtration method to obtain a thin poly(ethylene oxide) (PEO)–aramid nanofiber (ANF)–LiTFSI composite electrolyte film with a small thickness of  $25-42 \ \mu$ m. Compared with the solution-casting method, the rapid vacuum filtration process leads to the formation of a 3D interpenetrating ANF network structure and also a continuous ion conductivity of  $3.27 \times 10^{-5}$  S cm<sup>-1</sup> and a high strength of 5.19 MPa, which is 26 times that of the solution-casted PEO–LiTFSI electrolyte. Furthermore, the thin electrolyte shows excellent lithium dendrite suppression capability, and the thin electrolyte-containing lithium metal batteries deliver a capacity retention of 78% after 180 cycles with an average Coulombic efficiency of 99.9%. The thin electrolyte with the 3D nanofiber skeleton developed in this work possesses great potential for high-performance lithium metal batteries.

# 1. INTRODUCTION

Lithium-ion batteries (LIBs) have been widely adopted in new energy vehicles, consumer electronics, and energy storage stations due to their high energy density, high voltage platform, low self-discharge rate, and absence of memory effect.<sup>1–5</sup> However, there is an increasing demand for enhanced safety, energy density, and cycle life of the secondary batteries.<sup>6–8</sup> Solid-state electrolytes, characterized by their nonflammability, noncorrosiveness, and nonvolatility, are considered as an ideal alternative to commonly used liquid electrolytes.<sup>9,10</sup>

Compared to inorganic electrolytes, solid polymer electrolytes (SPEs) are thought as promising candidates in solid-state LIBs for their ease of fabrication, low cost, excellent film-forming property, good flexibility, and low interfacial impedance with electrodes, which could fundamentally address safety issues associated with liquid electrolytes.<sup>11–14</sup> However, the development of SPEs is challenged by the low room-temperature ionic conductivity ( $10^{-8}$  to  $10^{-6}$  S cm<sup>-1</sup>), poor mechanical properties, and susceptibility to lithium dendrite

penetration through the electrolyte membrane, severely limiting their application in solid-state lithium batteries.<sup>15–17</sup>

A few important methods such as copolymerization, polymer blending, and nanofiller incorporation are commonly used to modify polymer electrolytes.<sup>18–21</sup> In comparison with other modification techniques, the addition of inorganic nanofillers can enhance the overall performance of polymer electrolytes. The nanofillers primarily serve in the polymer matrices for three functions: increasing the amorphous regions of the polymer matrices, which facilitates the Li<sup>+</sup> migration;<sup>22,23</sup> generating rapid Li<sup>+</sup> pathways on the nanofiller surfaces;<sup>24,25</sup> and enhancing the mechanical properties of the polymer

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Figure 1. Preparation of thin electrolytes. (a) Schematic description of the preparation procedure of the PEO–ANF–LiTFSI CPE by a vacuum filtration method; (b) interactions among PEO, LiTFSI, and ANF; (c) merits of the filtrated electrolyte films.

electrolytes.<sup>26</sup> However, the inorganic nanofillers with high specific surface areas are prone to aggregate in the polymer matrices, and thus, it is difficult to form a continuous nanofiller/polymer interfacial phase, which limits the further improvement in the electrical and mechanical properties of the SPEs.<sup>27–29</sup> Furthermore, solution casting is commonly used to prepare polymer electrolytes; however, this method presents a few drawbacks such as the large electrolyte thickness and the solvent evaporation in the drying process, resulting in environmental pollution and solvent wastage.<sup>30–32</sup> Therefore, there is an urgent need to develop an environmentally friendly method to prepare thin composite polymer electrolytes (CPEs) with excellent mechanical and electrical properties for high-performance LIBs.

In this study, we exploit a straightforward vacuum filtration method to fabricate thin CPEs by using aramid nanofibers (ANFs) with abundant amide groups as a multifunctional nanofiller (Figure 1a). This preparation approach yields thin  $(25-42 \ \mu m)$  yet high-strength poly(ethylene oxide) (PEO)-ANF-LiTFSI CPE films with 3D interpenetrating ANF networks because of the strong hydrogen bonding interactions among the amide groups in the ANFs (Figure 1b,c). The hydrogen bonding interactions between the amide groups in the ANFs and the -O- groups in the PEO chains and the -N- groups in TFSI<sup>-</sup> can also effectively prevent ANF aggregation within the polymer matrices, suppress the PEO crystallization, and promote LiTFSI dissociation, thereby enhancing the ionic conductivity of the CPEs. Simultaneously, substantial fast-ion pathways created at the 3D continuous PEO/ANF interfaces would further increase the ionic conductivity. Besides, the solvents are easily recycled by using this fabrication method, avoiding environmental pollution and solvent waste caused by the solvent drying process in the commonly used solution casting method. As verified by theoretical calculations and experimental measurements, the thin CPE films exhibit high ionic conductivity and mechanical strength, a wide electrochemical window, and

excellent capacity to inhibit the lithium dendrite growth, and the thin CPE-containing LIBs also display enhanced electrochemical cycling stability. Therefore, this work holds significant potential for achieving high-performance LIBs by employing the 3D nanofiber framework-supported thin CPEs.

## 2. EXPERIMENTAL SECTION

2.1. Preparation of the Electrolytes. 4.0 g of potassium hydroxide (KOH, Aladdin, ≥99.99%) was added into 200 mL of anhydrous dimethyl sulfoxide (DMSO, Alfa,  $\geq$ 99.99%) and stirred for 30 min to ensure that most of the KOH was dissolved in DMSO, and then 4.0 g of long Kevlar 69 microfiber (DuPont,  $\geq$ 99.99%) sheared to a length of 2 cm was added, and the stirring process was continued for 14 days to obtain a dark-red 20 mg  $mL^{-1}$  of ANF solution. 25, 75, 125, 175, 225, and 275 mg of the ANF solution were taken, respectively, and then dropped slowly into 72 mL of dimethylformamide (DMF) and stirred for 4 h to obtain an ANF/DMF solution. Then 1.835 g of PEO (Macklin,  $M_w$ : 600,000) was added into the ANF/DMF solution and stirred for 12 h at 40 °C to obtain an ANF/PEO/DMF solution. 0.665 g of LiTFSI (Aladdin, ≥99%) was dissolved in 3 mL of DMF to obtain a LiTFSI/DMF solution. Subsequently, the LiTFSI/DMF solution was slowly dripped into the ANF/ PEO/DMF solution with a plastic dropper and stirred for 24 h to obtain an ANF/PEO/LiTFSI/DMF solution. The speed of dripping should be slow to ensure that the mixture solution did not solidify.

The thin PEO–ANF–LiTFSI electrolyte membranes were prepared by a vacuum filtration method followed by a vacuum drying process. First, 10 mL of the ANF/PEO/LiTFSI/DMF mixed solution was taken for vacuum filtration under a low pressure of –0.05 MPa for 30 min to obtain a PEO–ANF– LiTFSI gel film. After that, 2 mL of a 1 M LiTFSI/ethanol solution was dripped in the gel film under the same vacuum conditions, and the film was immediately removed from the filter membrane after the vacuum filtration process. Then the



Figure 2. Morphology of the electrolytes.  $(a_{11}a_{22}b_{13}b_{23}c_{11}c_{23}d_{13}d_{23})$  Surficial and  $(e_{11}e_{23}f_{13}f_{23}g_{13}g_{23}h_{13}h_{23})$  cross-sectional SEM images of  $(a_{11}a_{22}e_{12}e_{23})$  ANF1,  $(b_{11}b_{23}f_{13}f_{23}g_{13}h_{2$ 

film was vacuum-dried in an oven at 40  $^{\circ}$ C for 48 h to obtain thin PEO–ANF–LiTFSI electrolyte films. Note that the filtrate collected in the vacuum filtration process should be evaporated at 60  $^{\circ}$ C in vacuum to remove water for reusing DMSO and DMF solvents. The PEO–ANF–LiTFSI CPEs were labeled ANF1, ANF3, ANF5, ANF7, and ANF9 according to the weight percentage of the ANF in the electrolytes.

PEO-LiTFSI electrolyte films were prepared by a traditional solution casting method as a control group. The PEO/ LiTFSI/acetonitrile mixed solution was obtained by pouring 0.665 g of LiTFSI and 1.835 g of PEO into 40 mL of acetonitrile (ACN, Aladdin,  $\geq$ 99.90%) and stirring strongly for 24 h. The mixed solution was poured into a plastic mold and dried at 60 °C under vacuum for 48 h to obtain the PEO-LiTFSI electrolyte film.

2.2. Characterizations. In this experiment, a field emission scanning electron microscope (SEM) SU8010 manufactured by Hitachi was used to characterize the micromorphology of the electrolyte films. A D8 Focus X-ray diffractometer (XRD) was utilized to investigate the crystallinity of the electrolytes. Fourier infrared (FTIR) spectroscopy in the mode of ATR with a wavenumber range of 500-4000 cm<sup>-1</sup> was used to determine the changes of chemical bonds and functional groups in the composition of the electrolyte films. Thermogravimetric analysis (TGA) tests were performed on the electrolytes in nitrogen at 30-800 °C with a temperature increase rate of 10 °C min<sup>-1</sup> to study the thermal stability. A solid-state nuclear magnetic resonance spectrometer (ssNMR) was employed to perform <sup>7</sup>Li magic angle spinning at 12 kHz. A mechanical tensile tester was used to obtain the tensile stress-strain curves of the electrolytes. To evaluate their mechanical strength, the Young's modulus of the electrolyte films was calculated by eq 1

$$E = \frac{\sigma}{\epsilon} \tag{1}$$

where  $\sigma$  is the stress (MPa) obtained by stretching the electrolyte and  $\varepsilon$  is the strain (%) obtained by stretching the electrolyte.

Differential scanning calorimetry (DSC) tests were performed on the electrolytes; i.e., the difference in heat flow between the substance and the reference with temperature or time was measured under a programmed temperature control and a certain flow atmosphere, and the crystallinity of the electrolytes was calculated from the enthalpy of fusion of the samples according to eq 2

$$X_{\rm c} = \frac{\Delta H_{\rm m}}{\Delta H_{\rm m}^*} \tag{2}$$

where  $X_c$  is the degree of crystallinity (%),  $\Delta H_m$  is the enthalpy of melting of the crystallized portion of the polymer, and  $\Delta H_m^*$ is the enthalpy of melting of 100% crystallization of the polymer. The test condition of this experiment was as follows: the temperature was reduced to -90 °C at a rate of -5 °C min<sup>-1</sup> and held at -90 °C for 10 min, and then the temperature was increased to 110 °C at a rate of 5 °C min<sup>-1</sup>. The DSC curve of the electrolytes was obtained during the temperature increase process from -90 to 110 °C.

**2.3. Electrochemical Measurements.** The electrochemical AC impedance test was carried out using a ZAHNER electrochemical workstation in the frequency range of 0.01 Hz to 1 MHz on the assembled stainless steel (SS)|SPE|SS cells so as to calculate the ionic conductivity of the electrolytes by eq 3

$$\sigma = \frac{l}{RS} \tag{3}$$

where *l* is the electrolyte thickness (cm), *R* is the impedance of the electrolyte ( $\Omega$ ), and *S* is the contact area between the electrolyte and the electrodes (cm<sup>2</sup>).



**Figure 3.** Physical characteristics of the electrolytes. FT-IR spectra of ANF1, ANF3, ANF5, and ANF7 electrolytes with the wavenumber range of (a) 500–4000 cm<sup>-1</sup> and (b) 600–800 cm<sup>-1</sup>; (c) XRD patterns of ANF1, ANF3, ANF5, ANF7, and PEO–LiTFSI electrolytes; (d) DSC curves of ANF1, ANF3, ANF5, ANF5, ANF7, and PEO–LiTFSI electrolytes.

The electrochemical window of the assembled SSISPEILi cells was tested by a linear voltametric scanning method with a voltage range of 0–6 V and a scanning rate of 0.001 V s<sup>-1</sup>. The electrochemical cycling performance of the assembled LilSPEI Li and LilSPEILiFePO<sub>4</sub> cells was obtained by using a Neware battery test system. The assembled LilSPEILi batteries were tested at constant charge/discharge currents of 0.1 mA cm<sup>-2</sup> with a charge/discharge time of 1 h. The assembled LilSPEI LiFePO<sub>4</sub> batteries were tested under a charging/discharging voltage ranging from 2.5 to 3.8 V. The nominal specific capacity of the LiFePO<sub>4</sub> batteries was defined as 170 mA h g<sup>-1</sup>.

### 3. RESULTS AND DISCUSSION

**3.1. Microstructure of the Electrolytes.** The average diameter of the ANFs in the DMSO solution was 11.21 nm because of the deprotonation of the Kevlar 69 microfibers by KOH (Figure S1). The PEO–ANF–LiTFSI electrolytes (denoted as ANF1, ANF3, ANF5, ANF7, and ANF9) were successfully prepared by the novel vacuum-assisted filtration method, and their optical photographs are shown in Figure S2. It can be observed that the film-forming capability of the composite electrolytes is good. As the ANF content increases, the CPE films gradually become more yellow and the color is also uniform, indicating a relatively homogeneous distribution of the ANF frameworks in the electrolytes.

SEM was employed to characterize the surface and crosssectional morphology of the electrolytes, as illustrated in Figures 2 and S3. The ANF1 electrolyte had a few cracks on the surface (Figure 2a), while an increase in the ANF content resulted in a much smoother and denser surface (Figure 2b,c). This suggests that the increment in the ANF content enhances the interfacial bonding between PEO and ANF, which may in turn improve the mechanical properties of the electrolytes. However, the PEO-LiTFSI electrolyte membrane prepared via the conventional solution-casting method displayed a surface with numerous pores (Figure 2d), potentially resulting in inferior mechanical strength. Upon observation of the crosssectional morphology, it was found that the thicknesses of the ANF-containing CPEs were below 50  $\mu$ m (Figures 2e-g and S3c,d). Specifically, the ANF1, ANF5, and ANF7 electrolytes were 41, 31, and 30  $\mu$ m in thickness, respectively. These thicknesses are comparable to those of the commercial porous polymer separators. On the contrary, the thickness of the PEO-LiTFSI electrolyte membrane was as high as 262  $\mu$ m (Figure 2h). In short, thin PEO-ANF-LiTFSI CPE membranes were successfully fabricated by a novel vacuum filtration method.

To elucidate the interactions between PEO and ANF, FT-IR analyses were performed on the electrolytes in the wavenumber range from 500 to 4000 cm<sup>-1</sup> (Figure 3a,b). The characteristic absorption bands observed at 788, 947, 1061, and 1100 cm<sup>-1</sup> in the electrolytes are attributed to the stretching and bending vibrations of the C–O and C–O–C bonds within the PEO matrix. Furthermore, the presence of – CF<sub>3</sub> and C–F moieties in LiTFSI results in additional vibrational peaks at 568, 740, 760, and 1280 cm<sup>-1</sup> in the electrolytes. Concurrently, ANF exhibits distinct vibrational peaks at 3320 and 1660 cm<sup>-1</sup>, corresponding to the N–H and C==O groups, respectively, while the double vibrational peaks at 1517 and 1548 cm<sup>-1</sup> are indicative of the N–H and C–N groups. With an increase in the ANF content, the C–O–C bond shifts from 960 cm<sup>-1</sup> in the ANF1 electrolyte to 949



**Figure 4.** Ion conduction mechanism of the electrolytes. (a) Ionic conductivity of ANF1, ANF3, ANF5, ANF7, and ANF9 electrolytes; (b) <sup>7</sup>Li NMR spectra of PEO–LiTFSI and ANF5 electrolytes; Li<sup>+</sup> migration energy barriers (c) in PEO bulk and (d) at the PEO/ANF interface.

cm<sup>-1</sup> in the ANF3 electrolyte. These spectral shifts are ascribed to the hydrogen bonding interactions between the N–H groups of ANF and the C–O–C groups of PEO, which is conducive to preventing the aggregation of the ANFs within the PEO matrix and disrupting the orderly arrangement of the PEO chain segments. Additionally, as the ANF content of the electrolytes increases, the vibrational peak of the  $-SO_2$ – group at 1340 cm<sup>-1</sup> and the S–O bond at 652 cm<sup>-1</sup> in the ANF1 electrolyte have undergone change in shape and position, indicating the presence of strong hydrogen bonding interactions between the TFSI<sup>-</sup> anions and the N–H groups of ANF, which is helpful for promoting the dissociation of LiTFSI to emancipate more Li<sup>+</sup>.

To investigate the impact of the ANF introduction on the structure of the electrolytes, XRD was employed to obtain the diffraction patterns (Figure 3c). The PEO–LiTFSI electrolyte prepared by the solution-casting method exhibits two distinct characteristic peaks near  $19^{\circ}$  and  $23^{\circ}$ , corresponding to the typical crystalline peaks of PEO. In the ANF1 electrolyte, the characteristic peaks at  $19^{\circ}$  and  $23^{\circ}$  are somewhat reduced. As the content of ANF further increases, the crystalline peaks gradually diminish, indicating that the addition of ANF can greatly increase the amorphous regions within the electrolytes and reduce the crystallinity of PEO. This is beneficial for facilitating the movement of the PEO segments and the transport of lithium ions within the electrolytes.

The electrolytes were tested by DSC to further explore the influence of ANF on the PEO crystallization (Figure 3d). It is found that the glass transition temperatures of the ANF1, ANF3, ANF5, and ANF7 electrolytes are -55.8, -59.0, -54.2, and -52.3 °C, respectively. In addition, the melting enthalpies of the ANF1, ANF3, and ANF7 electrolytes were calculated to be 79.3, 13.4, and 32.7 J g<sup>-1</sup>, respectively, and the ANF5 electrolyte is almost in an amorphous state. In sharp contrast,

the PEO–LiTFSI electrolyte shows a high melting enthalpy of 164.8 J g<sup>-1</sup>. The crystallinities of the ANF1, ANF3, ANF7, and PEO–LiTFSI electrolytes are calculated to be 27.1%, 4.6%, 11.2%, and 77.1%, respectively. The results show that the introduction of appropriate ANFs can effectively inhibit PEO crystallization, consistent with the XRD results.

**3.2. Electrical Properties.** Figure 4a shows the Arrhenius plots of the ionic conductivity of the electrolytes at various temperatures from 30 to 80 °C. The results demonstrate that the ionic conductivity of the ANF5 electrolyte at 30 °C is higher than that of other electrolytes, reaching up to  $3.27 \times 10^{-5}$  S cm<sup>-1</sup>, which is closely related to the amorphous state of the ANF5 electrolyte at 30 °C (Figure 3c,d). When the temperature is in the range of 50–80 °C, the ionic conductivity of the electrolytes decreases with the increase of the ANF1 electrolyte reaches  $3.83 \times 10^{-4}$  S cm<sup>-1</sup>, while that of the ANF9 electrolyte is only  $5.75 \times 10^{-5}$  S cm<sup>-1</sup>. This is because the ANF1 itself is relatively nonconductive, while the high temperature would facilitate the movement of the PEO segments in the amorphous state.

To delineate the transport pathways of Li<sup>+</sup> ions within the electrolytes, density functional theory (DFT) calculations were performed to ascertain the migration energy barriers for Li<sup>+</sup> ions (Figure 4c,d). The migration barrier for Li<sup>+</sup> ions along the PEO chains is determined to be 0.245 eV, whereas the migration barrier at the PEO/ANF interfaces is reduced to 0.227 eV. This indicates a preference for Li<sup>+</sup> to migrate along the PEO/ANF interfaces, which function as a fast-ion conduction channel in the composite electrolytes. The ssNMR spectroscopy further demonstrates that the addition of the ANFs results in an increased line width of the <sup>7</sup>Li peak in the composite electrolytes (Figure 4b), again proving the

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Figure 5. Electrochemical and mechanical properties. (a) LSV curves, (b) tensile stress and strain curves, (c) TGA curves, and (d) optical photos of the electrolytes at 160  $^{\circ}$ C for 0, 0.5, 1, 2, 5, and 10 h in an oven.

presence of the rapid ion pathway in the ANF-containing composite electrolytes.

3.3. Electrochemical and Mechanical Properties. Electrochemical stability is one of the critical parameters of an electrolyte as it pertains to its application in LIBs. Figure 5a illustrates the LSV curves of the composite electrolytes, and it is observed that the ANF1, ANF3, ANF5, and ANF7 electrolytes all exhibit onset oxidation decomposition at potentials above 4.5 V. The addition of the ANFs enhances the oxidation stability of the PEO-LiTFSI electrolyte, which is attributed to the hydrogen bonding interactions between the amide groups of the ANFs and the ether oxygen groups of the PEO chains and the TFSI<sup>-</sup> in LiTFSI, thereby inhibiting the decomposition of PEO and TFSI-. This indicates that these composite electrolytes possess a broad electrochemical window, which is conducive to their chemical compatibility with high-voltage cathode materials for high-energy-density LIBs.

Meanwhile, the mechanical properties of the electrolytes were tested, and the tensile-strain curves of the electrolytes are depicted in Figure 5b. The ultimate tensile strengths of the ANF5 and ANF7 electrolytes are 2.02 and 5.19 MPa, respectively, while their Young's moduli are 0.50 and 3.22 MPa, respectively. These mechanical properties significantly exceed those of the traditional PEO-LiTFSI electrolyte (0.20 and 0.07 MPa). This indicates that the incorporation of the high-modulus ANFs substantially contributes to the improvement of the mechanical strength of the films. Furthermore, the elongation at break for the ANF1 and ANF3 electrolytes is higher than that of other electrolytes, which is closely attributed to the inherent flexibility of PEO itself. In short, the prepared thin composite electrolytes possess excellent mechanical properties, which is conducive to effectively inhibiting the growth of lithium dendrites and reducing the risk of battery short circuiting.

TGA was conducted to ascertain the thermal stability of the electrolyte films (Figure 5c). The electrolytes had a weight loss of approximately 2% at a low temperature of  $\leq 100$  °C, which was attributed to the evaporation of absorbed water. The

weight loss at 120-350 °C was likely due to the decomposition of LiTFSI, and the variation in the weight loss behavior potentially was related to the differences in the content of LiTFSI and the microstructure of the ANFs within the electrolytes. Furthermore, an intensified weight loss at 380–500 °C was primarily associated with the decomposition of PEO. Additionally, the main decomposition temperatures for the ANF1, ANF3, ANF5, and ANF7 electrolytes were 406, 412, 414, and 426 °C, respectively. At 800 °C, the residual amount of the PEO–LiTFSI electrolyte was 2.67%, while the ANF5 electrolyte had a high residual mass of 13.46%, demonstrating enhanced thermal stability upon ANF incorporation.

To assess the dimensional stability of the electrolytes at elevated temperatures, the electrolytes were subjected to a high temperature of 160 °C in air, and the optical photographs were taken at intervals of 0, 0.5, 1, 2, 5, and 10 h (Figure 5d). It was noted that the ANF1 electrolyte soon melted at 160 °C, due to the low melting point of PEO. In contrast, the ANF3 and ANF5 electrolytes demonstrated satisfactory dimensional stability even after 10 h without change in size, indicating that the incorporation of an appropriate amount of ANFs can greatly enhance the thermostability of the polymer electrolytes, which is beneficial for ensuring stable battery operation under high-temperature conditions.

**3.4. Resistance against Lithium Dendrites.** In order to investigate the electrochemical stability of the polymer electrolytes with the lithium metal electrodes, solid-state Lil SPEILi symmetric cells were assembled and then charged and discharged at various current densities. Critical current density (CCD) is an indicator of the effectiveness of solid-state electrolytes in inhibiting lithium dendrite formation. As shown in Figure S4, the CCD value of the LilLi symmetric cells is affected with the ANF content in the electrolytes, and the Lil ANF5ILi cell shows the highest CCD value of 0.75 mA cm<sup>-2</sup>, because of the high ionic conductivity and mechanical strengths of the ANF5 electrolyte.

In order to further investigate the effect of the electrolytes on the cycling stability of the batteries, the LilSPELLi

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**Figure 6.** LilelectrolytelLi battery performance. Galvanostatic cycling curves of (a) ANF1, (b) ANF5, and (c) ANF7 electrolyte-based LillLi symmetric batteries under 0.10 mA cm<sup>-2</sup> at 60 °C; surficial SEM images of the electrochemically cycled Li electrodes coupled with  $(d_1-d_4)$  ANF1 and  $(d_5-d_8)$  ANF5 electrolytes.



Figure 7. Solid-state lithium metal battery performance. (a) Rate performance of LilSPElLiFePO<sub>4</sub> batteries at 60  $^{\circ}$ C, and the corresponding charge/discharge voltage profiles of (b) ANF5 electrolyte-based batteries at various rates; (c) cycling performance and (d) Coulombic efficiency of the solid-state batteries at 0.1 C and 60  $^{\circ}$ C; corresponding charge/discharge voltage profiles of (e) ANF5 and (f) PEO-LiTFSI electrolyte-based batteries.

symmetric cells were cycled at 60 °C and 0.1 mA cm<sup>-2</sup> (areal capacity: 0.1 mA h cm<sup>-2</sup>). As shown in Figures 6a–c and S5a,b, the LiPEO–LiTFSILLi cell soon short-circuited after

280 h, while the low-content ANF-containing LillLi cells also easily short-circuited after short-time cycling, but the addition of ANF was able to make the cells maintain more stable potentials. When the ANF content was further increased, the LilANF5lLi and LilANF7lLi cells worked stably for 1600 and 2200 h, respectively. This is closely related to the introduction of more high-modulus ANFs in the electrolytes and the greatly enhanced mechanical strengths, which are conducive to inhibiting the lithium dendrites from penetrating into the electrolyte films and improving the safety of the cells.

The surface morphology of the lithium foil electrodes after galvanostatic cycling was characterized by SEM, and the results are shown in Figure 6d. It can be seen that after 180 h of cycling, a lot of lithium grains deposited unevenly on the lithium electrodes of the ANF1 electrolyte-based cell. However, after 1600 h of cycling, only a few cracks appeared on the surface of the lithium electrodes of the ANF5 electrolyte-based cell, and the lithium deposition was also relatively uniform, proving the high dendrite resistance of the high-content ANF-containing electrolytes. The EIS spectra in Figure S6 further show that the addition of appropriate ANFs can greatly reduce the interfacial resistance between the electrolytes and lithium electrodes, which is helpful for improving the cycling stability of the LillLi symmetric cells.

3.5. Solid-State Lithium Metal Battery Performance. In order to evaluate the practicability of the composite electrolytes in solid-state lithium metal batteries, the LilSPEI LiFePO<sub>4</sub> cells were assembled and cycled with different C rates at 60 °C. As shown in Figures 7a,b and S7, the discharge capacities of the LilANF1|LiFePO4 and LilANF3|LiFePO4 batteries reached 149 and 154 mA h  $g^{-1}$  at 0.1 C, respectively, which were higher than that of the LilANF5|LiFePO<sub>4</sub> battery (146 mA h  $g^{-1}$ ). As the C rate increased to 0.2 C, the LilANF3 LiFePO<sub>4</sub> battery still showed a high capacity of 146 mA h  $g^{-1}$ , which was slightly higher than that of the LilANF5|LiFePO<sub>4</sub> battery (144 mA h g<sup>-1</sup>), but the capacity of the LilANF1 LiFePO<sub>4</sub> battery decreased to 123 mA h  $g^{-1}$ . When the C rate increased to 0.5 C, the LilANF5lLiFePO<sub>4</sub> battery showed the highest discharge capacity of 114 mA h  $g^{-1}$ . Moreover, when the C rate returned to 0.1 C, the LilANF5/LiFePO4 cell exhibited good capacity recovery, which should be attributed to the high mechanical strength and thermostability of the ANF5 electrolyte.

We further investigated the cycling stability of the batteries. As depicted in Figures 7c,d and S8, the capacity of the Lil PEO-LiTFSILiFePO<sub>4</sub> cell decreased quickly to 0 mA h  $g^{-1}$ after 135 cycles at 0.1 C and 60 °C. In contrast, the LilANF5 LiFePO<sub>4</sub> cell exhibited a high initial capacity of 143 mA h  $g^{-1}$ , and it still maintained a reversible capacity of 112 mA h  $g^{-1}$ after 180 cycles with an average Coulombic efficiency of 99.9% and a capacity retention of 78%. Compared to commercial nonaqueous batteries, solid-state batteries usually showed high Coulombic efficiencies because of the effective inhibition of liquid electrolyte-induced side reactions and formation of the SEI on the electrodes. As shown in Figure 7e,f, the polarization voltage of the LilANF5|LiFePO<sub>4</sub> cell was much less than that of the LilPEO-LiTFSIlLiFePO4 cell, indicating the good cycle reversibility of the LilANF5|LiFePO<sub>4</sub> cell. The decrease in the discharge platform voltage value over cycling is related to the polarization. With the prolonged cycling, the formation of a solid electrolyte interphase and the growth of the dendrites would result in the increase of the resistance of the batteries. The EIS spectra were further recorded and fitted using an equivalent circuit model (Figure S9). It can be seen that the resistance of all of the cells increased after the long-term

galvanostatic cycling, and the high-content ANF-containing cells had low interfacial resistances.

The cycling stability of the LillLiFePO<sub>4</sub> cells at 0.3 C is also shown in Figure S10. The LilANF5lLiFePO<sub>4</sub> cell still had the best cycling performance with a high capacity retention of 105% after 150 cycles, and the Coulombic efficiencies were nearly 100% during the cycling process. Compared to previous reports,<sup>33-42</sup> the LilANF5lLiFePO<sub>4</sub> battery exhibits excellent cycle stability (Table S1), indicating its promising application in long-life lithium metal batteries.

#### 4. CONCLUSIONS

Overall, we exploited an environmentally friendly yet facile vacuum filtration method to obtain a thin (approximately 25-42  $\mu$ m) PEO-ANF-LiTFSI composite electrolyte film with a 3D ANF network structure, which made the mechanical strength increase to 26 times that of the solution-casted PEO-LiTFSI electrolyte. Simultaneously, the fast-ion conduction channels at the PEO/ANF interfaces can facilitate the Li<sup>+</sup> transport, and thus, the ionic conductivity of the composite electrolyte reached  $3.27 \times 10^{-5}$  S cm<sup>-1</sup> at room temperature. The composite electrolyte-based LillLi batteries cycled stably for 2200 h at 0.1 mA cm<sup>-2</sup>, demonstrating excellent lithium dendrite suppression capability. Furthermore, the composite electrolyte-based LillLiFePO<sub>4</sub> batteries exhibited better cycling stability than the PEO-LiTFSI electrolyte-based batteries during 180 cycles (78% vs 0 in capacity retention). The thin composite electrolyte with the 3D nanofiber framework developed in this study shows great application potentials in high-performance solid-state LIBs.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.5c00814.

TEM image of the ANFs; optical image of the PEO– ANF–LiTFSI electrolyte; SEM images of ANF3 and ANF9 electrolytes; CCD tests of LillLi symmetric cells; galvanostatic cycling curves of PEO–LiTFSI and ANF3 electrolyte-based LillLi symmetric batteries; EIS spectra of the LilSPE/Li batteries; charge/discharge voltage curves of solid-state LillLiFePO<sub>4</sub> batteries based on ANF1, ANF3, and ANF7 electrolytes; cycling performance of the solid-state batteries based on ANF1, ANF3, and ANF7 electrolytes; EIS spectra of the solid-state batteries; cycling performance of the solid-state batteries at 0.3 C; and property comparison of PEO-based electrolytes (PDF)

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# **Author Contributions**

The manuscript was prepared with contributions from all authors, who have approved the final version. J.M. and T.Y. prepared the electrolytes and conducted the morphology characterizations. R.X. and J.T. conducted the battery measurements. Q.Z., M.Z., and D.Z. helped to analyze the data. L.L. and M.L. supervised the whole experimental and conceived the original thoughts. L.L. and R.Z. wrote the manuscript. All the authors reviewed the manuscript.

#### Notes

The authors declare no competing financial interest.

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