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A strong Lewis acid imparts high ionic conductivity and interfacial stability to polymer composite electrolytes towards all-solid-state Li-metal batteries

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ABSTRACT The development of high-performance solid polymer electrolytes is crucial for producing all-solid-state lithium metal batteries with high safety and high energy density. However, the low ionic conductivity of solid polymer electrolytes and their unstable electrolyte/electrode interfaces have hindered their widespread utilization. To address these critical challenges, a strong Lewis acid (aluminum fluoride (AlF₃)) with dual functionality is introduced into poly(ethylene oxide) (PEO)-based polymer electrolyte. The AlF₃ facilitates the dissociation of lithium salt, increasing the ion-transfer efficiency due to the Lewis acid-base interaction; further the *in-situ* formation of lithium fluoride-rich interfacial layer is promoted, which suppresses the uneven lithium deposition and continuous undesired reactions between the Li metal and PEO matrix. Benefiting from our rational design, the symmetric Li/Li battery with the modified electrolyte exhibits much longer cycling stability (over 3600 h) than that of the pure PEO/lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) electrolyte (550 h). Furthermore, the all-solid-state LiFePO₄ full cell with the composite electrolyte displays a much higher Coulombic efficiency (98.4% after 150 cycles) than that of the electrolyte without the AlF₃ additive (63.3% after 150 cycles) at a large voltage window of 2.4–4.2 V, demonstrating the improved interface and cycling stability of solid polymer lithium metal batteries.

Keywords: all-solid-state battery, composite electrolyte, interfaces, Li-ion conductivity, polyethylene oxide

INTRODUCTION

The development of solid-state lithium metal batteries weeding out flammable liquid organic electrolytes is considered to be a promising solution to meet the demands for safety and energy density in next-generation energy storage devices [1,2]. In addition to their non-flammable nature, solid-state electrolytes with high thermal stability and mechanical strength can mitigate the safety issues and eliminate the need for dynamic security

monitoring systems associated with liquid batteries [3]. Currently, the commercial graphite anode (372 mA h g⁻¹) used in lithium-ion batteries is approaching its energy density limit of 770 W h L⁻¹ and 260 W h kg⁻¹ [4,5]. Solid electrolytes make it possible to directly use lithium metal anodes (3860 mA h g⁻¹) and obtain a much higher energy density. Several types of solid electrolytes have been proposed and widely investigated, including oxides, sulfides, halides, and polymers [6–10]. Among the various solid electrolytes, the polymer electrolytes are particularly attractive due to their excellent mechanical properties, good workability, and scalability for the current lithium-ion systems [11–13].

Solid polymer electrolytes generally comprise an ionic-conductive polymer matrix and lithium salts, where the lithium ions can be solvated by intermolecular interactions. Lithium-ion diffusion in polymer electrolytes is mediated by the hopping of lithium ions coupled with the local segment motion in the amorphous region [14]. The complex of poly(ethylene oxide) (PEO) polymer matrix with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) is one of the most practical and widely studied systems for solid polymer electrolytes owing to their numerous advantages in terms of excellent solvation ability for lithium salts, acceptable mechanical stability, and low gravimetric density [15]. Nevertheless, PEO-based electrolytes still suffer from low ion transference efficiency, severe parasitic reactions with Li metal (Fig. 1a), and limited oxidation potentials (less than 4.0 V). To date, a considerable amount of studies have been devoted to addressing such issues and improving the electrochemical performance of PEO-based polymer electrolytes, such as new lithium salt design [16], blending with other polymers, and the use of additional inorganic fillers [17,18]. Among them, introducing ceramic fillers into the polymer matrix is widely reported to enhance the ionic conductivity, through which the amorphous region can be enriched by the physical/chemical interaction between the polymer chains and the fillers [19,20]. Nevertheless, the unstable lithium/polymer interface, including the formation of Li dendrites and severe side reactions, still hinders the cycling stability [21,22].

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Figure 1 Illustration of the design strategy for the PEO-based composite electrolyte: (a) the traditional PEO/LiTFSI electrolyte with an unstable interface induced by the undesirable reactions; (b) our rational design of the Lewis acid-PEO/LiTFSI composite electrolyte with high ionic conductivity and a LiF-rich interface.

To address the aforementioned challenges affecting PEO-based electrolytes, we introduce a strong Lewis acid, AlF_3 , into PEO for the first time to increase the ion transport kinetics and improve interface stability of the PEO-based electrolyte in all-solid-state Li-metal batteries. In particular, the Lewis acid-base interaction between AlF_3 and TFSI^- facilitates the dissociation of Li salt and increases the concentration of free Li^+ ions, while the LiF-enriched interfacial layer is *in-situ* generated during the initial cycling, facilitating the homogeneous lithium ion deposition and inhibiting the undesired reactions between lithium and the PEO matrix (Fig. 1b). Both symmetric Li/Li and all-solid-state $\text{LiFePO}_4/\text{Li}$ full cells with the modified solid electrolyte demonstrate significant improvements in cycling stability and electrochemical performance. Our work highlights the mechanism for the construction of stable composite electrolytes by increasing ion mobility and stabilizing the Li/PEO interface.

RESULTS AND DISCUSSION

Structural characterization and kinetics of the PEO-based composite electrolytes

The fabrication diagram of PEO/LiTFSI polymer electrolyte membranes blended with AlF_3 is given in Fig. S1. Firstly, the micro-sized AlF_3 particles with diameters of approximately 30–40 μm (Fig. S2) were introduced into the PEO/LiTFSI system, which was further confirmed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS, Fig. S3). Subsequently, AlF_3 was partially dissolved in acetonitrile (ACN) and the apparent size of the undissolved AlF_3 was reduced to the

nanoscale (100–200 nm). The decreased nanoscale fillers generally had more interfacial ion transport paths for improving the ion conductivity [23,24]. The detailed morphology of the surface and cross-section of the as-obtained composite electrolyte is shown in Fig. S4. The cross-section scanning electron microscopy (SEM) image shows that the dense membrane has a thickness of around 110 μm (Fig. S4b). The composite membrane exhibits a smooth surface (Fig. S4c, d), and the energy dispersive spectrometer (EDS) mapping images show that both the Al and the F elements have a uniform distribution (Fig. S4c, d).

The structure and crystallinity of the as-fabricated PEO composite electrolytes with various amounts of AlF_3 additive were determined by XRD, as shown in Fig. 2a and Fig. S5. The soft PEO matrix acted as the critical ingredient in the electrolyte. Several intense and strong peaks in the XRD pattern indicate a high crystallinity at room temperature. The XRD analysis of PEO/LiTFSI suggests that the crystallinity reduced with the addition of LiTFSI salts in the PEO matrix, which was attributed to the effect of the formation of ion-dipole complexes on the ordered arrangement of the PEO chains and the enhancement of the amorphous content [25,26]. For the PEO/LiTFSI + x wt% AlF_3 ($x = 2, 5, 8, 12, 15, 20, 30$) composite electrolytes, the intensity of the PEO/LiTFSI peaks gradually decreased, while the intensity of the AlF_3 peak gradually increased. Furthermore, the weakened intensity of the PEO matrix can be attributed to the disruptive effect of AlF_3 on the ordered arrangement of the polymer chains, which also promoted the increase in the amorphous phase [27]. The weakened characteristic peaks of PEO with more amorphous regions can wrap the TFSI^- anions

Figure 2 (a) XRD patterns of pure PEO/LiTFSI, AlF_3 , and the composite electrolytes with various amounts of AlF_3 . (b) Arrhenius plots of the composite membranes with varying weight percentages (wt%) of AlF_3 . (c) Raman spectra of pure PEO/LiTFSI and PEO/LiTFSI + 15% AlF_3 membranes, fitted with the P1 and P2 bands. (d) Schematic representation of the proposed mechanism for the promotion of ion-paired LiTFSI dissociation by the Lewis acid. (e) Chronoamperometry curves of Li|PEO/LiTFSI + 15% AlF_3 |Li cell at a potential of 10 mV. The inset shows the EIS spectra before and after polarization. (f) Comparison of ion transference numbers of the PEO/LiTFSI electrolyte and composite electrolytes with various amounts of AlF_3 .

and induce high ionic conductivity of the composite electrolyte [28].

The ionic conductivity of the polymer-based electrolyte is regarded as a key requirement for practical applications, which is affected by polymer chain segmental motion and hopping in the amorphous phase. The temperature-dependent ionic conductivities of PEO/LiTFSI + x wt% AlF_3 composite electrolytes were evaluated by electrochemical impedance spectroscopy (EIS, Fig. S6) [29,30]. Fig. 2b depicts the temperature dependence (from 30 to 80°C) of the ionic conductivities for the composite electrolyte, along with the corresponding Arrhenius plot. With the increase of temperature, the ionic conductivity of all electrolytes increased due to the improved movement of PEO segments. The detailed temperature conductivities of composite electrolytes with varying amounts of AlF_3 are plotted in Fig. S7. It is also worth noting that the PEO/LiTFSI + 15% AlF_3 composite electrolyte had a preferable ionic conductivity of $1.2 \times 10^{-3} \text{ S cm}^{-1}$ at 60°C, whereas pure PEO/LiTFSI exhibited a conductivity of $6.2 \times 10^{-4} \text{ S cm}^{-1}$. Further, the conductivity of the PEO/LiTFSI + 15% AlF_3 composite electrolyte approached $3.7 \times 10^{-5} \text{ S cm}^{-1}$ at 25°C, which was higher than that of PEO/LiTFSI ($2.2 \times 10^{-5} \text{ S cm}^{-1}$). The PEO/LiTFSI + 15% AlF_3 electrolyte demonstrated an obvious improvement in terms of ionic conductivity, which was attributed to the increased amorphous region. In addition, the fast ion-conducting pathways on the interface could be another reason for the favorable electrochemical features. The much higher concentrations of ions diluted the polymer electrolyte and blocked the ion transfer channel in the polymer matrix, inducing a decreased ionic conductivity. Therefore, the optimized composition was PEO/

LiTFSI + 15% AlF_3 .

Raman spectroscopy was conducted to confirm the presence of ion-PEO- AlF_3 interactions, along with the conformation isomerism of TFSI^- anions. The Raman spectra of PEO/LiTFSI and PEO/LiTFSI + 15% AlF_3 are shown in Fig. 2c. The two fitted Lorentzian peaks, located at 741 cm^{-1} (P1) and 747 cm^{-1} (P2), correspond to the dissociated TFSI^- anions and the anionic cluster $[\text{Li}(\text{TFSI})_2]^-$, respectively [31,32]. The lower anionic cluster $[\text{Li}(\text{TFSI})_2]^-$ content indicates more free Li^+ coordinated with ether oxygen atoms on the PEO chains, causing inefficient ion transport in the polymer matrix. The spectrum of the PEO/LiTFSI + 15% AlF_3 membrane demonstrates a strong P1 band and a relatively weak P2 band, proving the existence of more free TFSI^- . Furthermore, the percentage of free TFSI^- anions can be calculated using the following equation:

$$[\text{free TFSI}^-] = \frac{A(\text{P1})}{A(\text{P1}+\text{P2})} \times 100\%, \quad (1)$$

where $A(\text{P1})$ and $A(\text{P2})$ represent the intensity of the P1 and P2 bands, respectively. The percentage of free TFSI^- anions in the PEO/LiTFSI + 15% AlF_3 system is 85.6%, which is much higher than that of pure PEO/LiTFSI (43.2% without AlF_3). This result demonstrates the better dissociation of ion clusters in the composite electrolyte.

In addition to the ionic conductivity, the ion transference number (t^+) is another crucial parameter that determines the performance of electrolytes and can be used to calculate the contribution of Li-ion transport. In accordance with the Lewis acid/base theory, the heterostructure inorganic Lewis acid AlF_3 can bond with the TFSI^- by sharing an electron pair. F is the

most electronegative element. Owing to the large energy difference between the 2p orbitals of F and the empty 3d orbitals of Al, the Al atom can accept electrons. Hence, AlF_3 is more highly Lewis acidic and has a greater tendency than Li^+ to accept a pair of electrons. Therefore, the affinity between the surfaces of AlF_3 fillers and anions facilitates the immobilization of TFSI^- and a higher ion transference number (Fig. 2d). In particular, Fig. 2e shows the current change during the direct current (DC) polarization process, with the inset showing the EIS spectra of the initial and final state. In addition to the relatively high ionic conductivity, the PEO/LiTFSI + 15% AlF_3 composite electrolyte also demonstrates a high Li^+ transference number (0.46), which is 1.70 times higher than that of PEO/LiTFSI (0.17, Fig. S8) without any rigid filler. This is consistent with the interaction between the AlF_3 Lewis acid and TFSI^- . Furthermore, increasing the AlF_3 load was found to increase the transference number; there was an optimal value (15%) found in this study. Excess amounts of AlF_3 led to a decreased transference number and limited the ion transfer in the polymer (Fig. 1f), which corresponded with the ion conductivity results and the percolation model. The increased Li^+ transference number and ion conductivity indicate that moderate amounts of AlF_3 can reduce the

interaction between Li^+ and TFSI^- , increase the free Li^+ concentration, and immobilize anions. The high Li^+ ion transference number demonstrates the efficient transmission of Li^+ ions, which could reduce the negative effects of space charge on the interface between the electrolyte and electrode [18]. Thus, the PEO/LiTFSI + 15% AlF_3 composite electrolyte, with a higher ion transference number, is expected to suppress lithium dendrite proliferation in working batteries [33,34].

Stability of the composite electrolyte contacting Li metal anode

The electrochemical compatibility and stability of the composite electrolyte with a metallic Li anode were evaluated using symmetric $\text{Li}||\text{Li}$ cells. The PEO/LiTFSI + 15% AlF_3 composite electrolyte was sandwiched between two identical Li anodes to simulate practical Li stripping/plating behavior. Fig. 3a shows the rate performance and long-term cycling stability at various current densities at the deposition capacity of 0.2 mA h cm^{-2} . For comparison, the pure PEO/LiTFSI membrane was also tested. Firstly, it was found that the overpotential of cells with the composite electrolyte increased slightly, from 32 to 131 mV, along with an increase in the current density from 0.1 to 0.5 mA cm^{-2} , suggesting an excellent rate performance and high

Figure 3 (a) Galvanostatic cycling and rate voltage profiles of symmetrical cells with PEO/LiTFSI + 15% AlF_3 electrolytes under current densities of 0.1, 0.2, 0.3, 0.4 and 0.5 mA cm^{-2} with a fixed capacity of 0.2 mA h cm^{-2} . (b) Nyquist plots of the impedance spectra of symmetric cells using PEO/LiTFSI + 15% AlF_3 electrolytes and PEO/LiTFSI after various numbers of cycles at a current density of 0.1 mA cm^{-2} at 60°C . Comparison of the surface SEM images of Li metal after 200 cycles contacted with (c) PEO/LiTFSI + 15% AlF_3 electrolytes and (d) PEO/LiTFSI electrolytes.

interface stability with metallic Li. It should be noted that the sudden drops of overpotential during long periods of cycling could be attributed to the temperature decrease caused by opening the test incubator since the ionic conductivity of the PEO-based electrolyte increases with temperature. Therefore, the overvoltage returned to normal after the temperature reverted to the test point. In comparison, it is apparent from Fig. S9 that the cell based on pure PEO/LiTFSI exhibits a higher overpotential (50 mV) at 0.1 mA cm^{-2} and could not run well at higher current densities, which is probably caused by the dendrite growth and short-circuiting. The symmetric cell assembled with the composite electrolyte demonstrates ultra-long cycle stability with negligibly increased voltage polarizations over 3600 h. The cell without AlF_3 has a higher overpotential and much shorter lifespan (550 h, Fig. S10), which is induced by the uneven Li deposition and continued deterioration of the interface. The improved electrochemical performance afforded by AlF_3 additives can be attributed to the enhanced ionic conductivity and ion transference number [35].

To further understand the fundamental mechanism affecting the stability of the interface of the composite electrolyte with metallic lithium, impedance measurement was performed and tracked after cycling for 1, 10, 50, 100, and 200 cycles (Fig. 3b). The semicircles of the Nyquist plots in the high-frequency region indicate the charge-transfer resistance on the electrode/electrolyte interface. The interfacial resistance can be obtained by fitting the Nyquist plots using the equivalent circuit depicted in Fig. S11. After initial cycling, the symmetric Li||Li cell with the composite electrolyte exhibited a lower interface impedance of 55Ω which is lower than that of the electrolyte without any rigid fillers (62Ω). This could be attributed to the improved interface contact. Further, the impedance of the PEO/LiTFSI electrolyte increased obviously after 200 cycles. The increased impedance could have been induced by the continuous side reactions on the interface of Li metal/electrolyte, which destroy the previously generated solid electrolyte interphase (SEI) [36], leading to a thickened and uneven Li/PEO interface. In comparison, the PEO/LiTFSI + 15% AlF_3 composite demonstrated fewer impedance changes and stabilized at around 62Ω . The AlF_3 additive was partially insoluble in the composite electrolyte, which led to a relatively stable SEI and inhibited the continuation of side reactions, enhancing the interface stability.

To visually analyze the influence of the PEO/LiTFSI + 15% AlF_3 composite electrolyte on the Li deposition, the surface morphologies of the electrolyte and Li metal anode after cycling were determined, as shown in Fig. 3c, d and Fig. S12. In comparison to the pristine Li metal before cycling (Fig. S13), the Li surface contacting the composite electrolyte (Fig. 3c) demonstrated a smooth surface and a few bumps after 200 cycles. In contrast, micro-sized Li particles and dendrites were found on the Li surface contacting the pure PEO/LiTFSI electrolyte. Simultaneously, as shown in Fig. S12, small wrinkles and fractures appeared on the cycled surface of the PEO/LiTFSI electrolyte. Once the dendrites keep growing along with the cracks, short-circuiting will occur. The smooth surface morphology in the presence of the composite electrolyte is consistent with the effect of Li metal and the rigid additive is effective for dendrite inhibition [37]. Further, as demonstrated in Fig. S14, compared with the pure PEO/LiTFSI electrolyte, the mechanical strength of the composite electrolytes increased from 0.98 to 1.94 MPa, making it possible to hinder the propagation of Li dendrites [38].

Therefore, the PEO/LiTFSI electrolyte modified by AlF_3 not only contributes to the improvement of the rigidity of the electrolyte membrane, but also enhances the Li-ion transfer efficiency, which could lead to a homogeneous ion distribution and inhibit the puncturing of the electrolyte by Li dendrites.

Evolution mechanism of the composite electrolyte/metallic Li interface

Furthermore, the evolution mechanism of the electrolyte interface composition was detected using XPS. The pristine and cycled detailed spectra of C 1s, F 1s, Li 1s, S 2p, N 1s, and O 1s signals of the PEO/LiTFSI and PEO/LiTFSI + 15% AlF_3 are shown in Fig. 4, Figs S15 and S16. Firstly, the binding energy scale of both the survey scan and narrow spectra were calibrated by the C 1s signal of aliphatic carbon (284.8 eV). Fig. 4 shows the C 1s and F 1s spectra from the outermost surface of the two electrolyte systems. As demonstrated in Fig. 4a, the peaks of the pristine composite electrolyte at 286.7 eV show a lower content of C–O–C with the addition of AlF_3 . This result corroborates the implication from the XRD graphs that the crystalline volume in the PEO matrix decreases with the addition of AlF_3 [39]. Furthermore, the new peaks at 290.9 eV on both surfaces of cycled electrolytes can be attributed to ROOLi, which is associated with the decomposition of PEO [40,41]. However, the C 1s spectral evolution indicates that the cycled electrolyte without AlF_3 modification has an obvious decline of the C–O (286.7 eV) configuration, which is induced by the undesired side reactions between metallic Li and the PEO matrix. Considering the ultrahigh thermodynamic instability of Li metal, severe degradation of PEO to generate C_2H_2 , H_2 , and alkoxide species occurred at the Li/PEO interface. Furthermore, during the repeated Li metal plating/stripping process, continuous side reactions caused the deterioration of the interface. In contrast, the composite electrolyte demonstrated no obvious decreases in C–O bonding, which reconfirmed that the AlF_3 in the composite electrolyte could suppress the Li dendrite growth and the continuous generation of fresh interfaces, improving the stability of the Li/electrolyte interface.

The fitted high-resolution XPS spectra of F 1s for the pristine and cycled specimens are given in Fig. 4b. There was a unique peak on the initial surface of the composite electrolyte, which can be attributed to the presence of AlF_3 (685.8 eV). Interestingly, it shifted to lower binding energy (684.8 eV) after cycling, demonstrating that the AlF_3 had reacted with Li metal and transformed into LiF [42–44]. Furthermore, in comparison with the pure PEO/LiTFSI electrolyte, the cycled composite electrolyte exhibited an increased generation of LiF on the surface. LiF was recognized for its ability to inhibit dendrite growth and its existence had been widely verified to stabilize the Li/electrolyte interface [45–47]. As all the LiF generated in the subsequent cycling process comes from the decomposition of the TFSI[−], it can be inferred that more fresh interfaces had been generated in the pure PEO electrolytes. Owing to the *in-situ* generated LiF interface during the initial cycling, the composite electrolyte with AlF_3 additive can inhibit the continuous side reactions between metallic Li and the PEO matrix. Similar results can be found in the spectrum of Li 1s, which is shown in Fig. S16. The Li 1s peak of the cycled composite surface had a stronger intensity than the pristine surface, indicating the formation of LiF and other compounds. Further, the Li-containing compounds of Li_2SO_4 , LiN_3 , and ROLi were detected on the cycled

Figure 4 High-resolution spectra of (a) C 1s and (b) F 1s of the pristine and cycled PEO/LiTFSI and PEO/LiTFSI + 15% AlF₃ electrolytes, demonstrating better polymer matrix stability and more LiF generation of the hybrid electrolyte after cycling.

electrolyte surface, which were also beneficial to stabilizing the metallic lithium/electrolyte interface.

To further determine the evolution mechanism of the composite electrolyte/Li interface, the morphologies and XPS depth profiles of the cycled Li metal anode were investigated (Fig. 5). As demonstrated in Fig. 5a, certain amounts of F and Al were evenly distributed on the surface of the cycled Li metal anode, suggesting that a conversion reaction of AlF₃ occurred during the cycling, as follows: AlF₃ + Li → AlLi_x + LiF. As expected, the metallic AlLi_x alloy was detected by the XPS spectrum after the cycling (Fig. S17), which corroborated the implication from the SEM images that there were reactions between the metallic Li and AlF₃. In addition, the detailed compositions of the cycled Li metal surface contacting the pure and composite electrolytes were investigated using the XPS depth profiles (Fig. 5b–d). The Li 1s spectrum demonstrated a single peak, and LiF constitutes a large portion of the whole [48]. With increases in the etching time, the peak shifted to lower binding energy and became more apparent, indicating baseline XPS spectra for RCOO–Li and Li⁰ (Fig. 5b). The fitted detailed C and F XPS spectra of the cycled Li metal were consistent with the results of those contacting the pure and composite electrolytes. As demonstrated in Fig. 5c, the intensity of the –CF₃ in LiTFSI and PEO peaks significantly decreased, which was consistent with the results for Li 1s [49]. In contrast, the signals of C 1s in Li metal contacting the PEO/LiTFSI electrolyte without AlF₃ exhibited a sharp decline, which was consistent with the surface of the PEO/LiTFSI electrolyte. This was likely caused by the undesirable reactions between the Li metal and PEO membrane. Further, the –O–C=O signal, related to the formation of RCOO–Li of the PEO/LiTFSI electrolyte without AlF₃, became more apparent after sputtering, indicating a much more passive layer on the Li metal surface. The fitted F XPS spectrum also exhibited two peaks, and the

content of LiF was dominant after etching (Fig. 5d). In comparison with the membrane without AlF₃, there was more F content in the interface layer of the Li metal contacting the composite electrolyte, indicating the formation of a LiF-rich interfacial layer on the Li metal surface. In addition, it should be noted that the LiF was mainly concentrated near the surface of the Li metal, which was the origin of the improvement in interface stability and the prolonged cycling life of symmetrical cells containing the composite electrolytes.

To better illustrate the mechanism of AlF₃ for stabilizing the Li/PEO interface, the Li-ion transfer behavior in both electrolytes was compared, as shown in Fig. S18. Particularly, three main contributions of AlF₃ additives can be summarized from the results described above. First, the Lewis acid-base interaction between AlF₃ and TFSI[–] facilitated the dissociation of Li salt and immobilized the anions, lowering the interface polarization. Second, the rigid additive effectively increased the amorphous volume of the PEO matrix and improved the amount of free Li, which could enhance Li-ion conduction. Third, the *in-situ* generated LiF-rich interface during the initial cycling could inhibit the continuous side reactions between metallic Li and the PEO matrix, enhancing the stability of the Li/PEO interface.

All-solid-state Li-metal batteries with composite electrolyte

Because the Li-ion transmission efficiency and interface stability were improved by using this electrolyte, all-solid-state Li-metal batteries with LiFePO₄ cathodes were assembled to evaluate the electrochemical performance of the composite electrolytes for practical applications. The main issue faced by the PEO-based electrolyte was the unsatisfactory oxidative stability on the cathode/electrolyte interface, which restricts their widespread application at voltages higher than 3.9 V [16,50,51]. Evaluating the leakage current during electrochemical floating has been

Figure 5 (a) Morphologies and EDS mapping of the Li metal anode after cycling. The high-resolution fitted (b) Li 1s, (c) C 1s, and (d) F 1s XPS depth (etching time) analysis of the cycled Li electrodes compared with those for pure PEO/LiTFSI and PEO/LiTFSI + 15% AlF₃ electrolytes.

identified as a good method for assessing antioxidation performance. The results of electrochemical floating, shown in Fig. 6a, demonstrated that the PEO/LiTFSI with the AlF₃-modified electrolyte had a small leakage current at voltages as high as 4.2 V. In contrast, the pure PEO/LiTFSI electrolyte had a smaller leakage current at 4.0 V. Further, the as-assembled Li|PEO/LiTFSI + 15% AlF₃|lithium-iron-phosphate (LFP) solid-state battery had a total resistance of 80 Ω, which was smaller than that of the PEO/LiTFSI electrolyte-based battery (Fig. S19). The improved oxidative stability of the composite electrolyte can be attributed to the strong interaction between the Lewis acid sites and TFSI⁻ anions, which could prevent the oxidation of the anion and enhance the electrochemical stability of the composite electrolyte.

To identify the fast-charging ability of the solid-state batteries, the rate performances are compared in Fig. 6b. The specific capacity of the solid battery with PEO/LiTFSI + 15% AlF₃ electrolytes was 146, 143, 138, 126, 114, and 88 mA h g⁻¹ at 0.1, 0.2, 0.3, 0.5, 1, and 2 C, respectively, which are higher than those for the PEO/LiTFSI, especially at higher rates, benefiting from the higher Li-ion conductivity and smooth Li deposition. Further, as shown in Fig. 6c, the PEO/LiTFSI + 15% AlF₃ composite electrolyte also had higher capacity retention (105 mA h g⁻¹ and 92.1% retention) and high Coulombic efficiency (higher than 98%) for 150 cycles at 1 C in the voltage range of 2.4–4.2 V. Fig. 6d presents the detailed selected voltage profiles of solid-state batteries with the two electrolytes. All of the voltage profiles

exhibited flat and smooth voltage plateaus, representing the limited leakage current and electrochemical stability of the electrolyte and electrode interface. In addition, the battery with the composite electrolyte exhibited lower voltage hysteresis and higher Coulombic efficiency. In contrast, the cell with the PEO/LiTFSI electrolyte could only be stably operated for less than 50 cycles. The Coulombic efficiency of the 150th cycle was about 63.3%, which was mainly induced by the uneven Li consumption, large interfacial resistance, and PEO decomposition. These features indicate that the as-prepared composite electrolyte, with improved ion transmission efficiency and stability of the cathode, solve two critical challenges for PEO-based electrolytes in practical applications.

CONCLUSIONS

In summary, we introduce a strong Lewis acid into the PEO-based polymer electrolyte to improve both the ion transference number of composite electrolyte and interface stability of the Li metal/electrolyte. The AlF₃ additive in the PEO matrix increased the amount of amorphous volume and free Li for enhancing Li-ion conduction. The Lewis acid-base interaction between the AlF₃ and TFSI⁻ facilitated the dissociation of Li salts and immobilized the anions, resulting in sufficient Li ions transfer and homogeneous Li ion deposition. In addition, the *in-situ* generated LiF-rich interface during the initial cycling could inhibit the continuous side reactions between the metallic Li and PEO matrix and enhance the stability of the Li/PEO interface.

Figure 6 (a) Electrochemical floating analysis of the PEO/LiTFSI + 15% AlF_3 electrolyte and pure PEO/LiTFSI electrolyte using LFP cathodes. (b) Rate performances, (c) cycling performance, and (d) the charge/discharge curves of $\text{Li}|\text{PEO/LiTFSI} + 15\%\text{AlF}_3|\text{LFP}$ and $\text{Li}|\text{PEO/LiTFSI}|\text{LFP}$ solid-state batteries from 0.1 to 2 C at 60°C.

Compared with the PEO/LiTFSI electrolyte, the composite electrolyte with AlF_3 additive delivered enhanced ion conductivities by 190% and a higher ion transfer number (0.46). Benefited from our rational design, the Li symmetric cells demonstrated ultralong cycling stability over 3600 h, and the solid-state LFP full cells displayed a stable cycling performance during the voltage range of 2.4–4.2 V. This work provides an alternative strategy for high-performance composite electrolytes, as well as the practical application of all-solid-state Li-metal batteries.

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Author contributions Wang L, Hong G and Tang Y designed the research and wrote the manuscript. Hong G and Tang Y supervised the project and analyzed the data. Wang L, Zhong Y, and Wen Z carried out the experiments and discussions. Li C, Zhao J, Ge M, Zhou P and Zhang Y analyzed the data and refined the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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强路易斯酸诱导构筑高离子电导率和界面稳定的复合电解质及其全固态锂金属电池

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摘要 开发高性能固态聚合物电解质是高安全、高比能固态锂金属电池的关键。然而, 固态聚合物电解质的低离子电导率和不稳定的电解质/电极界面阻碍了其广泛应用。针对上述关键问题, 本文基于聚环氧乙烷(PEO)基电解质, 引入具有双功能的氟化铝(AlF_3)做为添加剂, 以提高复合电解质的离子电导率和界面稳定性。一方面, AlF_3 做为一种强路易斯酸, 在和锂盐阴离子相互作用下可以促进锂盐的解离, 同时可以固定阴离子, 从而提高锂离子传输效率; 另一方面, AlF_3 在电解质/电极界面可以和锂金属原位反应生成富含LiF的界面层, 从而抑制锂金属的不均匀沉积以及和PEO基体之间持续的副反应。得益于我们的合理设计, 匹配改性后电解质的Li/Li对称电池可以稳定循环3600 h以上。同时, 在2.4–4.2 V电压区间内, 匹配复合电解质的全固态 LiFePO_4 全电池在150个循环之后库伦效率比没有 AlF_3 添加剂PEO基电解质大大提升(98.4% vs. 63.3%), 匹配复合固态电解质的固态锂金属电池显示出优异的界面稳定性和循环稳定性。