Polysulfide-Shuttle Control in Lithium-Sulfur Batteries with a Chemically/Electrochemically Compatible NaSICON-Type Solid Electrolyte

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A NaSICON-type Li"-ion conductive membrane with a formula of Li_{1+x}Y_{2-x}Zr_2PO_{12} (LYZP) (0 ≤ x ≤ 0.15) has been explored as a solid-electrolyte/seperator to suppress polysulfide-crossover in lithium-sulfur (Li-S) batteries. The LYZP membrane with a reasonable Li"-ion conductivity shows both favorable chemical compatibility with the lithium polysulfide species and exhibits good electrochemical stability under the operating conditions of the Li-S batteries. Through an integration of the LYZP solid electrolyte with the liquid electrolyte, the hybrid Li-S batteries show greatly enhanced cyclability in contrast to the conventional Li-S batteries with the porous polymer (e.g., Celgard) separator. At a rate of C/5, the hybrid Li ||LYZP|| Li_2S_6 batteries developed in this study (with a Li-metal anode, a liquid/LYZP hybrid electrolyte, and a dissolved lithium polysulfide cathode) delivers an initial discharge capacity of ~1000 mA h g\(^{-1}\) (based on the active sulfur material) and retains ~90% of the initial capacity after 150 cycles with a low capacity fade-rate of <0.07% per cycle.

1. Introduction

Rechargeable batteries with the lithium-sulfur chemistry are gaining overwhelming attention as one of the most promising candidates for next-generation electrochemical energy storage systems.[1] Coupling the sulfur cathode with a theoretical capacity of 1675 mA g\(^{-1}\) with a lithium-metal anode with a theoretical capacity of 3800 mA g\(^{-1}\), the lithium-sulfur (Li-S) battery system can deliver a significantly high energy density of ~2600 Wh kg\(^{-1}\) (Li + S) at an average voltage of 2.1 V.[2] As such, the Li-S batteries have a strong potential to be a power source in almost all application areas including small electronic devices, electric vehicles, and large-scale stationary energy storage.[3] However, despite many years of efforts into this novel battery system, major technical obstacles still remain to be overcome.

Due to its unique electrochemical characteristics, charge and discharge of a Li-S battery involve a sequence of polysulfide intermediate products, which are soluble in the liquid-phase organic electrolyte. During the electrochemical cycling of the cells, these dissolved polysulfides have a tendency to diffuse through the battery separator to react with the Li-metal anode. Such a process (generally named as a “polysulfide shuttle” behavior) has generally been recognized as one of the most serious challenges.[4]

To overcome the polysulfide-shuttle issue, many attempts have been made during the past years toward the encapsulation of the polysulfides in the cathode.[5] The important efforts include the development of advanced cathode structures, designation of unique cell configurations, development of proper functional groups on the cathode matrix to anchor the polysulfide species etc. However, all of the above approaches are only able to partially alleviate the polysulfide diffusion, and they are not able to provide a completely radical solution to eradicate the polysulfide-shuttle issue. Alternative strategic approaches need to be considered to totally eliminate the diffusion of the dissolved polysulfide species from the sulfur cathode to the Li-metal anode surface.

The progress made with Li"-ion conductive solid electrolytes based on inorganic materials provides a possibility to prevent the migration of polysulfides into the Li-metal anode. The first stage for integration of the solid electrolyte into the Li-S battery system was based on a concept of “all-solid-state Li-S battery”. However, these previous endeavors with the “all-solid-state” approach were unfortunately not able to provide satisfactory cell performances in terms of the utilization of the sulfur cathode, cyclability of the Li-S cells etc.[7] It was realized that the liquid electrolyte would still be necessary in the polysulfide-involved Li-S batteries. Therefore, the second stage for the advancement of Li-S batteries with a solid-electrolyte was the recently proposed approaches based on a “hybrid-electrolyte (or dual-electrolyte)” concept.[8] In such a “hybrid” Li-S battery system, the solid electrolyte played both as a separator/shield to prevent the polysulfide diffusion and as a Li"-ion conductor for the electrochemical reaction. The liquid electrolyte here served as an ionic medium not only for the redox reactions of sulfur-polysulfide-sulfide within the cathode, but also to maintain the ionic path at the electrode/solid-electrolyte interface.
From only a few reports on the “hybrid Li-S batteries”, the NaSICON-type Li_{1+x}Al_{2-x}Ti_{2-x}(PO_4)_3 (LATP) solid electrolyte was primarily considered as the first choice. This is due to its relatively high Li^+-ion conductivity at low temperatures and the commercial availability of the LATP membrane. However, the relatively narrow electrochemical-stability window and the facile reduction of Ti^{4+} in LATP by polysulfides impose both chemical and electrochemical incompatibility concerns of the LATP in Li-S batteries.

Herein we exploit an alternative NaSICON-type Li^+-ion conductive membrane with a general formula of Li_{1-x}Y,Zr_{2-x}(PO_4)_3 (LYZP) as a solid-electrolyte/separating layer to address the polysulfide-crossover issue in Li-S batteries. The LYZP membrane prepared with the inexpensive zirconium as the major element and with a series of facile solid-state reactions show favorable chemical/electrochemical compatibility with the cell components under the operating conditions of the Li-S batteries. Integration of the LYZP solid electrolyte significantly enhances the cyclability of the Li-S batteries.

2. Results and Discussion

2.1. Characteristics and Properties of the LYZP Solid-Electrolyte

Preparation of the dense LYZP membranes is as detailed in the Experimental Section through a series of solid state reactions and a series of mold–sintering processes. After the final process, the surface of the as-prepared membrane had lots of impurities such as ZrO_2 and Y(PO_4)_3 (Figure 1a). Upon removal of the skin layer, the LYZP pellets showed pure NaSICON phase with a well-crystallized rhombohedral NaSICON structure, as reflected in Figure 1a. It should be noted that the X-ray diffraction (XRD) pattern shown in Figure 1a was obtained with a membrane prepared under the optimized conditions. Actually, the phase purity of the LYZP membrane was very sensitive to the synthesis/processing conditions such as sintering temperature, sintering duration, and the excess amount of lithium precursor, as deliberated with Figure S1 in the Supporting Information. Figure 1b shows the scanning electron microscopy (SEM) image of the cross-section of the LYZP membrane, from which we can see that the particles are in good contact with each other in spite of some pin holes existing in the membrane. The density of LYZP membrane obtained under the optimized conditions was ≈96% of its theoretical density. Distribution of the elements was characterized with energy dispersive X-ray spectroscopy (EDS) in an area of the cross-section of the membrane, as provided in Figure S2 in the Supporting Information. Y, Zr, P, and O were homogeneously distributed in the LYZP membrane. Since Li is not detectable with the EDS, the mapping of Li is not provided in Figure S2 in the Supporting Information. The EDS spectrum of the LYZP membrane is provided in Figure S3 in the Supporting Information, in which the peaks of Y, Zr, P, and O are clearly seen. The atomic ratio of Y, Zr, P, and O was summarized in Table S1 in the Supporting Information.

2.2. Electrochemical Performances of the Hybrid Li-S Cells with the LYZP Solid Electrolyte

The hybrid-electrolyte Li-S batteries were prepared with a lithium-foil anode and a dissolved polysulfide (in a normalized form of Li_2S_{x}, named as catholyte in this study) cathode. A free-standing activated carbon nanofiber (CNF) paper was used as the electrode-matrix to accommodate the polysulfide catholyte. The lithium anode and the liquid-phase polysulfide cathode were separated by a piece of LYZP membrane as schematized in Figure 2a. The LYZP membrane here serves both as a separator to electrically insulate the anode/cathode and as a Li^+-ion conductive electrolyte to sustain the Li^+-ion transport. In order to build up a facile ionic interface, according to our previous study, a piece of polypropylene (PP) thin film (25 μm thick) was inserted as an interlayer between the Li-foil anode and the LYZP separator to hold a thin-layer of liquid electrolyte compressing 1.0 M LiCF_3SO_3 (with or without 0.1 M LiNO_3) dissolved in 1:1 (volume ratio) dimethoxy ethane/1,3-dioxolane (DEM/DOL) mixture solvent. Based on our experience, the polypropylene thin film used here plays...
an important role to ensure the cycling performances of the Li-metal-anode batteries with a solid electrolyte. It helps to build a facile ionic path between the Li-metal and the solid electrolyte by holding a thin layer of liquid electrolyte for the transport of Li$^{+}$ ions at the interface.[8b] The Li-S battery fabricated in the above manner (termed as IILYZPII Li$_2$S$_6$ battery) was in an intermediate discharge–charge state with an open circuit voltage (OCV) of \(\approx 2.3\) V. With the intermediate charge–discharge product (Li$_2$S$_6$) as the starting sulfur source at the cathode, this cell can either be first discharged or be first charged with a single voltage plateau, respectively, in the initial discharge or the initial charge profile (Figure 2b). After either a first discharge or a first charge, the voltage profiles of the cell show the normal two-plateau characteristics as that for the regular Li-S batteries with the elemental sulfur as the starting cathode.

Figure 2c shows the cyclic-voltammogram (CV) profiles of the Li IILYZPII Li$_2$S$_6$ cell with the potential initially swept in a negative direction from the OCV (\(\approx 2.3\) V) to 1.5 V to discharge the cell. Then, ten full cyclic scans were performed between 1.5 and 3.0 V. The single discharge wave in the first half-scan and the anodic/cathodic waves in the following full CV profiles are consistent with the discharge–charge characteristics of the Li IILYZPII Li$_2$S$_6$ cell as shown in Figure 2b. In addition, as seen in Figure 2c, the CV profiles for the initial 1.5 cycles exhibited an anodic peak with a relatively more positive potential and the cathodic peaks with a relatively more negative potential in comparison to those in the following cycles. After the second cycle, there are no obvious differences in the potential positions. The above phenomena indicate that the cells need a full electrochemical cycle for pre-conditioning. Figure S5 in the Supporting Information compares the CV profiles (the 5th cycle) of the Li IILYZPII Li$_2$S$_6$ cell and a Li/Li$_2$S$_6$ cell with the conventional Celgard separator (termed as Li IICelgardII Li$_2$S$_6$ cell). In contrast, use of the LYZP solid electrolyte shifts the anodic wave to a high-voltage direction and the two cathodic peaks to the low-voltage direction. In addition, relatively sharper waves are observed for the Li IICelgardII Li$_2$S$_6$ cell either in the anodic or in the cathodic scans. The above CV characteristics for the Li IILYZPII Li$_2$S$_6$ cell are supposed to be attributed to the relatively sluggish kinetics of the Li$^{+}$-ion transport in the solid electrolyte in contrast to that in the liquid electrolyte.

Figure 2d presents the rate capabilities of the Li IILYZPII Li$_2$S$_6$ cells with the charge–discharge profiles obtained at different C-rates (the 3rd cycle in each case are shown here for a comparison). Upon normalized with the net sulfur in the cathode, the specific discharge capacities of the Li IILYZPII Li$_2$S$_6$ cells at C/10, C/5, C/3, and C/2 rates are, respectively, \(\approx 1100\), \(\approx 1000\), \(\approx 880\), and \(\approx 780\) mA h g$^{-1}$ based on sulfur. With a 150 μm thick LYZP membrane, the Li IILYZPII Li$_2$S$_6$ cells showed reasonable rate capability. With the progress of the fabrication techniques, the thickness of the LYZP membrane can be further reduced. With a thinner LYZP membrane, the over-voltage of the cells is expected to be even lower than the results shown in Figure 2d and the cells will be able to sustain even higher discharge–charge rates. Due to the poor conductivity of the charge/discharge products at the cathode and the resistivity of the ionic transport within the hybrid electrolyte (as well as that at the electrode–electrolyte interface), the cells exhibit increasing voltage gaps between charge and discharge with an increase in the charge–discharge rates. The 3rd-cycle charge–discharge profiles for the Li IICelgardII Li$_2$S$_6$ cells cycled at different C-rates are provided in Figure S6 in the
Supporting Information. The discharge capacities of the Li IIICelgardII Li2S6 cells at the corresponding rates are generally a little higher than those for the Li IILYZPII Li2S6 cells (comparison of Figure 2d and Figure S6 in the Supporting Information). However, the benefits of using the LYZP solid electrolyte are by no means for the initial cycling performances of the Li-S batteries.

Figure 2e,f compare the prolonged cycling performances of the Li IILYZPII Li2S6 cells and the Li IICelgardII Li2S6 cells. Although the Li IICelgardII Li2S6 cell shows relatively higher initial discharge capacity relative to those of the Li IILYZPII Li2S6 cells, capacity decline of the Li IICelgardII Li2S6 cell is significantly faster than those of the Li IILYZPII Li2S6 cells. Within the 60-cycle frame, the Li IICelgardII Li2S6 cell shows superior performance compared to the Li IILYZPII Li2S6 cell. However, with prolonged cycling, the benefit from the LYZP membrane is more and more significant. Table 1 summarizes the initial capacities, 150-cycle capacities, capacity retention, and the fade-rate of capacity for the Li IILYZPII Li2S6 and the Li IICelgardII Li2S6 cells at C/5 rate.

<table>
<thead>
<tr>
<th></th>
<th>Initial capacity [mA h g⁻¹]</th>
<th>150-cycle capacity [mA h g⁻¹]</th>
<th>Capacity retention [%]</th>
<th>Capacity fade rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li IICelgardII Li2S6</td>
<td>1180</td>
<td>240</td>
<td>20.0%</td>
<td>0.53</td>
</tr>
<tr>
<td>Li IILYZPII Li2S6</td>
<td>950</td>
<td>850</td>
<td>89.5%</td>
<td>0.07</td>
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2.3. Polysulfide-Retention Ability, Chemical Compatibility (with the Polysulfides), and Electrochemical Stability (under Operating Conditions of the Li-S Batteries) of the LYZP Membrane

The LYZP membrane in the hybrid Li-S batteries has a “trifunctional” role as (1) a Lithium-ion conductor, (2) an electrical insulator to separate the anode and the cathode, and (3) a lithium polysulfide shield to prevent the diffusion of the soluble polysulfides from the positive sulfur electrode to the negative Li-metal electrode. The first two functions are similar to those in the regular solid-electrolyte battery systems. The third role of the LYZP membrane is a unique function, especially in the Li-S batteries involving soluble intermediates (lithium polysulfides). Figure 3 displays the polysulfide-retention ability of the LYZP membrane tested with a simple experiment (as detailed in the Experimental Section and in Figure S7 in the Supporting Information). As expected, the LYZP membranes exhibit a super effective function to prevent the polysulfide from diffusing through. There was no color change in the blank solvent (mixture of DME/DOL) even after 30 d of test (Figure 3), indicating no migration of the long-chain polysulfides from the upper reservoir to the opposite side DME/DOL solution through the LYZP membrane. For a comparison, the same test was also performed with a piece of Celgard separator (Figure S8, Supporting Information). Unfortunately, diffusion of the polysulfides was observed within only 1 h of experiment (light yellow color was observed for the DME/DOL solution).

As a general scenario, the electrochemical process of the Li-S battery involves a series of soluble polysulfide intermediate products. The negative aspect of the appearance of throughout the 150 cycles. It should be mentioned that after ≈180 cycles, the capacity fade of the Li IILYZPII Li2S6 cell started to be faster (>0.07% per cycle), most likely due to the evaporation/consumption of the liquid electrolyte at the anode based on our post-mortem analysis.
polysulfides has been well known as they may diffuse from the cathode through the separator to react with the Li-metal anode. However, another negative aspect of the polysulfide species when using the solid Li\(^+\)-ion conductor has never been recognized: the liquid-phase polysulfides are potential reducing regents for the solid electrolytes consisting of reducible transition-metal ions. Figure 4 presents the chemical compatibility of the two NaSICON-type solid electrolyte materials: the Li\(_{1+x}\)Al\(_{2-x}\)Ti\(_2\)(PO\(_4\))\(_3\) (prepared the same way as we previously presented\(^8\)b) and the Li\(_{1+x}\)Y\(_{2-x}\)Zr\(_2\)(PO\(_4\))\(_3\) with lithium polysulfides. Permanent color change (due to the reduction of Ti\(^{4+}\) to Ti\(^{3+}\)) was observed for the LATP membrane only upon a 1 d submerging into the polysulfide solution. On the other hand, there was no permanent color change at all for the LYZP membrane after a 7 d duration of submerging (into the polysulfide solution). The XRD analysis results displayed in Figure 4g,h further confirm the stability of LYZP and the instability of LATP under the liquid-polysulfide environment. Therefore, although the well-developed LATP exhibits relatively high Li\(^+\)-ion conductivity, it is hard to be considered as a candidate solid electrolyte for application in Li-S batteries. Whereas the compatible LYZP is relatively more promising.

Figures 3 and 4 provide information about the polysulfide-suppression effect of the LYZP membrane under the natural gravity and the chemical compatibility of the LYZP material with the polysulfide species under non-electrochemical processes. In order to evaluate the polysulfide-blocking ability of the LYZP separator and electrochemical compatibility of the LYZP membrane in the Li-S batteries under the cycling conditions, a series of post-mortem analyses were performed for the LYZP membranes taken from the cycled Li ILYZPII Li\(_2\)S\(_6\) cells. To verify that there is no polysulfide penetration through the LYZP membrane, cross-section of the cycled LYZP separator was analyzed with SEM/EDS, as presented in Figure 5a,b. The elements zirconium, phosphor, oxygen, and yttrium originated from the LYZP material are also shown here as references. There is no obvious sulfur signal observed in the line-scan profile along the cross-sectional area of the cycled LYZP separator, attesting to a good shield of the LYZP membrane for preventing the polysulfide-shuttle during the operation of the cell. A visual examination of the cycled LYZP membrane (Figure S9, Supporting Information) indicates that there is no color change of the membrane after cycling. Its electrochemical stability is further confirmed by the XRD analysis that there is no phase change of the membrane after cycling (Figure 5c).

### 2.4. Hybrid Li ILYZPII Li\(_2\)S\(_6\) Batteries without LiNO\(_3\) Additive

In the traditional Li-S batteries with the Celgard separator, it is well known that the LiNO\(_3\) additive in the electrolyte plays a critical role to suppress the negative effects induced by the polysulfide-shuttle behavior. For the Li ILYZPII Li\(_2\)S\(_6\) batteries in this study, since the LYZP membrane can circumvent the diffusion of the dissolved polysulfides to the Li-metal anode, the LiNO\(_3\) additive is expected to be excluded from the electrolyte. To verify this additional benefit from the use of LYZP membranes, a hybrid Li ILYZPII Li\(_2\)S\(_6\) cell and a Li IICelgardII...
Li$_3$S$_6$ cell were prepared and tested without LiNO$_3$ additive. Figure 6a,b compare the charge–discharge profiles of the above two cells at various C rates. As expected, due to the polysulfide-shuttle effect, the Li ICelgardII Li$_3$S$_6$ cell exhibits a large time difference between charge and discharge in each cycle whenever C rate is applied (Figure 6a). Therefore, without the LiNO$_3$ additive, the Li ICelgardII Li$_3$S$_6$ cell shows much lower Coulombic efficiency than the case with the LiNO$_3$ additive (comparison of Figure 6c to Figure 2f). On the other hand, for the Li IIIYZPII Li$_3$S$_6$ cell, the charge-and discharge times in each cycle are reasonably “symmetric” (Figure 6b). As a result, no obvious difference in Coulombic efficiencies was observed for the Li IIIYZPII Li$_3$S$_6$ cells with and without the LiNO$_3$ additive (comparison of Figure 6d to Figure 2e). But the LiNO$_3$ additive has a huge effect on the Li IIICelgardII Li$_2$S$_6$ cell in terms of the discharge capacity and capacity retention during cycling (comparison of Figure 6d to Figure 2e).

3. Conclusion

In summary, we presented a polysulfide-shuttle-free Li-S battery study with a NaSICON-type Li$^+$-ion conductive solid electrolyte, Li$_{1+x}$Y$_x$Zr$_{1-x}$(PO$_4$)$_3$ ($x$ = 0–0.15). The LYZP membrane synthesized with a facile method shows a reasonable Li$^+$-ion conductivity and a superior polysulfide-retention ability. More importantly, the LYZP exhibits both chemical compatibility with the cell components and electrochemical stability under the charge–discharge conditions of the Li-S cells. With a strategically designed ionic interface between the Li-anode and the LYZP membrane, the hybrid Li-S batteries with the liquid/LYZP hybrid electrolyte provide both a reasonable rate capability and a superior long-term cycling stability.

4. Experimental Section

Synthesis/Preparation of the NaSICON-Type Li$_{1+x}$Y$_x$Zr$_{1-x}$(PO$_4$)$_3$ ($x$ = 0–0.15) Membrane: The LYZP powder was synthesized through a series of solid-state reactions with Li$_2$CO$_3$, NH$_4$H$_2$PO$_4$, ZrO$_2$, and Y$_2$O$_3$ as the starting materials. First, a mixture of the above starting materials with a proper ratio was ball-milled for 24 h, followed by a calcination process at 750 °C for 24 h. Then the calcined powder was vibrate-milled for 120 h. After this process, the Brunauer–Emmett–Teller (BET) surface area of the resulting LYZP powder was $\approx$8.0 m$^2$ g$^{-1}$.

With the synthesized LYZP powder, a green pellet was prepared by a uniaxial cold-pressing at 100 MPa, followed by an isostatic pressing at 170 MPa. Then the obtained pellet was sintered at different temperatures and for a variety of durations.

LATP membrane was prepared the same way as we previously presented.$^{[8b]}$

Characterization: The SEM images and elemental mappings of the materials were obtained with a FEI Quanta 600 instrument equipped with an EDS. The XRD patterns of the materials were obtained with a FEI Quanta 600 instrument equipped with a CuKα radiation on a Philips X-ray diffractometer with a step width of 0.02° and 4 s counting time per each step. The Li$^+$-ion conductivity of the LYZP solid-state membrane was measured with the traditional AC impedance method employing two blocking stainless steel electrodes. Prior to the impedance measurement, the LYZP membrane was coated with a thin layer of gold on each side. The impedance data were collected on a Solatron 1287 electrochemical system with the frequency measured from 10$^4$ to 10$^{-1}$ Hz. The BET surface area of the powder materials was measured with a Quantachrome NOVA 2000 volumetric adsorption analyzer.

Preparation of Cathode Matrix, Liquid Electrolyte, and Polysulfide Catholyte: A free-standing (without binder)CNF paper was used as the cathode matrix in this study. Prior to the cell assembly, the CNF paper electrode was activated with a heating process under CO$_2$ atmosphere. The original CNF powder material (PR-24-XT-PS) was purchased from Pyrograf Products Inc. Fabrication and activation of the CNF paper electrodes are as described in our previous publication.$^{[11]}$ After activation, the areal density of the final CNF paper electrode was 2.0 mg cm$^{-2}$.

The liquid electrolyte used in this study was 1.0 M LiCF$_3$SO$_3$ (98%, Acros Organics) dissolved in a mixed dimethoxylethane (Acros Organics) and 1,3-dioxolane (Acros Organics) solvent with or without 0.1 M LiNO$_3$ (99%, Acros Organics) as the additive (named as blank electrolyte). The lithium polysulfide (in the form of Li$_2$S$_6$) catholyte with 1.5 M sulfur was
prepared the same way as that in our previous publication\cite{12} through a reaction of an elemental sulfur (99.5%, sublimed powder, Acros Organics) with a lithium sulfide (Li$_2$S, 99.9%, Acros Organics) in the blank electrolyte (1.0 M LiCF$_3$SO$_3$ in DME/DOL with or without LiNO$_3$ additive).

**Polysulfide Retention Test:** Diffusion of the dissolve polysulfides through the LYZP membrane or the Celgard separator was visually determined with a simple setup (Figure S7, Supporting Information). For these experiments, a 4.0 mL of 0.25 M Li$_2$S$_6$ catholyte (dissolved in 1:1 DME/DOL solution) was filled inside a transparent container with a piece of separator (either Celgard or LYZP) embedded in the cap (Figure S7, Supporting Information). The other side of the Celgard or LYZP separator was a beaker filled with the DME/DOL blank solvent. During the permeation tests, the entire setup was kept steady without any external movement. The color change of the blank solvent (DME/DOL) was visually examined.

**Coin Cell Assembly and Testing:** The Li IILYZPII Li$_2$S$_6$ cells were prepared with a coin-type configuration and were assembled in a glove box filled with argon gas. First, a certain amount of Li$_2$S$_6$ catholyte (with or without LiNO$_3$ additive) was injected into the CNF paper electrode. The sulfur loading was controlled at 2.0 mg cm$^{-2}$. Then, the LYZP membrane (with a diameter of 16 mm, thickness of 150 μm, and areal density of ≈50 mg cm$^{-2}$) was put on top of the CNF/Li$_2$S$_6$ cathode. Afterward, a piece of PP membrane (pre-soaked with the LiCF$_3$SO$_3$/DME-DOL electrolyte with or without LiNO$_3$ additive) was placed on the LYZP separator. Finally, a piece of Li-metal foil was attached onto the PP membrane. The coin cell was then sealed under the Ar atmosphere inside the glove box. The battery performances were tested with a BT2000 Arbin instrument at ambient temperature.

**Supporting Information**
Supporting Information is available from the Wiley Online Library or from the author.

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