Cationic Covalent Organic Framework as Separator Coating for High-Performance Lithium Selenium Disulfide Batteries

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Abstract: Selenium disulfide that combines the advantages of S and Se elements is a new material for Li-chalcogen battery cathodes. However, like Li-S batteries, the shuttle effect seriously restricts the performance of Li-SeS\(_2\) batteries. In this work, we have synthesized a kind of nitrogen-rich lithophilic covalent organic framework (ATG-DMTZ-COF) as a separator coating material for Li-SeS\(_2\) batteries. Here, the N atom in the ATG-DMTZ-COF channel preferentially interacts with the lithium ion in the electrolyte to form N . . . Li bond, which significantly improves the diffusion coefficient of lithium ions during the charge and discharge. More importantly, we prove that the pore size of ATG-DMTZ-COF will decrease sharply because there is a large amount of TFSI\(^-\) in the channel, and finally the shuttling of polysulfide and polyselenide is suppressed by the sieving effect. As a consequence, Li-SeS\(_2\) batteries using the ATG-DMTZ-COF separator coating show excellent performances with an initial discharge capacity of 1028.7 mAh g\(^{-1}\) at 0.5 C under a SeS\(_2\) loading of 2.38 mg cm\(^{-2}\). Furthermore, when the current density is 1C, the specific capacity of 404.7 mAh g\(^{-1}\) can be maintained after 700 cycles.

Keywords: shuttle effect; Li-SeS\(_2\) battery; covalent organic framework; sieving effect

1. Introduction

At present, rechargeable batteries, such as lithium-ion batteries (LIBs), lithium-chalcogen batteries, lithium-oxygen batteries and so on, are regarded as a kind of environmentally friendly energy storage system. Among them, lithium-ion batteries, which are used for mobile phone and electric vehicles (EVs), could become a prospective candidate for EVs and other aspects of energy consumption due to their advantages of low self-discharge, long cycle life, and safety [1–4]. However, the low theoretical energy density of lithium-ion batteries compared with metallic batteries gradually exposed its disadvantages for large-scale energy consumption equipments [5,6], so it is urgent to seek the next-generation energy storage system. With high theoretical energy density, low cost, and environmentally friendly high theoretical specific capacity, lithium-chalcogen batteries have obtained tremendous attention in the recent years [7,8]. For example, lithium-sulfur batteries have high theoretical specific capacity (1675 mA h g\(^{-1}\)) and energy density (2600 Wh kg\(^{-1}\)), which is two to five times as much as LIBs [9–16]. But for lithium-sulfur batteries, there are still many challenges to overcome such as the insulation of sulfur, the dissolution of polysulphide, volume expansion, and so on [17–19].

Similar to the lithium-sulfur battery, lithium-selenium battery also attracts a lot of interest since it was reported by Amine in 2012 because of its satisfactory theoretical specific capacity (675 mA h g\(^{-1}\)) and high theoretical volumetric (3260 mAh cm\(^{-3}\)) [20]. More importantly, selenium is a semiconductor, and its conductivity is up to 1 × 10\(^{-3}\) S m\(^{-1}\),
which is far higher than that of sulfur \( (5 \times 10^{-30} \text{ S m}^{-1}) \) [21]. Therefore, it is better for electronic transmission with improvement of the utilization of active material. Nevertheless, its theoretical specific capacity \( (675 \text{ mA h g}^{-1}) \) is lower than Li-S battery \( (1675 \text{ mA h g}^{-1}) \) [22] and makes it difficult to commercialize. By comparison, selenium sulfide\( (\text{SeS}_2) \), since it contains sulfur element and selenium element, can not only solve the problem of conductivity of sulfur positive electrode, but also overcome the problem of low theoretical specific capacity of selenium positive electrode [23–26]. For example, the conductivity and theoretical specific capacity of selenium disulfide are between sulfur elemental and selenium elemental, reaching \( 1342 \text{ mAh g}^{-1} \) [27]. However, like lithium-sulfur batteries and lithium-selenium batteries, the shuttle effect caused by the dissolution of intermediate products will make the active materials decrease, reduce the specific capacity, and lead to the deterioration of the cycle performance [28,29]. To solve this problem, many researchers have adopted a strategy similar to that of lithium-sulfur batteries. They first select a carrier material that can adsorb polysulfide and polyselenide and then encapsulate selenium disulfide in the guest material by melting. For example, they use MYS-Co\(_4\)N@C [30], MOFs-derived 3D nanoporous Co-N-C architecture nanoboxes [31], hollow mesoporous carbon nanocubes [32], NiCo\(_2\)S\(_4\) hollow capsules [33], mesoporous carbon@titanium nitride hollow spheres [34], nitrogen-rich carbon foam [35], and so on [36–39]. This strategy greatly improves the specific capacity and cycle stability of lithium-selenium disulfide batteries, but it also sacrifices the content of the active material, resulting in a low surface load of the active material (generally less than 2 mg cm\(^{-2}\)) and the overall energy density of the battery [27].

Here, we have adopted a separator modification method to improve the performance of lithium-selenium disulfide batteries. We synthesized a nitrogen-rich covalent organic framework\( (\text{ATG-DMTZ-COF}) \). Using the PP membrane modified by ATG-DMTZ-COF as the separator coating and carbon nanotubes and selenium disulfide as the positive electrode, we assembled a lithium-selenium disulfide battery. A large number of nitrogen atoms in the nitrogen-rich covalent organic framework can interact with lithium ions in the electrolyte to form N . . . Li bonds, forming a cationic framework. In order to keep the frame electrically neutral, bistri fluoromethanesulfonic imide ions \( (\text{TFSI}^-) \) are adsorbed in the COF channels by an electrostatic field. Thus, when the negatively charged polysulfide and polyselenide try to shuttle from the positive to the negative electrode, the TFSI\(^-\) (negatively charged) in the COF modified separator will exert electrostatic repulsion on them, thereby preventing them from passing through the separator to reach the negative electrode, suppressing the occurrence of the shuttle effect and also increasing the diffusion coefficient of lithium ions; therefore, the rate performance of the battery is greatly improved. Through experimenting and calculating, it was found that the COF modified separator can effectively improve the diffusion coefficient of lithium ion during charge and discharge. As a consequence, with electrostatic repulsion sieving effect, Li-Se\(_2\)S\(_2\) batteries using the ATG-DMTZ-COF separator coating show excellent performances with an initial discharge capacity of 1028.7 mAh g\(^{-1}\) at 0.5 C under a Se\(_2\)S\(_2\) loading of 2.38 mg cm\(^{-2}\) and the specific capacity of 811.7 mAh g\(^{-1}\) can be maintained after 200 cycles. Even at 1C, the specific capacity is 957.1 mAh g\(^{-1}\) initially and still maintain at 404.7 mAh g\(^{-1}\) after 700 cycles with a capacity decay rate of only 0.082% per cycle.

2. Materials and Methods

2.1. Synthesis of ATG-DMTZ-COF

First, 0.8 mmol (16.8 mg) 1,3,5-Benzene tricarboxaldehyde (ATG), 0.4 mmol (8.4 mg) 3,5-Diamino-1,2,4-triazole (DMTZ) were dissolved in 2 mL 1,4-dioxane. Then the reactants were ultrasound for 10 min until they dissolved. We filled the system with argon after adding 6M acetic acid solution and put them in an oven to react for 72 h at 120 °C. Finally, the product was dried in vacuum oven at 85 °C for 24 h after washing with 1,4-dioxane, THF and acetone. The yellow powder was obtained; it was named ATG-DMTZ-COF.
2.2. Preparation of ATG-DMTZ- COF Composite Separator

The composite separator was prepared by mixing ATG-DMTZ-COF, super-P, and LA132 with the ratio of 3:1:1. Then the N-propanol aqueous solution (VN-propanol/V water = 3/1) was added to form suspension. The ATG-DMTZ-COF coated separator was dried in vacuum oven at 55 °C after the suspension was covered on the ceramic membrane by using a scraper. Finally, the composite separator was cut into disk with a size of 19 mm in diameter, and ~30 μm in thickness.

2.3. Characterization

Powder X-ray diffraction patterns (Bruker D8 Advance, Cu Ka radiation) were used to prove the crystallinity of ATG-DMTZ-COF at 40 kV. Scanning electron microscopy (SEM) image and energy-dispersive X-ray spectrometry (EDX) elemental mapping analysis were recorded on Tescan Maia3. The thermogravimetric analysis (TGA) curves were tested in a nitrogen atmosphere with a flow rate of 20 mL/min by temperature rising from 25 °C to 900 °C with the heating rate of 10 °C/min. The pore size, volume, and surface area were measured at 77 K by Bel sorp Max surface area size analyzer.

2.4. Electrochemical Measurements

CR2032 coin cells were used to electrochemical experiments test. The pure SeS2 and multi-walled carbon nanotubes (MWCNs, with length of 10~30 μm) with the ratio of 4:1 were mixed in stainless steel reactor lining and heated at 120 °C for 8 h to obtain MWCNs/SeS2. After this, MWCNs/SeS2, super-P and LA132 with the ratio of 8:1:1 were mixed in N-propanol aqueous solution (VN-propanol/V water = 3/1). The cathode was dried at 55 °C under vacuum for 12 h after the suspension was covered on the Al foil by using scraper. Then the cathode was cut into disk with a size of 12 mm in diameter and the loading of Se was about 2.0–2.5 mg cm⁻². The coin cell with MWCNs/SeS2 cathode, ATG-DMTZ-COF/PP composite separator, electrolyte (1M LITFSI in DME/DOL (1:1, v/v), with 0.1M LiNO3 as additive) and lithium metal anode were assembled in the glove box filled with argon. The galvanostatic charge/discharge tests were carried out on LAND CT2001A multichannel battery testing system at 25 °C with the voltage range of 1.7–2.7 V (vs. Li/Li⁺). The rate performances of cell were tested at 0.5 C, 1 C, 1.5 C, and 2 C, respectively, and finally returned to 1.5 C, 1 C and 0.5 C. Cyclic voltammetry (CV) was examined at a scan rate of 0.1, 0.2, 0.3, and 0.4 mV s⁻¹.

3. Results

Figure 1a shows the XRD diffraction pattern of ATG-DMTZ-COF. The diffraction peaks at 8.8°, 13.08°, 16.6°, and 27.2° are respectively consistent with the [110], [020], [210], and [003] crystal plane of ATG-DMTZ-COF. Figure 1b is the absorption curve of N2 with the BET specific surface area of 201 m²/g, which is basically consistent with that reported in the literature [40]. Because of the extremely rich nitrogen atoms in the ATG-DMTZ-COF channel, its lithium affinity is great. Therefore, when coated on a commercial PP separator, the lithium ions anchored by nitrogen atom will adsorb the negatively charged TFSI⁻ into the pores, which sharply decreases the pore diameter of ATG-DMTZ-COF, thereby blocking polysulfide and polyselenide on the positive side. The XRD diffraction pattern of ATG-DMTZ-COF/PP separator was shown in Figure S1, from which we can figure out that the intensity of the diffraction peak of ATG-DMTZ-COF is weakened but still exists, indicating that ATG-DMTZ-COF still maintains good stability with the interaction of the binder and conductive.
Figure 2a,b show the SEM of ATG-DMTZ-COF/PP composite separator, from which we find that both COF and conductive are uniformly coated on the surface of separator. Figure 2e is a SEM image of a blank PP separator. Since a large number of holes exist in the blank PP separator, polysulfide, and polyselenide can pass through the separator to the negative electrode easily, thus causing the decay of batteries’ capacity. Figure 2f is a SEM image of the cross section of ATG-DMTZ-COF/PP composite separator. The thickness of 4.82 µm can improve the cycle performance of lithium-selenium disulfide batteries without reducing the overall energy density. In order to verify the barrier effect of COF on polysulfide and polyselenide, we conducted a group of screening experiments on ATG-DMTZ-COF/PP composite separator, blank PP separator, and Super P/PP separator respectively. As shown in Figure 3, 0.1 M Li2S6/DME solution was added to the left side of the tube. In order to keep the osmotic pressure on both sides consistent, the blank solution on the right side held 0.1 M LiTFSI/DME solution. And before carrying out the experiment, we immersed the three kinds of separator in the electrolyte of 1 M LiTFSI for two hours and dried them before assembling the H-tubes.
blocked the shuttle of polysulfide. As for blank PP separator and Super P/PP composite separator, the polysulfide on the left have shuttled through the separator to the right after 5 h and 10 h respectively, which was inferred by the color of the solution: from colorless to yellow.

To illustrate the interaction between ATG-DMTZ-COF and LiTFSI, we immersed the COF in a 1M LiTFSI methanol solution to form the ATG-DMTZ-COF/LiTFSI composite. Figure S3 shows XPS spectra of ATG-DMTZ-COF and ATG-DMTZ-COF/LiTFSI. In Figure S3, the characteristic peaks of fluorine atom and sulfur atom appeared at 691.3 eV and 168.7 eV, respectively. It can be shown that there is a large amount of LiTFSI in the COF channels. Figure S4 shows the adsorption experiment of Li$_2$S$_6$ by ATG-DMTZ-COF/LiTFSI complex. In this experiment, Super P and ATG-DMTZ-COF/LiTFSI did not adsorb polysulfides, indicating that there is not enough space for polysulfide adsorption, and this result can be seen from Figure S4. After the ATG-DMTZ-COF/LiTFSI complex was activated at a high temperature to remove some gas molecules, its specific surface area was tested and compared with that of Figure 1b. Here, we figured out that the specific surface area decreased sharply to only 10 m$^2$/g and the pore size also decreased from 1.3 nm to 0.06 nm.

Figure 3. The sieving effect experiments with different separators: (a) ATG-DMTZ-COF/PP separator. (b) blank PP separator. (c) Super P/PP separator.

The lithium ion diffusion coefficient methods of the three separators are shown in Figures S5 and S6 and according to the Randles-Sevcik equation Formula (1) [41]:

$$I_p = 2.69 \times 10^5 n^{1.5} A D_{Li^+}^{0.5} C_{Li^+}^{0.5} v^{0.5}$$

(1)

where $I_p$ is the value of the peak current (A), $n$ is the number of transferred electrons (for a lithium-selenium disulfide battery, $n = 2$), $A$ is the area of active material(cm$^{-2}$), $D_{Li^+}$ is the diffusion coefficient of lithium ions, $C_{Li^+}$ is the concentration of lithium ions (mol/mL), and $v$ is the scan rate (V/s). In Figure S5a–c, peak A and B correspond to the long-chain polysulfide and polyselenide that are reduced from selenium disulfide and the corresponding potential is 2.1–2.3 V. Peak C represents the reduction of long-chain polysulfide and polyselenide to lithium sulfide and lithium selenide, respectively, and the reduction potential is about 1.85 V. Peak D shows that lithium sulfide and lithium selenide are first converted into polysulfide and polyselenide and finally oxidized to selenium disulfide, corresponding to oxidation potential of about 2.4 V. The $I_p$-$v^{0.5}$ curve is shown in Figure S6 and from it, the lithium ion diffusion coefficients of the three types of separator at different peak positions can be calculated according to the Randles-Sevcik equation. At
Peak A, the diffusion coefficients of ATG-DMTZ-COF separator, blank PP separator and Super P separator are $6.81 \times 10^{-9}$, $3.11 \times 10^{-9}$, and $4.01 \times 10^{-9}$, respectively. Comparing with the blank PP separator and Super P/PP separator, the diffusion coefficients of ATG-DMTZ-COF/PP separator at the peaks B, C, and D are all larger, as Figure S5d shows.

As shown in Figure 4, the electrochemical performance of coin battery assembled with the ATG-DMTZ-COF separator, lithium metal, and selenium disulfide electrode was tested. For comparison, there are batteries assembled with blank PP separators and Super P separators. Figure 4a,b are the galvanostatic discharge and charge profiles of the battery at a current density of 0.5 C and the cyclic voltammetry curve of a scan rate of 0.1 mV/s, respectively. We can clearly see that three reduction peaks appear at around 2.35 V, 2.23 V, and 2.05 V. The first two peaks correspond to the conversion of solid selenium disulfide to liquid lithium polysulfide and lithium polyselenide, while the last peak represents lithium polysulfide and lithium selenide are converted into solid lithium sulfide and lithium selenide, and the discharge specific capacity in the first cycle is as high as 1028.7 mAh g$^{-1}$.

In charging, lithium sulfide and lithium selenide firstly generate polysulfide and polyselenide and finally selenium disulfide. The whole charging and discharging process is similar to the reaction mechanism of lithium-sulfur batteries, which is the solid-liquid-solid state transformation. Figures S7 and S8 are charge and discharge curves and cyclic voltammetry curves of blank PP separators and Super P separators at 0.5 C and comparing with Figure 4a,b, the platform for the conversion of selenium disulfide into liquid lithium polysulfide and lithium polyselenide is not obvious, which indicates that the shuttle effect occurs in batteries assembled with blank PP separators and Super P separators with the initial specific discharge capacity of only 722.6 mAh g$^{-1}$ and 999.2 mAh g$^{-1}$. Since Super P is a conductive carbon material, it has a small barrier effect to the intermediate product so the performance of Super P separator is slightly better than blank PP separator.

Figure 4c shows the cycle performance of the lithium-selenium disulfide battery with three kinds of separators at a current density of 0.5 C. For ATG-DMTZ-COF separators, the specific discharge capacity of the first cycles reaches 1028.7 mAh g$^{-1}$ and remains at 839.2 mAh g$^{-1}$ after 100 cycles. Even after 200 cycles, the capacity maintains at 811.7 mAh g$^{-1}$, which means that the attenuation rate is only 0.09% per cycle and the coulomb efficiency is up to 99.8%. For blank PP separators and Super P separators, the discharge specific capacity of the first cycles is only 722.6 mAh g$^{-1}$ and 999.2 mAh g$^{-1}$. After 100 cycles, the capacity remains at 408.4 mAh g$^{-1}$ and 746.1 mAh g$^{-1}$. At 200 cycles, the capacity is only 418.1 mAh g$^{-1}$ and 573.4 mAh g$^{-1}$. At the same time, the capacity decay rate is 0.21% and 0.213% per cycle and the coulomb efficiency is only 93% and 95%. This is because the two kinds of separators cannot stop polysulfide and polyselenide from reaching the negative electrode. Figure 4d is the rate performance of the three separators with different current densities. Even at a current density of 2C, the discharge specific capacity of ATG-DMTZ-COF separators can maintain at 772.2 mAh g$^{-1}$, while the other two separators are only 192.5 mAh g$^{-1}$ and 578.7 mAh g$^{-1}$, far lower than ATG-DMTZ-COF separators. When the current density returns to 0.5 C, the specific capacity of ATG-DMTZ-COF separators is still 999.9 mAh g$^{-1}$, showing its excellent performance; however, the specific capacity of PP separator and Super P separator are only 409.4 mAh g$^{-1}$ and 694.5 mAh g$^{-1}$, which is far from the first discharge density of 0.5 C. This shows that ATG-DMTZ-COF can not only block polysulfide and polyselenide but also speed up the transport of lithium ions and increase the diffusion coefficient of lithium ions. Figure 4e is a long cycle performance at a current density of 1C. The discharge specific capacity of ATG-DMTZ-COF separators is 957.1 mAh g$^{-1}$ initially (area capacity: 2.088 mAh cm$^{-2}$) and still maintains at 404.7 mAh g$^{-1}$ after 700 cycles with the capacity decay rate of only 0.082% per cycle. The initial discharge specific capacities of PP separators and Super P separators at a current density of 1C are 397.1 mAh g$^{-1}$ and 908.2 mAh g$^{-1}$, respectively, with the capacity decay rate up to 0.098% and 0.12%. Therefore, it is possible that in terms of the sieving effect on polysulfide and polyselenide, ATG-DMTZ-COF separators have greatly improved.
Figure 4. (a) The galvanostatic charge-discharge curve of ATG-DMTZ-COF/PP separator at a current density of 0.5 C. (b) CV curve of ATG-DMTZ-COF/PP separator at a sweep speed of 0.1 mV s$^{-1}$. (c) The electrochemical cycling performance of three kinds of separator at a current density of 0.5 C. (d) The rate performance of Li-SeS$_2$ batteries with different separator. (e) The long cycle performance of different separator at a current density of 1 C.

4. Conclusions

The nitrogen-rich covalent organic framework contains a large number of N atoms, which can preferentially form N···Li bonds with Li$^+$ in the electrolyte. At the same time, TFSI$^-$ anions are adsorbed in the channels of the COF, so the size of the channels in diameter is drastically reduced, achieving a sieving effect on polysulfides and polyselenides. Through cyclic voltammetry tests with different scan rates, it is concluded that the ATG-DMTZ-COF separators can not only suppress the shuttle of polysulfide and polyselenide but also improve diffusion coefficient of Li$^+$ in the battery. When the current density is 1C and the mass of selenium disulfide is 2.4 mg, the initial discharge specific capacity of ATG-DMTZ-COF separators is 957.1 mAh g$^{-1}$ (the corresponding surface capacity is 2.03 mAh cm$^{-2}$) and the specific capacity still maintains at 404.7 mAh g$^{-1}$ (0.858 mAh cm$^{-2}$) after 700 cycles with an average capacity decay rate of only 0.082% per cycle. Compared to previously reported Li-SeS$_2$ studies using commercial separators (Table S1), it provides another new idea for solving the problems encountered by lithium-selenium disulfide batteries. In this method, a cationic framework, which can adsorb TFSI$^-$ and prevent polysulfide and polyselenide from shuttling, is formed by a modifying separator with a kind of lithophilic porous material. Obviously, this strategy, which achieves a win-win situation that not only
screens the intermediate products but also improves the diffusion coefficient of lithium ion, will pave the way for the future development of high-performance Li-SeS$_2$ batteries.

**Supplementary Materials:** The following supporting information can be downloaded at: [https://www.mdpi.com/article/10.3390/coatings12070931/s1](https://www.mdpi.com/article/10.3390/coatings12070931/s1) [42–44], Figure S1: The XRD of ATG-DMTZ-COF and ATG-DMTZ-COF/PP separator; Figure S2 The electrolyte contact angles of (a) blank PP separator and (b) ATG-DMTZ-COF/PP separator; Figure S3: The XPS spectra of ATG-DMTZ-COF and ATG-DMTZ-COF/LiTFSI; Figure S4: The adsorption experiment of Super P and ATG-DMTZ-COF; Figure S5: The CV curve of Li-SeS$_2$ batteries with different separator at a sweep speed of 0.1 mV s$^{-1}$, 0.2 mV s$^{-1}$, 0.3 mV s$^{-1}$ and 0.4 mV s$^{-1}$; (a) ATG-DMTZ-COF/PP separator. (b) blank PP separator. (c) Super P/PP separator. (d) The lithium ion diffusion coefficients of the three types of separator at different peak positions; Figure S6: The $I_p$-v$^{0.5}$ curve of different separator at peaks A, B, C and D. Figure S7: The galvanostatic charge-discharge curve of (a) blank PP separator, (b) Super P/PP separator at a current density of 0.5 C; Figure S8: CV curve of (a) blank PP separator, (b) Super P/PP separator at a sweep speed of 0.1mV s$^{-1}$; Table S1 The performance of Li-SeS$_2$ batteries comparison chart of different literatures.

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