The application of Cr-MOF@MWCNT modified separator in high-performance lithium-sulfur batteries

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Abstract: Lithium-sulfur batteries have attracted attention when competing with the next-generation of rechargeable batteries due to their higher theoretical specific capacity, lower cost, and non-toxic and harmless feature. However, there are many obstacles towards the practical application of lithium-sulfur batteries such as low conductivity of the positive electrode and discharge products, the “shuttle effect” of polysulfides, and the unsafety of the lithium negative electrode. In this paper, Cr-MOF@MWCNT as a separator modification layer is introduced into lithium-sulfur batteries to solve the problem of “shuttle effect”. The Cr-MOF in the coating layer can adsorb polysulfides, and the MWCNT tightly combined with Cr-MOF helps to build a good conductive network, so that the adsorbed polysulfides can be converted. As the initial specific capacity and cycle stability of lithium-sulfur batteries with the Cr-MOF@MWCNT separators have been improved, the initial specific capacity is as high as 1377 mA h g⁻¹ at a rate of 0.2 C, while the average capacity attenuation per cycle after 300 cycles is 0.14%, with 99.8% of coulombic efficiency.

1. Introduction

With the development of information technology and electric vehicle industry in contemporary society, people’s demands have increased for environmentally-friendly energy storage batteries with high energy density. Among the system of rechargeable batteries, lithium-sulfur batteries have grabbed attention from scientific researchers ⁴ because of their higher theoretical specific capacity (1675 mA h g⁻¹), environmental benignity, and low cost. Although they boast promising future, there are still some problems needed to be solved urgently ⁵. First of all, the low conductivity of sulfur and Li₂S₂ have reduced efficiency of active materials. In addition, lithium polysulfide diffuses back and forth between the positive and negative electrodes, thus forming the “shuttle effect” which reduces the coulombic efficiency and cycle stability of batteries. Finally, uneven deposition of lithium ions on the surface of the negative electrode will generate lithium dendrites to pierce the SEI film, which makes lithium-sulfur batteries unsafe.

Separators is essential to lithium-sulfur batteries, which ensures safety of batteries and prevents short circuits. Nowadays, the widely-used ones are polypropylene separators and polypropylene/polyethylene/polypropylene three-layer composite separators. Traditional polyolefin separators exhibit good mechanical strength and electrochemical stability, but they fail to solve such problems as the shuttle effect of polysulfides. As metal organic framework materials (MOFs) possess the advantages of large specific surface area and high porosity, if applied to the separators of lithium-sulfur batteries, they can adsorb polysulfides dissolved in the electrolyte. In recent years,
extensive researches \cite{5,6} have been carried out in modifying separators with MOFs materials. Bai et al., \cite{7} synthesized a new type of Cu-HKUST@GO separator to be used in lithium-sulfur batteries. MOF@GO separators obstruct polysulfides through their size effects and chemical adsorption capacity, while hardly blocking the transportation of lithium ions, which enables ion to be selectively permeated. By using Cu-HKUST@GO separators, the average attenuation per cycle of lithium-sulfur batteries within 1500 long cycles is only 0.019%. Hong et al., \cite{8} combined Ce-MOF and CNT to modify separators of lithium-sulfur batteries, as Ce-MOF enjoys high specific surface area and catalytically active metal sites, which makes it faster to adsorb and catalytically convert polysulfides. The batteries have an initial specific capacity of 1022 mAh g\(^{-1}\) at a rate of 1 C, while coulombic efficiency is close to 100%. Song et al., \cite{9} used 3D Co/NCS/CNT nanomaterials as the separator coating layer of lithium-sulfur materials, which can adsorb polysulfides and speed up their conversion.

In this paper, a tightly connected Cr-MOF@MWCNT material is prepared, and Cr-MOF@MWCNT as a separator coating layer is adopted to modify the separator of lithium-sulfur batteries by using knife coating. The active metal center Cr\(^{3+}\) lies in the Cr-MOF in the coating layer, which can adsorb polysulfides and prevent trans-layer transport. The MWCNT tightly combined with Cr-MOF increases the conductivity of the positive electrodes of the separator, and the polysulfide restricted on the positive electrode is reused in subsequent cycles to improve the cycle performance of batteries. Thanks to the above advantages, lithium-sulfur batteries using Cr-MOF@MWCNT to modify the separator exhibit good electrochemical performance. The specific discharge capacity of the batteries at 0.2 C reaches 1377 mAh g\(^{-1}\); the average capacity attenuation after 300 cycles is 0.14%, with 99.8% of coulombic efficiency. Besides, lithium-sulfur batteries with the Cr-MOF@MWCNT separator possess good rate capability, with a specific capacity of 679 mAh g\(^{-1}\) at a rate of 2 C.

2. Materials and Methods

2.1. Preparations for Cr-MOF@MWCNT

First, 60 mg of polyvinylpyrrolidone (PVP) was dissolved in 30 ml of water to obtain 30 ml of PVP aqueous solution with a concentration of 2 mg mL\(^{-1}\). Then 160 mg, 240 mg, and 320 mg of multi-walled carbon nanotubes (MWCNTs) with a diameter of 20-40 mg were respectively added to 30 ml of PVP aqueous solution; after one hour of ultrasonic treatment, vacuum filtration was performed to obtain 3 groups of solid samples of MWCNT with activated surfaces.

Three groups of MWCNT samples were placed in 15 ml of deionized water and received an hour of ultrasonic treatment to make the samples uniformly dispersed. Two mmol of cadmium nitrate nonahydrate (Cr (NO\(_3\))\(_3\)•9H\(_2\)O) and 2 mmol of terephthalic acid (PTA) were added before putting them into the reaction kettle after one hour of ultrasonic treatment, and then heating them in a hydrothermal oven at 218°C for 18 hours. The heated solution was then taken out and filtered to obtain 3 groups of products with different MWCNT content; the products were washed twice with hot dimethylformamide (DMF) and ethanol to remove impurities, and finally they were dried in a vacuum at 150°C for 12 hours to obtain three groups of Cr-MOF@MWCNT samples with different MWCNT content. According to the MWCNT content from least to most, the three samples were respectively named as Cr-MOF@MWCNT-1, Cr-MOF@MWCNT-2 and Cr-MOF@MWCNT-3.

2.2. Preparations for Modified Separator of Cr-MOF@MWCNT and MWCNT

Prepared 150 mg of Cr-MOF@MWCNT materials and 18.8 mg of PVDF solid binder (Cr-MOF@MWCNT: PVDF=8:1) were put into a mortar and were ground for 10 minutes. Then an appropriate amount of n-methylpyrrolidone solution was added to the mixture and was converted into a liquid slurry. After three hours of magnetic stirring and an hour of ultrasonic treatment, the mixed slurry was uniformly dispersed, and Cr-MOF@MWCNT was coated on the Celgard separator on one side with the method of knife coating. The coated separator was dried in a vacuum oven at 60°C for 12 hours, then taken out and cut into a disc with a diameter of 18 mm on a cutting machine, and the Cr-MOF@MWCNT separator was therefore obtained and placed in a glove box for later use. When
the MWCNT separator was prepared, the mass ratio of the material to the binder (MWCNT: PVDF=8:1) as well as the thickness of the scraper remained unchanged. The surface load of the coating layer of Cr-MOF@MWCNT in this paper was about 0.3 mg cm⁻².

2.3. Assembly of Lithium-sulfur Batteries
Sulfur powder, Super P and PVDF were mixed and ground at a mass ratio of 7:2:1 and then were added to the N-methylpyrrolidone (NMP) solution, and stirred for 6 hours to obtain positive electrode slurry uniformly dispersed. The slurry was evenly coated on the aluminum foil through knife coating, was dried in a vacuum at 60 °C for 24 hours, and was sliced to obtain a circular pole piece with a diameter of 12 mm. After being weighted, it was placed in a glove box for later use. The surface load of the active materials of positive electrode mentioned in this paper was about 1.4 mg cm⁻². Then lithium-sulfur batteries were assembled in a glove box under argon atmosphere by using positive plates, lithium plating, separators, nickel foams, and cathodes and anodes, and about 30 μL of electrolyte was added to each battery. The electrolyte was a DOL/DME mixed solution (volume ratio 1:1) containing LiTFSI and 1% by mass of lithium nitrate additive. After being assembled, the batteries were sealed with a sealer, taken out of the glove box, and stood at room temperature for 12 hours before electrochemical testing.

2.4. Characterization and Testing
In the paper, a Rigaku Ultima IV X-ray diffractometer was used to perform X-ray diffraction analysis on Cr-MOF@MWCNT, with the radiation source Cu-Kα, the working voltage hitting 40 kV, and the 2θ scanning ranging between 10 and 90°. A FEI-Quanta FEG 250 electronic microscope was adopted to analyze the Cr-MOF@MWCNT material and the separators by scanning electron microscope to observe the morphology of surfaces. In the adsorption test of Li₂S₄, three vials with a capacity of 10 mL were prepared, and 3 mL of 0.4 M Li₂S₄ solution and 4 mg of sample were respectively added to each vial. Then, the vials stood for 3 hours to observe whether the color of the solution changed to characterize the strength of different samples for adsorbing polysulfide. When galvanostatic charge-discharge test was performed, the assembled battery needed to stand for 12 hours, and then the charge-discharge test was performed on the test system of Xinwei battery, with the discharge voltage ranging between 1.6 and 2.8 V. Produced by Shanghai Chenhua Company, an CHI660 electrochemical workstation was used for cyclic voltammetry testing, with the voltage scan ranging between 1.5 and 2.8 V and the scan rate reaching 0.1 mV s⁻¹. In this paper, the PARSTAT2273 electrochemical test system, with alternating-current signal frequency ranging between 0.01 and 105 Hz, and amplitude hitting 5 mV, produced by Princeton University, was used to conduct alternating-current impedance tests on lithium-sulfur batteries with different separators to understand how the internal resistance of the batteries changed and why it changed.

3. Results & Discussion

3.1. Physical and Chemical Characterization of Cr-MOF@MWCNT Materials with Different MWCNT Additions
To verify whether Cr-MOF@MWCNT was synthesized, three groups of Cr-MOF@MWCNT materials with different MWCNT additions were characterized by XRD, with the scan range between 5° and 80°, and the scanning speed reaching 5° min⁻¹, as shown in figure 1. Cr-MOF@MWCNT-1, Cr-MOF@MWCNT-2 and Cr-MOF@MWCNT-3 respectively represented Cr-MOF@MWCNT samples with MWCNT additions of 160mg, 240mg and 320 mg. In the figure, it could be observed that the XRD patterns of the three Cr-MOF@MWCNT samples all showed diffraction peaks at 6°, 9° and 17°, corresponding to the characteristic peaks of Cr-MIL-101. In addition, the patterns demonstrated a diffraction peak at about 26°, which corresponded to the characteristic peak of CNT, and the peak height increased as MWCNT was added. It proved that Cr-MOF@MWCNT materials with different MWCNT content were synthesized.
To observe the surface morphology of the three groups of Cr-MOF@MWCNT samples and verify whether they were synthesized, three sets of samples of Cr-MOF@MWCNT-1, Cr-MOF@MWCNT-2 and Cr-MOF@MWCNT-3 were characterized by scanning electron microscopy (SEM), as shown in Figure 2. It could be seen from the three images (a, b, c) that the diameter of MWCNT was between 20 and 40 nm. Cr-MOF particles grew uniformly on the surface of MWCNT in quantities, and MWCNT was interspersed in the Cr-MOF particles and combined with the MOF particles. SEM characterization revealed that the tightly bonded Cr-MOF@MWCNT materials were obtained through the method of hydrothermal synthesis. Images (d, e, f) indicated element distribution of Cr-MOF@MWCNT-3, showing how three elements C, O and Cr, which constituted Cr-MOF@MWCNT, were evenly distributed. The experimental results revealed that Cr-MOF grew uniformly on MWCNT.

3.2. Research of MWCNT Addiction in Cr-MOF@MWCNT Material
To study the optimal amount of MWCNT addition when Cr-MOF@MWCNT material was prepared, the cycle performance of lithium-sulfur batteries with Cr-MOF@MWCNT-1, Cr-MOF@MWCNT-2, and Cr-MOF@MWCNT-3 separators were tested, as shown in Figure 3. The initial specific capacities of the three sets of lithium-sulfur batteries at 0.2C were respectively 1078 mAh g⁻¹, 1340 mAh g⁻¹ and 1377 mAh g⁻¹. Their average coulombic efficiencies were 99.8%, 99.9%, and 99.8%, respectively, which were all close to 100%, but discharge specific capacity and cycle performance of batteries with Cr-MOF@MWCNT-2 and Cr-MOF@MWCNT-3 separator in the first cycle at 0.2 C were higher than that of battery with Cr-MOF@MWCNT-1 separator. This was because when the MWCNT content in
the coating layer was not enough, it was difficult to form an effective conductive network to quickly convert the adsorbed polysulfides; meanwhile, MWCNT of less content reduced the conductivity of the coating layer facing the positive electrode, which made it difficult to utilize the positive electrode active materials. After that, the cycle performance of the two sets of batteries with Cr-MOF@MWCNT-2 and Cr-MOF@MWCNT-3 separator under 1C magnification was compared. The specific discharge capacity of batteries with Cr-MOF@MWCNT-3 separator in the first cycle and the 100th cycle was respectively 1008 mAh g⁻¹ and 810 mAh g⁻¹, which were higher than that of batteries with Cr-MOF@MWCNT-2 separator which were 926 mAh g⁻¹ and 714 mAh g⁻¹. In summary, the lithium-sulfur batteries with Cr-MOF@MWCNT-3 separator performed the best. Therefore, in the subsequent experiments, Cr-MOF@MWCNT-3 material with 320 mg of MWCNT additions were selected as the separator coating layer for testing and characterization.

Figure 3 Cycle performance and coulomb efficiency of lithium-sulfur batteries with Cr-MOF@MWCNT separators with different MWCNT addition at (a) 0.2 C (b) 1 C.

3.3. SEM Characterization and Polysulfide Adsorption Experiment of Cr-MOF@MWCNT-3 Separator
Then, SEM characterization of the Cr-MOF@MWCNT-3 separator was performed to observe the influence of thickness of the coating layer and the separator modification on the microstructure. The SEM image and cross-sectional SEM image of the obtained Cr-MOF@MWCNT-3 separator were shown in Figure 4. Image (a) showed that, after coating, on the surface of the Cr-MOF@MWCNT-3 separator, a large amount of Cr-MOF was uniformly formed on the interwoven multi-walled carbon nanotubes. There was no significant change in the microstructure of the coated Cr-MOF@MWCNT-3. From image (b), the thickness of the Celgard separator was about 25 μm, and the coating layer of Cr-MOF@MWCNT was closely attached to the surface of the Celgard separator, with a thickness of 20 μm.

Figure 4 (a) SEM image (b) cross-section image of Cr-MOF@MWCNT-3 separator.

To verify the adsorption effect of Cr-MOF@MWCNT-3 materials on polysulfides, 4 mg of Cr-MOF@MWCNT-3 and MWCNT materials were added to 3ml Li₂S₄ solution and allowed to stand for 3 hours, with a blank Li₂S₄ solution prepared, which was shown in Figure 5. It could be seen that the color of the Li₂S₄ solution with MWCNT remained unchanged after 3 hours, while the color of the Li₂S₄ solution with Cr-MOF@MWCNT-3 were fading. The adsorption experiment proved that the Cr-MOF in Cr-MOF@MWCNT-3 interacted with polysulfides, and inhibited the “shuttle effect” of lithium-sulfur batteries.
3.4. Electrochemical Performance Test of Cr-MOF@MWCNT-3 Separator

To study the influence of Cr-MOF@MWCNT-3 separator exerted on lithium-sulfur batteries, the cycling performance was compared and tested of three sets of lithium-sulfur batteries with separators of Cr-MOF@MWCNT-3, MWCNT and Celgard, as shown in Figure 6. At 0.2 C, the initial specific capacity of the battery with Celgard separator was 737 mAh g⁻¹, and after 50 cycles it remained only 492 mAh g⁻¹, with the average coulombic efficiency hitting 96.8%. The rapid decay of the battery with Celgard separator was because of the loss of active materials caused by the continuous dissolution and diffusion of polysulfide ions into the electrolyte. When MWCNT was used as the separator coating layer, the specific discharge capacity of the battery in the first cycle increased to 1021 mAh g⁻¹, and reached 601 mAh g⁻¹ after 150 cycles, with an average coulombic efficiency of 97%. The improvement of the cycle performance of the battery was attributable to the physical adsorption of polysulfides by the MWCNT coating layer and the reduction of the battery’s internal resistance. When the Cr-MOF@MWCNT-3 coating layer was introduced into the lithium-sulfur batteries, the performance of the battery was improved. This is because when the charge-discharge cycle started, Cr-MOF with adsorption capacity restricted the polysulfide dissolved in the electrolyte to the positive side of the separator, and an effective conductive network, where the MWCNT closely was connected with Cr-MOF, was built to convert and use adsorbed polysulfide, thus improving the cycle performance of the battery. The initial specific capacity of the lithium-sulfur batteries with the Cr-MOF@MWCNT-3 separator reached 1377 mAh g⁻¹, and remained 752 mAh g⁻¹ after 300 cycles. The capacity attenuation per cycle was only 0.14%, which exhibited good cycle performance. In addition, the average coulombic efficiency of the battery reached 99.8%, which showed that the battery showed good electrochemical stability.

![Figure 6 Cycle performance and coulomb efficiency of lithium-sulfur batteries with different separators at 0.2 C.](image)

To study the rate performance of the lithium-sulfur batteries with the Cr-MOF@MWCNT-3 separator, batteries were respectively charged and discharged at 0.2 C, 0.5 C, 1 C, 2 C, 3 C rates for 5 times, as shown in Figure 7(a). As the current density increased, the specific discharge capacity of the batteries decreased stepwise. The specific capacity of the batteries was, respectively, 1433 mAh g⁻¹, 1108 mAh g⁻¹, 884 mAh g⁻¹, 679 mAh g⁻¹ and 446 mAh g⁻¹ at discharge rates of 0.2 C, 0.5 C, 1 C, 2 C, and 3 C, which exhibited good rate performance and proved that the batteries possessed good electrochemical kinetics. The figure (b) illustrated charge/discharge voltage profiles at different magnifications. Under 0.2 C, 0.5 C and 1 C magnification, the ΔE value of the batteries was 0.19V,
0.30V and 0.38V, respectively. The polarization of the batteries increased as the current densities of charging and discharging grew, but the charging and discharging curve of the batteries still maintained a stable voltage platform, which proved that the batteries with Cr-MOF@MWCNT-3 separator provided high-rate discharge capability.

Figure 7 (a) Rate performance of lithium-sulfur battery with Cr-MOF@MWCNT-3 separator (b) Charge/discharge voltage profiles of Cr-MOF@MWCNT-3 separator at different current densities.

To study how the coating layer of Cr-MOF@MWCNT-3 influenced the polysulfide during the conversion process, the CV curve of lithium-sulfur batteries based on Cr-MOF@MWCNT-3 separator and Celgard separator were tested, as shown in Figure 8. It could be seen that the lithium-sulfur batteries based on the Cr-MOF@MWCNT-3 separator showed reduction peaks at about 2.02 V and 2.30 V, which respectively demonstrated sulfur was converted to long-chain polysulfides, and long-chain polysulfides to short-chain ones. Plus, the oxidation peak at about 2.45 V showed that the lithium sulfide was converted to elemental sulfur. Compared with the Celgard separator, the CV curve of the batteries with the Cr-MOF@MWCNT-3 separator shifted to the right on the reduction peak at 2.02 V, while it to the left on oxidation peak at about 2.45 V, which proved that the coating layer of Cr-MOF@MWCNT-3 made it faster to mutually convert sulfur into lithium sulfide.

Figure 8 CV curves of lithium-sulfur batteries based on Cr-MOF@MWCNT-3 separator and Celgard separator

To further study the electrochemical kinetics of the batteries with Cr-MOF@MWCNT-3 separator, electrochemical impedance test was performed on the lithium-sulfur batteries based on Cr-MOF@MWCNT-3 separator and batteries with Celgard separator before cycling. In the figure (b), W represented the Warburg impedance; CPE1 was the phase angle component related to the double layer capacitance; Re the electrolyte resistance; Rct the charge transfer resistance. From figure (a), it could be seen that the AC impedance spectrograms of both batteries were composed of a semicircular curve and a straight line. The intercept of the curve on the horizontal axis corresponded to Re, while the semicircle diameter corresponded to Rct of electric circuit. The Re of the two sets of batteries was within 5 Ω, while the Rct value of the batteries with Cr-MOF@MWCNT-3 separator was only 38 Ω, which was lower than the value of 78 Ω of the batteries with Celgard separator. This was because the high conductivity of Cr-MOF@MWCNT-3 coating layer speeded up the conduction of electrons in the batteries and accelerated the electrochemical conversion between sulfur and lithium sulfide. The lower Rct value of the batteries with Cr-MOF@MWCNT-3 separator reflected the faster reaction
kinetics on the electrode interface during cycling.

Figure 9 (a) Nyquist curve and (b) equivalent circuit diagram of lithium-sulfur batteries with Cr-MOF@MWCNT-3 and Celgard separators.

4. Conclusions
To sum up, the tightly bonded Cr-MOF@MWCNT materials by hydrothermal synthesis as the functional coating layer of the separator have been applied to the lithium-sulfur batteries. The Cr-MOF in the coating layer adsorbs polysulfides and restricts them to the positive electrode of the separators to inhibit the “shuttle effect”. MWCNT, tightly combined with Cr-MOF, acts as a current collector and a well-built conductive network allows stored polysulfides to be converted quickly and massively. Compared with MWCNT and Celgard separators, the initial specific capacity and cycle stability of lithium-sulfur batteries with Cr-MOF@MWCNT separators has been improved, with the initial specific capacity reaching 1377 mAh g⁻¹, average capacity attenuation per cycle after 300 cycles hitting 0.14%, and the coulombic efficiency 99.8%, which shows that the batteries possessed high-rate discharge capability. All this provides an effective method for applying MOFs materials to the modified separators in lithium-sulfur batteries with high energy density.

References
[1] Manthiram, A. Fu, Y Z. Su, Y S. (2013) Challenges and prospects of lithium-sulfur batteries. Acc. Chem. Res, 46: 1125-1134.
[2] Armand, M. Tarascon, J M. (2008) Building Better Batteries. Nature, 451(7179): 652-657.
[3] Zhang, C. Wu, H. Yuan, C. Guo, Z. Lou, X. (2012) Confining sulfur in double-shelled hollow carbon spheres for lithium-sulfur batteries. Angew. Chem. Int. Ed.,51: 9592-9595.
[4] Zhou, G. L, Li. Wang, L D. Shan, X. Pei, S. Li, F. Cheng, H. (2015) A Flexible sulfur-graphene-polypropylene separator integrated electrode for advanced Li-S batteries. Adv. Mater., 27: 641-647.
[5] Lee, D H. Ahn, J H. Park, M S. Eftekari, A. Kim, D W. (2018) Metal-organic framework/carbon nanotube-coated polyethylene separator for improving the cycling performance of lithium-sulfur cells. Electrochimica Acta, 283: 1291-1299.
[6] Li, M. et al. (2017) Metal-organic framework-based separators for enhancing Li-S battery stability: mechanism of mitigating polysulfide diffusion. ACS Energy Lett., 2: 2362-2367.
[7] S, Bai.Liu, X. Zhu, K. Wu, S. and Zhou, H. (2016) Metal-organic framework-based separator for lithium-sulfur batteries. Nature Energy, 1: 16094.
[8] Hong, X. Song, C. Yang, Y. Tan, H. Li, G. Cai, Y. Wang, H. (2019) Cerium based metal-organic frameworks as an efficient separator coating catalyzing the conversion of polysulfides for high performance lithium-sulfur batteries. ACS Nano, 13: 1923-1931.
[9] Song, C. et al. (2020) 3D catalytic MOF-based nanocomposite as separator coatings for high performance Li-S battery. Chemical Engineering Journal, 381: 122701.