Research progress of high performance cathode materials for lithium-sulfur batteries

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Abstract. Lithium-sulfur battery is supposed to be a key for the next generation of energy storage devices due to its advantages of high energy density, high theoretical specific capacity, low cost and environmental friendliness, and has attracted extensive attention from researchers. However, the intermediate products of lithium-sulfur batteries are easily dissolved in the electrolyte to produce shuttle effect. In addition, there is volume expansion, low inherent conductivity, slow dynamics and other factors, which limit its commercial application. This paper describes the working principle of lithium-sulfur batteries, reviews the current research status of lithium-sulfur battery cathode materials, analyzes the existing problems of lithium-sulfur batteries, summarizes the improvement methods of cathode materials, and prospects the future development direction of lithium-sulfur batteries.

Key words: lithium-sulfur battery; cathode materials; cycle life; organic polymer; graphene.

1. Introduction

Lithium-ion battery is a widely used energy storage device in electronic equipment. However, with the large-scale development and application of electric equipment, higher requirements are put forward for lithium-ion batteries [1, 2]. Lithium-sulfur batteries with elemental sulfur as the positive electrode and lithium metal as the negative electrode have high theoretical energy density [3, 4]. At the same time, sulfur has many advantages, such as abundant reserves, low price, environmental friendliness, and easy availability, etc., so it is considered to be a potential lithium cathode material [5]. However, some disadvantages of traditional lithium-sulfur batteries, such as slow dynamics, shuttle effect and volume expansion, make it difficult to achieve large-scale production [6-9]. In order to solve the problems listed above, the research in recent years mainly focuses on the following three aspects: (1) incorporation of metal elements with high conductivity; (2) Introducing mesoporous carbon to inhibit the dissolution of polysulfide; (3) Design special morphology structure to restrain volume expansion [10-11].

Based on the above mechanism, the research progress of various cathode materials for lithium-sulfur batteries which are widely used in recent years is reviewed in this paper. The reasons for poor cycle stability, low coulomb efficiency and low sulfur utilization rate of lithium-sulfur batteries were analyzed. Finally, the modification methods of cathode materials were summarized, and the development of lithium-sulfur batteries was prospected.
2. The working mechanism of lithium-sulfur batteries

It is widely considered that lithium-sulfur originated in 1980s. In 1988, Peled et al. [12] dissolved lithium multisulfide in tetrahydrofuran and drip-coated glassy carbon electrode, and carried out cyclic voltammetry test: one oxidation peak and three reduction peaks were detected, which proved that the redox reaction of lithium multisulfide was reversible. Since then, lithium-sulfur batteries have caught the attention of more and more researchers because of their high energy density [13].

In fact, lithium-sulfur batteries have been around since the 1960s. In 1962, Herbet and Ulam first prepared the first lithium-sulfur battery using sulfur as the cathode material and lithium metal as the cathode material [14]. Different from the energy storage mechanism embedded in the "rocking chair" lithium-ion battery [15], in the first discharge process, the elemental sulfur in the lithium sulfur battery gets electrons, forming a chain of polysulfide lithium easily soluble in ether electrolyte, which reaches the negative electrode through the membrane as the electrolyte diffuses.

At room temperature, the discharge process of a typical lithium-sulfur battery can be divided into four stages, as shown in Fig 1. Phase 1: Solid/liquid two-phase transition of sulfur elemental (S8) opening long-chain polysulfide (Li2S8) on a high-potential platform (about 2.3V); The second stage: liquid/liquid single-phase transition process of long-chain polysulfide (Li2S8) to short-chain polysulfide (Li2Sx, 4 ≤ x ≤ 8); The third stage: the liquid/solid two-phase conversion process of dissolved short-chain polysulfide (Li2Sx) to insoluble Li2S2/Li2S at the low potential platform (about 2.0V); The fourth stage: solid/solid single-phase transition from insoluble Li2S2 to Li2S.

![Fig. 1 Schematic diagram of lithium-sulfur battery][2]

In general, as the reaction proceeds, the lithium-sulfur battery undergoes solid-liquid-solid conversion, which is different from the reaction mechanism of traditional lithium-ion batteries. There are many reasons hindering the application of lithium-sulfur batteries, among which the most important problem is that the electrode of lithium-sulfur batteries itself has yet to be improved. In the above reaction process, with the progress of battery charge and discharge, some reactions or products will not be conducive to the commercial application of lithium-sulfur batteries.

First, the intermediate polysulfide occurred in the first and second stages dissolves in the electrolyte. During the cycle, intermediate long-chain polysulfides (Li2S4 to Li2S8) tend to dissolve in the ether-based electrolyte, which results in continuous loss of active materials. At the same time, the polysulfide will have a shuttle effect, resulting in self-discharge during the cycle, resulting in low coulomb efficiency. In addition, the electrical insulation of sulfur and lithium sulfide results in underutilization of the active material, and deposition of insulating lithium sulfide during discharge also leads to passivation of the cathode surface, thus reducing the reaction rate.
Second, the volume of the positive sulfur electrode changes as it is lithified. Due to the density difference between sulfur and lithium sulfide, severe volume expansion occurs when the sulfur is completely lithified to lithium sulfide, which may lead to electrode damage.

3. Anode material
Elemental sulfur is an electronic insulator, so it is difficult to be used as electrode material alone. In addition, the final discharge products of sulfur, Li2S and Li2S2, are also electronic insulators, which will lead to that once generated Li2S and Li2S2 are wrapped on the surface of the electrode, the electrons will be stuck on the surface of the material and cannot be transferred to the inside of the material, resulting in a serious decline in battery performance. Therefore, elemental sulfur can be compounded with metal oxides, carbon materials and organic materials to make cathode materials.

3.1. Metallic composites
The research work of metal composite materials mainly focuses on the composite of sulfur and metal oxides. By compounding elemental sulfur with nanoscale metal oxides, the dissolution of polysulfides in ether electrolytes can be inhibited by the adsorption of polysulfides in nanoscale metal oxides [16].

Choi et al. [17] prepared a cathode material doped with metal oxide Al2O3 nanoparticles in elemental sulfur. After 25 cycles of testing, the specific capacity reached 1.6 times of elemental sulfur. Song et al. [18] compound Mg0.6Ni0.4O nanoparticles in elemental sulfur, and the discharge specific capacity of Mg0.6Ni0.4O nanoparticles can reach 1180mAh/g for the first time.

Seh et al. [19] prepared a core-shell structure of S-TiO2 (Fig. 2). The material has an S core and a TiO2 shell, with internal voids to accommodate the bulk expansion of sulfur atoms as they are lithified. When the current density is 0.5C, the first specific discharge capacity can reach 1030mAh/g. After 1000 cycles, the coulomb efficiency can be maintained at 98.4%, and the capacity loss rate of each cycle is as low as 0.033%. Undoubtedly, this high performance is due to the core-shell structure that can accommodate volume expansion.

![Fig. 2 Schematic diagram of the synthesis steps of S-TiO2 composites [19]](image)

3.2. Inorganic composites
At present, the hot spot of inorganic composites focuses on the composite of sulfur and nanoscale carbon materials. This is mainly because the design of spatial structure using carbon skeleton can make carbon adsorb polysulfides and thus effectively inhibit the dissolution of polysulfides. Second, carbon can enhance the electrical conductivity of the electrode [20].

3.2.1. Sulfur/carbon nanotube materials. Zhang et al. [21] prepared the composite material of sulfur and carbon nanotubes and used highly active CNTs to adsorb sulfur evenly. The physical material is shown in Fig. 3. This method relies on steam to carry sulfur. The main advantage of this method is that the sulfur and CNTs are in close contact and evenly distributed, so that CNTs can fully absorb polysulfides and thus inhibit the dissolution of polysulfides in the electrolyte. The specific capacity of the battery assembled by this method can reach 1300mAh • g⁻¹ at 0.16A • g⁻¹ current density. After a long cycle, the capacity decay rate of the battery per turn is 0.22%.
Chen et al. [22] composite sulfur with carbon nanotubes co-modified by cobalt metal nanoparticles and nitrogen atoms. The volatilization of cobalt metal is beneficial to the formation of microporous structure, which can adsorb polysulfide and inhibit the dissolution of polysulfide. In the half battery assembled with this material, the specific discharge capacity of the sulfur positive electrode containing 80% sulfur reaches 1240 mAh g⁻¹ for the first time and still maintains 60% of the specific discharge capacity after 1500 cycles.

3.2.2. Sulfur/mesoporous carbon materials. Ma et al. [23] prepared mesoporous carbon nanotubes by carbonizing glucose onto the wall of carbon nanotubes. The mesopores provide a space for storing polysulfides during the cycle, thus inhibiting the dissolution of polysulfides. At the same time, carbon nanotubes have excellent electrical conductivity, which can effectively shorten the ion and electron transport path in the process of charge and discharge, thus improving the ionic conductivity of the material.

Zhang et al. [24] prepared a kind of mesoporous carbon sphere with hollow structure. This material not only effectively increases the sulfur loading capacity, but also can adsorb polysulfides into the hollow structure of the sphere and the mesoporous pores of the shell, thus inhibiting the dissolution of polysulfides. The specific discharge capacity of the half battery assembled with this material can reach 1608.6 mAh g⁻¹ for the first time, and remains at 863.4 mAh g⁻¹ after 100 weeks of cycle.

3.2.3. Sulfur/graphene materials. Wu et al. [25] doped RGO with sulfur. This structure not only enables the sulfur to be evenly distributed among the graphene sheets, but also can be effectively encapsulated by the graphene sheets. The battery assembled with this material has a capacity of 1197.3 mAh g⁻¹ at a current density of 0.2 C, and remains at 730 mAh g⁻¹ after 1,200 cycles.

Gao et al. [26] doped the graphene aerogel with sulfur. The preparation flow chart is shown in Fig. 4. When the sulfur content of the battery is 70%, the first specific discharge capacity reaches 1290 mAh/g at the current density of 0.1 A/g. At a current density of 1.0 A/g, the retention rate is 71.4% after 100 cycles.

Fig. 3 CNTs synthesis device [21]

Fig. 4 Schematic diagram of preparation of GM-S complex [26]
3.3. Conducting polymer

Conducting polymers have the advantages of excellent electrical conductivity and good toughness. The ionic conductivity can be improved when used in lithium-sulfur batteries. At the same time, the good toughness of the polymer can effectively alleviate the volume expansion of sulfur in the process of lithium. Therefore, the composite of sulfur and conductive polymer has also received extensive attention.

Zhou et al. [27] coated the surface of sulfur nanoparticles with polypyrrole to generate nanospheres with sulfur as the core and polypyrrole as the shell, and then coated the nanospheres with graphene to produce sandwich structure composite electrode materials. The polypyrrole structure can alleviate the volume change during the charge and discharge process of positive electrode, and the graphene can effectively improve the ionic conductivity. At 0.1C, the specific discharge capacity can reach 1014mAh g⁻¹ for the first time; The discharge capacity can reach 537.8mAh g⁻¹ after 200 cycles at 0.2C.

In addition to the sandwich structure, a conductive spherical network structure can also be used to optimize the sulfur anode. Wang et al. [28] prepared a spherical conductive network structure of polyaniline. Then sulfur molecules are deposited through the liquid phase to make the sulfur enter the hole and form a conductive polymer with carbon and sulfur as the core. At 0.1C discharge, the first discharge capacity reaches 1453mAh g⁻¹, 1,200 cycles, and the stable capacity of 948mAh g⁻¹ can still be maintained. This high performance benefits from, first of all, the significantly improved electrical conductivity of the cathode material through the dual role of the conductive network and the carbon black oxide. Secondly, the conductive network can alleviate the volume change of the electrode during charging and discharging.

4. Improvement scheme of cathode material

In order to improve the electron and ionic conductivity of the positive electrode, a conductive material and sulfur are usually polymerized to form a compound. At present, the common cathode materials mainly include sulfur/metal compound, sulfur/carbon composite material, sulfur/conductive polymer.

In the aspect of metal compounds, metal oxides as cathode materials are the research hotspots. Metal oxides (such as Al₂O₃ and TiO₂) not only have good electrical conductivity. More importantly, the nanoscale metal oxides can adsorb polysulfides and inhibit the dissolution of polysulfides in the electrolyte, thus improving the cycle stability of the battery.

Among them, the main forms of carbon in sulfur/carbon composites include carbon nanotubes, mesoporous carbon and graphene. For these sulfur/carbon composites, the specific surface area of the cathode material can be effectively improved by changing the structure, and the adsorption capacity of polysulfides can be improved, thus reducing the loss of active substances. At the same time, carbon element has excellent electrical conductivity, by doping carbon element can improve the ionic conductivity. The studied cathode structures mainly include layered porous structure and porous sphere structure design.

Conductive polymers have also attracted extensive attention due to their excellent conductive properties and flexibility. Good electrical conductivity improves the ionic conductivity. At the same time, the flexibility of the polymer after the volume expansion of sulfur still does not occur a large morphological change, to ensure the stability of the electrode material.

To sum up, the modification and optimization of cathode materials can be carried out from three aspects: (1) Adding metal compounds with high conductivity to accelerate electron transport and ion diffusion rate. (2) The mesoporous carbon morphology was designed by physicochemical strategy, and the "shuttle effect" of polysulfides was limited by the physical confining of "carbon pore sulfur storage" and the chemisorption of polarity sites.(3) Design special morphology structure to alleviate the expansion of the active site in the process of lithium.

5. Conclusion

With the rapid development of electronic devices, the construction of electrochemical storage devices with high energy density, long service life, high safety and low cost has become a research hotspot.
Among them, lithium-sulfur batteries are expected to become the next generation of widely used batteries. Lithium-sulfur batteries have made significant progress over the past decade, with significant improvements in specific capacity and cycle stability, but challenges remain. The problems of the dissolution of polysulfide in electrolyte, the volume expansion of lithium anode and the dendrite of lithium anode all need to be solved.

The design of sulfur cathode materials is still the key direction of future research, which not only ensures the filling rate of sulfur, but also ensures the high energy density and good cycling stability. The modification and optimization of cathode materials can follow three principles: (1) incorporation of metal elements with high conductivity; (2) Introducing mesoporous carbon; (3) Design special morphology structure. The design of suitable cathode materials is one of the key problems to be solved before the industrialization and commercial application of lithium-sulfur batteries.

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