Progress study on the development of lithium-sulfur batteries

Weixuan Han¹a*, Zheya Li¹b*, Rizhou Wang¹c*
¹Department of Electric Engineering, Northeast Electric Power University, Jilin, China
a*jp2018303550@qmul.ac.uk, b*1824503024@stu.suda.edu.cn
² 2018301040526@neepu.edu.cn
† These authors contributed equally

Abstract—With the rapid development of the new energy industry in recent years, the demand for lithium batteries is very urgent, and at the same time, the requirements for the performance of lithium batteries are getting higher and higher. Lithium-sulfur batteries, as a very competitive lithium battery, can reach as much as five times the energy density of traditional lithium batteries. However, due to various limitations in the reaction process, Li-S batteries also need to undergo various performance improvements to improve the efficiency of Li-S batteries and industrial applications. This paper introduces the advantages and disadvantages of lithium-sulfur batteries as well as future challenges. It also introduces the recent developments in lithium-sulfur batteries from three different aspects, i.e., material modification, structure-based modifications, and discussion from the perspective of electrolyte additives.

1. Introduction
The research of Li-S batteries began in the 1970s. At that time, the American chemist M.S. Whittingham used titanium disulfide (TiS₂) as the positive material of the battery, Li sheet as the negative material, and potassium perchlorate/dioxane as the electrolyte to form the initial metal cell, which is the initial configuration of lithium battery and also marks the birth of Li secondary battery. The battery can stably cycle 1000 times, but there will be dendritic crystals on the surface of Li during use. The dendrites may prick the membrane diaphragm, cause a short circuit between the positive and cathodes, and finally make the battery explode.

The fire accident of Li and Al-S battery system in 1989 led to the loss of public trust in the battery system. Due to the dendritic problem and the selection of diaphragm materials subject to technical restrictions, the research on the battery was stagnant in the 1980s, and the application of Li-battery was only limited to the military.

Given various problems of Li, researchers used graphite as an embedded reaction material instead. This battery is called "rocking chair battery". Sony Corporation of Japan successfully commercialized the "rocking chair battery" in 1990 and named it "Li-ion battery". This battery has many advantages, such as good safety, good high/low-temperature performance, stable working state, abundant stock of raw materials and low cost.

The research of Li-S batteries is synchronized with the research of Li batteries. Later, the development of Li-S batteries is slow due to the high research upsurge of Li-ion batteries. For historical reasons, on the one hand, the lack of advanced characterization technology cannot deeply understand the micro-level of the battery's internal structure. The cultivation soil of lithium-ion is relatively fertile, and a large number of scientific research funds have been invested in the Li-ion market, which hinders...
the rapid development of Li-S batteries.

This paper introduces Li-S batteries' working principle and mechanism and briefly explains the advantages and challenges of Li-S batteries. Since there are still many problems to be solved for Li-S batteries, and it may be at the bottleneck stage of research, combined with the current research results of Li-S batteries, we summarized or discussed the feasible schemes from three aspects: battery material, structure and electrolyte, in order to provide convenience for subsequent researchers and save time and cost in direction selection.

2. Advantages and Challenges of Li-S Battery

2.1 Working principle and mechanism

Li-S battery comprises the S-composite anode, metal lithium cathode and intermediate electrolyte. Unlike a Li-ion battery, a Li-S battery is very close to the principle of a traditional battery. Because S is a poor conductor of electrons, the anode material is generally composed of S, conductive agent and polymer binder; the cathode adopts Li; The electrolyte between the poles is an organic (ether) electrolyte based on organic solvents and lithium salts.

Unlike Li-ion batteries, whose charge-discharge process relies on the ion de-intercalation mechanism, the charge-discharge of Li-S batteries is an electrochemical process. The Li of the cathode loses electrons and becomes ions. The S of the anode reacts with Li-ions and free electrons to form sulfide. The potential difference which stimulates the simultaneous electron transfer during this is the discharge voltage of the Li-S battery. The applied potential triggers the reverse reaction during the charging process, and the sulfide transforms into S and Li. From a macro point of view, the oxidation reaction occurs during the discharge process, in which Li loses electrons. Subsequently, the oxidative product gets reduced back to Li during the charging process.

According to the electric energy provided by the complete conversion of unit mass sulfur into sulfur ions (S^2^-), sulfur's theoretical discharge specific capacity is 1675 mAh·g^{-1}. Similarly, the theoretical discharge specific capacity of Li is 3860 mAh·g^{-1}. The theoretical discharge voltage of a Li-S battery is about 2.287 V. If Li and S react completely, the theoretical energy density of the Li-S battery is 2600 Wh·kg^{-1}.

However, the charging and discharging reactions of the S electrode are more complex under working conditions. Firstly, the cyclic S8 molecule becomes small molecule S to form Li sulfide or Li persulfide, while the small molecule S refers to the chain negative divalent ion S_n^{2-}(3 \leq n \leq 7), combined with Li^+ to form Li_2Sn. Then the chain structure of S_n^{2-} becomes S^2-, which combines with Li^+ to form Li_2S and Li_2S_2.

Fig. 1 Structure diagram of Li-S battery
Fig. 2 Charge discharge curve of Li-S battery

From the discharge curve, there are two discharge platforms for Li-S battery, a high-voltage platform of about 2.4 V and a low-voltage platform of about 2.1 V, which correspond to the two processes of "S8 molecule becomes small molecule S" and "small molecule S finally forms sulfide", respectively. Among them, the second discharge platform is the main discharge area of the Li-S battery.

2.2 Advantages
Compared with traditional Li-ion batteries, Li-S batteries have many advantages, especially the advantages of S cathode:

2.2.1 High energy density
S can provide a theoretical specific capacity of 1675 mAh·g⁻¹, more than 5 times the current commercial Li-ion battery cathode material (LiCoO₂), and more than 10 times the actual specific capacity. Its energy density of 2600 Wh/kg is also much higher than that of 500 Wh·kg⁻¹ of traditional Li-ion batteries. Therefore, Li-S battery has great application potential in high-energy electric equipment.

2.2.2 Low price
S is abundant in nature. The abundance of S in the earth's crust is 0.05 %. The raw material price of the positive active material of the Li-S battery is about 1/60 of the lithium cobalt oxide battery, and the preparation cost of Li is also low, which makes the cost performance of the Li-S battery outstanding. The cost-effectiveness makes Li-S battery a promising candidate for large-scale production and utilization.

2.2.3 Environmentally friendly
The cathode materials of traditional lithium-ion batteries, whether large-scale commercial LiCoO₂, other LiNO₂, LiMn₂O₄ and ternary material Li(NiₓCoₙMn₁₋ₓ)O₂, contain heavy metal elements, increase the recovery cost and easily cause environmental pollution; The S composite cathode material of Li-S battery can be degraded in nature.

2.3 Challenges

2.3.1 Relatively low volumetric energy density
Despite the conductive agent added in the anode promotes the conductivity of S composite, it reduces the battery's energy density. Further effort is needed in exploring new multi-component material or synthetic material with good conductivity and light volume and mass to replace the S to idealize the weight of the battery further or increase the capacity without changing weight. The above-mentioned goals significantly impact future application in equipment with strict weight requirements or lightweight equipment.
2.3.2 The discharge curve is not ideal
Li is used as the cathode of the battery, which has high activity and is suitable for oxidation. However, the oxidation-reduction reaction of the Li tends to be fierce, and the reaction process involves the generation of heat, which may cause safety issues during the discharge process. In addition, the boiling point of ether electrolyte is low, which is not conducive to high temperature working conditions. Future work needs to investigate the surface-active inhibiting materials to control the reaction rate and stability. In addition, adding impurities to Li may also improve the discharge characteristics of the Li-S battery. The voltage attenuation lag and temperature stability are controllable to expand the theoretical and practical scope. For example, the constant output voltage is demanded in the four-rotor aircraft to ensure the correct implementation of the flight control module.

2.3.3 The natural life of the battery is still short
As mentioned above, the electrolyte of Li-S battery adopts ether electrolyte based on organic solvent and lithium salt, which is different from the ester electrolyte used for Li-ion battery. The positive intermediate products of the Li-S battery dissolve in it, cannot migrate well between the two poles, and the reduction reaction is insufficient, resulting in the decline of battery cycle performance (service life). This problem is also a major problem hindering the development of Li-S batteries.

In general, the current problems of Li-S batteries are concentrated in the above three aspects: achieving high energy density, improving working voltage, increasing the proportion of elemental sulfur in the anode, and improving discharge safety and cycle stability.

3. Material-Based Modification Methods
Overcome the shuttle effect, and provide more localization points to enhance cycling stability, this can be achieved by research and modification of polar materials.

Currently, the polar materials used in lithium-sulfur batteries can be classified as heteroatomic reference carbon, metal oxides, sulfides, nitrides, and carbides.

3.1 Carbon material modified lithium-sulfur batteries
Graphene, as an ideal S-clad material for Li-S batteries, has the advantage of being only a single atomic layer thick, the thinnest material available, with a thickness of only 0.335 nm, and high electron mobility (15000 cm$^2$/V·s), low resistivity (~106 Q·cm), high strength, and good thermal conductivity at room temperature.

In 2010, Wang et al. made the first sulfur/graphene composite by heating and mixing graphene and sulfur, and the first discharge capacity reached 1611 mAh/g at a current density of 50 mA/g. However, the composite did not have confinement and could not effectively trap polysulfides, and the cycle stability and Coulomb efficiency were not high.[2] In 2011, Cui’s group prepared a sulfur/graphene
anode composite with 56% sulfur loading by coating submicron sulfur particles with polyethylene-diol (PEG) and then coating sulfur with acetylene black-modified graphene. The PEG and graphene layers can effectively solve the problems of excessive volume changes in the charge and discharge of lithium-sulfur battery cathode and polysulfide dissolution in the electrolyte [3].

In this research, N-NGN (5 h) yielded maximum area capacities of 12.0 and 11.0 mAh‧cm⁻² at 15 and 12 mg‧cm⁻² sulfur loadings, respectively. This area capacity limit is significantly higher than the area capacity of Li-S batteries required for commercial applications, suggesting a clear advantage of N-NGN as an excellent separation coating for Li-S batteries.[4]

![Fig.4 N-NGN coated Celgard PP separator and their mechanism to chemically bind the PS through multifunctional effects.[4]](image)

For the modification of graphene, there are many more possibilities. In the same year, MuyaChabu et al. obtained a double cone sulfur/graphene oxide composite anode with 92% sulfur content by a room temperature bottom-up method with the help of polyvinylpyrrolidone. Material characterization shows that each sulfur particle is uniformly encapsulated by a thin graphene oxide layer and residual polyvinylpyrrolidone molecules. The robustness and compactness of the protective graphene oxide shell facilitated electron and ion transport and inhibited the diffusion of polysulfides through interfacial chemistry.[5]

![Fig.5 Fabrication process of the S@GO composites.[5]](image)

### 3.2 Metal oxides in lithium-sulfur batteries

In recent years, efforts have been made to improve positive materials with a mixture of metal oxides or sulfur coatings. Initially, by simply mixing metal oxide with sulfur particles, the results were not ideal.

Such as an egg yolk-shell designed as a TiO₂ shell wrapped in s-particles forms a thio. The void between the core material and yolk-shell provides enhanced tolerance for volumetric expansion during the charging process. Hydroxylide Ti-O and hydroxyl with a hydrogenic shell surface can effectively suppress polysulfide soluble in electrolytes. This composite material has a first capacity of 1030 mAh/g at 0.5 °C, an electro charging efficiency of 98.4% after 1000 repeated charges, and remains 600 mAh/g in volume, which is reduced by only 3.3% per 100 charging cycles. Composite materials exhibit excellent cyclic stability due to the use of TiO₂. The wrapped core-shell can contain both changes in S volume and effective polysulfide dissolution suppression. This completed core structure also offers broad researchers a new way to improve thinking.[6]
4. Structure-Based Modifications

The high theoretical capacity and energy density of Li-S batteries have brought a new research hotspot in rechargeable batteries. Nevertheless, technical problems remain in this field, such as the poor conductivity of sulfur, the volume expansion of cathodes, and the shuttling of polysulfides [7].

To solve the problems, a proven solution is inserting an intermediate layer between the electrode and the separator. The interlayer materials, including CNT, graphene, MXene, and metal compound, can capture polysulfide by physical and/or chemisorption and further promote their conversion. Among them, CNT and GO composite interlayers have been confirmed in effectively suppressing the diffusion of polysulfides with the GO layer thickness of ~700 nm or content of 33 wt%.

Thus, a relatively large amount of auxiliary GO components was necessitated to help with the sulfur inhibition. However, in this work, researchers report a double-layer structured GO coated CNT film interlayer. It is demonstrated that adding a small amount of GO can significantly improve the cycling stability of Li-S batteries. The nanometer thickness GO coating facilitates the interception of polysulfides and promotes their conversion process. As a result, the battery's capacity remains at ~600 mAhg⁻¹ after 300 cycles at 0.5 °C, which is superior to those without interlayer or with only CNT film interlayer. [8]

Fig. 7. (a) CV curves, (b) the 1st cycle charge-discharge curves, (c) cycling performance of Li-S batteries with no interlayer (PP), CNT film interlayer (CNT), and GO/CNT interlayer with the GO densities of 15, 25, or 35 μg·cm⁻². (d) Charge-discharge curves at different cycles and, (e) rate performance.
5. Discussion from the Perspective of Electrolyte Additives

For the conventional liquid Li-S battery, the discharge process goes through cyclic S8 molecule and small molecule S to form lithium polysulfide. When the reaction is halfway through, soluble Li polysulfide is formed. Polysulfide ions inevitably pass through the porous polymer membrane, flow to the cathode, react directly with metal lithium, and leave the intermediate products in the cathode. The stability between the metal lithium itself of the cathode and the conventional ether electrolyte is also poor. The negative product has non-uniformity and tendency in the deposition process, forming dendritic crystals. If the dendrites pass through the diaphragm to the anode, they form an internal short circuit. The reaction is also easy to form "dead lithium" of the cathode (during charging, the reaction product cannot be completely reduced and covered on the surface of Li to prevent the next reaction, reduce the kinetic rate of the reaction and reduce the cycle performance). In addition, the density of S is greater than that of products Li2S and Li2S2. According to the principle of mass conservation, the reaction product is fluffier than that of reactants. In addition, the reaction product itself is easy to decompose, and the volume will inevitably expand, especially in soft pack batteries [10].

The ideal electrolyte in solid-state Li-S batteries ought to possess good chemical and electrochemical stability, good thermal stability, good compatibility with anodes and cathodes, and a wide electrochemical window. The sulfide electrolyte and polymer matrix electrolyte are the most widely used solid-state electrolytes in solid-state Li-S batteries systems. The organic-inorganic composite electrolyte has the advantages of high chemical and electrochemical stability and good mechanical properties. It is an ideal electrolyte material for the solid Li-S battery. However, its room-temperature ionic conductivity has not achieved a big breakthrough, and the active filler is expensive. Meanwhile, the complex preparation process of the agglomeration problem also hinders it from large-scale battery application [11-12].

In the Li-S batteries system, the positive material with high sulfur surface load changes greatly in volume during charging and discharging. Polymer solid electrolyte can alleviate the volume change of active material, effectively preventing electrode pulverization and inhibiting the formation of lithium dendrite. In addition, has excellent mechanical properties and is easy to form a film. This kind of polymer electrolyte generally takes polymer as the matrix. The lithium salt is dissolved in the matrix to realize the ion conductivity of the electrolyte. At present, polyethylene oxide (PEO) polymer matrix is the most widely studied solid-state Li-S battery. The recognized ion transport mechanism of PEO is that Li+ and -C-O-C- on the PEO chain constantly undergo complexation de complexation reaction, and the migration of Li+ is completed through the chain segment movement of PEO (Fig. 8)[13-15].

Fig.8 Diagram of Li+ conduction mechanism of PEO based electrolyte

Marmorstein et al. compared the electrochemical performance of PEO and PEO-based polymer electrolytes applied to the solid-state Li-S battery. The ionic conductivity of PEO based polymer electrolyte was 4.9×10^{-4} S cm^{-1} at 90 ℃, the initial discharge specific capacity of the assembled solid-state Li-S batteries is 1620 mAh g^{-1} when the current density is 0.1 mA cm^{-2}, which is very close to the theoretical specific capacity of S (1675 mAh g^{-1}). In addition to the polymer matrix, the appropriate lithium salt is also of great significance for constructing stable ion transport channels and the cycling of batteries. The electrolyte is cost-effective, and it has good interface compatibility with the anodes and cathodes, making it feasible for large-scale commercialization [16].
Different from liquid batteries, interface contact is one of the biggest challenges faced by solid-state batteries. The contact area of the solid-solid interface in solid-state Li-S batteries is limited, and the solid electrolyte is immovable, which is not conducive to the transmission of charge at the interface, resulting in large interface resistance. Secondly, there are serious side reactions and insufficient stability at the interface between electrode and electrolyte. Therefore, constructing an effective and stable interface (interface modification) is very important to improve the electrochemical performance of solid-state Li-S batteries [17].

Interface stability is one of the key problems in the development of solid-state Li-S batteries. The volume of the active material in the anode changes continuously during charging and discharging. The resulting stress will lead to material pulverization, destroy the electrolyte ion diffusion channel, increase the interface impedance, and reduce the battery life. Charge transfer in a solid-state battery completely depends on the solid-solid interface between solid electrolytes and active material. Therefore, increasing the interface contact area and improving the interface stability is the key to solving the problem. Therefore, many studies have constructed micro nanostructures between cathode and interface from the perspective of nanotechnology to improve the utilization of active materials. Nagao et al. reduced the size of Li2S particles by high-energy ball milling and then combined with other components to obtain the anode. The results show that the active material after ball milling is evenly distributed in the cathode material, providing more active sites, and effectively improving the coulomb efficiency and cycle stability of the battery. The enhanced performance is because the high specific surface area of nanostructures effectively improves the contact between cathode and electrolyte, and the utilization of active substances can be effectively improved by constructing nanochannels [18].

6. Conclusion

Accelerating the reversible reaction of sulfur becomes the key to achieving the revolutionary breakthrough of lithium-sulfur batteries. We focused on the following solutions.

A solid electrolyte consists of a polymer in which lithium salts are dissolved. The advantages of solid electrolytes are as follows: it overcomes dendrite problem, volume expansion problem, by-product problem and dead lithium problem caused by the reaction of lithium and ether electrolyte and has stronger mechanical properties. Its disadvantage is that the reaction rate at the interface is reduced, but this problem can be solved by interface modification.

In the future development, the prospect of solid electrolytes shows great potential, and the preparation of functional diaphragms is also very good. However, from the current development, the future of doping direction of composite materials may be difficult to predict.

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