

Nanotechnology in Lithium-Sulfur Batteries: Addressing the Challenges in Battery Cycle Life and Safety

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Abstract. Lithium-sulfur (Li-S) batteries, with their high energy density and affordable material prices, are a viable alternative to ordinary lithium-ion batteries, especially for electric cars. Their actual application is limited by challenges such as substantial volume expansion, low electrical conductivity, and the polysulfide shuttle effect, despite their advantages. This research investigates how incorporating nanomaterials into Li-S battery cathodes, anodes, and electrolytes might improve battery performance and analyzes the potential of nanotechnology to address these problems. The application of metal oxides, graphene oxide, and carbon nanofibers to improve the stability and conductivity of sulfur cathodes is covered. Additionally, it examines anode protection strategies using nanocoating and protective layers to inhibit dendrite growth and improve safety. The incorporation of nanoparticles in electrolytes to improve ionic conductivity and reduce side reactions is also analyzed. Despite the progress, challenges such as the polysulfide shuttle effect and volume changes remain. The paper concludes with recommendations for future research to develop commercially viable Li-S batteries with higher capacity, longer lifespan, and improved safety.

Keywords: Li-S battery; nanomaterials; battery cycle life and safety.

1. Introduction

Conventional lithium-ion batteries are finding it difficult to keep up with the high energy requirements of electric vehicles due to the quick development of new energy vehicles. Because of its greater energy density and cheaper material prices, lithium-sulfur (Li-S) batteries show great promise as a replacement for conventional lithium-ion batteries [1]. With a theoretical specific energy of up to $2,567 \text{ Wh kg}^{-3}$, Li-S batteries are roughly seven times more powerful than traditional lithium-ion batteries [2]. Sulfur is also cheap, plentiful, and eco-friendly, which makes Li-S batteries very appealing. Li-S batteries do, however, suffer a few difficulties. Sulfur and Li_2S have low electronic conductivity, which lowers their electrochemical performance. Furthermore, sulfur has a large volume expansion (about 80%) during charge and discharge cycles, which causes a quick decline in capacity. The polysulfide shuttle effect further reduces Coulombic efficiency during cycling. Nanotechnology offers promising solutions to these issues. For instance, coating electrode surfaces with nanoparticles increases the surface area, allowing more charged particles to pass through and generate additional current, which not only reduces battery weight but also enhances the efficiency of hybrid vehicles. Nanomaterials can also be used to separate the liquid electrolyte from solid electrodes, significantly improving the battery's shelf life [3]. Through a thorough review of the literature, the goal of this report is to explain how nanotechnology can enhance the safety and performance of lithium-sulfur batteries. For example, we can apply nanotechnology to the cathode, anode, and electrolyte to increase the batteries' cycle life and produce higher-performing lithium-sulfur batteries.

2. Fundamental Challenges in Lithium-Sulfur Batteries

The three primary parts of a battery are the electrolyte, cathode, and anode. Chemical energy is converted into electrical energy throughout the charging and discharging cycles. Lead, nickel, or lithium are common metals used to make anodes. The anode becomes the negative terminal during discharge because it oxidizes and loses electrons. Conversely, the cathode, which acts as the positive

terminal, consists of active materials that are reduced during discharge. These processes are reversed during charging. The battery can maintain a comparatively constant electrical potential for lengthy periods of time because the electrolyte acts as a conduit to help charged particles move between the cathode and anode.

The typical components of Li-S batteries are an organic electrolyte, a sulfur-based composite cathode, a lithium anode, and a diaphragm that separates the two electrodes (Figure 1). During discharge, the lithium anode oxidizes, losing electrons and releasing lithium ions. Lithium ions go through the electrolyte to reach the positive electrode while electrons travel from the external circuit to the positive electrode. Concurrently, the sulfur-based cathode accepts the electrons, initiating a chemical reaction that releases energy. Sulfur atoms often form lengthy chains or homocycles of different diameters during this discharge process. A chemical equation that is inverted during charging can be used to describe the whole discharge process.

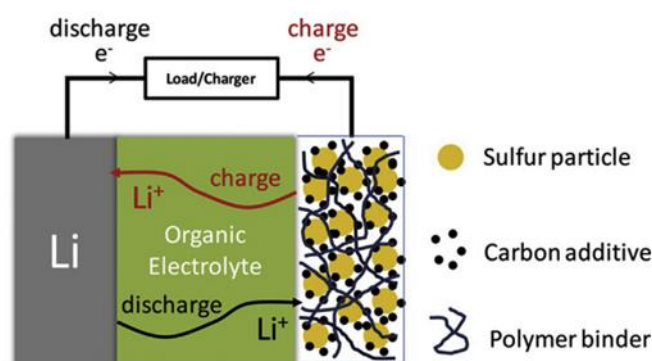
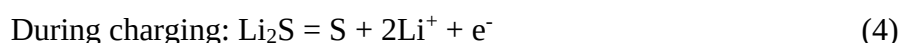
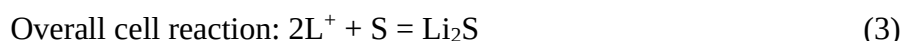
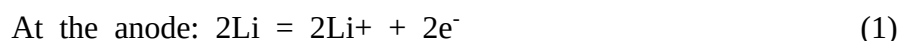
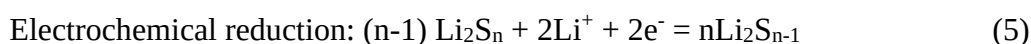


Fig 1. Scheme for LiS battery [3].

Although lithium-sulfur batteries have great development potential, LiS still faces many problems. The first problem to be faced is that sulfur has poor electrical conductivity, about $10\text{-}30\text{ S/cm}^{-1}$, which makes it difficult for electrons to flow in the battery. Furthermore, during the discharge process, many intermediate substances (Li_2S_x) are generated. These are polysulfide ions that are easily able to travel back and forth between the two electrodes. This phenomenon is called the redox shuttle effect between the Li negative and LiS positive electrodes. The steps involved can be expressed as follows:



During discharge, the sulfur is completely dissolved in the electrolyte, leaving a large hole in the cathode where the dissolved polysulphides can re-deposit as Li_2S_2 and Li_2S . The lithium anode corrodes because of these processes, which also causes ongoing active material loss. Once the shuttling effect is enhanced, it leads to a rapid increase in the internal resistance of the battery, which in turn leads to a rapid degradation of the battery capacity. In addition, it leads to reduced charging capacity and inefficient charging. In addition, S undergoes a volume expansion of about 80% upon complete lithiation to Li_2S , leading to structural damage to the battery. When cycling repeatedly, this can cause lithium dendrites to develop. This causes the battery to lead to short circuits and equipment fires [3].

With the development of nanotechnology, it has been found that there are many benefits of using nanotechnology in battery manufacturing. For example, the use of nanocoating to cover the surface of the electrodes to increase the surface area of the electrodes allows more charged particles to pass

through, which generates additional current. This can significantly reduce the weight of the battery, which is crucial for the development of electric vehicles. Examples include the use of graphene and carbon nanotube (CNT), nanomaterials with a high surface area [4]. Because of its vast surface area, carbon can hold a considerable quantity of sulfur, which makes it easier for electrons to flow between molecules. Furthermore, the carbon's hollow shape permits sulfur to expand during charging and discharging and restricts the migration of polysulfides, enhancing the battery's efficiency and cycle life [5]. Electrolytes and electrodes can also be kept apart using nanomaterials. This significantly extends the battery's shelf life and keeps the battery from self-discharging. These results suggest that nanotechnology is essential to enhancing Li-S battery performance.

3. Nanostructured Cathodes

An S-positive electrode, a diaphragm, a Li-negative electrode, and an electrolyte make up a conventional lithium-sulfur battery. During discharge, an electrochemical redox reaction occurs in the sulfur-positive electrode. Once solid S₈ is reduced, it first forms smaller Li₂S_x substances (x = 3, 4) and then extremely soluble long-chain PS (Li₂S₈, Li₂S₆), before becoming insoluble lithium sulfides (Li₂S₂ and Li₂S) [6]. Low coulombic efficiency and rapid capacity decline are thought to be caused by the disintegration and migration of PS. However, insulating solid sulfur and lithium sulfides build up and create a thick layer of passivation on the surfaces of both electrodes, which stops further reactions and obstructs the flow of electrons and ions. This means that to ensure smooth electron access to sulfur and Li₂S and to assist electrochemical kinetics, highly conductive materials must be incorporated [7].

The pore shape plays a critical role in controlling PS diffusion and allowing Li⁺ to pass through throughout cycle. Pore volume is inversely related to the relationship between pore size and the material's total surface area. Given the size of PS, 2 nm micropores can efficiently regulate PS diffusion. It's also important to remember that materials with lower surface areas and pore sizes have less room to hold sulfur, which leads to less sulfur loading. Pore size is hence another factor in material design that needs to be carefully considered. One of the main things that has been influencing the growth of LSBs is high sulfur loading. In LSB research, sulfur concentration (wt%) and area loading (mg/cm²) are crucial factors to consider. In addition to enhancing Li⁺ conduction while cycling, a high surface area cell also performs better electrically. Greater surface area and greater area loading materials are what we require [7].

To address the issues of poor electrical conductivity, volume expansion in Lithium-ion batteries, and polysulfide shuttle effect, attempts have been made to add nanomaterials to the sulfur electrode to improve the electrical conductivity of the active material and to suppress the polysulfide shuttle effect during cycling. Many carbon compounds, such as graphene oxide (GO) and carbon nanofibres (CNF), have been discovered to be highly successful in adjusting to volume changes and suppressing the shuttle effect. Because of their porous structure and huge surface area, these materials also have excellent electrical conductivity. For instance, because of its strong structural integrity and excellent conductivity, CNF is frequently used as an electrode material. CNF can minimize polysulfide shuttling by forming a structure resembling a network. Particles of sulfur easily enter the CNF pores. During charge-discharge cycling, the sulfur electrode and the electrolyte can compress enough thanks to the porous CNF, which also allows for volume expansion. Furthermore, the composite could transfer lithium ions and electrons quickly, reducing transmission distance and enhancing battery performance [8]. Graphene is a carbon allotrope characterized by a large surface area and its flexibility. By applying it to the electrode, it can lessen the amount of polysulfides that dissolve in the electrolyte [9]. S-prGO, or partially reduced graphene oxide, is an effective addition that helps lessen the shuttle effect and enhances the sulfur cathode's performance. The lamellar structure of the S-prGO layer effectively covers the sulfur particles and allows for the active substance's volume expansion during cycling.

Because of their large surface area, customizable pore structure, and high electrical conductivity, a variety of carbon compounds and conductive polymers have been investigated. Because PS has poor physical limits that restrict its useful life to fewer than 200 cycles, scientists have redirected their research efforts toward different metal-based materials that exhibit stronger chemical interactions with PS, potentially providing 1000 cycles or more of cycle stability. Because the oxygen anion (O_2) provides a high number of active polar sites for PS adsorption, metal oxides frequently have strongly polar surfaces [10]. As a sulfur host, the conductive Magnéli phase Ti_nO_{2n-1} ($3 < n < 10$) has been proposed to increase the capacity of LSBs and extend their cycle life [11].

4. Anode Protection Strategies

Due to the deposition of dendrites, extremely poor Coulombic efficiency, and safety factors, lithium metal anodes are still difficult to apply in practical production. Various methods have been investigated, such as enhancing the performance of lithium electrodes and electrolytes through the use of electrolyte additives and applying nano-coatings and protective layers to anodes. All these techniques are aimed at controlling the lithium surface reaction to inhibit dendrite growth [12].

It has recently been discovered that an insertion layer based on Li-Nb-O sits between the electrode and electrolyte, providing protection against undesired reactions and facilitating rapid lithium transport at the interface. Recently, niobium-based oxides have been deemed appropriate anode materials for ultra-fast charging high-power Li^+ batteries due to their ability to facilitate rapid and safe energy storage in lithium-ion batteries [13]. Furthermore, improved cycle stability and increased capacity may be attained by shrinking Li-Nb-O entities to nanoscale sizes. The performance of the lithium metal anode was found to be enhanced by the $LiNbO_3$ coating. This is due to the fact that the nano-coating keeps the lithium metal away from the liquid electrolyte, which stops the metal from reacting in an unintended way and stops lithium dendrite formation. Compared to uncoated lithium metal, the surface of lithium metal covered by $LiNbO_3$ is more stable [14].

It has been found that doping nanoparticles such as carbon or graphene into the anode can improve its mechanical strength and conductivity, reduce the lithium consumption rate and enhance the uniformity of lithium ion flux across the anode surface. In recent years, research on composite lithium metal anodes has made great progress, greatly optimising the performance of lithium batteries. Because of their various benefits, materials based on carbon are being employed in composite lithium metal anodes more and more. Carbon-based materials, such as graphene, carbon fibers, carbon nanotubes, reduced graphene oxide, and others, can be used as lithium metal anode scaffolds because they have a larger specific surface area and electrical conductivity, which helps to reduce the effective current density and allow for uniform deposition of lithium metal [15].

In addition to blocking lithium polysulfides, the application of a thick inorganic layer (CIL) prevents the shuttle effect. Lithium polysulfides induce surface erosion of bare lithium during cycling by destroying the initial flat surface, interfering with the SEI's homogeneity, and producing a lot of pinholes. Consequently, the fast buildup of dead lithium and deterioration of batteries occurred due to the predominance of lithium dendrite development and growth. In the end, the CIL-Li anode guarantees that lithium-sulfur batteries have an extraordinarily long service life by preventing the majority of polysulfides and inhibiting lithium corrosion, preserving the original surface and uniform lithium deposition on the SEI. Due to the dense structure of CIL, it can block lithium polysulfide shuttle and inhibit lithium corrosion. The study found that in lithium-sulfur batteries with CIL-protected lithium anodes, the CE was 96.7%, compared to 82.4% for bare lithium anodes when lithium nitrate was not used. This study shows that CIL can effectively block most of the diffused PS and inhibit the side reactions, thus greatly improving the performance of Li-S batteries [16].

5. Electrolyte Modifications

In recent years, metal oxides have emerged as electrolyte additives that can and do promote sulfur redox reactions. Aluminium oxide (Al_2O_3), as a common metal oxide, has a strong polysulfide adsorption capacity, which can promote polysulfide capture, thus reducing the "shuttle effect" and improving the cycling stability of the battery. In addition, the low cost of Al_2O_3 is favourable for practical applications. However, Al_2O_3 has several drawbacks, such as low electrical conductivity, which is not conducive to sulfur utilisation, and small surface area, which is not conducive to providing sufficient active sites for the capture and conversion of polysulfides [17].

Inhomogeneous growth of Li can be inhibited using ionic liquid electrolytes containing SiO_2 nanoparticle additives. SiO_2 can bind ionic liquid molecules, which are then inorganic-organic nanostructures constructed in the electrolyte. Inorganic nanoparticles can modulate Li^+ flux by attaching to charge carriers (Li^+ or anions) in the electrolyte. Vapour phase silicon oxide (SiO_2) is a multipurpose electrolyte addition that improves the battery's capacity to charge in adverse circumstances. In this environment, tiny SiO_2 particles have the ability to spontaneously absorb Li^+ . [18]. Therefore, SiO_2 functions as a pump, promoting Li^+ migration close to the electrode/electrolyte contact, giving Li^+ an extra transport channel, and reducing side reactions. After over 200 cycles, this yields a comparatively large reversible capacity. It has also been discovered that adding LiX ($\text{X} = \text{Cl}, \text{Br}$) can increase the conductivity of Li_2S . The introduction of LiI in solid-state batteries can both improve the sulphide tolerance to lithium metal and enhance the dissolution/deposition of lithium during cycling. By adjusting the proportion of LiX in $\text{Li}_2\text{S} - \text{LiX}$ electrodes one can balance the ionic dynamics and the effective active substances, resulting in suitable electrodes with excellent electrochemical performance and high energy density [19].

MoS_2 is one of the most researched potential materials for transition metal sulfides, which can greatly enhance the reaction kinetics of Li-S batteries in liquid electrolytes. Therefore, a MoS_2 nanosheet-modified advanced carbon fibre has been designed, which can significantly improve the problems of interfacial instability and poorer electronic and ionic conductivity in sulfide SSE. MoS_2 nanosheets grown on carbon fibres prevented the severe decomposition of sulphides at high voltages. A significant number of lithium ions may be introduced into the special lamellar structure of MoS_2 , improving the ionic conductivity. It produces a battery with an extremely high initial coulombic efficiency by removing the shuttle effect and enabling the interface to be stable and devoid of side reactions [20].

6. Challenges and Future Perspectives

One of the most promising choices for next-generation rechargeable batteries is lithium-sulfur (Li-S). In compared to traditional lithium-ion batteries, viable Li-S batteries are expected to have a higher energy capacity, safer operation, and a longer lifespan. Additionally, elemental sulfur has a large deal of economic potential for industrial uses due to its non-toxicity and natural availability.

In recent decades, Li-S batteries have received a lot of attention. Many of the challenges that have hampered the commercialization of energy storage devices have been overcome, including the shuttle effect of polysulfides, anode volume expansion, volume fluctuation, and lithium dendrite development at the anode. Significant research efforts will be required in materials and technology development for cathodes, anodes and electrolytes. Although some progress has been made, cathode material chemistry and associated nanostructure engineering still need to be improved. For instance, the requirements at the industrial level might not be consistent with the synthesis and production of cathode materials in a laboratory context. Therefore, long-term evaluation of sulfur host materials is necessary before commercialization in order to guarantee the long-term stability of lithium-sulfur battery cathodes in real-world applications. The study also discovered that lithium-sulfur battery systems may be efficiently made to last longer by adding an intermediary layer made of carbon. However, because the process is more complicated, using this technique will require extensive, inexpensive, environmentally acceptable synthetic control, which is unlikely to be achieved. It is also

important to develop interlayers with high mechanical strength to inhibit dendrite formation. There is an urgent need for a hybrid interlayer that can transport lithium ions faster and encapsulate polysulfides [21].

Therefore, before the commercialisation of lithium-sulphur batteries, it is necessary to conduct comprehensive research on conductive anodes, new or modified electrolytes, new functionalised diaphragms and protected anodes so that lithium-sulphur batteries can actually be put into commercial production.

7. Conclusion

Since nanotechnology has advanced, researchers have used it to lithium-sulfur batteries in a variety of ways to increase the batteries' lifetime and electrochemical performance. For example, the use of sulphur cathodes with nanoscale designs can improve sulphur utilisation and limit polysulphides. Or the use of nano-coatings and protective layers, etc. to protect the lithium anode, or the incorporation of nanoparticles in the electrolyte to enhance the overall stability of the battery, among other measures, are intended to enable lithium-sulfur batteries to be truly commercially produced. However, issues including the polysulfide shuttle effect, the anode's volume change, and the development of lithium dendrites in the anode are still not fully resolved. We need to explore more methods in order to develop batteries with higher capacity, longer service life, greater safety and the ability to meet high energy demands.

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