

The advantages of Li-S car batteries and some solutions to the problems

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Abstract:

Rechargeable batteries has a significant impact in modern electronic devices, it powers various applications, from mobile phones or laptops that are portable devices to bigger machines including electric vehicles. Li-ion batteries, however, start to reach its limitation. It is urgent to find out new solutions, in many choices, lithium-sulphur batteries is a famous candidate due to the high ability of storing electricity in chemical energy within smaller volumes and lighter weight, the friendliness to the environment and the large number of raw materials. However, several challenges are obstacles of LSB practical deployment, including the insulating property of sulphur, the solving ability and migration of lithium polysulfides and the large changing in volume during cycling. This article mainly focuses on solving problems including overusing of electrolyte, “shuttle effect” and low conductivity, which strongly hold back the commercialisation process. In order to develop LSB and enable it to be a next-generation energy storage solution in recent future.

Keywords: Li-S battery; “Shuttle Effect”; electric vehicles

1. Introduction

In past few years, the popularity of electric vehicles (EVs) have increased significantly among customers, largely due to they are powerful, environmentally friendly and low maintenance cost. One of the cores of EVs is Li-ion batteries (LiBs), which is intermediaries that store electricity in the form of chemical. It converts electricity energy to chemical energy

during charging and vice versa during discharging. The components of LiBs include anode that typically is made of non-metal composites and with metallic current collector, the cathode consist of metal oxides, and a metallic current collector at the top of the cathode. The separator prevents short-cut and electrolyte has the function of allowing electrons and ions moves freely between cathode and anode [1].

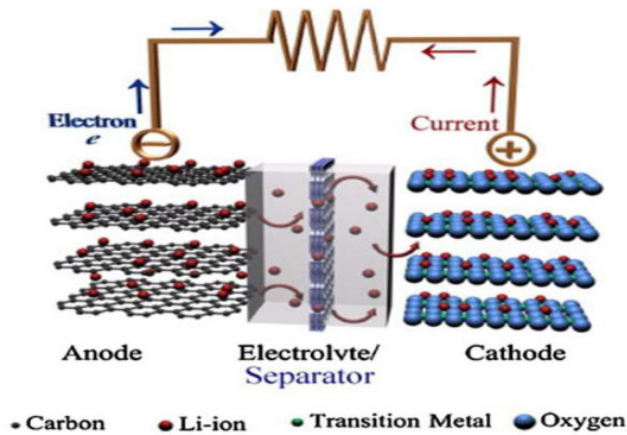


Fig. 1 The principle of Li-ion battery [1].

The structural characteristics of LiBs have a dominant effect on functions and application. Firstly, the high energy density, comparing to other types of commercial battery, making them capable of powering vehicles over long distance. Secondly, the technology of producing LiBs largely and shortly is significantly mature in the manufacturing factories, this implies that the cost of each individual battery is lower, which can reduce the overall vehicle price and making them more competitive. However, the LiBs still face significant challenges, one of the major issue is that the energy density is very low compared to internal combustion energy (ICE) vehicles. Therefore, if longer distance wants to be covered, the car should spend less time in charging. Even if some ultra-fast charging station is constructed, which does make charging time faster, meanwhile, higher current means that the condition of battery is unsafe and may lead to permanent damage and catastrophic failure. If the energy density can be improved to a higher level, producing a similar range of fuel cars. This can release the worries and doubts of EVs cannot handle long distance journey. This article presents Li-S battery, which hopefully a good solution to these problems.

This kind of battery is named as Lithium-sulphur batteries (LSB) and comparing to other types of cathode materials that currently using in batteries, including LiCoO_2 , Nickel Cobalt Aluminium Oxide (NCA) and LiFePO_4 , which usually have the energy density of 200-250 Wh/kg, and some of these materials are harmful to the environment and very expensive to made [2]. LSB can be a good solution, it has higher energy density, which is suitable for future smaller electronic devices or maintain higher ranger of EVs, cheaper and more environmentally friendly. If other additive materials are added to the battery, it can even provide a higher charging current. This article reports some problems and solutions to the LSBs and hope it can be commercialised in the recent future.

2. Main part

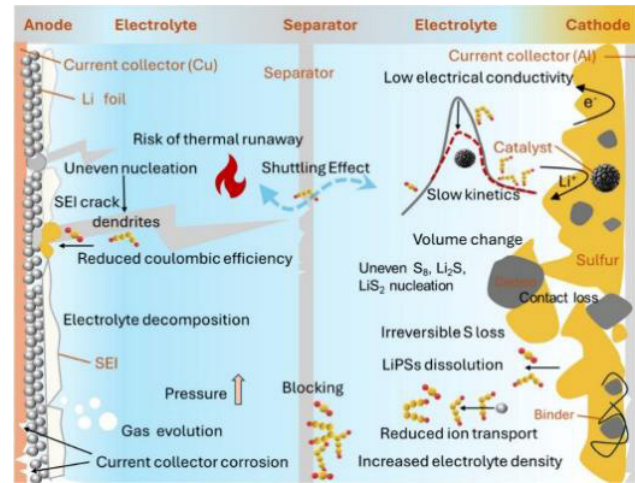


Fig. 2 Complex chemical reactions and structure of LSB [3].

2.1 Principle of the Li-ion battery

The fundamental principle of LSB isn't same with normal Li-ion batteries. The anode is a thin foil that made of Li metal. When the battery starts to discharge, the Li-metal is oxidized, and move through the electrolyte and separator to the cathode and react with Sulphur to form Li_2S compound ideally. When charging the battery, the compound cracks and the electrons moves through the outside circuit to the anode, the Li-ion moves back to anode through electrolyte and separator, they form Li metal at anode, prepared for another cycle [4].

2.2 Advantages of Li-S battery

Sulphur is very suitable for store Li-ions, it can store two ions compared to NCA or LiCoO_2 , which only available to store one or even less Li-ions, as their chemical formular expresses. Thereby, the energy density of LSB can reach 2600 Wh/kg [5], which is almost five times higher than commercial batteries that used in cars currently. Also, the price (lower than 1\$) of Sulphur is much cheaper than the LiCoO_2 (40\$ to 70\$). With the same amount of these two materials, the sulphur is 40 times cheaper than the traditional materials [2].

2.3 Problems and solutions of LSB

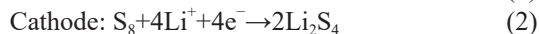
Three hard questions are raised if the LSB wants to be commercialised, which are "Shuttle Effect", low conductivity of cathode materials and over-consuming of electrolyte. In recent studies, there are numbers of solutions that target to settle these problems. The Carbon-based powder plays a role in increasing conductivity, hole structure may

capture the long chain Sulphur compounds and a brand new additives can be helpful in reducing the consumption of electrolyte.

2.3.1 “Shuttle Effect”

During discharge, the Li metal will react with sulphur to form Li_2S ideally, as the reaction below [4].

Discharge:



Charge:



The formation of the intermediate soluble Lithium polysulphides (LiPSs) Li_2S_n ($4 \leq n \leq 8$) is unsurable, so the final products Li_2S and active cathode material is reduced, the performance of the battery is negatively impacted, lower capacity, shorter cycle life and lower charging/discharging rates [3]. More seriously, the poly-sulphide compounds can be reduced to insoluble compound Li_2S_2 or Li_2S , by passing through electrolyte to anode when discharging. These insoluble compounds can also turn to soluble compounds again and migrate to cathode again when charging. This is a revisable reaction and always happens in the battery, causing a continuous shuttling effect, leading to low coulombic efficiency, self-discharge, formation of insulating layers on the electrodes, worst, short cut.

One research shows a way to use rGO-PEDOT: PSS compounds to cover on the separator, which stops the LiPSs pass through it and reduces to insoluble compounds at the anode. The rGO-PEDOT: PSS compound is a polar compound and it has a well-developed layer structure, which means the LiPSs can both be attracted to the layer chemically or physically. Also, using air-controlled electrospraying technology allows the surface of separator can cover with the rGO-PEDOT: PSS uniformly and quickly on the surface of separator [6]. Moreover, this conductive layer also increases the rate of electron transfer, thereby, reducing the polarization and increasing redox reactions. Another research shows that if V_2O_5 can be wrapped in hollow spheres, with the nitrogen-doped graphene surface on it, which is so called VOHS/NG, can react with LiPSs to transfer them to another form that is insoluble in the electrolyte [7]. Also, the nitrogen-doped graphene is a good conductor and its can also attract high-order LiPS easily by its high surface-volume rate. The result is the decay rate is reduced to 0.017% for each charging cycle.

2.3.2 Low conductivity of compounds

Low Conductivity and Volume Expansion of Sulphur [4, 8]. Sulphur and its discharge product Li_2S are electrically

insulating (5×10^{-30} and $3.6 \times 10^{-7} \text{ S cm}^{-1}$ respectively), which significantly increases the internal resistance of battery, lower the specific capacity of battery and reduce the cycle life. Moreover, sulphur undergoes up to ~80% volume expansion when converting to Li_2S , mainly because the considerable density difference between Li_2S and S is relatively big, which is 1.66 and 2.07 g/cm^3 [4, 9]. Each time the battery is charged or discharged, both electrodes must experience this volume changing and the force act on it. This can destabilise the electrodes and make it easy to break down and accelerate the degradation of electrochemical performance.

In order to make the Sulphur more conductive in the battery, nitrogen-doped graphene nanosheets (N-GNS) and carbon black powder (CB) have been widely employed as conductive additives. If these two conductive additives can be combined in some particular optimized proportion, the performance of LSB can be hugely increased. As these two additives have different chemical properties due to their crystallinity, morphology, chemical activity conductivity and chemical interactions with sulphur active materials [10]. The synergy of their properties not only provides continuous conductive electron channel but also helps the volume expansion happens when charging and discharging. Therefore, improving the charging stability and practical energy density.

2.3.3 Over consumption of electrolyte

The consumption of the electrolyte of LSB is significantly big. As mentioned before, the Sulphur and Lithium will form LiPSs, which is highly soluble in the electrolyte, and very hard to capture and store in cathode, which enable them to be used in the next cycle. These compounds can decline the concentration of electrolyte. Also, this decreases the efficiency of battery and the capacity of the battery, the over-consumption of the electrolyte means the concentration of additives that responsible for the conductivity or protection of internal materials decreases. This can lead to the increased internal resistance and lower electrons and ions moving speed. Or even cause safety risks.

To reduce the overusing of electrolyte. One group of researcher developed a type of electrolyte with high solubility, which is made of high-polarity solvents and high lithium salt concentrations. To enhance the solubility and reactivity of lithium polysulfides [12]. Enabling the recycle of LiPSs in the electrolyte. The electrolyte formulation is designed to optimize solvent-ion and solvent-polysulfide coordination, promoting efficient redox reactions and uniform sulphur utilization even at low electrolyte-to-sulphur (E/S) ratios. It allows stable cycling and high discharge capacities ($>1000 \text{ mAh g}^{-1}$), when low concentration of electrolyte is used ($\text{E/S} \approx 3 \text{ } \mu\text{L mg}^{-1}$) and

suppresses the polysulfide shuttle effect and reduces electrolyte consumption without compromising performance [12].

3. Conclusion

This article has examined in detail both the advantages of lithium–Sulphur batteries and the major problems that currently hinder the large-scale production. As an efficient electric energy intermediate, due to the reasons of the LSB has high theoretical energy density, sustainable reactants, environmentally friendly raw materials, making LSB is a good candidate that competes in next-generation batteries. Particularly in the application of electric vehicles, with large-scale renewable energy integration.

However, some problems including the shuttle effect of lithium polysulfides, the high electric resistance of sulphur and its compounds and the excessive consumption of electrolyte should take the responsibility for holding back the commercialisation process of the LSB. Recent research has provided a range of potential solutions, such as improving cathode conductivity with carbon-based additives, electrospinning separators to suppress polysulfide migration, and designing new electrolyte systems to enable stable cycling under lean conditions. These methods demonstrate continuous progress in enhancing the performance and stability of LSBs.

Although none of the current solutions can fully address all the problems in isolation, the combined advances in cathode engineering, separator design, and electrolyte optimisation indicate a bright future for lithium–sulphur technology. The development of Li–S batteries is not only a demanding scientific and engineering challenge but also an opportunity to achieve cleaner, safer, and more sustainable energy storage. With continuous innovation and integration of new strategies, it is reasonable to expect that the remaining barriers will be gradually overcome, paving the road for the eventual large-scale commercialisation of lithium–sulphur batteries and a cleaner environment.

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