



## Present status, electrochemical properties and future direction of Lithium sulphur batteries (LSBs)

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### Abstract

Lithium Sulphur battery (LSB) is the future of rechargeable batteries as its theoretical specific capacity and theoretical energy density are much higher than these of conventional Lithium ion battery (LIB). Another advantage of LSB is its relatively lower output voltage (2.1 V) which provides higher safety margin. However, life cycle, capacity fading and Coulombic efficiency are found to be serious problems for LSB. Several steps have been taken to improve the conductivity of Sulphur cathode and to slow down the solubility of polysulfides in electrolyte. Mostly, the Sulphur cathode has been encapsulated by different types of carbon to improve conductivity of the composite and to hinder dissolution of long chain polysulphides. At the same time, anode side also has been modified by suitable means like fabricating pre lithiated carbon or Ge-C composite. Similarly, research work on electrolyte modification has also been discussed.

**Keywords:** Energy density, power density, battery, lithium sulphur, cycling, electrode

### Introduction

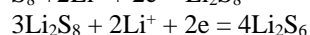
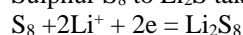
The demand to store electrochemical energy efficiently spurred the continued research interest in advanced batteries. The traditional lead acid or nickel cadmium batteries are found to be insufficient to cater the present needs due to lower energy density and power density, cycling of these batteries. On the other hand, lithium ion batteries (LIBs) have many superior attributes which make them a dominating player in battery market. In addition, conventional LIBs do not suffer from memory effect. The self-discharge rate of lithium ion battery is also very low for Lithium ion batteries (LIBs) (-5% per month) in comparison to Ni-Cd or Ni-MH batteries. The global reserve of lithium in earth crust is around 20 ppm which is sufficient to build more than 12 billion electric vehicles<sup>[1]</sup>. Therefore, lithium ion based. Batteries have become the central focus of researchers globally. Even though Li-ion batteries have higher energy density than sodium ion battery still they are not very suitable to be installed in electric vehicles. The energy density of Lithium ion battery (LIB) can be 200-300 Wh/kg, which cannot satisfy all the requirements of upcoming applications like vehicle electrification or high end electronic application. These new demands have been prompting the researchers to work on other alternative rechargeable batteries with higher energy density and longer life cycle. Among other battery chemistries, Li-S is most important candidate due to its low cost, high theoretical capacity (1675 mAh g<sup>-1</sup>) with a high theoretical specific energy of 2600 Wh kg, on the presumption of the complete reaction of Lithium with Sulphur to form Li<sub>2</sub>S<sup>[2]</sup>. The theoretical capacity of S is more than five times higher than that of traditional cathode materials based on transition metal oxides or phosphates. Another important aspect of Lithium-Sulphur Battery (LSB) is its low operating voltage (~2.1 V) which offer higher safety margin over the high-

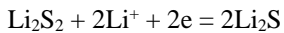
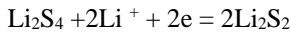
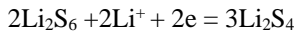
voltage oxide based cathodes (>4.3 V). It becomes more important in case large pouch cell configuration. Recently the role sulphate modification in enhancing electrochemical properties for battery application<sup>[3]</sup>, development of nanomaterials for flexible Lithium ion Batteries (LIBs) and super capacitors (SCs) play role in future electrochemical storage devices (FFSDs)<sup>[4]</sup>. The application process of nanomaterials development in Lithium ion batteries (LIBs), cathode materials of electrochemical performances<sup>[5]</sup>, etc have already been studied.

### Materials and Methods

#### Working principal of Lithium-Sulphur Battery(LSB):

Like any other secondary cell, Lithium-Sulphur battery (LSB) also consists of cathode where reduction takes place during discharge, anode where oxidation takes place during discharge, electrolyte through which ions migrates from one electrode to another internally and a separator to avoid physical contact between two electrodes. The working principle of a typical Lithium-Sulphur battery is slightly different from conventional lithium Ion battery. In conventional Lithium ion batteries (LIBs), lithium ions move from Lithium containing cathode to anode via electrolyte during charging process and in reverse direction during discharging process. However, in case of Lithium Sulphur Battery (LSB), the cells are made in charged state and initially discharging is done. During discharging, Lithium ion moves from Lithium anode to Sulphur or Sulphur composite cathode via separator soaked in electrolyte and reduce S to Li<sub>2</sub>S via a multi-step, multi-electron reduction process. In charging process, Li<sub>2</sub>S gets oxidized to S and releases Li ions which migrate to lithium anode again via electrolyte. Interestingly, the reduction of Sulphur S<sub>8</sub> to Li<sub>2</sub>S takes place in multiple steps.





Initially higher polysulfides ( $\text{Li}_2\text{S}_n$ ,  $x = 8, 6, 5$  and  $4$ ) form on reaction between lithium and sulphur which on further lithiation results lower polysulfides ( $\text{Li}_2\text{S}_n=1, 2$ ). The higher polysulfide ( $\text{Li}_2\text{S}_n$ ,  $x=8, 6, 5$  and  $4$ ) are highly soluble in organic solvent (mostly 1, 3-dioxolane and 1, 2-dimethoxyethane are used as solvent) used as electrolyte in LIB. On the other hand, the lower polysulfides ( $\text{Li}_2\text{S}_x$ ,  $1 < x < 4$ ) are insoluble and hence. Remain in solid state. The rate of reaction is faster in initial phase of lithiation at the solid-liquid interface, however, it is slower in second step as lithiation takes place on solid  $\text{Li}_2\text{S}_2$ . The voltage plateau for first reaction i.e. formation of  $\text{S}_4^{2-}$  from  $\text{S}_8$  via above mentioned steps is observed around 2.3 V with corresponding capacity  $418 \text{ mAhg}^{-1}$  ( $\sim 25\%$  of total capacity). The lower discharge plateau occurs at 2.1 V (vs  $\text{Li} / \text{Li}^+$ ) corresponding to subsequent reduction of  $\text{Li}_2\text{S}_4$ , to  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$  with a theoretical capacity of  $1254 \text{ mAhg}^{-1}$  ( $\sim 75\%$  of total capacity).

**Challenges ahead:** Even though there are myriad of advantages of Lithium-Sulphur batteries (LSBs), still the following challenges need to be addressed before its large-scale applications.

- High Resistivity of Sulphur and LIS.
- Shuttle Effect of Polysulfides.
- Huge Volume Expansion/Contraction during Lithiation/Delithiation.
- Use of Metallic Lithium Anode.

These problems are related to either electrodes or electrolyte and suitable modification of these components can improve the overall performance of Lithium-Sulphur battery (LSB), in the following sections highlight the important research on cathode, anode and electrolyte materials.

## Results and Discussion

**Research on Cathode Materials:** Mostly, elemental Sulphur is used as cathode material in Lithium-Sulphur battery (LSB). Sulphur has more than 30 allotropes and the most common and stable amongst them is cyclic octa Sulphur ( $\text{S}_8$ ) electronic conductivity of elemental Sulphur is vary ( $10 > 35 \text{ Scm}$ ), therefore, it needs to be made composite with conducting material like carbon. Several methods have been adopted so far by different groups to make Sulphur-carbon. Composites. Initially conventional carbons or carbon black were added with Sulphur to make it conducting. These carbon blacks are mostly fabricated by thermal cracking or partial combustion of carbon precursors, such as natural gas, at elevated temperatures and in an inert atmosphere or an inadequate air supply. Graphite, bio-derived carbon are also potential members in the list which can also increase the conductivity of the composite significantly. Typically, Sulphur is vaporized in presence of these carbon hosts and then cooled down to remove the Sulphur on the outer surface in carbon host by heating it<sup>[6]</sup>. The loading of Sulphur depends on porosity present in the matrix which in turn dictates the performance of the cathode. The optimal pore size required for excellent performance in LI-S batteries is not fully understood. However, a rough guideline might be deduced: (a) mesoporous and macroporous carbon (pore size more than 2

nm) are good in Sulphur leading but poor in cycling stability; (b) small micropores (less than 0.5 nm) are advantageous in utilization of Sulphur and good cycling stability but it has limitation in Sulphur loading on it; (c) large micropores (i.e. 0.5 nm to 2 nm) are found to be non-suitable for designing the Sulphur-carbon composite<sup>[7]</sup>.

Another candidate with which composite can be made efficiently is carbon nanotubes (CNT). Demonstrated loading of the elemental Sulphur on CNT by crushing the Sulphur powder in ball mill along with CNT<sup>[8]</sup>. The CNT bundles were acting as conducting medium in those heavily Sulphur loaded CNTs. Since Sulphur particles were on top of the nanotubes, cycleability of the composite was poor even though the interconnected CNTs provide a robust conductive network, the group observed a discharge capacity of around 560 mAhg Free standing 3D graphene were fabricated<sup>[9]</sup> on which 90 wt% Sulphur could be loaded. These interconnected graphene networker sured superior electronic conductivity and the pores therein allowed extra loading of Sulphur. The electrolyte also could seep into the structure which helps in migration of Lithium ion. However, the structure could also trap the polysulfides form during lithiation reaction. This Sulphur and 3D graphene composite is capable to deliver a high discharge capacity of 969 mAh g. Lu and co-workers. Sperepared a self-supported graphene sponges using hydrothermal reduction followed by freeze drying. The conductivity of 3D GO sponge is very high and the carbon network can support the conductivity whereas Sulphur can be incorporated inside carbon pores. The pores present in GO sponge also ensure electrolyte percolation, which essentially improve Sulphur utilization. Interestingly, the areal mass loading in this kind of structure is around 12 mg Sulphur/cm<sup>3</sup> which is more than commercial requirement, In this case high aerial capacity of the cathode could be achieved. Moreover, the authors observed slow decay rate (0.08% per cycle at 0.10) after 300 cycles. In addition to 3D graphene sponge researchers are also involved in development of interlayer of graphitic nitride coated on carbon fibre<sup>[10]</sup>.

Thereafter, many researchers have reported engineering of structure of graphene for further improvisation of electrochemical properties of Lithium-Sulphur batteries (LSBs). In this context, nitrogen doped 3D graphene has also been used as host matrix for Sulphur<sup>[11]</sup>. In addition, to the modification of the cathode, attempts have also been made to trap lithium polysulfides (LIPS) on the interlayer of graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) coated on carbon fiber paper (CFP), The resulting as-fabricated Lithium-Sulphur battery provided outstanding stability over 400 cycles with a reversible capacity of 1271 mAhg<sup>-1</sup> at 0.1C. The capacity fading (only 0.068% per cycle) was found to be much lower than the self-supporting graphene sponges.

Conducting polymers like polypyrrole (Ppy), polyaniline (PANI) are also widely used to fabricate yolk-shell type configuration. Conducting polymers helps to improve the electronic conductivity and also act as buffer to compensate the volume variation during charge-discharge<sup>[12]</sup>. Another approach at cathode side is insertion of graphene-based interlayer to reduce the dissolution of LIPS. Huge capacity retention could be observed in case of cells where interlayers have been introduced. It has been showed that Sulphur cathode with high Sulphur loading can show good cycling stability in presence of interlayers<sup>[13]</sup>. Sulphur

sandwiched between two graphene membranes is another suitable configuration. One graphene membrane with Sulphur coating acts as current collector and other graphene layer was deposited on commercial separator. Sulphur loading on current collector graphene layer was around 70% of total weight. The cell with this configuration delivers specific capacity of 750 mAh/g at current density 6 A/g which is 50 times higher than that of cell using aluminium current collector and polymer separator<sup>[14]</sup>. It is important to mention that addition of conductive interlayer increases the overall performances of Lithium-Sulphur battery, however, the weight of the interlayer should be considered during calculation of weight of cathode. The dead mass of inactive component increases the overall weight of the cathode which leads to decreased Sulphur content in the cathode. Hence, the dimension and density of the conductive interlayer should be selected judiciously.

Mostly, researchers are involved in modification of cathode material with superior life cycle, higher capacity, higher loading of Sulphur in lithium-Sulphur battery. Relatively, lesser attention has been paid towards anode material of LSB, Metallic lithium is most suitable choice as anode material for LSB. However, the issues arising due to formation of dendrite, formation of SEI layer in first few cycles, volume variation, short cycle life etc. need to be addressed. There are three important aspects for stabilization of lithium anode: (1) stabilization of Li-electrolyte interface (2) a 3D lithium host (3) a lithiophilic lithium host. A brief introduction to other kind of anode, i.e. Carbon and silicon has also been given. The lithium anode reacts swiftly with organic electrolytes inside the cell, therefore, it needs to be passivated. In order to do that mostly research is done more extensively in electrolyte material. Most of the articles focus on variation of components of the electrolytes or addition of oxidizing agents like LINO, in it<sup>[15]</sup>.

In order to stabilize the interface between lithium anode and electrolyte, addition of lithium nitrate to ether-based electrolyte is found to be more effective in improving Coulombic efficiency and cycle life. LINO, helps to form a passivation layer on the lithium anode, which prevents further reactions between lithium and polysulfides. However, addition of LINO, does not have much effect in suppression of dendrite formation. Although it is very difficult to form sufficiently sturdy passivation layers on lithium anode in liquid electrolytes, a self-healing electrostatic shielding mechanism has been proposed<sup>[16]</sup>. In this work, additives like Cs/Rb has been used in the electrolyte which get easily reduced before Li ions. Get reduced to Li metal. These lead to lesser amount of dendrite formation during charge-discharge.

Another approach to modify the anode is introduction of mechanically stable artificial layers, such as polymer or solid state blocking layers<sup>[17]</sup> to block the dendrite penetration. The interfacial layer suppresses the dendrite formation probability by reducing the activity of lithium anode. This also increases the coulombic efficiency. In this way, the dendrite is physically separated to avoid piercing the separator, however, the true nature of lithium anode could not be avoided. Another approach is to use 3D lithium host instead of planer lithium sheet. Generally, lithium dendrites grow on lithium surface due to inhomogeneous deposition of lithium ions on it. In this regard, 3D host

copper is found to show promising behaviour in preventing dendrite growth<sup>[18]</sup>.

Lithium anode undergoes volume variation due to lithium plating/stripping, and as a result of that the lithium surface gets pulverized after long cycling. SEI layer on the lithium surface can take care of the dimensional variation of the anode; however, during lithiation and delithiation the SEI layer breaks down which again forms in the subsequent cycles, As a result of that electrolyte gets consumed continuously which also increases the possibility of dendrite growth. It would be beneficial to build a host matrix which has excellent lithium affinity (lithiophilicity) for metallic lithium, Lin *et al*, introduced molten lithium inside the rGO layers<sup>[19]</sup>. It has been observed that the surface of Li-rGO film does not change with lithium loading. The volume variation of the anode was also found to be relatively lower. They also observed that after long cycling, the cell with planer lithium anode shows a voltage drop due to short circuit whereas the cell with infused lithium in rGO shows better stability, Also, the voltage hysteresis arising in the cell where rGO-Li film has been used is found to be comparatively lower.

Several alternative anodes have been considered in recent past in place of pure lithium to reduce the activity of lithium. It showed that a sufficiently stable Li-S cell could be fabricated using silicon-carbon (Si-C) composite as anode<sup>[20]</sup>. It has been observed that when the cell is made with Sulphur cathode and pristine lithium anode, the cell was able to achieve reversible cycling for 135 cycles at 167mA/g". However, when the same cathode could not be cycled at higher current density which might be due to rapid electrolyte depletion and formation of unstable SEI layers. On the other hand, the cell with Sulphur cathode and pre-lithiated Si-C shows stability for more than 1300 reversible cycles with high Coulombic efficiency nearly 99%. Pre-lithiated carbon is also used as anode in some cells which shows excellent cycle ability for more than 500 cycles. However, the pre-lithiated carbon has higher potential compared to pure lithium which decreases with overall energy density.

**Research on Electrolyte Materials:** Electrolyte is a very important part of Lithium-Sulphur battery as carbonate-based solvent is found to be inferior in this case. However, carbonate base solvent does not because many problems in case of short chain Sulphur cathode. In case of Lithium-Sulphur battery, it is observed that ether-based solvents are superior to carbonate based solvent as dissolution and redeposition of polysulfides is faster in ether based solvent which enables better Sulphur utilization, however, the formation of polysulfides cannot be restricted using these ether-based electrolytes. For optimum performance of LSB there are two important aspects *viz*, electrolyte concentration and electrolyte amount (Electrolyte/Sulphur ratio)

**Electrolyte concentration:** Dissolution of lithium polysulfides in electrolyte is a serious problem which not only decreases the specific capacity but also reduces the Coulombic efficiency. It is expected that the solubility of LIPS will decrease in presence of highly concentrated electrolyte due to common ion effect. A study has been carried out to investigate the impact of concentration of electrolyte on electrochemical performance of cells<sup>[21]</sup>. In their experiment, they used highly concentrated (7 mol/l) electrolyte and found limited dissolution of LIPS which

results enhanced cycling stability. Also, they observed poor Coulombic efficiency of the cell with low concentration of electrolyte. It is established now that highly concentrated electrolyte is beneficial for electrochemical performance; however, it comes with its own set of drawbacks. Firstly, highly concentrated electrolyte leads to higher viscosity and as a result of that the cell exhibit lower output voltage. Secondly, higher concentration also means higher unwanted weight of electrolyte which ultimately decreases the overall energy density. Third disadvantage is that the higher electrolyte concentration is not cost effective,

**Electrolyte amount:** It is very important to use optimum amount of electrolyte to get higher energy density. Lower amount of electrolyte ensures relatively lesser dissolution of LIPS which increases. The cycle-life. However, lower amount of electrolyte results in sluggish migration of lithium ion due to poor wetting of separator. On the other hand, cells with higher E: S (electrolyte and Sulphur) ratio leads to lower gravimetric and volumetric energy densities. However, cells with excess electrolyte can improve the overall cycle life because the electrolyte will get depleted quickly as the depletion of electrolyte is one of the main reasons for failure of cell. It has been established that E/S ratio should be 20 pl/mg (electrolyte concentration 50g/l<sup>[22]</sup>. Solid or polymeric gels are also found to be suitable option to be used as electrolyte. Solid electrolyte is superior to liquid counterpart with respect to LIPS dissolution, thermal stability, mechanical stability, non-flammability etc. Mostly, compositions from Li, S-P, S, solution are chosen as electrolyte in all solid-state Lithium-Sulphur battery (LSB). It has been have reported that a cell comprised of carbon/S composite as cathode, Li-In alloy as anode and Li,S-P,S, solid solution as electrolyte could be cycled for more than 100 cycles with capacity 1600 mAhg<sup>-1</sup><sup>[23]</sup>.

### Conclusion

The issues with Lithium sulphur battery (LIB) have been partially sorted out so far, however, lot of works needs to be done before this technology becomes viable for large-scale application. Most Lithium Sulphur batteries (LSBs) reported sofar contains cathode with relatively lower Sulphur loadings and excess electrolyte. This leads to cells having lower energy density and power density which cannot outperform the existing state-of-the-art Lithium ion batteries (LIBs). Novel conducting materials need to be searched for better electrochemical performance. Also, the parameters like Sulphur loading, electrolyte to Sulphur ratio need to be optimized to realize higher energy density in Lithium Sulphur Battery (LSB). The research on overall engineering of Lithium-Sulphur battery (LSB) packaging needs to be emphasized. In the anode side, more work should be focused towards suppression of dendrite formation, stabilization of SEI layer and improvement of safety of lithium anode.

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