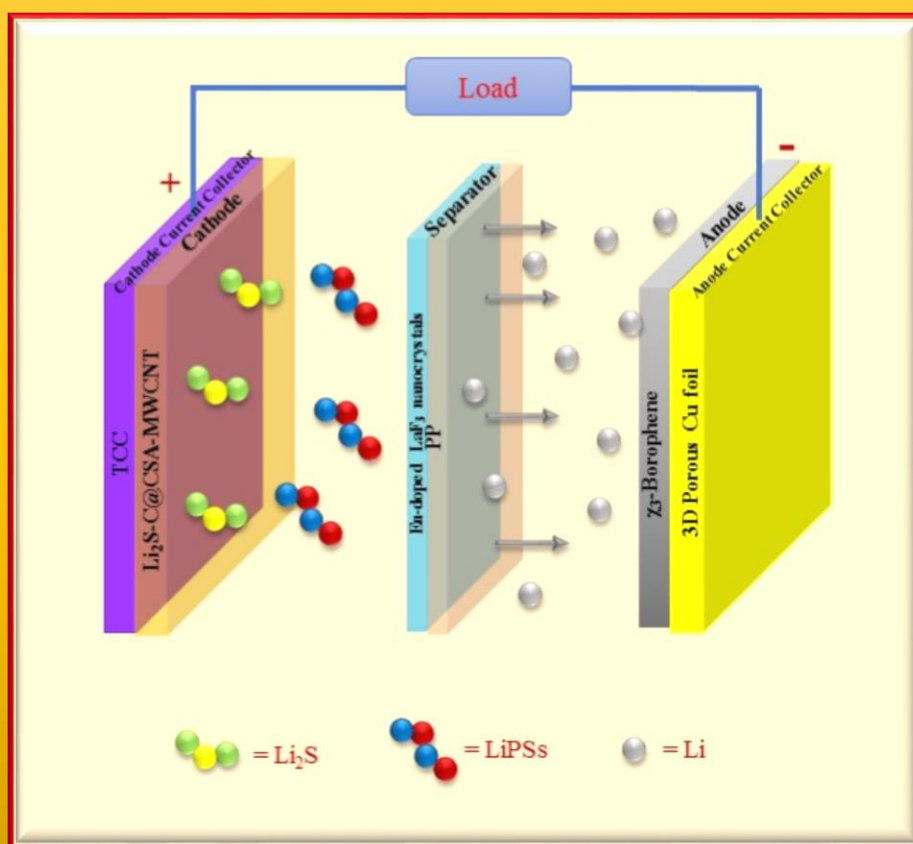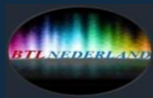# Towards High Energy Lithium-Sulfur Batteries: Hypothetical Strategies

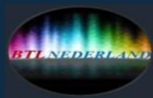# Table of contents

Towards High Energy Lithium-Sulfur Batteries: Hypothetical Strategies

Towards High Energy Lithium-Sulfur Batteries: Hypothetical Strategies

Atef S. Iskander

The increasing global demand for renewable energy storage systems requires a new era of batteries with high energy density, reliability and economic viability. One of the most promising candidates for those energy storage systems is the lithium-sulfur batteries due to its high energy density and low cost. This study provides a new insight for the development of the materials involved in lithium sulfide-based lithium-sulfur batteries. It introduces comprehensive novel hypothetical strategies as modeling approaches with the expected objective functions. These new scenarios include the cathode materials, cathode current collectors, electrolytes, anode materials, anode current collectors, electrolyte additives and trapping materials/separators. Prior to discussing these hypothetical approaches, a brief overview of the concept of lithium-sulfur batteries is highlighted including their major intrinsic challenges and the approaches to tackle these drawbacks. The proposed new scenarios can be generalized to other alkali metal ion batteries such as sodium or potassium batteries.

1. Introduction

The rapid technical progress of portable electronics and the increasing demand for other forms of electricity necessitate a high-capacity energy storage. Batteries fulfill these requirements by providing a direct route to the conversion of electrical to chemical energy. Thus, there has been a burgeoning interest in recent years in renewable energy storage systems, which necessitate a new era of batteries with high energy density, low-cost, reliability and environmental friendliness. In fact, the storage of energy through electrochemical reactions is a crucial technology for portable power needs and load leveling of many alternative and

conventional power sources. In a general sense, the basis for the conversion of electrical to chemical energy is the simultaneously shuttling of electrons to and from electrodes via complementary chemical reactions. During discharge, electrons are delivered from the cathode to the anode through an electrolyte medium by spontaneous reduction and oxidation, respectively, of chemical species at the electrodes. Electrons provide power by flowing from the anode back to the cathode through an external load. Applying an opposing voltage across the cell reverses the reactions at the electrodes, so recharging the battery capacity. Lithium ion batteries, which use lithium cations to transport charge between electrodes, are appropriate for rechargeable chemical energy storage due to the fast mobility and high energy density of lithium ions. Lithium also has a large negative reduction potential (E^o = -3.05 V) which generates a high-voltage output. The energy stored in the lithium batteries is a result of the difference in the redox potentials of lithium insertion into the two electrodes. As a consequence, the battery capacity depends on the weight or volume fraction of lithium that each electrode can hold, and the rate of charging and discharging depends on the electrical resistance of the electrodes and the rate of lithium diffusion in and out of the electrode materials.[1]

Lithium-sulfur (Li-S) rechargeable batteries are considered as one of the most favorable candidate for next-generation energy storage systems. The merits behind this expectation is mainly related to that the multi-electron-transfer cathode reaction of $S_8 + 16\ Li^+ + 16\ e^- \longleftrightarrow 8\ Li_2S$ provides the large theoretical specific capacity of sulfur positive electrodes (~ 1675 mAh g^{-1}), which is unique among existing cathode materials, permitting for high energy density storage.[2-4] Whereas lithium negative electrodes provide both the highest theoretical specific capacity (3860 mAh g^{-1}) and the lowest redox potential (-3.05 V vs SHE) among all known anode materials.[5] The average potential of Li-S cell is 2.15 V with respect to Li^o/Li^+, which is relatively low compared to other batteries. Furthermore, the high abundance of sulfur, its relatively low mass and low-price as well as coupled with lithium to form a unique solid-liquid-solid conversion processes are characteristic features. Herein, a brief highlight of the concept of Li-S batteries is outlined including their major intrinsic problems and the approaches to tackle these problems. Thereafter, a range of innovative hypothetical scenarios are presented for high energy lithium-sulfur batteries, including the cathode materials, cathode current collectors, electrolytes, anode materials, anode current collectors, electrolyte additives and trapping materials/separators.

2. Concept and critical issues in Li-S batteries

Generally, the concept of Li-S batteries relies on the reaction of the produced lithium ions, that ionized from the anode with the *cyclo*-octasulfur (S_8) of the cathode to form lithium sulfide (Li_2S) during the discharging process, whereas the electrons generate a current through the external load (Figure 1). The redox chemistry of sulfur in the cathode behaves a solid (cyclo-S_8)-liquid (chain-polysulfide (Li_2S_{4-8})-solid (Li_2S_2/Li_2S) reaction. This conversion reaction at the sulfur cathode is accompanied by two distinct plateaus. The first plateau, the reduction of S_8 forms a long-chain of the high-order lithium polysulfides Li_2S_n ($6 \leq n \leq 8$) at ~ 2.3 V *vs* Li^o/Li^+. These polysulfide ions (PSs) are soluble in organic electrolytes, such as dioxolane (DOL) and dimethoxy ethane (DME), so the reaction is fast, which is equivalent to 25% of the theoretical capacity of sulfur. The second plateau, as a result of continuing discharge, the polysulfide ion will reduce to a short-chain of lower-order lithium polysulfides Li_2S_n ($2 < n < 4$) at ~ 2.1 V *vs* Li^o/Li^+ as Li ions insert continuously, which are insoluble species with slower reaction kinetics, corresponding to the remaining 75% of the theoretical capacity of the system.[5-7] During the charging process, Li_2S is dissociated into elemental sulfur,

which migrates to the cathode for regeneration, while the lithium ions migrate to the anode and combine with electrons to form metallic lithium. Unlike the discharging process, the system during the charge process does not exhibit similar two distinct plateaus in the reverse reaction, which can lead to a variety of multistep reactions with different activation energy barriers.
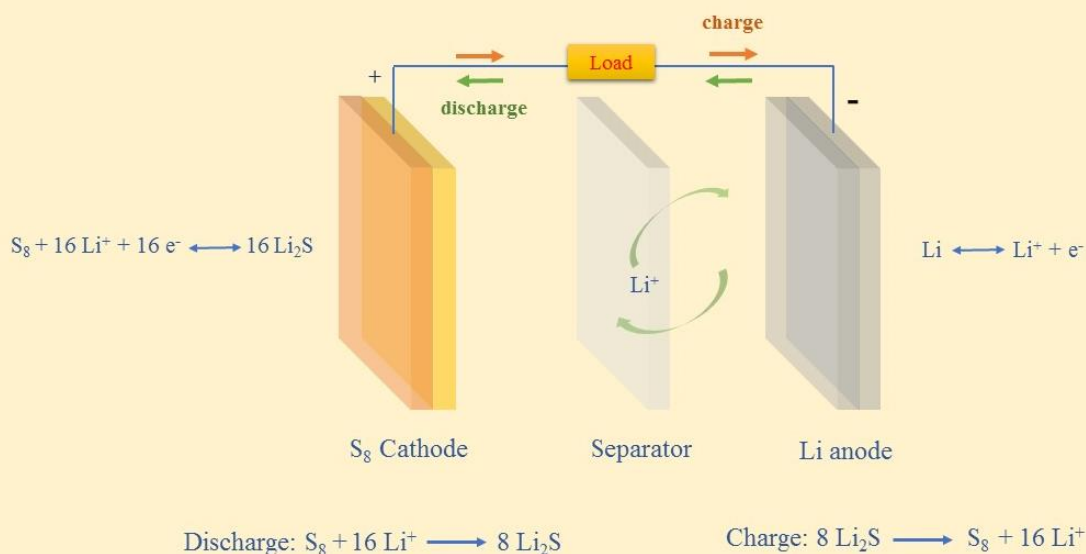
Figure 1. Li−S battery system conversion reaction. The conversion reaction during discharge at the sulfur cathode follows a progressive "solid− liquid−solid" transition process: $S_8 \rightarrow Li_2S_8 \rightarrow Li_2S_6 \rightarrow Li_2S_4 \rightarrow Li_2S_2 \rightarrow Li_2S$.
—{*Soluble Polysulfides*}—

Despite the various advantages of Li-S batteries, there are many aspects, that stand in the way of their commercialization and need to be addressed. Several practical problems are associated with the sulfur cathode. During discharge, the lithiation of sulfur to Li_2S results in an 80% volume expansion, due to the variation in the density of sulfur (2.03 g cm^{-1}) and that of Li_2S (1.67 g cm^{-1}). This large volume expansion can result in pulverization of the sulfur particles and the cathode, as well as passivation of the lithium electrode, inducing fast capacity fading.[5] Solvation and migration of polysulfides also leads to self-discharge. Even under the static state, solvated polysulfides are continuously consumed by the lithium electrode via chemical reactions, causing a low open-circuit voltage and a fast capacity degradation. To overcome this challenge, many cathode materials with three-dimensional (3D) porous structure have been developed, which have shown the ability to reduce the large volume expansion.[4] Thus, well-designed 3D porous morphologies can facilitate the reaction between Li ions and sulfur, and can improve the contact with electrolytes, as their structures have several void spaces. However, the reduced material loading within 3D electrode needs to be careful to ensure sufficient sulfur loading for practical applications.

Another issue associated with the sulfur cathode is the low conductivity of sulfur. Both S and Li_2S have low electronic and ionic conductivity (5×10^{-30} Scm^{-1} and 3.6×10^{-7} Scm^{-1} at 25 ^{o}C, respectively), leading to poor reaction kinetics as well as increasing internal resistance. The sulfur is a natural insulator, which restricts the movements of electrons, inhibiting redox reactions. This leads to low sulfur utilization and reduces the effective capacity of the electrode. The addition of conductive additives could be an option to solve this problem, but would result in a limitation of the energy density of the cathode.[8]

Additionally, the formation of soluble lithium polysulfides (LiPSs) intermediate poses the issue of dissolution and shuttle. The concentration gradient of soluble LiPSs in the electrolyte leads to diffusion to the anode through the separator. These shuttled LiPSs at the anode react irreversibly with the lithium ions present to form an unstable film of insulting lithium sulfide solid-electrolyte interphase (SEI), which has a negative effect on the cycling stability of the Li-S betteries.[9]

On the other side, the major problem associated with the lithium anode is lithium dendrite formation during the charging process. The nonuniform deposition on the surface electrode leads to uneven surface, which consumes more electrolyte via parasitic reactions, resulting in high internal resistance. Furthermore, dendrites (needle structures) can penetrate the separator, resulting in severe safety issues.[10]

3. Lithium sulfide (Li_2S)-based cathode materials

Li_2S with a prelithiated cathode has been shown to retain the high energy capacity while avoiding some of the challenges in the conventional Li-S cells utilizing elemental sulfur cathode and metallic lithium anode. The advantages of Li_2S-based cathode include: i) Achieving a high theoretical specific capacity (1166 mAhg^{-1}) with the same similarity of the chemical reaction between lithium and sulfur in the case of sulfur cathode; ii) creating a system where lithium already exists in the cathode, which allows for the use of lithium metal-free anodes; iii) eliminating problematic dendritic growth and the formation of insulting Li_2S SEIs at the anode; iv) allowing for manufacturing and modification methods using higher temperature mechanical or chemical processes, due to its high melting point (~938 ^{o}C) compared to elemental sulfur (~116 ^{o}C); v) reducing volume expansion issues during cycling, as the Li_2S cathode is prepared in its fully lithiated form with the largest volume in the Li-S system; vi) high compatibility with available high-capacity anodes for acquiring high energy density; and vii) eliminating the needs for designed voids in the porous matrix or deliberate measurement of buffer material to cater for sulfur expansion.[5]

However, the lithium-sulfur batteries based on the Li_2S cathode suffer from some similar problems. Li_2S is an insulator, requiring a conductive matrix or additives to function as a cathode. In addition, the formation of soluble LiPSs and their shuttling effect is still an issue, although with better control over the formation of a passivating layer with the variety of anode choices. Moreover, the main challenge is the high overpotential during the first charging process, which affects the electrochemical performance of the cell and causes safety risks. This overpotential arises from the high charge transfer resistance in the initial stage between Li_2S, the electrolyte, and the conducting electrode additives, due to the insulting nature of Li_2S. A potential of ~ 3.5V is required to overcome the initial stage. Once this initial barrier is overcome, the soluble LiPSs formed enhance ion and charge transfer, and the conversion reaction behaves at lower potential (~ 2.5V).[5]

4. Hypothetical strategies for Li_2S-based Li-S batteries architecture

Several strategies have been developed with promising solutions to overcome the aforementioned challenges, such as optimizing the electrolyte, synthesizing composite electrode of S/polymer, S/carbon, S/metal organic framework (MOF) and designing novelty structure of Li-S battery. Most of the strategies that overcome the challenges of the Li_2S cathode, are based on reducing the charge transfer distance by refining the Li_2S particles, and introducing functional elements that catalyze the reaction. However, the practical application of these strategies is still far from large-scale implementation. Inspired by these great efforts, facile and cost-effective hypothetical scenarios are presented to improve the performance of Li-S batteries.

4.1. $Li_2S@C$ composites as a Cathode

For electrode material, high capacity, suitable voltage, good electronic and ionic conductivity and maintaining good electrical connections to the current collector are crucial parameters. The instability of sulfur and Li_2S as an electrode material owing to its natural insulting necessitates the use of carbon as conductive additive in the Li_2S-based Li-S batteries. Carbon materials have excellent conductivity and good mechanical resilience. Such a channel promotes charge transfer in the cell and improves the sluggish carrier migration dynamics.

The proposed strategy for a high performance cathode electrode in the Li_2S-based Li-S cell is based on a facile synthetic route for Li_2S-carbon composites (denoted as Li_2S-C@CSA-MWCNT). A densely packed structure of multiwalled carbon nanotubes (MWCNT) film is proposed, which serves as a host to store carbon coated Li_2S. In fact, the discharge capacity at various rates was found to improve with decreasing nanotube wall thickness, consistent with the shorter lithium diffusion lengths.[11] Furthermore, the nanotubes retained good electronic connections to the current collector through many charge/discharge cycles. To reduce the high first charge overpotential of Li_2S cathodes, the elements that form the electrode with Li_2S must possess high electric conductivity. Thus, a densely packed MWCNT film is proposed, which is characterized by its ultra-high electric conductivity.[12] To obtain a densified MWCNT film, a chlorosulfonic acid (CSA) treatment method was developed by Wang *et. al.*, which the densely packed structure of MWCNT in the film is attributed to the zipping effect.[12] Briefly, the MWCNT film was synthesized by a floating chemical vapor deposition method. The precursor solution of ferrocene and thiophene in n-hexane/ethanol was injected in a furnace at 1300-1500 ºC using nitrogen as the carrier gas, and collected out the reactor by a roller at a winding speed. The obtained pristine-MWCNT film for the direction parallel to the winding direction was annealed at 1000 ºC under inert atmosphere, and then purified with concentrated HCl. Finally, the film was immersed in CSA in a petri dish and heated at 150 ºC for densification (Figure 2). The obtained MWCNT film exhibited ultra-high electrical conductivity of ~ 9.92 MS/m and a thickness of ~ 0.64 μm.[12]
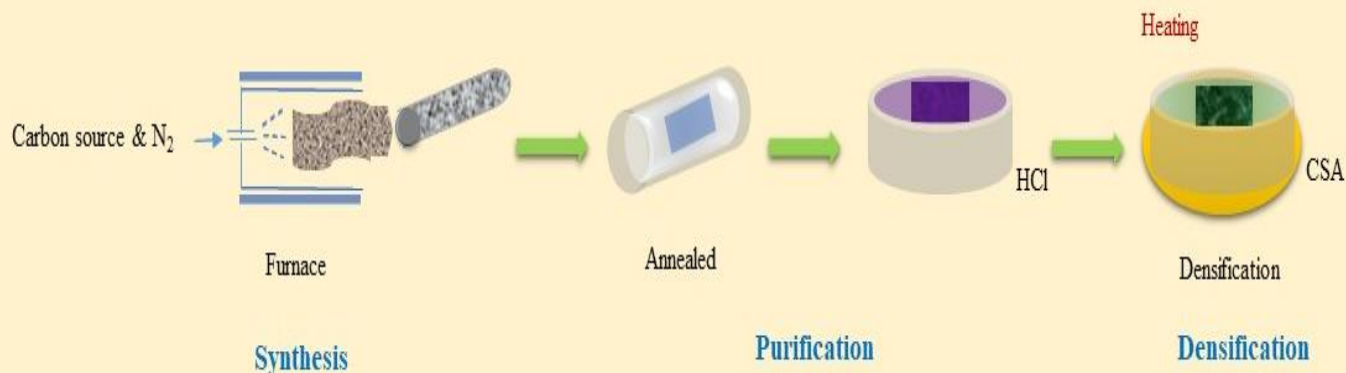
Figure 2. Schematic illustration of the synthesis of MWCNT film.[12]

To obtain a heterostructure matrix of Li_2S-C and composite CSA-MWCNT, a facile liquid-phase method would be employed using a solution of lithium sulfate salt (Li_2SO_4) and resorcinol-formaldehyde (RF) as a carbon source. A solution of Li_2SO_4@RF particles would attach to the dispersion of the composite CSA-MWCNT, which would then spray dried to form granules of hierarchical structures. The carbothermal reduction of these granules would produce Li_2S nanoparticles with a well-tuned nanopore size distribution, whereas the agglomeration would be prevented by the RF coating during the drying process.[15] The Li_2SO_4 salt is converted into Li_2S through carbothermic reduction:[16] $Li_2SO_4 + C \longrightarrow Li_2S + CO_2/CO$

4.2. *Hydrophilic carbon cloth (TCC) as a cathode current collector*

In fact, both of the current collector and the electrolyte are contributed to the high first charge overpotential of Li_2S cathodes. The Li_2S conversion reaction depends on solution-based redox of LiPSs, which, in turn, depends on facile ion transport. Thus, hydrophilic current collectors can enhance the wettability of the cell, in which the liquid electrolyte can completely envelop the cathode particles, and thereby facilitate electrolyte infiltration and promote LiPS conversion.[13] To achieve this goal, the commercial hydrophobic carbon cloth must first be chemically activated via an oxidation process using a mixture of concentrated acid (H_2SO_4:HNO_3) followed by a treatment with ammonium hydroxide (NH_4OH) to obtain the hydrophilic treated carbon cloth (TCC).[14] The incorporation of TCC would result in enhancing the surface area, improving the electrochemical active surface area, and specific capacitance retention rate as well as lower charge-transfer resistance. These collective properties would greatly accelerate electron transport, leading to enhancing the dynamic process of carrier migration. Moreover, they would facilitate LiPS binding, boosting its conversion and attainable capacity.

4.3.   2-Methyltetrahydrofuran (MeTHF) as Electrolyte

The nature of discharge in Li_2S-based Li-S cells relies on the dissolution of redox-active LiPS, which mediates the reaction kinetics of charge transfer. Due to the solution-mediated reaction mechanisms, the electrolyte must be able to accommodate and solvate a wide array of lithium polysulfide species. Therefore, the electrolyte must ensure excellent ionic conductivity and favorable solubility of LiPSs. The major used ether-based electrolyte represents the best-identified solvent realizing these considerations. Conventional ether-based electrolytes can dissolve up to 8 M sulfur in the form of LiPSs in solution.[17] Thus, the proposed electrolyte is 2-methyltetrahydrofuran ((MeTHF). MeTHF is a commercially available aprotic ether solvent, that is produced from renewable resources. It is an excellent solvent for low-temperature lithiation reactions due to its low mp (-136 ºC), and low viscosity at low temperature (1.85 cp at -70 ºC).[18] It exhibits resistance to reduction by lithium. Moreover, it is very stable to bases and is stable to acids at moderate concentrations. Table 1 shows its properties. The solvent polarity of MeTHF compared to THF and Et_2O places it between them (Table 2).[19] It is reasonable to hypothesize that this electrolyte would display quite favorable ionic conductivity and LiPSs solubility.

Table 1. Properties of MeTHF

Property	MeTHF
Molecular weight	86.1
Density at 20 ºC (g/mL)	0.854
Boiling point (ºC)	80.2
Melting point (ºC)	-136
Dielectric constant	6.97
Dipole moment, Debye	1.38
Vapor pressure at 20 ºC (mm)	102
Viscosity at 25 ºC (cp)	0.46
Viscosity at -70 ºC (cp)	1.85
Water solubility, g/100g	4
Refractive index at 20 ºC	1.408
Flash point (ºC)	-11
Heat of vaporization (cal/g) at bp	87.1
Hildebrand, $MPa^{1/2}$	16.9
Solvation energy, kcal/mol	0.6
Donor number	18
Azeotrope bp (ºC)	71

Table 2. Solvent polarity properties

| Property	MeTHF	THF	Et₂O
Dielectric constant	6.97	7.5	4.42
Dipole moment, Debye	1.38	1.69	1.11
Water solubility, g/100g	4	miscible	1.2
Hildebrand solubility, $MPa^{1/2}$	16.9	18.7	15.5
Solvation energy, kcal/mol	0.6	0	2.3

4.4. Additives

During charging, the Li ions migrate to the anode surface, relay itself in the Schottky vacancy inside the solid electrolyte interphase (SEI) layer, and then accept electrons from the current collector to deposit as lithium metal.[20] Thus, the diffusion resistance of Li ions affects the uniform deposition of lithium metal. Many approaches have been developed to address this issue for realizing practical applications of the batteries. Among them, the addition of electrolyte additives is an effective method to establish stable electrode electrolyte interfaces, which would result in improved battery performance. Two dual-additives are hypothetically proposed to enhance the regulation of SEI layer.

4.4.1. Tris(dimethylamino)phosphine/tris(2-pyridyl)phosphine as electrolyte additive

Tris(dimethylamino)phosphine ($(Me_2N)_3P$) has a phosphine center bound to three amino groups, which could offer donor sites for LiPSs. It has a high propensity for sulfur. It serves as a base and reacts with sulfur to form hexamethylthiophosphoramide ($S=P(NMe_2)_3$). It can also coordinate with lithium. It is cost-effective and has low toxicity. Whereas the co-additive, tris(2-pyridyl)phosphine, has strong donor sites towards the lithium. The pyridinic nitrogen with lone-pair electrons could be regarded as Lewis base, which enhance the even distribution and nucleation of Li^+ ions (Lewis acid) on the anode surface *via* acid-base interaction. Moreover, the pyridinic- nitrogen will improve the electrochemical response. It is assumed that these multifunctional electrolyte additives could be able to dissociate lithium polysulfides and to improve the regulation of SEI layer on the anode as a result of the flexibility and mechanical stability of the formed components in SEI layer. In addition, their high electronic conductivity and strong affinity to LiPSs would result in reducing the charge transfer resistance at the cathode, and hence overcoming the overpotential barrier, as well as forming a stable cathode electrolyte interface (CEI). These features would benefit the cycling performance of the cell.

4.4.2. Tris(dimethylamino)phosphine/D-limonene as dual-electrolyte additive

It is well known that the conversion of limonene into *p*-cymene can be accomplished *via* the reaction with sulfur. Furthermore, this reaction forms a low-molecular-weight polysulfides (Scheme 1).[21] The co-additive, d-limonene, is derived from natural resources, and has solubility properties close to those of chlorofluoro-carbon compounds (CFCs). It is safe and cheap. From these points of view, it is assumed that once in contact
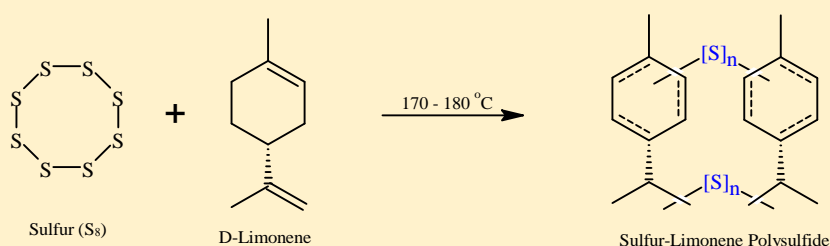
Scheme 1. The reaction of D-Limonene with Sulfur.[21]

with Li_2S, limonene is likely to be reduced to lithium-limonene-sulfides ($C_{10}H_{16}S_nLi_4$), lithium-limonene-polysulfides ($C_{10}H_{16}S_4Li_4$), and lithium polysulfides (Li_2S/Li_2S_2). The components containing limonene polysulfides can improve the toughness and flexibility of the SEI layer. Whereas the lithium polysulfides could enhance the necessary Li^+ ions conductive pathways and mechanical strength for the SEI layer. Furthermore, the course of the reaction with LiPSs in the presence of tris(dimethylamino)phosphine in the electrolyte (MeTHF) would boost the cycling performance of the battery, due to charge transfer reactions *via* radical formation as hypothetically proposed. It is believed that these dual-additives would promote the dissolution of Li_2S and hence reduce the loss of capacity caused by the precipitation of Li_2S; passivate the surface of the anode, thus eliminating the polysulfide shuttle phenomenon; and improve the even distribution of SEI layer. In addition, they could be able to alleviate the polysulfide nucleation around the Li_2S particles, which would result in a reduction of the high overpotential.

4.5. χ₃-Borophene as an anode

To tackle the fast capacity fading induced by the shuttle effect, a suitable sulfur anchoring material can suppress such shuttle effect and improve the cycling performance. Borophene is the lightest 2D material and has high theoretical specific capacities, excellent electronic conductivity and outstanding ion transport

properties.[22,23] χ_3-Borophene belongs to a group of epitaxial monolayer sheets, which has moderate to weak interactions. The adsorption energies of Li_2S_4, Li_2S_6 and Li_2S_8 on χ_3-borophene are 2.67, 2.53 and 2.89 eV, respectively, indicating that it is a suitable anchoring material.[24] Such suitable adsorption strength is beneficial to suppress the shuttle effect and maintain their cyclic structure undecomposed during the charging and discharging processes, and to facilitate the lithium plating. In addition, borophene exhibits a metallic electronic structure during the whole battery cycling. A thin film of χ_3-borophene would maximize the electrode surface area while maintaining good electrical connections to the current collector.

4.6. 3D Porous Cu foil as an anode current collector

The current collector is a crucial component of the anode, which has a great influence on the anode. It affects the nucleation in the initial stage of lithium plating, which determines the morphology of subsequently plated layers. Copper is well-known as an anode current collector because of its high conductivity and stability at low potential. In view of these features, a three-dimentional (3D) porous Cu foil with a submicron-sized skeleton is proposed as an anode current collector. Such a current collector would be useful not only to regulate the nucleation in the initial stage of lithium plating, but also the growth of subsequent layers. Consequently, the lithium would fill the pores of the 3D submicro-sized Cu skeleton and regulate the growing of subsequent layers on the anode.[25] The 3D porous Cu foil can be fabricated from a commercial planar Cu foil via the immersion in ammonia solution to allow $Cu(OH)_2$ deposition by self-assembly. Then, the foil with $Cu(OH)_2$ would be heated at 180 ℃ for 10 h for dehydration and reduced at 400 ℃ for 10 h in a H_2/Ar mixed flow to obtain the 3D porous Cu foil.[25]

### 4.7. Eu-doped LaF₃ nanocrystals coated PP as separator

For separator material, high specific area, strong interaction with polysulfides, high conductivity, high catalytic activity and good electrolyte wettability are important parameters. In view of these parameters, a europium (Eu)-doped lanthanum fluoride (LaF_3) nanocrystals coated polypropylene (PP) is proposed as a separator for Li_2S-based Li-S cells. Lanthanum fluoride matrixes have high thermal and chemical stability, tunable crystal phase and low toxicity. It is believed that decorating the PP separator with a conductive layer of Eu-doped LaF_3 nanocrystals would enhance electrolyte wettability and electrode-separator interfacial adhesion due to its high polarity. The proposed separator can serve as a host for LiPSs, which would form a shielding barrier against the shuttle effect. It would act as potential active sites for reaction with Li_2S and LiPSs and boost sulfur utilization leading to a significant reduction in the first charge overpotentials as well as improve capacity retention after cycling. In addition, such crystals would effectively improve the migration of Li^+ ions due to the high mobility of fluoride ion and the doping with Eu. Generating fluoride ions at a confined nanoscale would be helpful to promote uniform lithium deposition and form a stable SEI.
On the other side, this separator can be used as an additional current collector due to its outstanding luminescence dynmics.

The preparation of Eu-doped LaF_3 nanocrystals can be accomplished *via* a facile coprecipitation method at room temperature as demonstrated by Yamada *et al.*[26] Briefly, a mixed solution of $La(NO_3)_3$, $Eu(NO_3)_3$ and NH_4F in water is stirred for 1 h, followed by the addition of NaOH to adjust the pH to 10. Finally, the obtained white precipitation is washed and then dried at 60 ^{o}C for 2 h.

A suspension of Eu-doped LaF_3 can further be used as coating agents on PP separator.

5. Discussion of proposed scenarios

Li_2S-based Li-S batteries are considered as the most favorable option to avoid some of the challenges in the conventional Li-S cells. For reasons, lithium sulfide based cathodes have an exceptional capacity (1166 $mAhg^{-1}$); high compatibility with various high-capacity anodes; eliminating volume expansion pre-lithiated species; excellent thermal stability; allowing the use of lithium metal-free anodes and insoluble in organic electrolytes. However, they suffer from some issues such as the formation of soluble LiPSs and their shuttling effect; as well as high overpotential during the first charging process. This study presented a series of innovative hypothetical strategies to address these issues. Figure 3 shows a schematic illustration of the construction of the proposed L_2S-based Li-S cells.
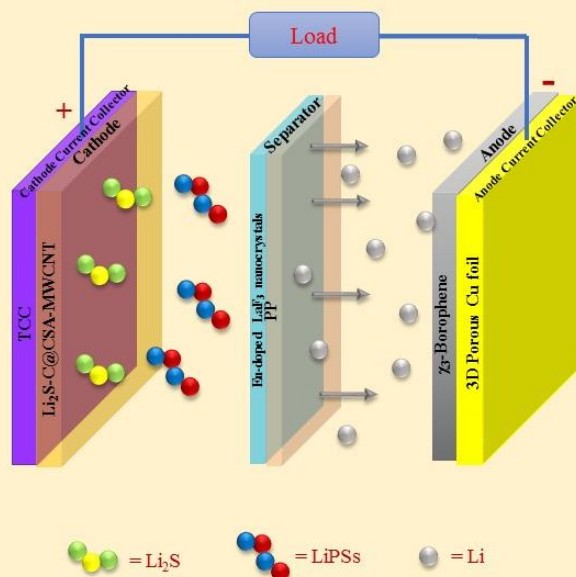
Figure 3. Schematic illustration of proposed construction of Li_2S based Li-S cells.

The proposed cathode electrode is based on a simple fabrication method of a densely packed structure of MWCNT film serving as a host to store carbon coated Li_2S. this cathode material has various advantages including thin nanotube wall, good electronic connections to the current collector, and high electronic conductivity. These synergic properties would expect to reduce the high first charge overpotential of Li_2S cathodes. Further support to these synergic properties of the cathode materials, a hydrophilic treated carbon cloth cathode current collector is proposed. Through enhancing the wettability of the cathode, the electrolyte infiltration into the cathode would be facilitated, which in turn would promote LiPSs conversion, leading to improving the dynamic process of carrier migration.

Electrolyte is a key active component of the Li_2S-based Li-S battery, which mediates the reaction mechanisms. It is believed that MeTHF has the ability to display quite favorable ionic conductivity and LiPSs solubility. To establish stable electrode electrolyte interfaces, two dual-additive electrolytes are proposed to tackle the uneven deposition of lithium metal on the anode and the regulation of SEI layer. Tris(dimethylamino)-phosphine/tris(2-pyridyl)phosphine electrolyte additives have a high electronic conductivity and strong affinity for LiPSs, which would result in improving the even distribution and nucleation of Li^+ ions on the anode surface, improving the electrochemical response, and reducing the charge transfer resistance at the cathode. Alternatively, tris(dimethylamino)phosphine/D-limonene electrolyte additives have advantages of alleviating the polysulfide nucleation around Li_2S particles, promoting the dissolution of Li_2S/LiPSs, passivating the surface of the anode and even distribution of SEL layer.

On the other hand, a high-capacity anode is proposed, which would be compatible with L_2S cathode. χ_3-Borophene has outstanding properties including a high theoretical specific capacity (1240 mAhg^{-1}) that far exceeds that of graphene, silicene, phosphorene and $Li_4Ti_5O_{12}$,[27] excellent electronic conductivity, superior ion migration and moderate interactions with substrates. These properties make it suitable for anchoring LiPSs and facilitate the lithium ions plating and regulate its deposition, leading to suppression the fast capacity fading. As an integral component of the anode, the anode current collector influences the nucleation of the initial stage of lithium plating, which is crucial for the morphology of subsequently plated layers. It is assumed that a 3D porous Cu foil with a submicron-sized skeleton would regulate the nucleation at the initial stage of lithium plating as well as the growth of subsequent layers. Such skeleton would provide the migrated lithium ions with electrons to deposit on the anode and regulated them to form an even SEI layer.

The key role of separators is to mitigate the harmful processes in the battery. The proposed Eu-doped LaF_3 nanocrystals coated PP separator is believed to be an optimal separator because of the following features: i) possessing high polarity to improve wettability and electrode-separator interfacial adhesion; ii) have a strong susceptibility to trapping the polysulfides; iii) exhibit good sulfur utilization leading to a reduction in the first charge overpotential and enhancement of capacity retention after cycling; iv) with high mobility of ions resulting in good migration of Li^+ ions; v) are nanocrystals that improve discharge kinetics, promoting even lithium deposition and stable SEI; and vi) possessing outstanding luminescence dynamics enabling it to be used as an additional current collector paving the way for new engineering avenues.

6. Conclusion

This study presents a series of novel hypothetical strategies for high energy Li_2S-based Li-S batteries. A comprehensive scenarios of the development of the involved materials in those cells as modeling approaches with their expected objective functions were demonstrated. For cathode material, thin nanotube wall with high electronic conductivity of Li_2S-C@CSA-MWCNT is proposed, supported by TCC hydrophilic cathode current collector to promote wettability of the cathode. While, the anode electrode is composed of χ_3-borophene and supported by 3D porous Cu foil anode current collector. The solubility of LiPSs and ion migration are mediated by Me-THF electrolyte. To improve the electrochemical performance of the cell, two dual-electrolyte additives with high electro conductivity and strong affinity to LiPSs are proposed. Either tris(dimethylamino)phosphine/tris(2-pyridyl)phosphine or tris(dimethylamino)-phosphine/D-limonene would improve the cycling performance of the Li_2S-based Li-S cells. To further enhancement of the chemical confinement of LiPSs, eu-doped LaF_3 nanocrystals coated PP separator is proposed. The construction of Li_2S-based Li-S battery with viability for massive energy storage requires an effective combination of these materials to gain the best advantage of the properties of the individual building blocks. It is important to point out that these novel scenarios can be generalized to other alkali metal ion batteries such as Na or K batteries.

7. References

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Insights
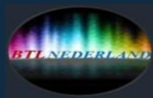
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