A review on Li-S batteries as a high efficiency rechargeable lithium battery

Marzieh Barghamadi, Ajay Kapoor, Cuie Wen*

Faculty of Engineering and Industrial Sciences, Swinburne University of Technology
Hawthorn, Victoria, 3122, Australia

Abstract

Energy production and storage are critical research domains where the demands for improved energy devices and the requirement for greener energy resources are increasing. There is particularly intense interest in Lithium (Li)-ion batteries for all kinds of electrochemical energy storage. Li-ion batteries are currently the primary energy storage devices in the communications, transportation and renewable-energy sectors. However, scaling up the Li-ion battery technology to meet current increasing demands is still problematic and issues such as safety, costs, and electrode materials with higher performance are under intense investigation. The Li-sulphur (S) battery is a promising electrochemical system as a high-energy secondary battery, particularly for large-scale applications, due to its low cost, theoretically large specific capacity, theoretically high specific energy, and its ecofriendly footprint. The Li-S battery exhibits excellent potential and has attracted the attention of battery developers in large scale production in recent years. This review aims to highlight recent advances in the Li-S battery, providing an overview of the Li-ion battery applications in energy storage, then detailing the challenges facing Li-S battery and current applied strategies for improvement in its efficiency.

Keywords: Energy Storage; Li-ion Batteries; Li-S Batteries; Advances and Improvements in Cathode

*Corresponding author. Tel.: +61 3 92145651; Fax: +61 3 92145050
E-mail address: cwen@swin.edu.au (C. Wen).
Contents

1. Introduction .................................................................................................................. 3
2. Current Li-ion batteries ............................................................................................... 4
3. Li-S battery .................................................................................................................. 8
   3.1. Fundamental aspects of the Li-S battery .............................................................. 8
   3.2. Challenges for the Li-S battery .......................................................................... 10
   3.3. Advances in Li-S battery ................................................................................... 12
      3.3.1. Advances in cathode .................................................................................. 12
      3.3.2. Advances in anode .................................................................................... 17
      3.3.3. Development in electrolyte ...................................................................... 19
   3.4. Application of Li-S battery in electric vehicles .................................................... 21
4. Conclusions and outlook ............................................................................................. 22
   Acknowledgements .................................................................................................... 23
   References .................................................................................................................. 24

*Corresponding author. Tel.: +61 3 92145651; Fax: +61 3 92145050
E-mail address: cwen@swin.edu.au (C. Wen).
1. Introduction

An energy economy based on fossil fuels is at a serious risk due to the continued increase in demand for oil, the depletion of non-renewable resources, and with the rate of CO$_2$ emissions showing a dramatic increase in the last 30 years. This increase has also resulted in a rise in global temperature and a series of associated climate changes. Energy is, therefore, a vital global issue and attempts are being made to rectify current problems by utilizing new energy resources. In this regard, electrical energy storage is recognized as an essential element for both stationary and mobile power equipment.

Electrical energy storage systems play a crucial role in managing the gap between energy generation and demand, especially for electricity generation from renewable and sustainable sources, such as solar and wind, and in portable electronics such as personal computers, cordless tools, and electric vehicles. There are several technologies available such as flywheels and compressed air, but batteries are at the forefront of energy storage systems, especially for electricity.

Battery Energy Storage Systems (BESSs) have appeared as promising storage technologies for power applications, offering a wide range of power system applications. The batteries are made from cells that convert chemical energy to electrical energy and vice versa. They are rated in terms of their energy and power capacities. The amount of energy per mass or volume that a battery can deliver is a function of the cell’s voltage and capacity. Significant development is going on in the battery technology. Different types of batteries have been commercially developed, while some are still in the experimental stage. Safe, low-cost, high-energy-density and long-lasting rechargeable batteries are urgently needed to address important issues in energy generation, such as the increased energy consumption of portable devices. Rechargeable batteries are used in portable electronics, power tools,
electric vehicles (EVs), and in stationary electrical energy storage (EES) for a grid supplied by wind, radiant-solar, and nuclear power. Among all the types of batteries, lithium batteries have attracted the most attention because the theoretical energy density (both gravimetric and volumetric) of lithium metal is the highest for all solid electrodes. Lithium-ion batteries have been under intense scrutiny over the past 20 years because of their advantages, such as high energy density, high operating voltage and low rate of self-discharge.

2. Current Li-ion batteries

Lithium-ion batteries employ lithium storage compounds as the positive and negative electrode materials. During the battery’s cycling, lithium ions (Li$^+$) exchange between the positive and negative electrodes. Li-ion batteries have been discussed as rocking chair batteries because the lithium ions “rock” back and forth between the positive and negative electrodes as the cell is charged and discharged. The working mechanism of a typical Li-ion battery is presented in Figure 1.

Sony commercialized the lithium ion battery (LIB) first in the early 1990s. Until now, lithium-ion batteries have offered the most practical solutions to a wide variety of electrical energy storage applications, such as mobile phones, lap-top computers, MP3s, due to their high voltage, high energy density, light weight and good environmental compatibility in comparison to other kind of batteries. Lithium ion batteries have also found applications in satellites and in biomedical device clinical trials, such as Neurostimulator, Ventricular Assist, Artificial Heart. However, the maximum energy density of current lithium ion batteries is too low to satisfy the demands of key markets such as transport and they need to be improved. Some of the major challenges facing this kind of battery are as follows: (i) The obtainable or usable capacity is inadequate (and much lower than the theoretical limit) and diminishes with the rate of cycling; (ii) The power density is insufficient for the intended applications, especially in EVs; (iii) The energy efficiency is too low due to large polarization
losses for charge and discharge, with the situation worse at higher cycling rates; (iv) The cycling life is limited due to capacity fading with cycling; and (v) The price is high. Overall, the existing Li-ion batteries often suffer from deterioration in their microstructure or the architecture of the electrodes accompanied by volume expansion or contraction, phase transformation, and morphology changes of the active electrode materials during cycling.\(^4\) In addition, safety of lithium metal oxide cathodes is an issue because of their intrinsic thermal properties. The thermal runaway is caused by the exothermic reactions between the electrolyte, anode and cathode, with temperature and pressure increasing in the battery.\(^{19}\) For example, a fully charged lithium cobalt oxide can release oxygen, which oxidizes the solvent and causes the battery thermal runaway.

In order to improve the energy and power density of LIB, the use of anode materials with larger capacity and higher Li diffusion rate is required. Different materials such as nano carbon, alloys and metal oxides have been developed. Nano carbons like graphite can effectively store Li and improve storage ability due to their high surface area and morphology. Li anode can be alloyed with some elements such as Sn, Si, Al to improve the capacity and safety. But this will result in large volume change which causes cracking of the electrode and capacity fading. Metal oxides like Fe\(_3\)O\(_4\), SnO\(_2\) and CuO have been proposed as potential materials for LIB anode, but their capacity decrease rapidly because of large volume changes.\(^{20}\) SnO\(_2\)-nanofiber carbon composite\(^{21}\) and Fe\(_3\)O\(_4\)/reduced graphene oxide nanocomposite\(^{22}\) were applied as anode to deal with this issue.

The main LIB cathode materials are lithium metal oxides like LiCoO\(_2\) which have high energy density, but they suffer from some intrinsic and safety issues in addition to high cost. Although using nanostructured lithium metal oxides can solve some problems like low conductivity, it causes more safety issues due to higher surface area.\(^{23}\) Better stability has
been achieved by coating the cathode LiCoO₂ with ZnO, which suppresses the cobalt dissolution.²⁴

Li-ion materials are currently the subject of intense research.²⁵ Several countries, including Japan, United States and European countries, are supporting R&D programs aimed at solving these problems in order to develop advanced and efficient LIB.²⁶ Indeed identifying new materials offering a better performance than those offered by the current common anode and cathode used in rechargeable Li battery is necessary. In general, the performance of any device depends on the properties of its materials; this is also true for lithium batteries. Thus, a new generation of rechargeable lithium batteries can only be achieved by a breakthrough in electrode and electrolyte materials.¹

Introducing positive electrode materials that offer higher capacity and improved safety properties, as well as negative electrode materials with improved specific energy, energy density, rate capability, and longevity are the main research and development goals in the lithium battery area. Adopting new electrolytes, additives and electrode material coatings to improve both the cycle life and calendar life of lithium batteries are also receiving increased attention.²⁷

Reaching beyond the horizon of rechargeable lithium batteries requires an exploration of new chemistry, especially electrochemistry, and new materials. Non-lithiated cathode materials not only exhibit higher specific capacities than lithiated cathode materials, but also provide enhanced safety as they cannot be overcharged. Rechargeable Li-S is highly efficient lithium rechargeable battery. Sulphur has one of the highest theoretical capacities for the cathode of lithium batteries in comparison with all other cathode materials in this kind of battery. Based on complete reactions with metal lithium to form Li₂S, it has a theoretical specific capacity of 1675 mA h g⁻¹.²⁸⁻³⁰ Table I compares the different kinds of lithium batteries.
### Table I. Comparison of lithium batteries.

<table>
<thead>
<tr>
<th>Battery</th>
<th>Cell voltage (V)</th>
<th>Theoretical capacity (mAh g(^{-1}))</th>
<th>Theoretical specific energy (Wh kg(^{-1}))</th>
<th>Theoretical energy density (Wh l(^{-1}))</th>
<th>Overall reaction</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional Li-ion</td>
<td>3.80</td>
<td>155</td>
<td>387</td>
<td>1,015</td>
<td>(\text{Li(C)} + \text{CoO}_2 \leftrightarrow \text{LiCoO}_2)</td>
<td>15, 31</td>
</tr>
<tr>
<td>Li-S</td>
<td>2.20</td>
<td>1672</td>
<td>2,567</td>
<td>2,199(^b)</td>
<td>(2\text{Li} + \text{S} \leftrightarrow \text{Li}_2\text{S})</td>
<td>31, 32</td>
</tr>
<tr>
<td>Li-air (non-aqueous)</td>
<td>3.00</td>
<td>3862</td>
<td>11,248(^a)</td>
<td>3,436(^a)</td>
<td>(2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2)</td>
<td>31, 33</td>
</tr>
<tr>
<td>Li-air (aqueous)</td>
<td>3.20</td>
<td>1861</td>
<td>5,789(^a)</td>
<td>2,234(^d)</td>
<td>(2\text{Li} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \leftrightarrow 2\text{LiOH})</td>
<td>31, 33</td>
</tr>
<tr>
<td>Zn-air</td>
<td>1.65</td>
<td>820</td>
<td>1,086</td>
<td>6,091(^e)</td>
<td>(\text{Zn} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{ZnO})</td>
<td>31, 34</td>
</tr>
<tr>
<td>Al-air</td>
<td>2.70</td>
<td>2980</td>
<td>8100</td>
<td>NA</td>
<td>(4\text{Al} + 3\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Al(OH)}_3)</td>
<td>34, 35</td>
</tr>
<tr>
<td>Mg-air</td>
<td>3.10</td>
<td>2200</td>
<td>6800</td>
<td>NA</td>
<td>(\text{Mg} + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2)</td>
<td>34</td>
</tr>
</tbody>
</table>

\(^a\) The molecular mass of \(\text{O}_2\) is not included in these calculations.

\(^b\) Based on the sum of the volumes of \(\text{Li}\) at the beginning and \(\text{Li}_2\text{S}\) at the end of discharge.

\(^c\) Based on the sum of the volumes of \(\text{Li}\) at the beginning and \(\text{Li}_2\text{O}_2\) at the end of discharge.

\(^d\) Assuming the product is anhydrous \(\text{LiOH}\) and alkaline conditions.

\(^e\) Based on volume of \(\text{ZnO}\) at the end of discharge.
3. Li-S battery

The lithium–sulphur (Li-S) battery, which is composed of a sulphur composite cathode, a polymer or liquid electrolyte, and a lithium anode, is a promising candidate for high energy systems. Figure 2 presents a schematic configuration of a Li-S battery. It is based on the lithium/sulphur redox reaction, given by:

\[ 16 \text{Li} + S_8 \rightarrow 8\text{Li}_2S \]  \[1\]

Assuming complete conversion, it has a high theoretical specific capacity of 1675 mA h g\(^{-1}\) and a high theoretical specific energy of 2600 Wh kg\(^{-1}\).\(^{36, 37}\)

3.1. Fundamental aspects of the Li-S battery

Sulphur is a promising positive electrode material for lithium batteries due to its high theoretical specific capacity of approximately 1675 mA h g\(^{-1}\). The Gibbs energy of the Li/S reaction is more than five times the theoretical energy of a Li-ion system, ~ 2600 Wh kg\(^{-1}\). The concept of electrochemical energy conversion and storage utilizing sulphur as the positive electrode in an alkali metal anode battery dates back to the 1960s.\(^{38}\) During recent decades, there has been strong incentive to develop a rechargeable Li/S battery.\(^{39, 40}\) Many articles regarding the electrochemical properties of the Li–S cell, such as discharge capacity,\(^{36, 41, 42}\) cycling,\(^{42-44}\) and self-discharge\(^{45}\) have been published.

Among the various types of rechargeable batteries, this system is a very attractive candidate, because of its high theoretical capacity, high theoretical power density and wide temperature range of operation. Moreover, elemental sulphur benefits from advantages such as natural abundance, low cost, excellent safety due to its intrinsic protection mechanism from overcharge, and its non-toxicity.\(^{46-48}\)

In the nature sulphur exists in more than 30 allotropes, and ring-structural cyclooctasulphur (S\(_8\)) is the most stable form.\(^{28}\) In the discharge process of a fresh Li-S battery, an S–S covalent bond of S\(_8\) is first broken to form a chain-structural polysulphide
(PS) anion \((S_x^{2−}, x = 8)\), and then it is further reduced into \(Li_2S\) through multistage reactions.\(^{49,50}\)

The reaction mechanism of a Li-S battery is different from that of commercial secondary lithium batteries with an intercalation-deintercalation mechanism in lithium metal oxide and graphite. Reduction of sulphur in a Li-S battery is a multistep electrochemical process that can be composed of different intermediate species. In general lithium metal reacts with sulphur \((S_8)\) to produce lithium polysulphides with a formula of \(Li_2S_n\). Long chain polysulphides are produced first, such as \(Li_2S_8\) and \(Li_2S_6\), which are shortened during further reduction of sulphur. The final product of discharge is lithium sulphide \((Li_2S)\) and the overall reaction is given by Eq. 1.\(^{39,51}\) In this process, sulphur accepts electrons from an open-circuit voltage \((OCV)\) to 2.1V, forming lithium polysulphide and then lithium polysulphide is reduced. From the viewpoint of phase transitions, the discharge can be divided into four stages, as follows:

I: Reaction of elemental sulphur with \(Li\) is given by:

\[
S_8 + 2Li^+ + 2e^- \rightarrow Li_2S_8 \quad [2]
\]

II: A reaction between dissolved \(Li_2S_8\) and lithium is described as:

\[
Li_2S_8 + 2Li^+ + 2e^- \rightarrow 2Li_2S_4 \quad [3]
\]

III: A transition from the dissolved \(Li_2S_4\) to insoluble \(Li_2S_2\) or \(Li_2S\) by the coexistence of Eqs. 4 and 5:

\[
Li_2S_4 + 2Li^+ + 2e^- \rightarrow 2Li_2S_2 \quad [4]
\]

\[
Li_2S_4 + 6Li^+ + 6e^- \rightarrow 4Li_2S \quad [5]
\]

IV: An equilibrium reaction of insoluble \(Li_2S_2\) and \(Li_2S\) is described as:

\[
Li_2S_2 + 2Li^+ + 2e^- \rightarrow 2Li_2S \quad [6]
\]

Eq. 3, is the most complicated of the four stages because it is affected by both the solubility of the polysulphides in the electrolyte and the chemical equilibrium between each
type of polysulphide in the solution. Therefore, this reaction is affected strongly by the type of electrolyte solvents. The outcome of stage III depends on the competition of Eqs. 4 and 5. The final discharge products are mainly a mixture of Li$_2$S$_2$ and Li$_2$S. As Eq. 5, is the predominant reaction, the Li-S cell has high capacity with slightly lower discharge voltages and a shorter stage IV. Stage IV is kinetically slow and suffers from high polarization because of the non-conductive nature of Li$_2$S$_2$ and Li$_2$S. Figure 3 shows the voltage profile of the first discharge of a sample of Li-S cell.$^{52, 53}$

As the current density increases, both the discharge capacity and the plateau voltage decrease. X-ray diffraction analysis of discharged sulphur electrodes proves that at low current density, only Li$_2$S peaks are displayed while at high current density, both elemental sulphur and Li$_2$S peaks can be observed. The discharge capacity of the sulphur electrode greatly decreases after discharging at high current density due to under-utilization of the active material.$^{54}$

3.2. Challenges for the Li-S battery

Although the Li-S battery has considerable advantages, it still suffers from a series of problems that have hindered its practical application. The discharge products precipitate during the second discharge step, covering the positive electrode surface and causing poor electrode rechargeability and capacity limitation. This is mainly linked to the passivation of the positive electrode. In fact the discharge stops when the surface is fully covered by these insulating species.$^{39, 55}$ The long-chain lithium polysulfides dissolve into the electrolyte and migrate to the anode to form lower-order polysulfides by reacting with lithium, and then they diffuse back to cathode to be deoxidized to a longer-chain. This causes the so-called internal “shuttle” effect, which leads to the corrosion of the lithium anode and consequently causes poor efficiency and a short cycle life in rechargeable Li-S batteries. Additionally, the continuous reaction of the soluble polysulfide to the Li anode leads to significant self-
discharge and the deposition of solid Li$_2$S$_2$ and Li$_2$S on the cathode, which results in active mass loss and capacity fading. Some amount of the insoluble Li$_2$S and Li$_2$S$_2$ accumulate on the Li anode. Another challenge is the volume change accompanied by morphology change which occurs in the electrode upon the active sulphur dissolution and the final products precipitation. These problems contribute to the fast aging of electrodes and a quick fading of the practical specific charge of the battery.$^{56-58}$

Therefore, the Li-S battery is unsuitable for a high energy density primary battery that is required to have a long calendar life and service time. Another problem is the very poor electronic conductivity of sulphur, which causes poor electrochemical contact of the sulphur and leads to low utilization of active materials in the cathode.$^3$ Thus, a large quantity of conductive agents is needed when making the sulphur cathode. Compositing elemental sulphur with carbon$^{50, 59}$ and conducting polymers$^{60-62}$ can significantly improve the electrical conductivity of a sulphur cathode.

The successful development of a Li-S battery, regarded as a candidate for the next generation of batteries, requires extensive research on the electrochemical behavior under various operating conditions.$^{36, 63}$ A lot of research has been conducted to mitigate the negative effect of the polysulphide shuttle. Much of this work has focused on either the protection of the lithium anode$^{42}$ or on the restriction of the ionic mobility of the polysulphide anions.$^{64, 65}$ However, since protection of the lithium anode causes a slow reaction rate at the anode during the discharge cycle due to passivation of the anode, this leads to a loss of power density in the battery. Gel electrolytes and solid electrolytes have been reported as a means of slowing down the polysulphide shuttle by reducing the ionic mobility of the electrolytes.$^{64, 66, 67}$ It is also necessary to introduce conductive additives and strong adsorbent agents with a large surface area to the cathode. The preparation of the sulphur-conductive polymer
composites, or sulphur-carbon composites, has been reported as softening the impact of the shuttle effects.\textsuperscript{52}

3.3. Advances in Li-S battery

3.3.1. Advances in cathode

Based on studies reported in the literature over the last few years, the ideal structure for a sulphur electrode requires the following characteristics: a closed structure for efficient polysulphide containment, a limited surface area for sulphur electrolyte contact, sufficient space to accommodate sulphur volumetric expansion and the small characteristic dimensions of a sulphur electrode to avoid pulverization, a short pathway for both electrons and Li ions to achieve high capacity at a high power rate, a large conductive surface area on which to deposit the insulating Li$_2$S$_2$ and Li$_2$S in order to preserve the morphology of the electrodes, and suitable electrolyte additives to passivate the lithium surface and so minimize the shuttle effect.\textsuperscript{68}

The literature reports on different strategies that have been considered to improve Li-S battery electrochemical performance, mainly focused on the combination of a conductive matrix with sulphur to form a highly conductive composite. In recent years, carbon-based nanomaterials, including 0-D fullerene, 1-D carbon nanotube and 3-D graphite, have attracted a great deal of interest.\textsuperscript{69, 70}

Several research attempts have focused on the development of carbon/sulphur nanocomposites, in which sulphur particles were embedded in the nanopores of the conductive carbon matrix. They can increase both the electrical and ionic conductivity of the sulphur cathode while at the same time suppressing the polysulphide shuttle phenomenon.\textsuperscript{40, 55, 71}

Using nanostructured sulphur-carbon composite cathodes can considerably improve both the cyclability of the battery and the utilization of sulphur in the battery cycles. The pores in this structure not only act as micro-containers for the elemental sulphur that provides
sufficient contact to the insulating sulphur and promotes the electrical conductivity, but also facilitates the transport of Li ions during the electrochemical cycling and accommodates the produced polysulphides and sulphide ions during the electrochemical reactions.\textsuperscript{3} Preparing a uniform mixture of carbon and sulphur or obtaining a composite of carbon-encapsulated sulphur requires multiple processing steps. Some related works will now be discussed.

Researchers have investigated the use of a sulphur cathode containing carbon nanotube (CNT) in a Li-S battery, and this has demonstrated great cycling stability and coulombic efficiency.\textsuperscript{72}

Composite cathodes containing a sulphur/acetylene black (AB) composite, in which the sulphur was embedded inside the nano-pores of the acetylene black, showed a high discharge capacity and good cycle performance.\textsuperscript{73}

A nano-sized S/PPyA (poly(pyrrole-co-aniline)) composite delivered a high initial discharge capacity and acted as a good conductive matrix, a strong adsorbing agent, and as a firm reaction chamber for the sulphur cathode materials, and it improved both the capacity and cycling stability of the cathode.\textsuperscript{60} It has been observed that the cycling life and specific capacity of the battery are improved when carbon nanofiber (CNF) is added into the sulphur electrode because CNF provides a good electrical connection and structural stability.\textsuperscript{68,74} Ji et al.\textsuperscript{75} showed that loading S in to the porous CNF improves the battery performance. It provides both high conductivity and high surface area for S and reduces the PS solubility. Also this structure can accommodate Sulphur volume changes. Figure 4 shows the SEM images for bare Sulphur and CNF-encapsulated sulphur electrodes. Figure 4(a) shows CNF formed inside the AAO template and Figure 4(b) shows CNF after sulphur infusion and AAO etching with a weight ratio of 3:1 (sulphur to carbon). The energy-dispersive X-ray spectroscopy (EDS) images in Figures 4(d) and (e) confirm the presence of carbon and sulphur in the electrode.
Zhang et al.\textsuperscript{76} introduced a novel polymer, polyaniline polysulfide (SPAN), which can hold an appropriate amount of sulphur. The polymer has polyaniline as the backbone chain and 2 four-member rings with S-S bonds as the side chains of aniline. An ordered mesoporous carbon (OMC) sphere with uniform channels is applied as the conductive agent in the sulphur cathode. Sulphur filled the holes of the OMCs by a co-heating method. The S-OMC composite exhibits excellent cycling performance compared to the bare S cathode.\textsuperscript{46,77} Applying spherical OMC-S as a cathode material provides a battery with high initial discharge capacity and cyclability.\textsuperscript{78} Wang et al.\textsuperscript{79} used microporous–mesoporous carbon which has a high adsorption capacity and conductivity as the sulphur immobilizer to provide a stable cathode and consequently a battery with good cyclability. Also cycle life of Li-S battery extends with encapsulated sulphur in mesoporous hollow carbon capsules. It showed 91\% capacity retention after 100 cycles.\textsuperscript{58}

Recent reports suggest that a multi-wall carbon nanotube (MWCNT) is a promising conductive material that could improve the cycling performance of the Li-S battery. It provides the electrochemical reaction sites with a large interface area, between the MWCNTs and the lithium polysulphides, on which the electrochemical reaction can take place, and accommodates Li$_2$S and Li$_2$S$_2$ without clogging the pores in the cathode.\textsuperscript{80-82} Choi et al.\textsuperscript{50} reported an improved discharge capacity and cycle performance of a Li-S battery with a carbon coating on the surface of the sulphur, which enhanced the electrical contact and adsorption of the lithium polysulphide.

A breakthrough for Li-S batteries is the application of a Graphene-S cathode in the battery.\textsuperscript{83-88} Graphene is a material that could not be imagined 70 years ago. Research on graphene is very new, having explosively started in 2004 following the development of a simple technique to prepare a single-layer graphene sheet.\textsuperscript{89}
Graphene is single layer of sp$^2$-hybridized carbon atoms found in graphite, known for its unusual electronic properties and possible applications.$^{90-92}$ In recent reports, two-dimensional graphene has been considered as a potential electrode material for battery applications, due to its superior electrical conductivity, high surface area, and broad electrochemical window. In comparison to CNT and CNF, it is typically impurity-free and much cheaper. They have many applications in a variety of industries and research.$^{93-96}$ An early example of an improvement achieved with graphene was the production of sulphur–graphene nano sheets (S-GNS) by heating a mixture of elemental sulphur and synthesized graphene nanosheets. The S-GNS composite showed a significantly improved capacity and cycle life compared to the pristine S cathode.$^{83}$ The use of graphene-wrapped sulphur particles as the cathode material in a Li-S battery has also been reported.$^{85}$

A functionalized graphene sheet-sulphur nanocomposite (FGSS) with sandwich-type architecture has been synthesized and studied as a possible cathode material for Li-S batteries. The unique composite structure and good conductivity of graphene contributes to the observed good cycling stability.$^{97}$. Ji et al.$^{84}$ investigated on the graphene oxide-sulphur (GO-S) nanocomposite cathode that displays good reversibility and excellent capacity stability. This improved performance may be related to the reduction of GO by incorporation of S which improves the conductivity of the GO, and diminution of Li polysulfides dissolution due to mild interaction between GO and S.$^{98}$

The design and synthesis of sulphur cathode coated with reduced graphene oxide (RGO) has been reported where the carbon framework serves as a conductive layer and nanoelectrochemical reaction chamber.$^{99}$ A layer-structured sulphur-expanded graphite (EG) composite has been employed as a cathode in Li-S batteries to improve the electrochemical performance.$^{100}$ The EG maintains a layered structure similar to natural flake graphite with a higher surface area that provides sufficient contact to the insulating sulphur and improves the
conductivity. Each layer of EG could be considered as a micro current collector to provide sufficient electrons for a reaction between the cathode materials and lithium ions. The development of graphene materials, and their applications in the electrochemical energy fields, is still in its infancy and many challenges remain.

A cathode should have uniform combination of active sulphur and conductive materials for better performance. Among the components in the sulphur cathode, the binder plays an important role in improving cell performance, especially in regards to the cycle life. A binder should not only have high adhesion between the electrode materials and the current collector, but should also facilitate electron transport and lithium ion diffusion because of the ability to form a good electric network between the active material and conductive carbon.37

Kim et al.101 investigated PTFE +CMC and PTFE + PVA as binder in Li-S battery. These cathodes have larger specific surface area with more contact area between the cathode materials and the electrolyte, leading to decreased interfacial resistance and consequently improved capacity. Jung et al.51 studied the mixed polymer binder system of PVP and PEI in order to maintain the initial morphology of cathode during charge–discharge cycles to improve the cycle performance of battery. The cycling property of polyethylene oxide (PEO) and polyvinylidene fluoride (PVdF) binder with a carbon nanofiber is also investigated and proved that the capacity increased by applying binders.74 Gelatine has been used as a binder in the sulphur cathode, which is electrochemically stable and functions as a highly adhesive which stabilize the structure of the cathode and effective dispersion agent for the cathode materials.37 Table II lists the discharge capacity of improved Li-S batteries by applying different cathode materials.
### Table II. Comparison the discharge capacity of cathode’s materials used in Li-S battery.

<table>
<thead>
<tr>
<th>Cathode materials</th>
<th>Discharge current rate</th>
<th>Initial discharge capacity (mAh g⁻¹)</th>
<th>Cycle number</th>
<th>Residual reversible capacity (mAh g⁻¹)</th>
<th>Electrolyte</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur</td>
<td>0.4 mA cm⁻²</td>
<td>710</td>
<td>50</td>
<td>230</td>
<td>LiCF₃SO₃-DME-DOL</td>
<td>102</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.1 mA cm⁻²</td>
<td>400</td>
<td>50</td>
<td>100</td>
<td>LiTFSI in Tetruglyme</td>
<td>103</td>
</tr>
<tr>
<td>Sulphur</td>
<td>160 mA g⁻¹</td>
<td>1094</td>
<td>80</td>
<td>&lt;150</td>
<td>LiPF₆-EC-DMC</td>
<td>88</td>
</tr>
<tr>
<td>S-MPC</td>
<td>250 mA g⁻¹</td>
<td>1584.56</td>
<td>30</td>
<td>804.94</td>
<td>LiTFSI-DOL-DME</td>
<td>3</td>
</tr>
<tr>
<td>S-Carbon</td>
<td>100 mA g⁻¹</td>
<td>1232.5</td>
<td>50</td>
<td>800</td>
<td>LiClO₄-DEGDME-DOX</td>
<td>25</td>
</tr>
<tr>
<td>S-PPy</td>
<td>50 mA g⁻¹</td>
<td>1280</td>
<td>20</td>
<td>800</td>
<td>LiTFSI-PEGDME</td>
<td>104</td>
</tr>
<tr>
<td>S-Carbon</td>
<td>50 mA g⁻¹</td>
<td>1300</td>
<td>30</td>
<td>700</td>
<td>LiTFSI-EMITFSI</td>
<td>46</td>
</tr>
<tr>
<td>S-PEG-CMK-3</td>
<td>168 mA g⁻¹</td>
<td>1320</td>
<td>20</td>
<td>1,100</td>
<td>LiPF₆-TEGDME</td>
<td>7</td>
</tr>
<tr>
<td>S-PAN</td>
<td>0.3 mA cm⁻²</td>
<td>893</td>
<td>50</td>
<td>600</td>
<td>PVDF Gel Electrolyte</td>
<td>59</td>
</tr>
<tr>
<td>S-MWCNT</td>
<td>168 mA g⁻¹</td>
<td>734.7</td>
<td>100</td>
<td>491.5</td>
<td>LiPF₆/EC/DMC</td>
<td>82</td>
</tr>
<tr>
<td>SPAn</td>
<td>0.2 mA cm⁻²</td>
<td>980</td>
<td>20</td>
<td>403</td>
<td>LiCF₃SO₃/DOL-DME</td>
<td>76</td>
</tr>
<tr>
<td>S-MWCNT</td>
<td>0.1 mA cm⁻²</td>
<td>485</td>
<td>50</td>
<td>300</td>
<td>LiTFSI in Tetruglyme</td>
<td>103</td>
</tr>
<tr>
<td>S-CNF</td>
<td>100 mA g⁻¹</td>
<td>1191</td>
<td>20</td>
<td>700</td>
<td>LiCF₃SO₃-TEGDME</td>
<td>74</td>
</tr>
<tr>
<td>S/PPy-MWCNT</td>
<td>0.1 mA cm⁻²</td>
<td>1309</td>
<td>100</td>
<td>725.8</td>
<td>LiCF₃SO₃-TEGDME</td>
<td>80</td>
</tr>
<tr>
<td>S–PPy Nanowire</td>
<td>0.1 mA cm⁻²</td>
<td>1222</td>
<td>20</td>
<td>570</td>
<td>LiCF₃SO₃-DOL-DME</td>
<td>61</td>
</tr>
<tr>
<td>S/T-PPy</td>
<td>0.1 mA cm⁻²</td>
<td>1151.7</td>
<td>80</td>
<td>650</td>
<td>LiCF₃SO₃-TEGDME</td>
<td>69</td>
</tr>
<tr>
<td>S-OMC</td>
<td>168 mA g⁻¹</td>
<td>934.9</td>
<td>50</td>
<td>500</td>
<td>LiPF₆/PC-EC-DEC</td>
<td>73</td>
</tr>
<tr>
<td>S-PPyA</td>
<td>0.1 mA cm⁻²</td>
<td>1138</td>
<td>80</td>
<td>800</td>
<td>LiTFSI-DOL-DME</td>
<td>71</td>
</tr>
<tr>
<td>S-CNF</td>
<td>335 mA g⁻¹</td>
<td>1285</td>
<td>40</td>
<td>866</td>
<td>LiCF₃SO₃-DOL-DME</td>
<td>60</td>
</tr>
<tr>
<td>S-OMC</td>
<td>0.1 mA cm⁻²</td>
<td>1200</td>
<td>150</td>
<td>730</td>
<td>LiTFSI-DOL-DME</td>
<td>68</td>
</tr>
<tr>
<td>S-MWCNT</td>
<td>60 mA g⁻¹</td>
<td>700</td>
<td>60</td>
<td>482</td>
<td>LiPF₆-EC-DMC-EMC</td>
<td>81</td>
</tr>
<tr>
<td>S-GNS</td>
<td>50 mA g⁻¹</td>
<td>1611</td>
<td>40</td>
<td>700</td>
<td>LiTFSI-PEGDME</td>
<td>83</td>
</tr>
<tr>
<td>S-GO</td>
<td>168 mA g⁻¹</td>
<td>1320</td>
<td>50</td>
<td>735</td>
<td>PYR₁₄TFSI-LiTFSI-PEGDME</td>
<td>84</td>
</tr>
<tr>
<td>S- EG</td>
<td>280 mA g⁻¹</td>
<td>1210.4</td>
<td>50</td>
<td>957.9</td>
<td>LiTFSI- DME/ DOL</td>
<td>86</td>
</tr>
<tr>
<td>S-FGS</td>
<td>168 mA g⁻¹</td>
<td>950</td>
<td>50</td>
<td>800</td>
<td>LiTFSI-DME-DOL</td>
<td>97</td>
</tr>
<tr>
<td>TG^c-S-RGO</td>
<td>200 mA g⁻¹</td>
<td>1290</td>
<td>100</td>
<td>928</td>
<td>NA</td>
<td>99</td>
</tr>
<tr>
<td>S- EG</td>
<td>25 mA g⁻¹</td>
<td>1588</td>
<td>50</td>
<td>1200</td>
<td>LiClO₄-DME-DOL</td>
<td>100</td>
</tr>
<tr>
<td>S- GNS</td>
<td>160 mA g⁻¹</td>
<td>1598</td>
<td>80</td>
<td>670</td>
<td>LiPF₆-EC-DMC</td>
<td>88</td>
</tr>
</tbody>
</table>

- ^a Mesoporous Carbon
- ^b Polypyrrole
- ^c Polyethylene glycol
- ^d The most well-known member of the mesoporous carbon family
- ^e Polyacrylonitrile
- ^f Tubular polypyrrole
- ^g Thermally exfoliated graphene nanosheet

### 3.3.2. Advances in anode

The use of elemental lithium as the anode in Li-S batteries remains a major issue due to safety concerns arising from the formation of lithium dendrites during cycling, which can penetrate the separator and lead to thermal runaway. One way to avoid this safety problem in the Li-S system is to use a high-capacity anode material other than elemental lithium. Some...
researchers have investigated this possibility. A novel lithium metal-free battery consisting of a silicon nanowire anode and a Li$_2$S/mesoporous carbon composite cathode, with high theoretical specific energy, has been reported.\textsuperscript{105} He et al.\textsuperscript{30} designed a Li-S cell with non-lithiated electrode materials. They used graphite anodes and a non-lithiated sulphur composite cathode (Sulphur- acetylene black- PTFE) by incorporating lithium metal foil to provide lithium and so enhanced the performance of the cells.

Li negative electrodes have also been replaced by a Sn–C–Li alloy which demonstrated higher chemical stability towards sulphides.\textsuperscript{106} Since lithium is so reactive, the protected Li anode was introduced to the Li-S battery to enhance the charge/discharge performance by reducing the growth of the solid electrolyte interface (SEI) layer and suppressing the reaction between the Li and soluble polysulphides.

A Li negative electrode with a Li–Al alloy layer can increase the cycle life of a battery.\textsuperscript{107} The protection layer on the Li anode can be prepared using a UV cured polymerization method\textsuperscript{42} It can be seen the protected anode has a smoother and denser surface morphology. The protected anode can suppress the overcharge during the charge process and form a stable SEI layer which causes stable discharge capacity up to 100 cycles in battery. Liu et al.\textsuperscript{108} used an anode of lithium-rich multiphase Li$_{2.6}$BMg$_{0.05}$ alloy foil for Li-S battery. This alloy is composed of Li$_3$B$_4$, Li, and Li$_3$Mg$_7$ and provides a battery with lower polarization and longer cycle life than the pure Li anode based battery due to its improved morphology. Figure 5 compares the surface morphology of a pure and alloyed anode. As shown in Figure 5, lots of dendrites are detected on the pure Li surface after 70 cycles, while Li$_{2.6}$BMg$_{0.05}$ anode inhibits the formation and growth of Li dendrites and shows a more homogeneous morphology.
3.3.3. Development in electrolyte

For the successful operation of a Li-S battery, the electrolyte should have high ionic conductivity and enough PS solubility, electrochemical stability, chemical stability regarding the lithium, and safety. Also it should stabilize the chemical composition and structure of the sulphur cathode by suppressing dissolution of polysulphide. The capacity of a sulphur electrode is insufficient when using conventional organic liquid electrolytes due to the high solubility of polysulphides during both the charge and discharge processes. A number of strategies have been explored to address the polysulphide solubility issue, including the design of adjusted organic liquid electrolytes, the use of ionic liquid-based electrolytes, and the application of polymer electrolytes.

Choi et al. studied the effect of different liquid electrolyte combinations based on DME, DEGDME, TEGDME and DIOX on Li-S battery efficiency; and Chang et al. researched on a mixed electrolyte of TEGDME and DOXL. It is found that a mixture of electrolytes is more suitable because of the lower viscosity and the better wetting of the electrodes which facilitate ion transportation. The electrochemical performance of Li-S battery has also been investigated using LiClO$_4$ DOL/DME as electrolyte and proved that an optimum mixture of these solvents led to better cycle performance. DME offers higher PS solubility and faster PS reaction kinetic, but high content of DME could increase the resistance of the battery due to the high solubility of polysulfide, whereas DOL could improve the interfacial contact between the electrodes and electrolyte.

Polymer electrolytes have attracted a great deal of research interest for use in the Li-S battery due to higher safety because of both the absence of flammable organic solvents and the much lower reactivity toward lithium; also they can control the dissolution of polysulphides. These electrolytes are divided into two groups: (i) Solid polymer electrolyte (SPE) in which polymer acts as both mechanical matrix and solvent to dissolve lithium salts;
(ii) Gel polymer electrolyte (GPE) in which a polymer is gelled by conventional electrolyte solutions. Here polymer only provides dimensional stability. GPE has been more attention-grabbing due to higher ion conductivity and major manufacturers of Li-ion batteries have incorporated this electrolyte.\(^{115}\) It has been reported that PEO with ceramic filler and lithium salts in the Li-S battery possesses good mechanical properties and ionic conductivity. This polymer electrolyte postpones diffusion of the lithium polysulphides and sulphur dissolution, leading to decreasing self-discharge, also the polar groups in the polymer chains can dissolve the ionic salts.\(^{116, 117}\) Scrosati et al.\(^{106}\) improved the overall operation and safety of the battery by replacing the common liquid organic solutions by a gel-type polymer membrane, with trapping (EC: DMC/LiPF\(_6\)) solution saturated with lithium sulfide in a (PEO/LiCF\(_3\)SO\(_3\)) polymer. In another work the discharge process of Li-S with PVdF gel polymer electrolyte has been investigated.\(^{118}\) The PVdF gel polymer electrolyte was prepared by LiCF\(_3\)SO\(_3\) as lithium-ion resource, tetraglyme as plasticizer, and PVdF as a gelling agent which shows a high first discharge capacity of 1268 mAh g\(^{-1}\).

Another approach is using ionic liquid-based electrolytes. An ionic liquid of N-methyl-N-butyl-piperidinium (PP14) was synthesized as an electrolyte in the Li-S battery and showed good chemical and electrochemical stability towards lithium and sulphur. The dischargeability and reversibility of battery were improved because of a stable structure of sulphur due to suppressed dissolution of polysulfides in the electrolyte.\(^{111}\)

Another efficient and economical strategy to modify electrode/electrolyte interface in Li batteries is using an additive at small concentration in the electrolyte. LiNO\(_3\) is mentioned as an additive in electrolyte for Li-S batteries by Aurbach and his co-workers\(^{119}\). It this case, solvents, polysulphide and LiNO\(_3\) additives reacted with lithium to form a protective surface film (SEI) on the surface of the Li anode; this layer not only protected the lithium anode from chemical reaction with the dissolved polysulphide but also prevented PS from
electrochemical reduction on the Li anode surface and inhibited the loss of active materials.\textsuperscript{53, 120} Although the cycle life and discharge capacity of the Li-S batteries improved, the safety was reduced because of the strong oxidation of LiNO$_3$. Thus, a new additive to the electrolyte for Li-S batteries has been explored, LiBOB (lithium bis(oxalato) borate).\textsuperscript{121} This is thermally more stable, and since its hydrolytic decomposition products are less toxic and corrosive, it is more environmentally friendly. In batteries with LiBOB, a passivating surface film on is formed on the lithium anode giving a higher discharge capacity, and a better cycle performance.

3.4. Application of Li-S battery in electric vehicles

Currently, the transportation sector is the main consumer of fossil fuels that are a contributing factor in global greenhouse gas (GHG) emissions. Over recent decades, extensive effort have been devoted to the development and introduction of electric drive vehicles, including both electric and hybrid vehicles (HEV), as a fundamental solution to the serious emission and pollution problems, to the benefit of society.\textsuperscript{46, 122} In 1996 General Motors released the EV-1, the first all-electric car from a major manufacturer.\textsuperscript{26} EVs eliminate or reduce toxic exhaust emissions from automobiles, especially in urban areas of high air pollution and consequently reduce carbon dioxide emissions, addressing concerns over global climate change. This generation of vehicles is considered to promise a saving of non-renewable energy sources by reducing dependence on oil and gas for transportation. Hybrid electric vehicles are now commercially available and growing in market share and there is increased interest internationally in the development and commercialization of modern battery-powered electric vehicles. Leading companies in this industry, such as BMW, Ford, Nissan, Tesla and Daimler Benz, use lithium-ion batteries as the energy supplier for the EVs they have produced.\textsuperscript{123, 124} However, in order to develop Li-ion batteries of adequate energy density for EVs to have an efficient driving range, it will be necessary to go beyond
present strategies and develop cells with higher energy density and lower costs. Li-S batteries are good candidates for this.\textsuperscript{125, 126} Sion Power Corporation\textsuperscript{127} is working on the application of the Li-S system for EV applications. They have developed a cell that can demonstrate 350 Wh kg\textsuperscript{-1} in unmanned aerial vehicle flights. High efficiency Li-S batteries could provide appropriate energetic and environmental performance. Applying the Li-S battery in EV’s can reduce the charge time and increase the cycle life of the EV batteries. It is predicted that Li-S batteries will be commercially available between 2020 and 2025.\textsuperscript{122}

4. Conclusions and outlook

In recent years, significant effort has been made to improve the performance of Li-S batteries as an electrochemical energy storage device with high power output/input, excellent cycle life and a low cost, for use in a number of applications ranging from portable electronics to electric vehicles. Although theoretically the energy density of Li-S cell is high, there are many challenges to be addressed before theory becomes practice. As highlighted in this review, such challenges are frequently rooted in materials discovery and optimization because the efficiency of a battery depends on the electrode and electrolyte performance.

This review presents the current status of the Li-S battery and discusses its challenges and its electrochemical reaction mechanism. Generally, one of the main problems of the Li-S battery is its poor cycle life, mainly caused by PS dissolving into the electrolyte. To overcome this hurdle, all cathodes, anodes and electrolytes should be modified. Research has demonstrated that applying a sulphur/carbon-based composite as the cathode has opened up a new way to Li-S batteries with high efficiency. Among of the many carbon-based materials, graphene provides hope because of its high electrical conductivity, high surface area and low cost. The Li metal anode can cause some safety problems. However, promising results have been achieved recently in Li/S battery efficiency by using a non-lithium metal anode such as silicon, or by applying protected anode technologies. As mentioned in this review, electrolyte
has a direct effect on cell performance and various electrolytes have been investigated for the Li-S battery and, among these, polymer electrolytes have been regarded as good candidate for future researches on Li-S battery because of their safety and easy design and fabrication.

Although there has been promising progress, many aspects of Li-S batteries are not fully understood, and will require additional investigation. High initial capacities above 1000 mA h g\(^{-1}\) can be achieved with an improved cell, but maintenance of the initial cathode morphology is difficult. To overcome these issues, researchers are explore more profound mechanisms and reasons of the capacity fading in Li-S batteries after cycling. These issues will be solved when all the problems are identified. In addition, Li-S batteries have to compete with other energy conversion and storage technologies, such as fuel cells, which are promising energy devices for the transport, mobile and stationary sectors. Meanwhile, Sion Power Corporation is focusing on developing the commercial Li-S battery and claims that the Sion Power's Li-S will be the next rechargeable power source for a wide variety of applications, including unmanned vehicle systems, military communications and electric vehicles.

The ultimate goal is to develop a low-cost, high-throughput, environmentally friendly battery. In order to reach this ambitious goal, there must be a better understanding of the current situation with Li-S batteries. This review may provide some new insights and opportunities into the challenges in this area, and so help move towards a commercially available Li-S battery.

Acknowledgements

This research is financially supported by the Australian Research Council (ARC) through ARC Discovery Project DP110101974.
References


Figure Captions

**Fig. 1.** Schematic illustration of a typical lithium ion battery.

**Fig. 2.** Schematic configuration of Li-S battery based on graphene- sulphur composite (G-S) cathode.

**Fig. 3.** Voltage profile of the first discharge of a Li-S cell. Reproduced from Zhang,53 (written permission has been obtained from the previous publisher).

**Fig. 4.** SEM characterizations of hollow carbon nanofiber-encapsulated sulphur: (a) anodic aluminum oxide (AAO) template after carbon coating, (b) hollow carbon nanofiber-encapsulated sulfur after etching away AAO template, (c) cross-sectional image of hollow carbon nanofiber/S array, (d) carbon elemental mapping of (c) and (e) sulfur elemental mapping of (c). Reproduced from Zheng et al.,68 (written permission has been obtained from the previous publisher).

**Fig. 5.** SEM images of surface morphologies after 70 cycles: (a) Li anode; (b) Li2.6BMg0.05 anode. Reproduced from Liu et al.,108 (written permission has been obtained from the previous publisher).
Figure 4
Click here to download high resolution image
Figure 3, black and white

Click here to download high resolution image

Graph showing the variation of potential (V) vs. Li/Li\(^+\) with capacity (mAh g\(^{-1}\) sulfur) at a constant current density of 0.2 mA cm\(^{-2}\). The graph is divided into four regions labeled I, II, III, and IV.