

Review on performance optimization of Lithium Sulphur Batteries (LiSBs) using carbon based electrodes

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ABSTRACT

Presently, researchers' and experts are currently dealing with ways to maintain and improve the best performance of several energy storage technologies. This review focuses on how adding carbon derivatives to lithium sulfur battery (LiSBs) electrodes can reduce capacity fade, resistance, breakdown and poor performance while also enabling the best possible use of LiSBs in a variety of devices. Their rate as regards specific capacitance, energy and power densities, life duration, lightweight, etc., are among these optimal performances. The global energy crisis focused more scientists' attention on how to enhance the performance of LiSBs devices for the benefit of humanity. Numerous carbon derivatives, including GO, rGO, carbon nanotubes (CNTs), etc., have advantageous properties that raise the efficiency of energy storage technologies. This review looked at LiSBs and the impact of carbon derivatives addition on their storage capability, cycle stability, life span and durability.

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1. INTRODUCTION

Climate change and environmental pollution are major challenges facing our world. The growing world pays for the dam-

aging effect of toxicity, global warming and depletions of fossil fuels, which technological advancement increased and sustained due to human activities [1–3]. Finding environmentally friendly sources of energy as alternative to usual hydrocarbons and developing high capacity batteries, solar cells, supercapacitors, etc., for energy fabrication and storage devices have kept

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Figure 1. Samples of sulphur batteries [14].

researchers all over the world in laboratories [2, 4, 5]. More also as the world is gradually transiting to electric vehicles; the need to review the impact of hydrocarbons, fossil fuels like petroleum oil, coal and natural gas, which have substantial percentage of the global electricity generation to our environment, is inevitable [6–8]. Environmental pollutions caused by constant depletion of fossil fuel resources have terrible health implications, and other adverse impacts to humanity; however, because of the ever increasing human population, the energy need of the society have drastically increased, requiring more effective energy fabrication and storage systems [8–11]. Since energy is an evitable need of man, there can only be an upgradation, and more environmental approaches toward its generation and storage. Especially as there is high demand in their most portable form, for usage in electrical and electronic gadgets like laptops, smart phones, wrist watches, ear pod and the likes [12, 13]. Recently, portable electric vehicles and hybrid electric vehicles have taken the centre stage enhancing the need of our mobility and information rich, global society [10]. Since LIBs are considered as the best energy storage preference for electric vehicles (EVs) and hybrid electric vehicles (HEVs), most electric controlled devices employ them for energy storage, as is shown from Figure 1. Lithium ion batteries (LIBs) has a remarkable property compared to most other energy storage devices due to its ability to operate with a constant voltage through charge or discharge process, while working voltage of other energy storage devices like supercapacitors decline linearly in their cycling process [15, 16]. However, main difficulties preventing the usage of LIBs in EVs and HEVs is still its thermal management [17]. Though already in commercial use, Lithium-ion batteries have their shortcomings, thus the need for further research on lithium batteries. One of the most promising energy conversion solutions that can satisfy the requirements for the proper driving range of battery electric vehicles (BEVs) is the use of LiSBs batteries. The theoretical capacity and energy density of a LiSBs system are 1675 mAhg^{-1} and 2500 Whkg^{-1} , respectively. Sulphur is abundant in nature and is therefore a cheap raw material, which lowers the cost of LiSBs systems [18]. LiSBs need to be improved despite being promising because their small active materials consumption, little sulphur stuffing and reduced cycling stabilities may diminish the effectiveness of their practical applications [18]. Compared to other carbon-sulphur composites that researchers have suggested in the literature to boost

the effectiveness of lithium-sulphur batteries, graphene offers a better promise for this use. Current collectors, electrolytes and anodes could all benefit from the use of graphene and its derivatives [19]. Since, LiSBs was capable of trapping polysulphur and increase the battery conductivity, a current collector made of graphene was able to achieve exceptional lifespan and rate capability. Therefore, in this review, we will concentrate on using carbon-based electrodes to increase the performance of LiSBs [20], aimed at ways of enhancing performance of LiSBs using carbon-based derivatives. These performances include storage capability, cycle stability, life span and durability. Since ether-based electrolytes are currently the most suitable electrolyte for LiSBs, the electrodes must meet a number of conditions in order to produce high energy density LISBs. One such need is compatibility with ether-based electrolytes. In order to get a relatively high voltage for LiSBs, the electrode material should also have a lower potential for Li^+ deintercalation and intercalation. Finally, the capacity needs to be on par with LiBs. The problems with LiSBs, potential solutions, and upcoming advancements in the search for an appropriate high energy and power density electrode material were all thoroughly examined in this review.

1.1. LISBS OPERATIONAL MECHANISMS

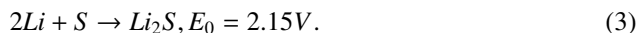
The market for rechargeable batteries for portable electronics, including smartphones, laptops, and other universal mobile technologies, has recently been dominated by Lithium ion batteries [21]. Contrarily, traditional Lithium ion batteries are expensive and have inadequate energy density (theoretically, $350 - 400 \text{ Whkg}^{-1}$, actually, $100 - 220 \text{ Whkg}^{-1}$) (typically, a graphite anodes and lithium transition metal oxides cathodes) [21]. These drawbacks prevent their usage in power-intensive applications like fixed energy storage and long range electrical vehicles [22]. The development of small, lightweight rechargeable batteries with improved performance as well as higher energy densities and longer cycling lifetimes was sparked by the search for such novel energy-storage devices. LiSBs have a high theoretical specific capacity of 1672 mAhg^{-1} of active material and cathodes that are primarily formed of elemental sulphur [23]. Sulphur composite cathode, electrolyte, separator, and metallic lithium anode make up LiSBs [24]. Electrons and Li ions are created during the discharge of the lithium metal anode and then diffuse to the cathode side through the electrolyte. While this is happening, electrons from the external circuit travel to the sulphur molecule in the cathode and reduce the elemental sulphur to lithium sulphide, as shown in the schematic design in Figure 2 [25]. Anode: oxidation process involves an electron loss. The ultimate electrochemical reactions of LiSBs can be streamlined using equations (1–3).



cathode: reduction reaction, electrons are obtained,



total battery reaction (discharge process),



Since charging is in opposite process from draining, when a battery is being charged, an exterior power sources drives electrons

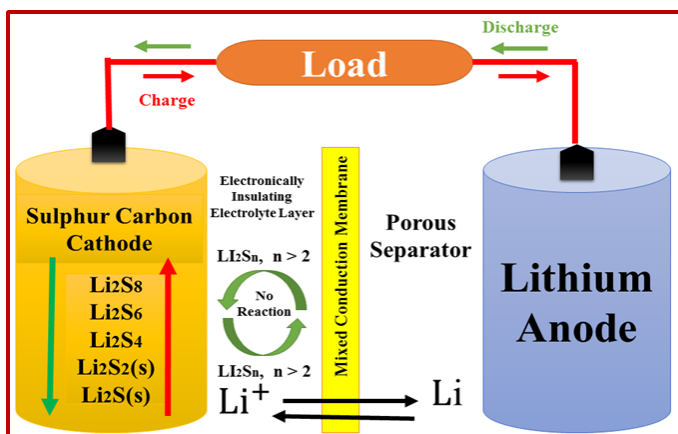


Figure 2. Operation features of LiSBs [25].

to travel from cathode to anode through an outside circuit while lithium ions diffuse through the separator and return to the anode [26]. In general, an LiSBs comprises a lithium anode, sulphur cathode and a separator with liquid or solid electrolyte as represented in Figure 2.

1.2. FUNDAMENTAL FEATURES OF LISBS

Sulphur is a new family of active material for LiSBs that has received several interests because of its exceptional features. Polysulfide migration can be effectively stopped thanks to the covalent bond (S-S bonds) between its atoms, which cannot be severed from the molecular chain [24]. Developing rechargeable LiSBs possessing high energy densities and long-term cycle capacities requires a complete understanding of sulphur and its redox processes [27]. With a potential specific capacity of $1,722 \text{ mAhg}^{-1}$, sulphur is a promising cathode material. This is five times greater than the specific capacities of conventional cathodes material centred on transition metal oxides or phosphates. Sulphur likewise has extra benefits, including affordability and environmental friendliness [28]. Other outstanding qualities that made sulphur the best cathode material for great specific capacity and unlimited cycle stability include: (1) sufficient sulphur content; (2) decent conductivities using mixed conductive materials within the cathodes; (3) elastic assembly to safeguard volume changes; and (4) techniques for trapping polysulphides within cathodes [26].

2. LISBS ELECTRODES

The appropriate investigation of electrochemical changes or reactions in order to get optimum or less performance within LiSBs electrodes during cycling leads to better understanding of appropriate materials or conditions to use in synthesis or fabrication of LiSBs electrodes. In addressing these issues, methodology adopted or considered to improve the performances should also consider availability, cost, and toxic nature of materials and methods. Several strategies such as controlled morphology, introduction of artificial defects (doping) in the nanostructured materials, nanostructured doping, surface coating and functionalization, etc., have been employed towards enhancing electrode performance. In addition, abundant interests have also been channeled in detecting new cathode materials that can accomplish the de-

sired equilibrium among performance, affordability, availability, and environmental requests [29].

2.1. LISBS CATHODE

As was already mentioned, the LISBs cathode presents a number of difficulties, including the shuttle effect, slow electrical and ionic transport, and high over potential voltage during first charging. Compared to the outcomes described by the early published works, the over potential voltage has been significantly decreased by synthesizing nanosize Li_2S , covering the Li_2S using Li^+ conductive materials or introducing a redox mediator in the electrolytes. The activation barrier does not now pose a significant obstacle to the practical use of Li_2S cathode material. Furthermore, the high over potential voltage only appears during the initial charging phase and disappears after subsequent cycles. Hence, the high over potential voltages difficulties are small. Low electronic conductivities and the shuttle effects are the hardest and most pressing issues for Li_2S cathode materials, and both will have a significant negative impact on the cycle life and practically available capacity. As a result, scientists have worked extremely hard to increase the electronic conductivities and reduce the shuttle effects for Li_2S cathodes. The most efficient way to accomplish these objectives is to form composites of Li_2S with carbon materials. Due to its great electrical conductivities, carbon materials can first establish sufficient electrons network in order to transfer of electrons from the current collectors to the active materials [30]. Subsequent, carbon materials have strong mechanical features that can preserve the structural integrity of the cathodes in the course of cycling [30]. However, different production methods enable carbon materials' morphology to be modified. Carbon compounds, for instance, can be converted into hollow spheres, sheets (like 2D graphene), and carbon nanotubes [31]. Carbon can be utilized in a variety of morphologies to generate electrodes with increased adaptability. Hence, to avoid the shuttle effects, it is easy to make porous carbon materials that can grip and absorb polysulfide. It is simple to add extra elements or groups to the surface of carbon materials or derivatives so that they can chemically bond to polysulfide and end forfeiture of electrodes active materials. The configurations, texture, conductivities and surface properties can all be specifically adjusted for the LiSBs electrodes when carbon material is fused as composites. Numerous researches have been concentrated on developing LiSBs/carbon composite in order to address the problems with LiSBs electrode materials.

2.1.1. Graphene Based LiSBs Cathode

Several features prompted the use of graphene in doping and forming composites of electrodes materials for energy storage devices as listed below:

1. In order to obtain high utilization of active sulfur material, the cathode can benefit from a good conductive network thanks to graphene's better electrical conductivity.
2. The enormous pore volumes that graphene frameworks can provide are essential for loading insulating sulfur, and they have a high tolerance for the volume fluctuations that occur in sulfur cathodes during frequent charging and discharging cycles.

- Materials made of graphene can satisfy the stringent specifications for Sulphur cathode frameworks.
- In order to provide rapid transit of Li⁺ during the redox process, the three-dimensional (3D) interconnected hierarchical macro porous networks of graphene materials may accommodate sulfur species, prevent the diffusion of polysulphides into the electrolyte, and favor the electrolyte's diffusion [32].

2.1.2. LiSBs Based Conductive Polymer Composite

For LiSBs cathode materials, conductive polymers have been thoroughly investigated [33, 34]. For instance, the use of polypyrrole on the LiSBs cathode has been documented in various articles. Conductive polymers can be advantageous to the cathode from the two perspectives listed below when used as a conductive addition, which includes the flexibility and malleability of the polymer allowing for customization of LiSBs by creating good contact with the active substance. However, the polymer's functional groups have the ability to efficiently absorb polysulfide, which reduces the shuttle effect and improves cycling efficiency. To our knowledge, much less study has been done on the LiSBs/conductive polymer composite than on the LiSBs cathode. High-performance Li₂S cathodes were made using an in situ synthesis of Li₂S/polypyrrole composites by Seh *et al.* [35] The N element in polypyrrole had an advantageous Li-N interaction with Li₂S, as demonstrated by high-resolution XPS, which allowed polysulfides to be tightly bound to the surface of LiSBs. In order to create effective electron routes, the polypyrrole was in close contact with the LiSBs, which led to the resultant composite's good cycling performance and rate capability.

2.2. GRAPHENE BASED LISBS ANODE

Anode is one of the essential and vital components in LiSBs; it shows an essential role in determination of general productivity of LiSBs. Recently, most LiSBs anodes are commonly fabricated using graphitic carbon; this graphite material possesses limited theoretical capacity and diffusion path for Li⁺ dispersion is very long, which results in small energy and power densities of LiSBs. However, researchers are looking for ways of enhancing anode material to withstand ever-expanding request for next-generation LiSBs. To solve problems associated with small theoretical capacity and long diffusion path length, properties of anode materials, varieties of nanostructured carbon derivatives like GO, rGO, CNTs, CNFs and their composites materials are receiving serious attention [36]. Carbon derivatives' morphology can be controlled to produce porous, hollow, needle, rods, etc. nanostructured nanocomposite materials that deliver an improved surface-to-volume ratio, electrode/electrolyte interactions, short ionic diffusion length, and increased conductivity [22]. The Li anode in the LiSBs has three main issues: (a) corrosion (b) small Coulombic efficiency and (c) uneven morphologies of the lithium coating, caused by parasitic interactions with dissolved polysulfide (PS) [26]. Both organic electrolyte solvents and PS cause the lithium to retreat. Various interactions deplete Li⁺ metal and produce an undesirable passivation coating, prompting LiSBs to lose capacity. The primary cause of the LiSBs thermal runaway at abundant temperature has also been

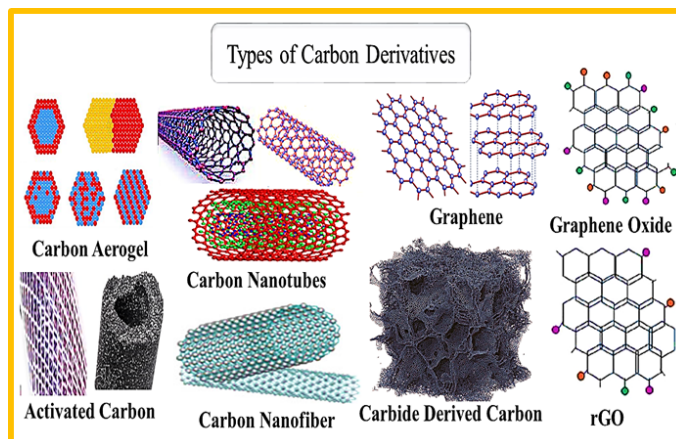


Figure 3. Types of carbon derivatives [37].

identified as the reactions amongst liquefied PS and Li anode [26].

3. CARBON AND ITS DERIVATIVES IN LISBS

There are many carbon derivatives as shown in Figure 3. Various carbon derivative affect sulphur differently as will be discussed in later sections

3.1. GRAPHENE MATERIALS IN LISBS

Graphene, a carbon material one atom thick with exceptional electrical conductivity and mechanical elasticity, recently triggered success in LiSBs. For instance, a graphene and Sulphur composites material by Zheng *et al.* [38] with sulphur particles coated in polyethylene glycol (PEG) and graphene sheets demonstrated consistent capacity of 600 mAhg⁻¹. While the manufacturing of graphene-sulphur composite cathodes is often difficult for large-scale use, they show promising electrochemical performance. Examples of materials that have been used to increase conductivity and prevent sulphur agglomerations include graphene/sulphur/polyaniline composite, graphene wrapped hair derived carbon/sulphur composite and graphene derived carbon sulphur nanocomposite. These materials may possibly enhance cycling stability and decrease the impedance of LiSBs [39, 40]. Graphene is a sheet of refined graphite in which the atoms are densely and closely packed. These graphite atoms that formed graphene are arranged systematically and neatly hexagonal configuration [37, 41]. Their unique features like great specific surface area, good electrical conductivity and established chemical reaction (inertness) make them a good candidate for energy storage devices. The high malleable characteristic gives graphene an edge over activated carbon because it can be reformed into many shapes, other derivatives have their unique characteristics too as shown in Figure 4. Graphene sheets can also be used directly as electrode materials without collectors for transferable supercapacitor application [42]. Additionally, graphene demonstrates effectiveness in improving the sulfur electrode's conductivity and reducing polysulphide migration to the anode, both of which have a major positive impact on the usage and cycle life of the active materials [37]. Due to its exceptional electrical conductivities, high specific surface areas, huge pore volume, and outstanding structural stability, graphene is considered as one of

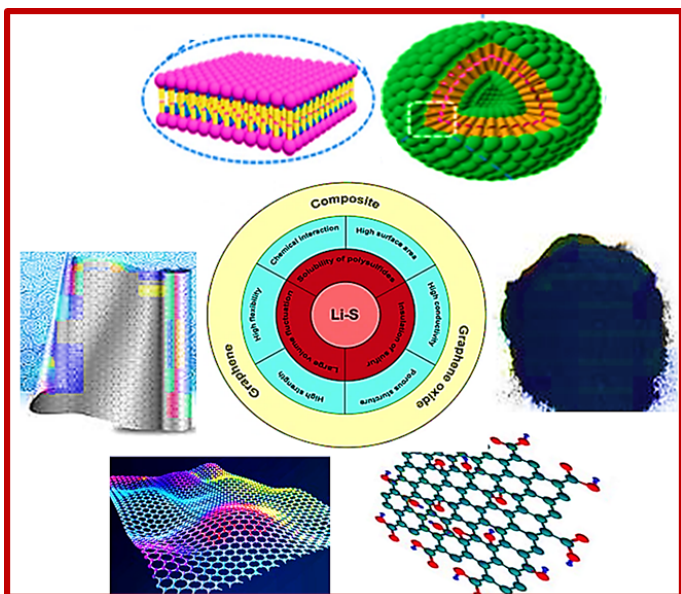


Figure 4. Graphene derivative performance in LiSBs [42].

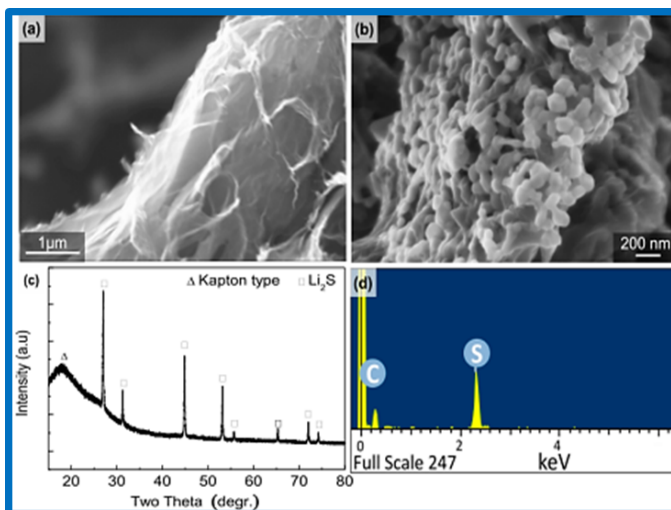


Figure 5. (a-d): Selected microstructure characterizations [39].

the greatest promising conductive matrixes LiSBs. Due to its many preparation techniques, it can also have a variety of traits and qualities, allowing it to be employed in various Li-S battery components [43]. A sulphur/graphene composite was created by loading elemental sulphur into three-dimensional graphene (3D graphene) and then being assembled using a metal ion aided hydrothermal process [44]. The S@3D graphene composite displayed a high specific capacity and steady capacity retention when the sulfur concentration was up to 73 wt%. High-rate discharge/charge capability was also made possible by the unique 3D structure. Their findings demonstrated the potential of the S@3D-graphene composite as a cathode for high-rate performance LiSBs. However, benefits of containing energetic sulphur, preventing the disbanding of soluble polysulphides and offering adequate electrical conduction. Park *et al.* studied the possible usage of sulphur-impregnated graphene composites as a cathode material by Park *et al.* [42], after 50 cycles were completed in a voltage range of 1.8 - 2.6 V vs. Li/Li⁺, they noticed virtuous cyclic retaining of 67% and a high discharge capacity of 1237 mAhg⁻¹.

3.2. LISBS BASED GRAPHENE OXIDE (GO) AND REDUCED GRAPHENE OXIDE (RGO)

The most important of graphene derivatives, known as graphene oxide (GO), is frequently made using Hummer's approach [14]. GO is more adaptable than defect-free graphene because it has respectable conductivity, mechanical characteristics, and a comparatively strong chemical connection with polysulfide [38]. The excellent qualities of graphene and GO are particularly advantageous for Li-S batteries. The cycle efficiency of lithium-sulphur batteries has also been reported to be significantly improved by graphene oxide (GO) by Wu *et al* [39] network anchoring sulphur [45]. Ex situ and in situ surfaces, coatings and layers were combined to prevent the nanostructured Li₂S electrodes used in Wu *et al.* [40], Li-S cells from unfavorable interactions with the electrolyte. Conductive graphene or carbon shell was coated on

micro-scaled Li₂S particles to improve the Li₂S performances and stability [39]. The rGO (multiwalled graphene) powder in Figure 5 (a) shows a typical shape with a highly clean surface and linked walls. They discovered 100 – 200 nm Li₂S nanoparticles that were coupled to one another after the Li₂S was deposited. Due to the high point of Li₂S, the CVD deposition did not visibly alter the particle size as shown in Figure 5 (b). We also intended to reduce damages within CCVD shell round the discrete particles for the duration of electrode fabrication and collaboration by generating these composites, where many interconnected Li₂S are deposited on graphene and bonded to each and the substrate surfaces. Through X-ray diffraction (XRD) experiments, Figure 5 (c) demonstrates that only the pure and singular crystalline phase of Li₂S was present following the CCVD step. Energy dispersive spectroscopy (EDS) data are shown in Figure 5 (d), illustrating the absence of elements besides S and C.

3.3. LISBS IN COMPOSITE OF GO AND RGO

The exceptional compatibility of graphene and its derivatives with other materials, such as carbon compounds, polymer and metal complexes, is their unmatched advantage. This compatibility opens up a variety of rational design options to address their inherent drawbacks, such as combining polysulphide with graphene, GO, rGO or other carbon derivatives with high conductivity. Carbonaceous materials are frequently used with graphene/GO/rGO to improve ions/electrons conductivities or capacity to capture polysulphides due to their availability and diversity [46]. Therefore, a different approach is to combine graphene/GO with conductive polymers to create a composite that not only physically encapsulates but liquefied polysulphides but also dampens volume fluctuations to avoid cathodes from being expanded [47]. Some polymers may improve chemical reactions or conductivity with sulfur or polysulphides. Additionally, carbon nanotubes (CNTs), a kind of carbon with a unique 1D shape and exceptional conductivity, have been used in a variety of applications [48]. Li-S battery performance was significantly enhanced by CNT reinforced graphene/GO composites [49]. Researchers have established that metal oxides fre-

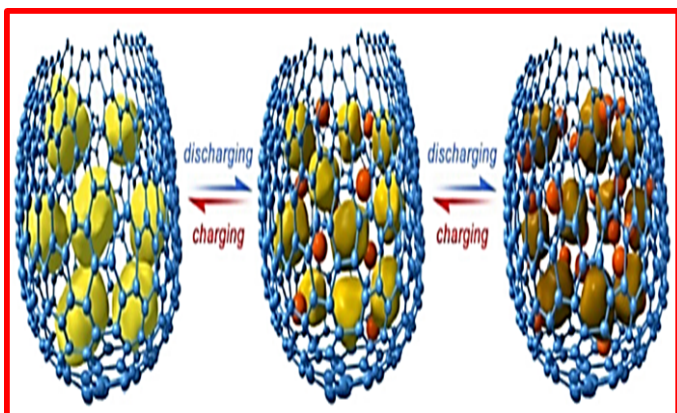


Figure 6. Sulphur entrapment in graphene support for LiSBs during the charge/discharge cycle [39].

quently display high ion and molecule absorption. Consequently, graphene/GO/rGO has been composited with metal oxides, metal nitrides, metal carbides, or metal sulphides, making such topologies attractive for high-performance Li-S batteries. In the end, different substances, oxides, and materials, including nanomaterials, can be mixed with graphene and graphene oxide to create the composites required for a specific output. Notably, graphene, GO, and even rGO can be combined to create an improved composite that can make up for each of their distinct shortcomings [26].

3.4. LISBS IN HIERARCHICAL-POROUS GRAPHENE (HPG)

The placement of components parts in a thoughtfully calculated structures, which nanocarbon frameworks serves as both an electronics conduits to the capture dynamic materials and a miniature electrochemical reaction chamber, is the key to creating a high performance electrode for Li-S batteries [23]. Moreover, nanocomposite for LiSBs was designed and created with sulphur trapped in hierarchical porous graphene. The sulphur/lithium polysulfide were thought to be trapped in the hierarchical porous graphene (HPG), as seen in Figure 6. The Li^+ ions will diffuse into the graphene during the discharge process and combine with the original sulphur particles to create soluble lithium polysulphides, which is anticipated to be contained by the graphene. Table 1 is the summary of LiSBs Performances using different carbon compounds

4. CURRENT PERFORMANCE OF LISBS

In this section, various advantages and disadvantages of LiSBs in present industries, homes, hospitals, technology and various uses are discussed.

4.1. BENEFITS OF LISBS

Sulphur, a major raw material fabrication of LiSBs cathodes, is inexpensive, plentiful and non-hazardous; hence, the LiSBs is better environmentally and economically friendly choice compared with LIBs. The cell cost of a LiSBs is lower compared to LIBs (approximately 100 USD per KWh) [60–62]. Additional remarkable advantage of LiSBs is it is discharged to a zero percent charged position and do not require successively recharging

for their storage [63, 64]. Therefore, LiSBs can stay without discharging for free long-standing storage days when it is not used since it is devoid of severe capacity degradation or damage. This is a significant feature of LiSBs, as LIBs must be recharged severally on the course of long-term storage in order to avert permanent capacity damage. Additionally, LiSBs constituents material permit very lightweight materials, as slight as 1.0 g cm^{-3} , which is much smaller compared to characteristic LIBs. There is additional important superiority that LiSBs have compared to LIBs, the aeronautical and submarine application need rechargeable batteries as small weight as possible, it is more reliable using LiSBs in aeronautical and submarine applications [65–67].

4.2. IMPERFECTIONS OF LISBS

Despite the LISBS extraordinarily high theoretical energy density, the LiSBs meaningfully lower real energy density values are major barriers to their commercialization. One of the main causes of the LiSBs low commercialisation is their intricate functioning mechanism. The problem is seen primarily in the transformation of elemental sulphur (S8) into the final reduction product, lithium sulphide (Li_2S). A lot of effort has been spent into finding a solution to this problem. During the discharge process, an intermediate known as LiSBs (Li_2S_x , $3 < x < 8$) is created when elemental sulphur is reduced. LiSBs can diffuse from the cathode after becoming soluble in the electrolyte.

The distance between soluble polysulphide chains shorten as the discharge procedure progresses, affecting the viscosity of electrolyte in use. The final discharge products, Li_2S_2 and Li_2S , are solid protecting compounds that can increase LiSBs resistance by passivating the cathodes conductive surfaces. The charging technique, which entails oxidizing solid products ($\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$) back into soluble form and then transforming them into elemental sulphur, is also challenging. This last stage is determined by the voltage charge cut [68]. It is difficult to detect distinct polysulphide varieties, because the reactions differs significantly dependent on the electrolytes/electrodes configurations. The electrolyte viscosity changes as the soluble polysulphide chains get shorter during the discharge process. The final discharge products, Li_2S_2 and Li_2S , are solid protecting compounds which increase LiSBs resistance by covering the cathodes conductive surfaces. This charging technique, which entails oxidizing solid products ($\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$) in reverse soluble arrangement and then transforming them to elemental sulphur, is also challenging. The voltage charge cut determines this final step [68]. Individual polysulphide species cannot be distinguished with clarity and the reactions fluctuates significantly dependent on the electrolytes/electrodes configuration. Since the primary reaction in a LIB is the movement of Li^+ ions amid anode and cathode, this tendency stands more pronounced in case of a LiSBs. Even this particular illustration is enough to complicate matters for researchers and make it harder for them to decide which material to use to create a LiSBs High-performance component materials may not be compatible with one another, thus research on each material must be done individually and in a different environment. Despite having a large theoretical and gravimetric energy capacity, using lithium metal as the anode can have drawbacks of its own; this is principally responsible for the limited lifespan of LiSBs. The reduction potential of lithium, a

Table 1. Summary of LiSBs performances with various carbon compounds.

S/N	Cathode	Anode	Specific Capacitance (F/g)	Retention Cycles Completed	Capacity@	References
1	Lithium Sulphide/Microporous Carbon	Graphite	660	91.0% @ 150		[50]
2	Ball-milled Li ₂ S/Graphene	Graphite	809	50.0% @ 100		[51]
3	Lithium Sulphide@Porous Carbon	Graphite	470	57.4% @ 30		[52]
4	Li ₂ S @ Graphene Nanocomposites	Graphite	730	60.0% @ 200		[53]
5	Li ₂ S/Mesoporous Carbon Nanocomposites	Silicon	423	51.0% @ 20		[54]
6	Li ₂ S/Carbon Mixture	Silicon	550	49.0% @ 70		[55]
7	Li ₂ S/C/Graphene Composite	Silicon	593	61.0% @ 30		[56]
8	Free-Standing Li ₂ S/rGO Film	MnO ₂	587.5	80.0% @ 150		[57]
9	Li ₂ S-Carbonised Wipe	SnO ₂	983	80.0% @ 150		[58]
10	Li ₂ S - C Mixture	Tin	600	66.0% @ 32		[59]

highly electronegative element, is 3.04 V. Numerous organic solvents unexpectedly reacts with sulphur due to its high potential, severely destroying the electrolyte in the process [20]. An irrevocable harm of various active ingredients within cathode occurs because of the polysulfide that forms around anode surfaces reducing to a diminutive polysulfide and reducing LiSBs coulomb efficiency. Lithium ions are stripped and plated as the reaction progresses, creating a rough lithium metal anode surfaces during charge and discharge. The current density over the LiSBs is therefore uneven. This raises a question since an excessively irregular surfaces can adversely affect other cell parts, particularly the cathode, which might result in a short circuit [69, 70].

Lithium metal substitutes have been tried in LiSBs anodes, along with carbon-based materials and materials based on silicon (Si) and tin (Sn)[71, 72]. It should be made clear that these materials need to be altered in order to serve as LiSBs anodes. The battery voltage is already smaller than that of Li-ion batteries at about 2.1 V, but the anodes that arise are less electronegative. Since Si or Sn is also significantly denser than lithium metal, a light materials, the overall weightiness of Si or Sn-based negative electrodes rises. This finished cells specific energy and gravimetric energy density are negatively impacted by this. Additionally, a Si or Sn-based anodes volume fluctuates significantly throughout the course of a charge-discharge cycle, resulting in a reduction in the LiSBs performance [73]. In order to optimize the potentials of the LiSBs multi electron reductions, lithium metal remains the optimum material for LiSBs anode.

Li₂S₂ and Li₂S are deposited at the cathode because of the breakdown of the carbon skeleton of the cathode and the polysulfide reactions with electrolytes, which significantly reduces the cycle life of the battery [74, 75]. Sulphur is an active component of a LiSBs, but due to its inherent insulating properties, it requires a significant amount of conductive carbon material to maintain the cathodes conductivity. As a result, different lengths of LiSBs are formed into porous structures that are vulnerable to collapsing under repeated charge/discharge cycle of the active materials depositions and dissolutions. LiSBs often require far more conductive carbon materials added to their cathodes than LIBs do, for this reason. Researchers have addressed this problem by altering the cathode to permit quick mass transfer and redox reactions [76, 77]. Rapid Li⁺ diffusion is also possi-

ble with an electrolyte of low density. The volume of a sulphur cathode fluctuates considerably during charge/discharge cycles, which is the foremost cause of electrodes eventual delamination from the current collector and subsequent slow degradation. In essence, intermediate reactions primarily cause the degradation of LiSBs. It becomes obvious from a closer look of cathode materials that conductive carbon or carbonaceous compounds are typically non-polar on the surface. Normally, modest interactions between polar LiSBs and non-polar surfaces cause LiSBs to disintegrate and significantly limit its capacity [78–80]. It would be desirable to use cathodes materials with polar surfaces, like oxides, nitrides or carbides, to stop LiSBs dissolution through chemisorption and chemical anchoring. Cell cycle time would rise and LiSBs shuttle would decrease. Some carbonaceous materials could have polar surfaces because of doping with transition metals like cobalt, nickel, or iron as well as with nitrogen, sulphur, or phosphor. Depending on their morphology and surface edge, other carbonaceous materials like carbon nanotubes and graphene may also exhibit specific non-polar surfaces [81–83]. Despite all of these difficulties, the LiSBs remains the most promising candidate for the upcoming rechargeable battery generation, in part due of its high theoretical capacity.

5. CONCLUSION

High performance energy storage is required by the world's technological advancements; lithium sulphur batteries appear to provide the desired characteristics, notwithstanding they do have some drawbacks. LiSBs technology is currently at a turning point, which made performance optimization of its electrodes a task that had to be undertaken by researchers. On the cathode side, graphene and its derivatives have the ability to enclose sulfur atoms, form bonds with polysulphides, and improve electronic/ionic conductivities. Hence, on anode part, they have the ability to maintain Li⁺ ions and stop side reactions. However, there are numerous ways to improve the physical and chemical interactions of carbon derivatives with sulphur and polysulphides, including creating porous architecture, functionalizing and doping etc. For low-cost, high-performance LiSBs, composites of carbon derivatives have proven to be a more efficient and effective technique of accomplishing a remarkable result. LiBS are still in the early stages of research and development, they have the potential to be inexpensive, high energy densities, and high

power capabilities. The knowledge of sulfur's electrochemical reactions in liquid electrolyte has advanced significantly. When building high-performance LiBS battery systems, reducing the shuttle effect and increasing coulombic efficiency are always crucial. These objectives can be met by graphene materials, which are perfect scaffold materials for improving LiBS battery performance and offering excellent prospects for commercialization. However, there are still the following issues that need to be resolved. Today's LiBS batteries are still in early prototype or coin cell form, and there are still a lot of issues that need to be worked out before they can be completely commercialized. It is believed that improving the electrode materials and designing new structures are efficient and successful ways to improve the cycle performance. Functionalized graphene, or rGO, represents a very promising frame structure configuration because it can trap polysulfides owing to oxygen functional groups on graphene surface, minimizing polysulfide dissolution and improving the reversibility of the charge/discharge process. Despite significant advancements in the field of nanostructured graphene-based electrodes for lithium-ion batteries, the precise response mechanisms remain unclear. Combining strong theoretical calculations with in situ and operando characterization techniques, such as density functional theory (DFT), molecular modeling, and synchrotron radiation analysis, can lead to a thorough understanding of interface interactions and the mechanisms underlying the degradation of component materials. These techniques can also help uncover the intricate mechanisms underlying the electrochemical reactions of conversion chemistry.

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References

- [1] E. Ali, "Low Voltage Anode Materials for Lithium-Ion Batteries", *Energy Storage Materials* **7** (2017) 157. <https://doi.org/10.1016/j.ensm.2017.01.009>.
- [2] J. Cao, Q. H. Mao, L. Shi & Y. T. Qian, "Fabrication of γ -MnO₂/ α -MnO₂/hollow core/shell structures and their application to water treatment", *Journal of Materials Chemistry* **21** (2011) 16210. <http://dx.doi.org/10.1039/C1JM10862J>.
- [3] H. Cui, J. Xue & M. Wang, "Synthesis of high electrochemical performance Ni(OH)₂ nanosheets through a solvent-free reaction for application in supercapacitor", *Adv. Powder Technol.* **26** (2015) 434. <https://doi.org/10.1016/j.apt.2014.11.016>.
- [4] X. Cao, X. Zheng, B. Shi, W. Yang, J. J. Fan, Z. Luo, X. Rui, B. Chen, Q. Yan & H. Zhang, "Reduced Graphene Oxide-Wrapped MoO₃ Composites Prepared by Using Metal-Organic Frameworks as Precursor for All-Solid-State Flexible Supercapacitors", *Adv. Mater* **27** (2015) 4695. <https://doi.org/10.1002/adma.201501310>.
- [5] H. A. A. Abdel, X. Yang, J. Yang, X. Chen & J. Y. Ying, "Graphene-wrapped nickel sulfide nanoprisms with improved performance for Li-ion battery anodes and supercapacitors", *Nano Energy* **26** (2016) 425 <https://doi.org/10.1016/j.nanoen.2016.05.046>.
- [6] Kim, et al, "Electrochemical Supercapacitors for Energy Storage and Conversion", John Wiley & Sons Ltd, 2015. <https://doi.org/10.1002/9781118991978.hces112>.
- [7] R. Dubey & V. Guruviah, "Review of carbon-based electrode materials for supercapacitor energy storage", *Ionics* **25** (2019) 1419. <https://doi.org/10.1007/s11581-019-02874-0W475W9026>.
- [8] M. Jayalakshmi & K. Balasubramanian, "Simple capacitor to supercapacitor an overview", *Int. J. Electrochem. Sci.* **11** (2008) 1196. [http://dx.doi.org/10.1016/S1452-3981\(23\)15517-9](http://dx.doi.org/10.1016/S1452-3981(23)15517-9).
- [9] S. Gopukumar, D. H. Gregory, H. S. Kim & D. Shu, "Lithium-Ion Batteries: Recent Advances and New Horizons", *International Journal of Electrochemistry* **1** (2012) 1. <https://doi.org/10.1155/2012/878416>.
- [10] Zhu, D & Shao, Y., "NiO/ZnO Nanocomposite as Electrode Material for supercapacitors", *Int. J. Electrochem. Sci.* **13** (2018) 3601. <https://doi.org/10.20964/2018.04.45>.
- [11] Y. Zhu, L. Peng, D. Chen & G. Yu, "Intercalation Pseudocapacitance in Ultrathin VPO₄ Nanosheets: Toward High-Rate Alkali-Ion-Based Electrochemical Energy Storage", *Nano Lett.* **61** (2016) 742. <https://doi.org/10.1021/acs.nanolett.5b04610>.
- [12] R. M. Obodo, H. E. Nsude, C. U. Eze, B. O Okereke, S. C Ezugwu, I. Ahmad, M. Maaza & F. I. Ezema, "Optimization of MnO₂, NiO and MnO₂@NiO electrodes using graphene oxide for supercapacitor applications" *Current Research in Green and Sustainable Chemistry* **5** (2022) 100345. <https://doi.org/10.1016/j.crgsc.2022.100345>.
- [13] R. M. Obodo, S. M. Mbam, D. C. Iwueke, M. Ramzan, R. Ijeh, I. Ahmad, M. Maaza & F. I. Ezema, "Annealing Optimization of Graphitized Co₃O₄@CuO@NiO Composite Electrodes for Supercapacitor Applications", *Energy Storage* **4** (2022) e347. <https://doi.org/10.1002/est2.347>.
- [14] S. Zhang, K. Ueno, K. Dokko & M. Watanabe, "Recent Advances in Electrolytes for Lithium-Sulfur Batteries", *Advanced Energy Materials*, **5** (2015) 1. <https://doi.org/10.1002/aenm.201500117>.
- [15] R. M. Obodo, T. C. Chibueze, I. Ahmad, C. E. Ekuma. A. T. Raji, M. Maaza, F. I. Ezema. "Effects of Copper Ion Irradiation on Supercapacitive Electrodes". *Journal of Applied Electrochemistry Springer Nature* **51** (2021) 829. <https://doi.org/10.1007/s10800-021-01543-3>
- [16] R. M. Obodo, M. Asjad, A. C. Nwanya, I. Ahmad, T. Zhao, A. B. C. Ekwealor, P. N. Ejikeme, M. Maaza & F. I. Ezema, "Evaluation of 8.0 MeV Carbon (C²⁺) Irradiation Effects on Hydrothermally Synthesized Co₃O₄@CuO@ZnO@GO Electrodes for Supercapacitor Applications", *Electroanalysis* **32** (2020) 2958. <https://doi.org/10.1002/elan.202060382>.
- [17] Y. Ye, Y. Shi, L. H. Saw & A. A. O. Tay, "Performance assessment and optimization of a heat pipe thermal management system for fast charging lithium ion battery packs", *International Journal of Heat and Mass Transfer* **92** (2016) 893. <https://doi.org/10.1016/j.ijheatmasstransfer.2015.09.052>.
- [18] M. U. M. Patel, N. D. Luong, J. Seppälä, E. Tchernychova & R. Dominko, "Low surface area graphene/cellulose composite as a host matrix for lithium sulphur batteries", *Journal of Power Sources* **54** (2014) 55. <https://doi.org/10.1016/j.jpowsour.2013.12.081>.
- [19] R. M. Obodo, H. E. Nsude, S. E. Ugwuanyi, D. C. Iwueke, C. Iroegbu, T. Mehmod, I. Ahmad, M. Maaza, & F. I. Ezema, "Graphene Oxide in Enhancing Energy Storage Devices", Taylor & Francis Group, CRC Press, United Kingdom, 2022, pp. 75-86. <https://doi.org/10.1201/9781003215196-7>.
- [20] R. M. Obodo, U. K. Chime, A. C. Nkele, A. C. Nwanya, A. K. H. Bashir, I. G. Madiba, M. Asjad, I. Ahmad, T. Zhao, N. Thovhogi & F. I. Ezema, "Effect of annealing on hydrothermally deposited Co₃O₄-ZnO thin films for supercapacitor applications", *Materials Today: Proceedings* **36** (2020) 374. <https://doi.org/10.1016/j.matpr.2020.04.229>.
- [21] R. M. Obodo, A. C. Nwanya, I. S. Ike, I. Ahmad & F. I. Ezema, "Role of Carbon Derivatives in Enhancing Metal Oxide Performances as Electrodes for Energy Storage Devices", in *Chemically Deposited Nanocrystalline Metal Oxide Thin Films*, USA, Springers, 2021, pp. 469 - 488. https://doi.org/10.1007/978-3-030-68462-4_18.
- [22] J. Kim, M. Eom, S. Noh & D. Shin, "Performance optimization of all-solid-state lithium ion batteries using a Li 2S-P 2S 5 solid electrolyte and LiCoO₂ cathode", *Electronic Materials Letters* **8** (2012) 209. <https://doi.org/10.1007/s13391-012-2037-7>.
- [23] X. Huang, T. Qiu, X. Zhang, L. Wang, B. Luo & L. Wang, "Recent advances of hollow-structured sulfur cathodes for lithium-sulfur batteries", *Materials Chemistry Frontiers* **4** (2020) 2517. <https://doi.org/10.1039/D0QM00303D>.
- [24] W. Ren, W. Ma, S. Zhang & B. Tang, "Recent advances in shuttle effect inhibition for lithium sulfur batteries", *Energy Storage Materials* **23** (2019) 707. <https://doi.org/10.1016/j.ensm.2019.02.022>.
- [25] F. Li, Q. Liu, J. Hu, Y. Feng, P. He & J. Ma, "Recent advances in cathode materials for rechargeable lithium-sulfur batteries", *Nanoscale* **11** (2019) 15418. <https://doi.org/10.1039/C9NR04415A>.

- [26] L. Chen & L. L. Shaw, "Recent advances in lithium-sulfur batteries", *Journal of Power Sources* **267** (2014) 770. <https://doi.org/10.1016/j.jpowsour.2014.05.111>.
- [27] S. Zhang, K. Ueno, K. Dokko & M. Watanabe, "Recent Advances in Electrolytes for Lithium-Sulfur Batteries.", *Advanced Energy Materials* **5** (2015) 1. <https://doi.org/10.1002/aenm.201500117>.
- [28] H. Wang, Y. Yang, Y. Liang, J. T. Robinson, Y. Li & A. Jackson, "Overview in Lithium Sulphur Batteries", *Nano Letters* **11** (2011) 2644. <https://doi.org/10.1021/nl200658a>.
- [29] Conway B. E., "Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications", Plenum Press, New York, USA, 1999, PP. 1–8.
- [30] D. Liu, C. Zhang, G. Zhou, W. Lv, G. Ling, L. Zhi & Q. H. Yan, "Catalytic effects in lithium–sulfur batteries: promoted sulfur transformation and reduced shuttle effect", *Adv Sci* **5** (2017) 1700270. <https://doi.org/10.1002/advs.201700270>.
- [31] Z. Yuan, H. J. Peng, T. Z. Hou, J. Q. Huang, C. M. Chen, D. W. Wang, X. B. Cheng, F. Wei & Q. Zhang, "Powering lithium–sulfur battery performance by propelling polysulfide redox at sulfiphilic hosts", *Nano Lett* **16** (2016) 519. <https://doi.org/10.1021/acs.nanolett.5b04166>.
- [32] M. Yu, R. Li, M. Wu & G. Shi, "Graphene materials for lithium-sulfur batteries", *Energy Storage Materials* **1** (2015) 51. <https://doi.org/10.1016/j.ensm.2015.08.004>.
- [33] H. E. Figen & S. Z. Baykara, "Effect of ruthenium addition on molybdenum catalysts for syngas production via catalytic partial oxidation of methane in a monolithic reactor", *Int. J. Hydrogen Energy* **43** (2018) 1129. <http://dx.doi.org/10.1016/j.ijhydene.2017.10.173>.
- [34] J. Wang, J. Yang, J. Xie & J. Xu, "A novel conductive polymer–sulfur composite cathode material for rechargeable lithium batteries", *Adv. Mater* **14** (2002) 963. <https://doi.org/10.1002/1521-4095>.
- [35] Z. W. Seh, H. Wang, P. C. Hsu, Q. Zhang, W. Li, G. Zheng, H. Yao & Y. Cu, "Facile synthesis of Li₂S–polypyrrole composite structures for high-performance Li₂S cathodes", *Energy Environ. Sci.* **7** (2014) 672. <https://doi.org/10.1039/C3EE43395A>.
- [36] X. Huang, T. Qiu, X. Zhang, L. Wang, B. Luo & L. Wang, "Recent advances of hollow-structured sulfur cathodes for lithium-sulfur batteries.", *Materials Chemistry Frontiers* **4** (2020) 2517. <https://doi.org/10.1039/D0QM00303D>.
- [37] R. M. Obodo, A. C. Nwanya, I. Ahmad, M. A. Kebede & F. I. Ezema, "Carbon Derivatives in Performance Improvement of Lithium-Ion Battery Electrodes, in *Electrode Materials for Energy Storage & Conversion*, Taylor & Francis Group, CRC Press, UK, 2021, pp. 23 – 33. <https://doi.org/10.1201/9781003145585-2>.
- [38] N. Li, M. Zheng, H. Lu, Z. Hu, C. Shen, X. Chang, G. Ji, J. Cao & Y. Shi, "High-rate lithium–sulfur batteries promoted by reduced graphene oxide coating", *Chemical Communications* **48** (2012) 4106. <https://doi.org/10.1039/C2CC17912A>.
- [39] F. Wu, J. T. Lee, E. Zhao, B. Zhang & G. Yushin, "Graphene-Li₂S-carbon nanocomposite for lithium-sulfur batteries", *ACS Nano* **10** (2016) 1333. <https://doi.org/10.1021/acsnano.5b06716>.
- [40] H. Wu, Q. Tang, H. Fan, Z. Liu, A. Hu, S. Zhang, W. Deng & X. Chen, "Dual-Confined and Hierarchical-Porous Graphene /C/SiO₂ Hollow Microspheres through Spray Drying Approach for Lithium-Sulfur Batteries", *Electrochimica Acta* **255** (2017) 179. <https://doi.org/10.1016/j.electacta.2017.09.140>.
- [41] R. M. Obodo, A. C. Nwanya, C. Iroegbu, I. Ahmad, A. B. C. Ekwealor, R. U. Osuji, M. Maaza & F. I. Ezema, "Transformation of GO to rGO due to 8.0 MeV carbon (C++) ions irradiation and characteristics performance on MnO₂–NiO–ZnO@GO electrode", *Int J Energy Res* **44** 2020 1. <https://doi.org/10.1002/er.5416>.
- [42] M. S. Park, J. S. Yu, K. J. Kim, G. Jeong, J. H. Kim, Y. N. Jo, U. Hwang, S. Kang, T. Woo & Y. J. Kim, "One-step synthesis of a sulfur-impregnated graphene cathode for lithium-sulfur batteries", *Physical Chemistry & Chemical Physics* **14** (2012) 6796. <https://doi.org/10.1039/C2CP40727B>.
- [43] R. Fang, S. Zhao, S. Pei, X. Qian, P. X. Hou, H. M. Cheng, C. Liu & F. Li, "Toward More Reliable Lithium-Sulfur Batteries: An All-Graphene Cathode Structure", *ACS Nano* **10** (2016) 8676. <https://doi.org/10.1021/acsnano.6b04019>.
- [44] C. Xu, Y. Wu, X. Zhao, X. Wang, G. Du, J. Zhang & J. Tu, "Sulfur/three-dimensional graphene composite for high performance lithium-sulfur batteries", *Journal of Power Sources* **275** (2015) 22. <https://doi.org/10.1016/j.jpowsour.2014.11.007>.
- [45] C. Zu & A. Manthiram, "Hydroxylated graphene-sulfur nanocomposites for high-rate lithium-sulfur batteries.", *Advanced Energy Materials* **3** (2013) 1008 <https://doi.org/10.1002/aenm.201201080>.
- [46] Y. Zhang, Z. Gao, N. Song, J. He & X. Li, "Graphene and its derivatives in lithium–sulfur batteries.", *Materials Today Energy* **9** (2018) 319. <https://doi.org/10.1016/j.mtener.2018.06.001>.
- [47] R. M. Obodo, A. C. Nwanya, A. B. C. Ekwealor, I. Ahmad, T. Zhao, M. Maaza & F. Ezema, "Influence of pH and annealing on the optical and electrochemical properties of cobalt (III) oxide (Co₃O₄) thin films", *Surfaces and Interfaces* **16**(2019) 114. <https://doi.org/10.1016/j.surfin.2019.05.006>.
- [48] E. Yoo, J. Kim, E. Hosono, H. Zhou & T. Kudo, "Large Reversible Li Storage of Graphene Nanosheet Families for Use", *Nano Letters* **8** (2008) 2277. <https://doi.org/10.1021/nl800957b>
- [49] M. M. Atabaki & R. Kovacevic, "Graphene composites as anode materials in lithium-ion batteries", *Electron Mater Lett.* **9** (2013) 133. <https://doi.org/10.1007/s13391-012-2134-7>.
- [50] N. Wang, N. Zhao, C. Shi, E. Liu, C. He, F. He & L. Ma, "In situ synthesized Li₂S@ porous carbon cathode for graphite/Li₂S full cells using ether-based electrolyte", *Electrochim. Acta* **348** (2017) 256 <https://doi.org/10.1016/j.electacta.2017.10.053>.
- [51] Z. Li, S. Zhang, S. Terada, X. Ma, K. Ikeda, Y. Kamei, C. Zhang, K. Dokko & M. Watanabe, "Promising Cell Configuration for Next-Generation Energy Storage: Li₂S/Graphite Battery Enabled by a Solvate Ionic Liquid Electrolyte", *ACS Appl. Mater. Interfaces* **8** (2016) 16053. <https://doi.org/10.1021/acsami.6b03736W475W9026>.
- [52] Y. Jin, B. Zhu, Z. Lu, N. Liu & J. Zhu, "Challenges and recent progress in the development of Si anodes for lithium-ion battery", *Adv. Energy Mater* **7** (2017) 1700715. <https://doi.org/10.1002/aenm.201700715>.
- [53] G. Q. Tan, R. Xu, Z. Y. Xing, Y. F. Yuan, J. J. Lu, G. Wen, C. Liu, L. Ma, C. Zhan, Q. Liu, T. P. Wu, Z. L. Jian, Y. R. R. Shahbazian-Yassar, D. J. Miller, L. A. Curtiss, X. L. Ji & K. Amine, "Burning lithium in CS₂ for high-performing compact Li₂S–graphene nanocapsules for Li–S batteries", *Nat. Energy* **2** (2017) 17090. <https://doi.org/10.1038/nenergy.2017.90>.
- [54] Y. Yang, M. T. McDowell, A. Jackson, J. J. Cha, S. S. Hong & Y. Cui, "New Nanostructured Li₂S/Silicon Rechargeable Battery with High Specific Energy", *Nano Lett* **10** (2010) 1486. <https://doi.org/10.1021/nl100504q>.
- [55] H. Jha, I. Buchberger, X. Cui, S. Meini & H. A. Gasteiger, "Li-S batteries with Li₂S cathodes and Si/C anodes", *J. Electro-chem. Soc.* **162** (2015) A1829. <https://doi.org/10.1149/2.0681509jes>.
- [56] S. Wang, H. Chen, Z. Zhong, X. Hou, S. Hu & J. Wu, "Graphene-decorated sphere Li₂S composite prepared by spray drying method as cathode for lithium-sulfur full cell", *Ionics* **24** (2018) 3385. <https://doi.org/10.1007/s11581-018-2493-7.s>
- [57] Y. Chen, S. Lu, Y. Li, W. Qin & X. Wu, "A high-performance Li₂S/MnO₂ rechargeable battery", *Mater. Lett.* **248** (2019) 157. <https://doi.org/10.1016/j.matlet.2019.04.018>.
- [58] M. Liu, Y. X. Ren, H. R. Jiang, C. Luo, F. Y. Kang & T. S. Zhao, "An efficient Li₂S-based lithium-ion sulfur battery realized by a bifunctional electrolyte additive", *Nano Energy* **40** (2017) 240. <https://doi.org/10.1016/j.nanoen.2017.08.017>.
- [59] J. Hassoun, B. Scrosati & Angew, "A high performance polymer tin sulfur lithium ion battery", *Chem., Int. Ed* **49** (2010) 2371. <https://doi.org/10.1002/ange.200907324>.
- [60] A. Manthiram, Y. Fu, S. H. Chung, C. Zu & Y. S. Su, "Rechargeable lithium - sulfur batteries", *Chem Rev* **114** (2014) 11751. <https://doi.org/10.1021/cr500062v>.
- [61] Y. Liu, C. Cui, Y. Liu, W. Liu & J. Wei, "Application of MoS₂ in the cathode of lithium sulfur batteries.", *RSC Adv* **10** (2020) 7384. <https://doi.org/10.1039/C9RA09769D>.
- [62] M. Zong et al, "A cost and energy density competitive lithium-sulfur battery", *Energy Storage Mater* **41** (2021) 588. <https://doi.org/10.1016/j.ensm.2021.06.037>.
- [63] R. Soni et al, "Lithium-sulfur battery diagnostics through distribution of relaxation times analysis.", *Energy Storage Mater* **51** (2022) 97. <https://doi.org/10.1016/j.ensm.2022.06.016>.
- [64] C. Barchasz et al, "Lithium/sulfur cell discharge mechanism: an original approach for intermediate species identification.", *Anal Chem* **84** (2012) 3973. <https://doi.org/10.1021/ac2032244>.
- [65] M. Hagen, D. Hanselmann, t. K. Ahlbrech, R. Maca, D. Gerber & J. Tübke, "Lithium–sulfur cells: the gap between the state-of-the-art and the requirements for high energy battery cell", *Adv Energy Mater* **5** (2015) 1401986. <https://doi.org/10.1002/aenm.201401986>.
- [66] A. Fotouhi, D. J. Auger, L. O'Neill, T. Cleaver & S. Walus, "Lithium-sulfur battery technology readiness and applications- A Review", *Energies*

- 10** (2022) 1937. <https://doi.org/10.3390/en10121937>.
- [67] S. Dörfler et al., “Recent progress and emerging application areas for lithium–sulfur battery technology”, *Energy Technology* **9** (2020) 2000694. <https://doi.org/10.1002/ente.202000694>.
- [68] T. Cleaver, P. Kovacic & M. Marinescu, “Commercializing lithium sulfur batteries: are we doing the right research”, *J. Electrochem Soc.* **165** (2018) A6029. <https://doi.org/10.1149/2.0071801jes>.
- [69] J. Luo, R. Lee, J. Jin, Y. T. Weng, C. C. Fang & N. L. Wu, “A dual-functional polymer coating on a lithium anode for suppressing dendrite growth and polysulfide shuttling in Li–S batteries”, *Chem Commun* **53** (2017) 963. <https://doi.org/10.1039/C6CC09248A>.
- [70] B. D. McCloskey, “Attainable gravimetric and volumetric energy density of Li–S and Li ion battery cells with solid separator-protected Li metal anodes”, *J Phys Chem Lett* **6** (2015) 4581. <https://doi.org/10.1021/acs.jpcclett.5b01814>.
- [71] F. Jeschull, D. Brandell, K. Edströma & M. J. Lacey, “A stable graphite negative electrode for the lithium–sulfur battery”, *Chem Commun* **51** (2015) 17100. <https://doi.org/10.1039/C5CC06666B>.
- [72] A. Krause, S. Dörfler, M. Piwko, F. M. Wisser, T. Jaumann, E. Ahrens, G. L. A. H. S. Schädlich, J. Grothe, A. Jeffery, M. Grube, J. Brückner, J. Martin, J. Eckert, S. Kaskel, T. Mikolajick & W. M. Weber, “High area capacity lithium-sulfur full-cell battery with prelithiated silicon nanowire-carbon anodes for long cycling stability”, *Sci. Rep.* **6** (2016) 27982. <https://doi.org/10.1038/srep27982>.
- [73] M. Piwko, T. Kuntze, S. Winkler, S. Straach, P. Hartel, H. Althues & S. Kaskel, “Hierarchical columnar silicon anode structures for high energy density lithium sulfur batteries.”, *J Power Sources* **351** (2017) 183. <https://doi.org/10.1016/j.jpowsour.2017.03.080>.
- [74] R. Cao, W. Xu, D. Lv, J. Xiao & J. G. Zhang, “Anodes fo rechargeable lithium-sulfur batteries”, *Adv. Energy Mater* **5** (2015) 1402273. <https://doi.org/10.1002/aenm.201402273>.
- [75] M. Ryohei, “Cathode materials for lithium-sulfur battery: a review”, *Journal of Solid State Electrochemistry* **27** (2023) 813. <https://doi.org/10.1007/s10008-023-05387-z>.
- [76] J. Yan, X. Liu & B. Li, “Capacity fade analysis of sulfur cathodes in lithium–sulfur batteries.”, *Adv Sci* **3** (2016) 1600101. <https://doi.org/10.1002/advs.201600101>.
- [77] Y. J. Choi, Y. D. Chung, C. Baek, Y. K. W. Kim & H. J. Ahn, “Effects of carbon coating on the electrochemical properties of sulfur cathode for lithium/sulfur cell.”, *J Power Sources* **184** (2008) 548. <https://doi.org/10.1016/j.jpowsour.2008.02.053>.
- [78] X. Ji, K. T. Lee & L. F. Nazar, “A highly ordered nanostructured carbon - sulphur cathode for lithium - sulphur batteries.”, *Nat Mater* **8** (2009) 500. <https://doi.org/10.1038/nmat2460>.
- [79] X. Liu, J. Q. Huang, Q. Zhang & L. Mai, “Nanostructured metal oxides and sulfides for lithium–sulfur batteries.”, *Adv Mater* **29** (2017) 1601759. <https://doi.org/10.1002/adma.201601759>.
- [80] J. He & A. Manthiram, “A review on the status and challenges of electrocatalysts in lithium-sulfur batteries”, *Energy Storage Mater* **20** (2019) 55. <https://doi.org/10.1016/j.ensm.2019.04.038>.
- [81] K. Zhang & et al, “Dual taming of polysulfides by phosphorus-doped carbon for improving electrochemical performances of lithium–sulfur battery”, *Electrochimica Acta* **354** (2020) 136648. <https://doi.org/10.1016/j.electacta.2020.136648>.
- [82] M. Zheng et al, “Carbon nanotube-based materials for lithium–sulfur batteries.”, *J Mater Chem A* **7** 2019 17204. <https://doi.org/10.1039/C9TA05347F>.
- [83] J. Guo, Y. Xu & C. Wang, “Sulfur-impregnated disordered carbon nanotubes cathode for lithium–sulfur batteries.”, *Nano Lett* **11** (2011) 4288. <https://doi.org/10.1021/nl202297p>.