https://doi.org/10.1149/1945-7111/ac4cd7

Journal of The Electrochemical Society

ACCEPTED MANUSCRIPT

Review—Contemporary Progresses in Carbon-Based Electrode Material in Li-S Batteries

To cite this article before publication: Utkarsh Chadha *et al* 2022 *J. Electrochem. Soc.* in press https://doi.org/10.1149/1945-7111/ac4cd7

Review—Contemporary Progresses in Carbon-Based Electrode Material in Li-S Batteries

Journal:	*Journal of The Electrochemical Society*
Manuscript ID	JES-106002.R2
Manuscript Type:	Review Paper
Date Submitted by the Author:	05-Jan-2022

Complete List of Authors:	Chadha, Utkarsh; Vellore Institute of Technology, School of Mechanical Engineering Bhardwaj, Preetam; Vellore Institute of Technology, School of Electronics Engineering; Vellore Institute of Technology, VIT University Vellore Padmanaban, Sanjeevikumar; Aarhus Universitet, Department of Business Development and Technology Suneel, Reyna Michelle; Vellore Institute of Technology Milton, Kevin; Vellore Institute of Technology Subair, Neha; Vellore Institute of Technology Pandey, Akshat; Vellore Institute of Technology Khanna, Mayank; Vellore Institute of Technology Srivastava, Divyansh; Vellore Institute of Technology, School of Mechanical Engineering Mathew, Rhea Mary; Vellore Institute of Technology SELVARAJ, SENTHIL KUMARAN; Vellore Institute of Technology, Department of Manufacturing Engineering Banavoth, Murali; University of Hyderabad Sonar, Prashant; Queensland University of Technology Badoni, Badrish; Bal Ganga Degree College Srinivasa Rao, Nalamala; MRR Government degree college Gopa Kumar, S; Rohini College of Engineering and Technology

Keywords:	Lithium-Sulphur Batteries, Carbon-Based Electrode, Conducting Polymers, Carbon Nanotubes, Graphene, Activated Carbon

Review—Contemporary Progresses in Carbon-Based Electrode Material in Li-S Batteries

Utkarsh Chadha,[1] Preetam Bhardwaj,[2,z] Sanjeevikumar Padmanaban,[3,z] Reyna Michelle Suneel,[4] Kevin Milton,[4] Neha Subair,[4] Akshat Pandey,[4] Mayank Khanna,[1] Divyansh Srivastava,[1] Rhea Mary Mathew,[1] Senthil Kumaran Selvaraj,[1] Murali Banavoth,[5] Prashant Sonar,[6] Badrish Badoni,[7] Nalamala Srinivasa Rao,[8] and S. Gopa Kumar[9]

[1]Department of Manufacturing Engineering, School of Mechanical Engineering (SMEC), Vellore Institute of Technology (VIT), Vellore, Tamilnadu, India – 632014

[2]Centre for Nanotechnology Research (CNR), School of Electronics Engineering (SENSE), Vellore Institute of Technology, Vellore 632014, Tamil Nadu, India – 632014

[3]Center for Electric Vehicles and Power, Department of Electrical and Electronics Engineering, Anna University, Chennai-600025, India **&** Department of Energy Technology, Aalborg University, Esbjerg, Denmark

[4]School of Chemical Engineering (SCHEME), Vellore Institute of Technology (VIT), Vellore, Tamilnadu, India – 632014

[5]Solar Cells and Photonics Research Laboratory, School of Chemistry, University of Hyderabad, Hyderabad, Telangana, India – 500046

[6]Centre for Materials Science, School of Chemistry and Physics, Queensland University of Technology, Brisbane, QLD 4001, Australia

[7]Department of Physics, Bal Ganga Degree College, Sendul Kemar, Tehri Garhwal Uttrakhand, India- 249155

[8]Department of Chemistry, M.R.R. Govt. Degree College, Udayagiri, SPSR Nellore, Andhra Pradesh, India- 524226

[9]Department of Electrical and Electronics Engineering, Rohini College of Engineering and Technology, Palkulam, Anjugramam, Tamilnadu, India- 629401

[z]E-mail: pbhardwaj105@gmail.com; sanjeevi_12@yahoo.co.in

Abstract

Lithium-sulfur batteries are among the rising rechargeable batteries due to their high energy density, theoretical capacity, and low cost. However, their large-scale application is delayed by several challenges, such as degradation due to polysulfide dissolution, low conductivity, and other restricting factors. Li-S batteries have undergone decades of development aimed at improving battery performance by altering the electrode material to overcome these challenges. In the meantime, due to the depletion of fossil fuels and growing energy demand, the need for changes in processes to improve battery performance is now more urgent than ever. Carbon-based materials like conducting polymers, carbon nanotubes, Graphene, and activated Carbon have gained extensive attention due to their low cost, easy availability, good cycling stability, and exceptional electrical, thermal, and mechanical properties. Here, we summarize recent progress in carbon-based electrode material in Li-S batteries, the development of electrolytes,

and progress in adopting lithium-sulfur batteries as flexible devices. Furthermore, a comparison of Li-S batteries based on similar parameters with its rechargeable battery competitors is discussed and a comparison with other non-carbon-based electrodes used in the lithium-sulfur battery is also examined. Finally, a general conclusion and future directions are given.

1. Introduction

Rechargeable batteries are said to be the key technologies for future energy storage and electric vehicle applications. Lithium-sulfur batteries are one of the major energy storage devices notable for their high specific energy.

Energy density measures the amount of energy a single battery can carry in proportion to its weight. Usually, energy density measurement is represented in terms of watt-hours per kilogram or Wh/kg. Li-ion batteries have one of the highest energy densities when in contrast with other rechargeable batteries.

Lithium-sulfur cells offer notable safety advantage over the other batteries due to their operating mechanism. The 'conversion reaction', which forms new materials during charge and discharge, eliminates the need to host Li-ions in materials, and reduces the risk of catastrophic failure (sudden failure from which recovery is not possible) of batteries. [1]. In a common lithium-sulfur cell, elemental Sulfur is used as the positive electrode, whereas metallic Lithium is used as the negative electrode. In an Li–S battery, cathode contributes the major part of the cell, making it an integral and indispensable part of the battery operation. Li-S batteries operating at normal room temperature can provide comparatively lower equivalent weight with high capacity, low cost, and environment-friendly factors. [2]

On the cathode side, Sulfur is used. Considering both the charge product, which is Sulfur, and the discharge product, which is lithium sulfide, are insulating in nature, this results in poor material utilization. Also, during the cycling process, a sequence of long-chain lithium polysulfides are forms that later dissolve into electrolytes. This led to the decrease in active material and increased capacity decay. It is also found that the elemental Sulfur goes through a volumetric expansion which leads to pulverization and damage in the structure. The semi-reaction can be expressed as [3]

$$S + 2Li^{+} + 2e^{-} \longleftrightarrow Li_2S$$

When it comes to the anode side, metal lithium is highly reactive and prevents the formation of dendrites. This might lead to short circuits and later safety hazards. Also, the sequence of long-chain lithium polysulfides that dissolve into electrolytes diffuses into lithium anode, leading to the formation of short-chain polysulfides on the surface. This results in the shuttle effect and reduced coulombic efficiency that destroys Li-S batteries. The half-reaction can be expressed as [4]

$$Li \longleftrightarrow Li^{+} + e^{-}$$

Lithium-sulfur batteries are said to have higher specific energy, low manufacturing cost, improved safety and are said to have 2-3 times higher performance when compared with other Li-ion cells. As a result, Li-S batteries and their applications are subjected to various research experiments [5]. These advanced batteries are not yet commercialized due to their limitations, such as short life-cycle, high self-discharge, etc. Most of the recent research concerns the development of Li-S batteries, including understanding materials used and cell behaviour and its construction. [6,7]

This review focuses on the structure, current developments, and the electrodes used in Li-S batteries. The merits of using Carbon as an electrode instead of Sulfur and the characteristics of various lithium-ion batteries are also discussed. The second part of this review consists of various parameters that influence the properties of lithium-ion batteries, alongside discussions and future directions.

2. Understanding Li-S Battery

Lithium-sulfur batteries are rechargeable batteries. They are the modern energy storage device known for their high specific energy, high theoretical density, and good kinetics. Sulfur being abundant and cheap makes the Li-S battery an economical technology. In the Li-S battery, dissolution of Lithium occurs at the anodic surface during discharge and reverse lithium plating to the anode while charging.

Li-S batteries still face the challenges of achieving high coulombic efficiency, high capacity, and long-life cycle arising due to sulfur utilization is limited due to the shuttle effect of polysulfides, formation of dendrites on the Li anode during cycling, low conductivity of Sulfur, and its massive volume change on discharging. All these obstacles have to be subdued in the process of commercialization. [8]

This can be made possible by using Sulfur as the Li-S cathode to meet its demands of low cost and high energy density since one sulfur atom can host a maximum of 2 electrons and has a theoretical capacity of 1675 mAh g^{-1}. Also, sulfur-metal batteries show superiority over other battery technologies in terms of energy density, specific capacity, and operation voltage, using Lithium as the anode material due to its high theoretical capacity and negative electrode potential; However, by selecting an electrolyte that can dissolve well while stabilizing the polysulfide, can solve the obstacles mentioned above. Selecting the electrolyte is crucial as it determines the temperature range of the battery, designing the battery well since it affects the cycling performance. While achieving improvement targets is necessary, one should not neglect that the main drivers behind Li-S are its low cost and sustainability.[9]

2.1. Design & Construction of Li-S Batteries

Lithium-sulfur batteries have, in general, four essential components which define them as Li-S. These include cathode, anode, electrolyte, and a separator. A lithium-sulfur battery is composed of metallic lithium on the anode part, whereas elemental Sulfur on the cathode part.[10]

Positive electrode: Here, elemental Sulfur is considered as cathode.

Lithium-sulfur batteries utilizes Sulfur as cathode as it is abundantly available on Earth. When used as an energy storage cell, Sulfur has a number of advantages. [11] The use of Sulfur allows lightweight materials to be produced using more cost-effective materials, while also reducing the environment and social concerns surrounding the production of nickel and cobalt. Sulfur also carries out an average voltage of 2.15V, making it suitable to function as a cathode. [12]

Negative electrode: The negative electrode is mainly metal or hydrogen, or an alloy. In a lithium sulfur battery, the anode by definition is made from metallic Lithium. [13]

Lithium is a very light metal which possess the least amount of ionization energy, 520 KJ/Mol, with increased shelf life. Lithium is an important component of rechargeable Li-S batteries that power electric vehicles (EVs), laptops and mobile phones. Lithium is also highly reactive which makes an excellent choice for the anode. Lithium-based batteries possess high specific energy and energy density of about 200 Wh/kg, 2-4 times more than that of the other conventional batteries. [15]

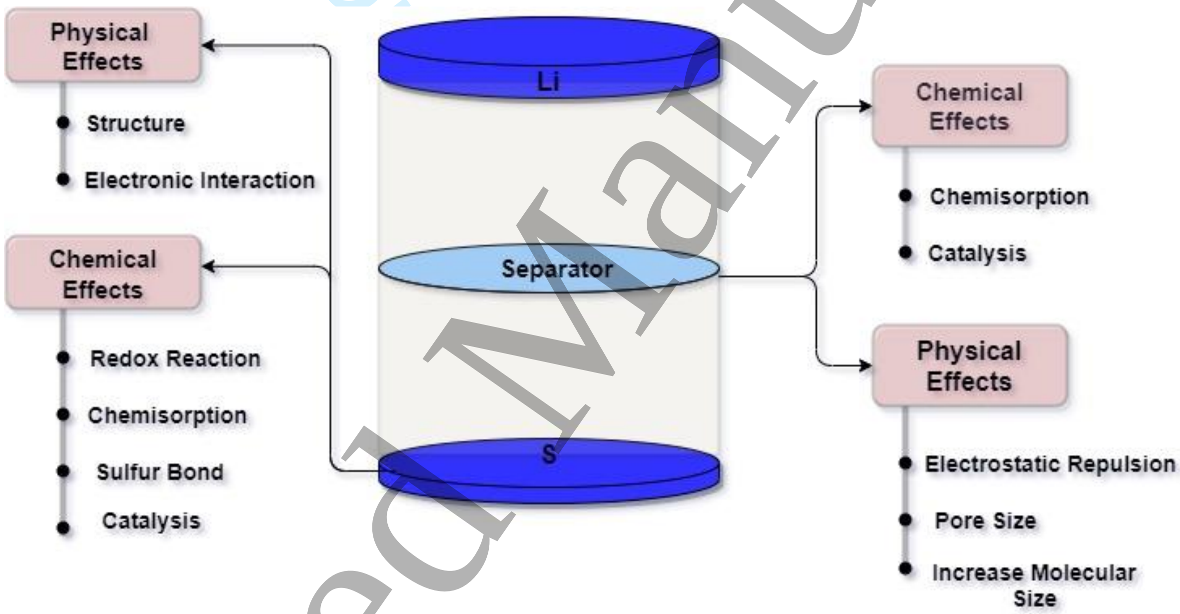

FIGURE 1. Physical and Chemical properties of Separators and Anodes

Electrolyte: The electrolyte in an electrochemical cell plays a major role in the transfer of positive lithium ions between anode and cathode.

Solvents, lithium salts and its additives are the major components of an electrolyte in a Li-S battery. Excess amounts of electrolyte and reduced sulfur loading resulted in the enhancement of cycle life and capacity maintenance. The most commonly used electrolyte is comprised of lithium salt and a wide range of other additives which results in providing the required properties to an electrolyte solution. The lithium salt concentration plays a significant role in reducing the shuttle mechanism and capacity loss. [16]

Electrolytes for Li-S batteries generally fit into four different types: non-aqueous, ionic liquids, solid polymer electrolytes, and superionic conductors.

Ionic liquids make good electrolytes due to their distinctive properties such as high ionic conductivity, eco-friendliness, non-flammability, and high electrochemical stability. Solid polymer electrolyte usually plays an essential role in reducing the dissolution of polysulfides [2]. This results in enhancing capacity retention and better cycling stability. The superionic conductors can be sulfides or oxides, or phosphates. Among these, oxides are more stable when compared with the other two and are safe, non-flammable, have thermal stability, and prevent polysulfide formation. In a non-aqueous electrolyte, the active cathode material is ambient oxygen and air electrode provides a site for the catalytic reduction of oxygen. [17]

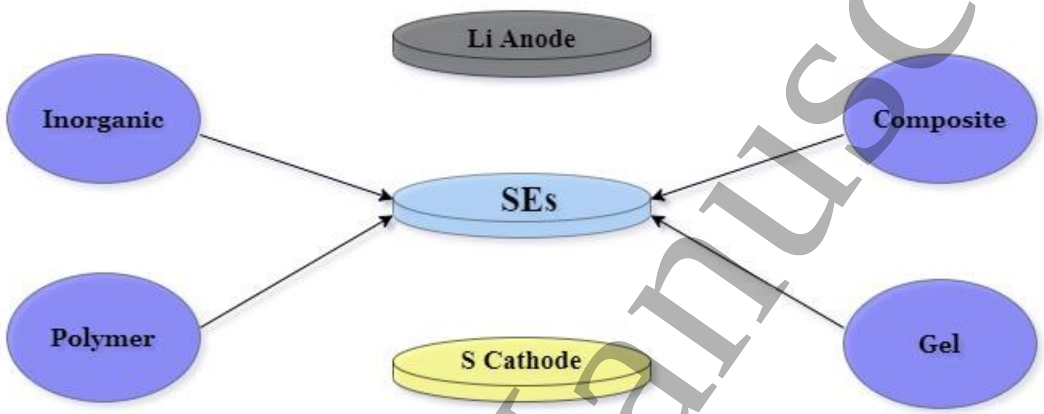

FIGURE 2. Different types of electrolytes used in a Lithium-Sulfur battery

Electrolyte additives play an essential role in electrochemical performance lithium-sulfur batteries. It improves the solid-electrolyte interface, improves thermal stability, increases temperature tolerance and other physical properties such as viscosity, wettability. (FIGURE 2) discuss about different types of electrolytes namely composite, gel, inorganic or polymer electrolytes. $LiNO_3$ has become the most-used additive in the Li-S battery. On the addition of $LiNO_3$, the electrochemical properties of the cell were enhanced that provided a stable and protective solid-electrolyte interference.

Problems pertaining to chemical contact mostly refers to side reactions between electrolyte and electrodes, which significantly decrease the stability and increase interfacial resistance. In short, the major solid-solid interfaces consist of cathode-electrolyte interface and anode-electrolyte interface. For a cathode-electrolyte interface, the formation of a highly resistive interphase and/or a Li-depleted layer at the interface between the sulfide electrolyte and the high-voltage cathode represents a critical problem. For an anode-electrolyte interface, the major issue is Li dendrite growth and penetration through solid electrolyte, coupled with the side reactions between the sulfide electrolyte and Li anode. Li-S batteries must be designed to meet the needs of a broad range of applications.[10]

Electrolytes have been evaluated for performance and designed with cost and performance in mind. Phosphorous(V) sulfide as an additive promotes the dissolution of lithium sulfide and reduces the shuttling of polysulfides. Shuttle effect represents the phenomenon in which soluble lithium intermediate sulfide bounces off the electrodes. [5]

Separator: The function of a separator is to electrically isolate the positive and negative electrodes to avoid self-discharge and short circuit. The separators are often made using fiber, polymer, or glass. The various functions of separators are mentioned in (FIGURE 3).

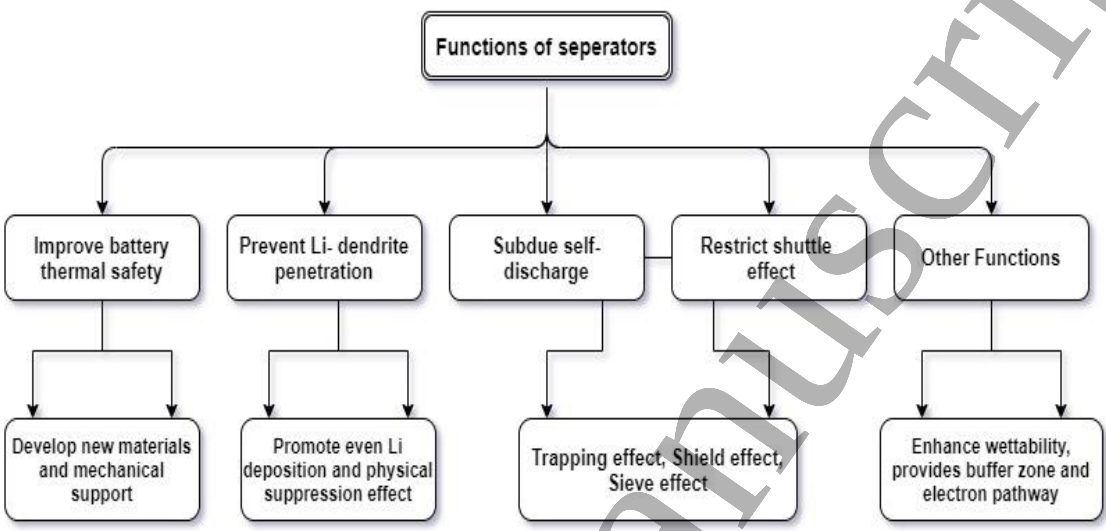

FIGURE 3. Various functions of separators in a lithium-sulfur battery

2.2. Current Developments in Carbon-based Li-S Batteries

This table (Table 1) gives a short review of the contemporary developments in Li-S batteries, mainly CNT's, conducting polymer, Graphene, biomass, activated Carbon, etc.

An understanding between their composition and structure, their columbic efficiencies, which is the ratio of discharge capacity to charge capacity multiplied by 100 is given since it helps to predict the lifespan of the battery; Furthermore, the battery's capacity retention is also given to determine the ability of the battery to retain stored energy during an extended open-circuit rest period, if the capacity retention is good the charge/discharge remains almost the same for many cycles. Overall, giving us a better understanding of the efficiency of different carbon-based Li-S batteries. [18,19]

Table 1. Contemporary developments in carbon-based Li-S battery

Electrode Materials/Parameters	Efficiency	Discharge Capacity	Reverse capacity/Capacity Retention	Remarks	Ref.

Nafion coated electrode	Columbic efficiency of 100%.	1084 mAh/g	Reversible capacity of 1091 mAh/g and about 879 mAh/g after 100 Cycles.	The cation conductivity and anion inconductivity is considered the supreme factor for the superior electrochemical properties.	[20,21]
Biomass-derived activated Carbon (Carbon derived from coconut shells and activated by KOH) (A polypropylene separator was used)	Coulombic efficiency of over 99% is achieved.	1233 mAh g^{-1}	929 $mAhg^{-1}$ after 100 cycles.		[22-26]
Carbon Nanotubes was fabricated on C/S cathode		1288 $mAhg^{-1}$. Initial areal discharge capacity of about 3.21 $mAh·cm^{-2}$.		It exhibited the highest sulfur utilization in comparison to the other cells.	[27-31]
CNF film has adhered to the Li metal anode	Stable Coulombic efficiency of 99.9%.	Specific capacity of 1.0 $mAh·cm^{-2}$.		This can be cycled for more than 300 cycles.	[32,33]
PANi is used as electrode material	Could improve its behavior by using various techniques in preparing suitable size, pore, etc.	High specific capacitance is shown		Good cycling stability	[34]

MXene phase Ti2C is used as the cathode host.	Using this method is highly effective for mitigating polysulfides.	1200 mAh/g	80% capacity retention is achieved over 400 cycles.	They show stable long term cycling	[35,36,]
Co/N-C-S electrode. (Used Co/N-C modified separator)	It is effective in confining shuttle effect	1614.5 mAh/g. It achieved 5.5 mAh/cm^2 area capacity.		It exhibits stable cycling properties for a long time.	[38]
N-doped porous carbon microspheres		692.3 mAh g^{-1}	Displays 91% capacity retention after 100 cycles. Reversible capacity of 1030.7 mAh g^{-1}	High-performance rate and remarkable cyclic stability.	[39-41]
The cathodes were fabricated with lithium metal powder onto a coated S/MC cathode electrode	Columbic efficiency of almost 100%.	It exhibited a stable capacity of around 600 mAh/g in 150 cycles.	It exhibited a reverse capacity of about 650 mAh/g even after 900 cycles.		[42]
graphite electrode (super-concentrated ether electrolyte)	Columbic efficiency nearing 100%	Specific capacity of 1031 mAh g^{-1} sulfur.	It exhibited a reversible capacity of 686 mAh g^{-1} Sulfur even after 105 cycles.		[43-45]

2.3. Development of electrolytes in Li-S batteries

The high solubility of lithium polysulfides in typical electrolytes contributes to and exacerbates the shuttling effect, resulting in rapid capacity fading, poor cycling performance, and low columbic efficiency Li-S battery [7,9]. The problem of the shuttle effect has been addressed via the development of new electrolytes. Liquid electrolytes at its best, reduce or inhibit the shuttling effect by using appropriate solvents, additives, and Li salts[16]. A solid electrolyte interface (SEI) is a conducting passivation layer, it is formed on electrode surface from decomposition products of electrolytes, it allows Li+ transport and blocks electrons in order to prevent further electrolyte decomposition [46]. This layer can suppress the shuttling effect, decrease the interfacial resistance, inhibit further reduction of the electrolyte; however, the formation of SEI can also lead to capacity fading, reduction in cycling and rate performance due to the limited ionic conductivity. Hybrid electrolytes combining soft polymer and sulfide based solid-state electrolyte have an edge over the single electrolyte system, enabling high ionic conductivity, improving flexibility and toughness. Designing resourceful and compatible electrode-electrolyte for a Li-S battery is a practical and effective way to achieve high-performance lithium-sulfur batteries.

Gel electrolyte has high ionic conductivity at room temperature which is as the same order of magnitude as liquid electrolyte. To protect the sulfur cathode and suppress shuttling effect, an integrated gel electrolyte/electrode can be constructed. However, due to gel electrolyte's low mechanical strength, the lithium dendrites cannot be easily inhibited.

In ceramic electrolyte-based lithium-sulfur batteries, the shutting effect can be controlled effectively by blocking the migration of polysulfides. However, the main disadvantage is the large ceramic electrolyte/electrode interfacial resistance leading to large polarization. Ceramic electrolytes with compact structure are critical to prevent lithium dendrite formation.

Utilizing composite electrolytes with special structures containing inorganic electrolyte and solid polymer electrolytes in Lithium-sulfur batteries can also productively supress the shuttle effect of Sulfur. However, due to the low ionic transportation in solid polymer electrolytes and grain boundaries separating the solid polymer electrolytes and sulfide, the polymer/ceramic composite electrolyte can only work at high temperatures,

A polymer/ceramic/polymer sandwich electrolyte also can effectively suppress dendrite nucleation and growth. [47,48]. In (FIGURE 4) we can see the development direction of electrolytes to improve Li-S battery's efficiencies.

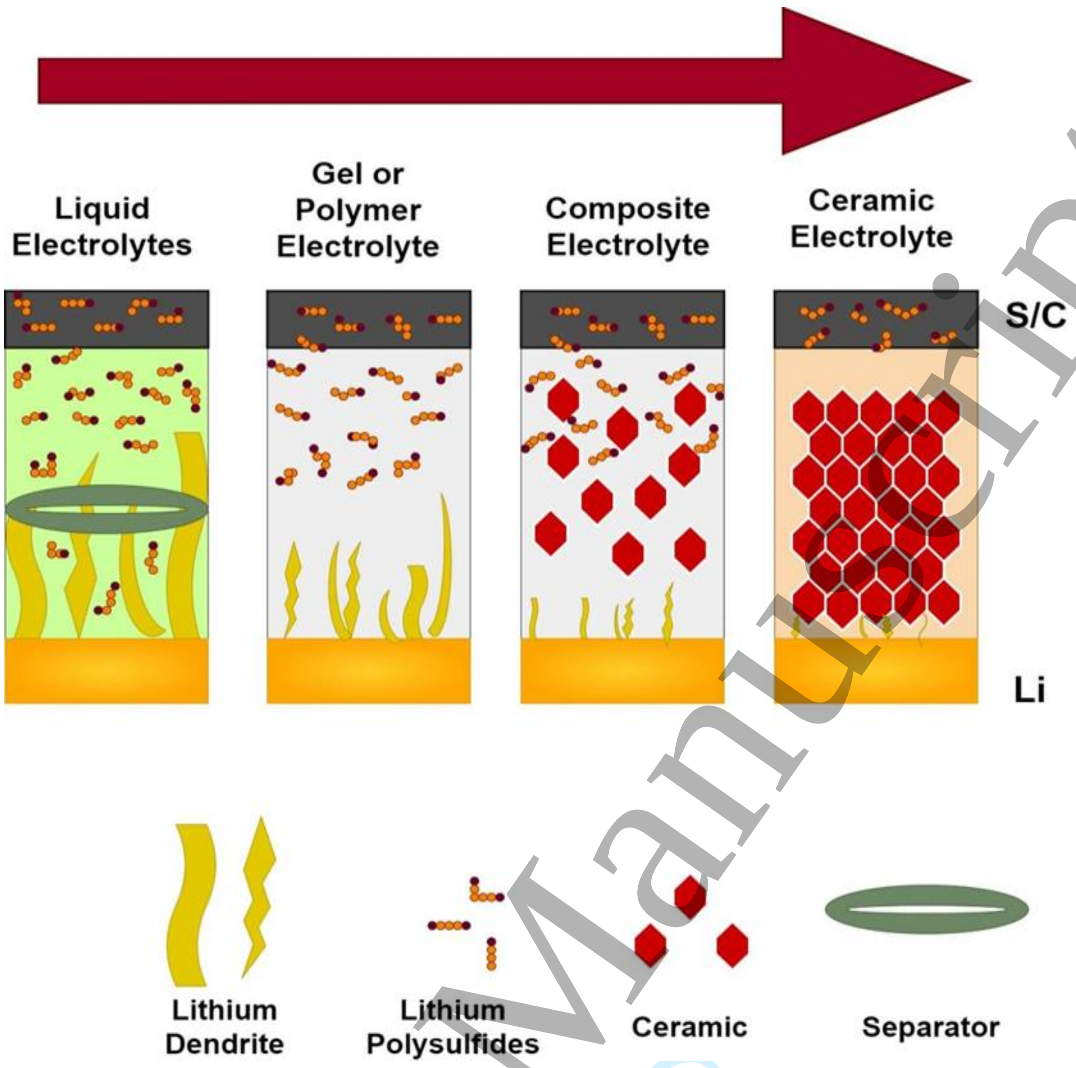

FIGURE 4. Development of electrolytes in Li-S batteries

The current developments of lithium-ion batteries are that they have primarily been used in laptops and cell phones. Li-ion batteries differ from each other in changing the cathode material. Thus, considering the different parameters such as cost, performance, etc., the efficiency of different lithium-ion batteries is evaluated discussed in this table (Table 2). [4]

Table 2. Various characteristics of different Li-ion batteries.

Characteristics	Cost	Specific Energy	Performance	Lifespan	Safety
$LiMnO_2$ Battery	Low	Moderate	Low	Low	Moderate
$LiFePO_4$ Battery	Low	Low	Moderate	High	High
$LiCoO_2$ Battery	Low	High	Moderate	Low	Low
Remarks	Thus, Li-ion batteries have	Lithium Cobalt	Li-ion batteries have	Lithium-ion	Lithium-ion phosphate

	a comparatively low cost.	oxide has higher specific energy, which makes it suitable for laptops & cell phones.	moderate performance when compared with the other batteries.	phosphate shows a high lifespan which makes it suitable for electric motorcycles.	provides high safety that makes it suitable for electric vehicles.
References	[6,20]	[11,50, 51]	[36,52,53]	[54, 55]	[10, 56]

High energy density Li-S batteries are ideal for flexible devices since they can store a lot of energy in a small amount of mass and work for a relatively long time. [50]

Polymer and carbonaceous materials produce higher energy density owing to the absence of an Al current collector. Li-S batteries can be fabricated using high electrical conductivity and good flexibility carbon nanotubes film, but its high cost and complex process obstruct its widespread application [57]. Polymer or biomass can be easily prepared for flexible carbon materials, but the sacrifice of their mechanical strength, electrical conductivity, and flexibility cancels out their built-in advantages. Due to the multistep reaction and dissolution of polysulfides, outstanding performance of flexible Li–S batteries needs the participation of multiple components[60]. Utilizing a polymer as a supporting substrate or as the binder could help in inhibiting the shuttling effect. Utilizing a solid-state electrolyte helps in boosting electrochemical performance and improving the safety of Li-S batteries compared to a single-component cathode.

The flexible cathode’s area capacity should be improved for practical application. Durability is essential for a flexible battery, and hence the battery should be able to exhibit strong tolerance against 10,000s deformations while maintaining the electrochemical performance [61].

2.4. Li-S Batteries Compared with Competitors

Batteries such as Li-S, Mg-S, Na-S, Ca-S, K-S, Al-S are rechargeable and trending energy storage devices. They use Sulfur based cathode since it is economical and abundantly found. They have various challenges that need to be overcome before their practical usage. [13]

Magnesium-sulfur batteries have gained attention because they are cheap, sustainable, and mainly dendrites-free. However, Mg-S batteries face many uncertainties due to the insufficiency of Mg ion conducting electrolytes, thus causing poor cycling stability. Mg-S batteries would be of great interest for a renewable and sustainable future, but due to the struggle of finding a compatible electrolyte, extensive efforts are needed before Mg-S batteries have their breakthrough and can be used at an experimental stage. [62,63]

Sodium-sulfur batteries are in the spotlight owing to their non-toxicity and low cost. Na-S batteries operating at high temperatures between 300-350°C have been used commercially for large-scale energy storage devices. However, using such high temperatures bring about safety issues and increases cost and maintenance. Due to this, tremendous efforts are being taken to reduce the working temperatures and promote room temperature Na-S batteries. Room temperature Na-S batteries face their challenges of low reversible capacity, low discharging capacity, and severe cycling problems. All these drawbacks obstruct the progress of room temperature Na-S batteries. [64-66]

Calcium-sulfur batteries show great promise for energy storage applications due to their relatively high energy and low cost. Calcium has a high volumetric capacity of ~2070 mAh cm^{-3} and a reduction potential of -2.8 V vs. SHE, which is near to that of Lithium and lower than that of magnesium. The voltage and energy density are higher than that of magnesium. In order to obtain an energy-dense system, calcium is said to be ideal for pairing with Sulfur. [51]

There are a number of reasons why potassium-sulfur cells will be particularly useful as an energy storage technology. Results show that the potassium sulfur battery can be operated at a relatively low temperature, about 150°C. K-S provides a comparatively lower energy density. The elemental abundance of both potassium and Sulfur is high, and the manufacturing cost is low. The performance is demonstrated with relatively high reversible capacity and stable cycling performance. The voltage range between 0.8–2.9 V vs. K^+/K is the most promising as the columbic efficiency is nearly 100%. [54]

Table 3. Comparison of Various Batteries/Power Sources with Li-S Battery.

Parameters	Electrode used	Efficiency	Voltage	Capacity Retention	Energy Density	References
Li-S Battery	Anode-Li Cathode- S/C composite	90% Columbic efficiency	2.1 V	70% after over 40 cycles	2500 Wh/kg	
Mg-S Battery	Anode-Mg Cathode- S/C composite	99.9 % Columbic efficiency	1.3 V	69% after 110 cycles	1722 Wh/kg	[62.63]
Na-S battery	Anode-Na Cathode- Molten Sulfur	79.1% Columbic efficiency	2 V	77.7 % after 200 cycles	150–240 Wh/kg	[64-66]
Ca-S Battery	Anode-Ca Cathode- S/C composite	-----------	2.1 V	-----------	1835 Wh/kg	[51]
K-S Battery	Anode-K	Nearing 100%	0.8–3.0 V	86.3% over 300 cycles	914 Wh/kg	[54]

	Cathode-Molten Sulfur	Columbic efficiency				

From Table 3, it is clear that the potassium sulfur batteries are the most desirable lithium ions batteries in terms of efficiency. It shows nearly 100% columbic efficiency, making it a suitable energy storage system for large-scale applications. It also uses molten Sulfur as cathode with a higher melting point and about 99.8% purity. However, the energy density is comparatively lower than that of other lithium-ion batteries.

3. Electrodes in Li-S Battery

3.1. Electrodes used in various research works

The electrode is easily the most important part of any battery, whose composition and design significantly influence the battery's capacity, energy density, and speed of storing Lithium. Generally, in Li-S batteries, the anode is made of metallic Lithium, while Sulfur is used for the positive electrode [24]. As pure Sulfur is not a good conductor of electrons, it is incorporated into a carbon matrix during the construction of the anode.

Porous Carbon is a popular material used for composites meant for Li-S battery electrodes and several have been discussed for the electrochemical performances, viability, and scope for improvement. Other electrode materials include nitrogen-doped graphene paper, lithium alloys, gel-based Sulfur, and many more.[30] Carbon materials, like Graphene, carbon nanotubes, meso/microporous carbons, hollow carbon spheres, and even carbon nanofibres and Carbon black, known for their conductance, is utilized by dissolving in Sulfur to magnify its electrochemical efficiency. The carbon structure also entraps dissolvable polysulfides during the cycling process.

Porous Carbon-based electrodes

Porous Carbon in carbon nanotubes is gaining more popularity as an innovative electrode material used in significant Li-S battery developments. The unique morphological and electronic structures of porous CNT's give them wide application in material science, energy storage, and biological and environmental technologies.

A hybrid CNT cathode using a sulfur-rich copolymer has been made for the sole benefit of double confinement of polysulfides when used in high-energy lithium-sulfur batteries. A sulfur-1,3-diisopropenylbenzene@CNT (S-DIB@CNT) membrane cathode was used for the experiment [67-69]. The two types of confinements occur when the CNT wall structure traps the polysulfide ion and when the Sulfur binds together with the sulfur copolymer (FIGURE 5). This strategy eliminates the use of binders as well as the metal current collector electrode to give an electrode with 880mAh/g specific capacity and 98% capacity retention over 100 cycles (Table 4), thus offering an innovative and efficient method for the manufacture of high-performance sulfur copolymer-carbon matrix electrodes for Li-S batteries. [70]

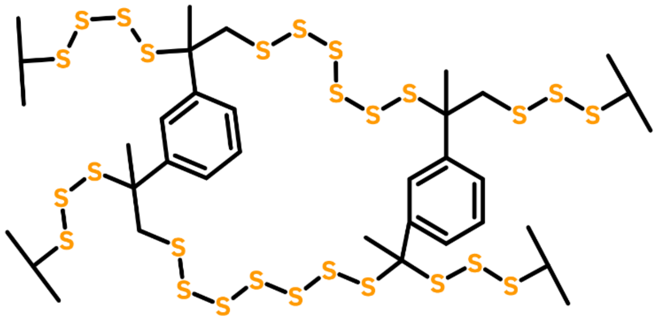

FIGURE 5. S-DIB@CNT structure

N-Doped Graphene paper made by pyrolysis of Poly-diallyldimethylammonium chloride (PDDA) when used as electrode material showed significant improvements like better charge capacity, absorptivity, and cycling stability as well as uniform thickness of the film due to enhanced binding of S containing species onto the N-sites of the electrode with an enhanced binding energy of 168.2 eV [71,72], usually forming at the edges of the graphene paper, as well as the decrease in sulfide concentration in the electrolyte. [73]

Sulfur vapor infiltrated CNT nanotubes with 3D structure have been considered for electrode manufacture due to their high areal loading and capacity. Utilization of capillary thermodynamics, which analyses the capillary rise and its properties for the infiltration of Sulfur into foam, enables the formation of a thick CNT conductive foam that maintains its charge conduction pathways and electrical accessibility, which are crucial for the areal performance of the cathode. [74]

Carbon nanoribbon (CNR) aerogels derived from bacterial cellulose have been used to form a gel-based sulfur cathode achieving both high sulfur loadings of 6.4 mg/cm² as well as 90% sulfur content giving excellent cell performance (943 mAh/g capacity and 99% coulombic efficiency over 200 cycles) which is mainly attributed to the gel-based structure of the cathode which can reduce the lithium polysulfide shuttling effect and store large amounts of catholyte [75]. The interconnected web structure enables fast electron transfer and Li+ migration, and its electrolyte retention ability prevents polysulfide dissolution.

Biomass-derived porous carbons with nanostructured (BDNPCs) have been used as interlayers and hosts for Sulfur in Li-S batteries, and they are cheap and eco-friendly alternatives to traditional sources, electrodes incorporated with BDNPCs showed excellent electrochemical properties like high initial capacity (1295 mAh/g, 1193 mAh/g), coulombic efficiency above 95%, large pore volume (0.38 and 1.05 cm³/g) and surface area (791.8 and 2269 m²/g), as shown in Table 4[69,60]

Table 4. Electrodes Compared based on specific Parameters applicable in a Li-S Battery.

Parameters/Electrode material	Discharge capacity	Energy density	Areal capacity	Coulombic efficiency	Hazards	Unique properties	Ref
N-doped Graphene Paper	1256 mAh/g	1675mA/g	10 mAh/cm²	99% over 300 cycles	N.A	Significantly improved uniformity and thickness of Li_2S film on cathode	[72]
S-vapor infiltrated CNT foam	1039 mAh/g	>500 Wh/kg	19.3 mAh/cm²	N.A	Ice formation in macropores reduce surface area	Can incorporate capillary forming and nanomaterials in 3D composite	[75]
Graphene foam	1059 mAh/g	1500 mA/g	13.4 mAh/cm²	95% over 1000 cycles	N.A	Excellent flexibility	[44]
Gel Based Sulfur	1260 mAh/g	3.22 mA/cm²	4.84 mAh/cm²	99% over 200 cycles	N.A	Large catholyte storage	[76]
Biomass-derived porous Carbon	1134 mAh/g	200 mA/g	N.A	98.3% over 400 cycles	N.A	High surface area and physiochemical stability	[24]

3.2. Carbon Electrodes in Li-S Batteries

Carbonaceous materials have been used in various formulations because of their positive impact on resulting conductivity and chemical stability. The use of carbons for batteries and fuel cells have been significantly increased due to these features. Carbonaceous materials also help out as a catalyst for electrochemical reactions. Materials derived from Carbon are also made into compact structures that are utilized by being the bipolar separator or by entrapping the current. [76]

Table 5 shows few materials doped and their effect on various parameters such as discharge capacity, efficiency, and capacity retention.

Lithium-carbon composites are also employed, wherein the lithium species are inserted in the middle of various layer planes like graphite or disordered carbons, and they act as a negative electrode in lithium-ion batteries. Graphitic carbon products are now starting to be excessively utilized as negative electrodes in lithium-ion cells. Mesoporous carbon materials of pore size 2-50 nm, which have better electrical conductivities than traditional graphites, are also used to aid the charge-discharge performance of the Li-S batteries. These three-dimensional materials have a large surface area and a considerable quantity of highly ordered, homogenous mesopores inside the matrix structure [77], these changes to the structure helps with the incorporation of more Sulfur and keep the volumetric change of Sulfur in check with the composite. This concept of design by pore structure is an important avenue of research regarding electrolyte selection and efficiency of the conducting matrix. The design has been considered to incorporate various types of solid electrolytes as well, which would help the ionic conducting network in the matrix. [78-80]

The drawbacks of using traditional Sulfur in Li-S batteries are numerous, despite its high theoretical capacity. Its drawbacks include rapid capacity degeneration and low coulombic performance, which occurs from mixing of decomposition products, like Li_2S and polysulfides in the electrolyte. This polysulfide dissolution is a leading cause of the erosion of active Sulfur and the repressing of its extensive lithiation, which becomes explicitly more serious during slow charge-discharge processes [45]. It is not suitable for electrochemical efficiency at low cycling rates. There is also a long cycle steadiness when high charge/discharge rates exist, which is another big issue with sulfur cathodes with extensive sulfur content.

The carbon-based derivatives from metal-organic frameworks (MOFs) have also arisen in their usage as cathode has for Li–S batteries. They are not just highly conductive and permeable to empower the speed increase of ion transfer and accommodation of volumetric development of sulfur cathode during cycling. Tuneable chemical active sites also advance them to empower the adsorption of polysulfides and advancement of their conversion reaction kinetics. Due of the different types of MOFs, the designs, formation process and morphology, primary prevalence of MOFs-derived carbon structures alongside their electrochemical performance as cathode have in Li–S batteries are seen to be beneficial.

The various materials in which carbon-based subsidiaries were derived include ZIF-8 (synthesized by Zn^{2+} and 2-methylimidazole with a SOD (sodalite) zeolite-type structure, which exhibits an exciting nanopore topology formed by four-ring and six-ring ZnN_4 clusters), ZIF-67 (formed by bridging 2-methylimidazolate anions and cobalt cations, resulting in a sodalite topology with a pore size of about 0.34 nm), bimetallic ZIFs, Prussian blue and Prussian blue analogs and AI-PCP (Al(OH)(1,4-naphthalene dicarboxylate)) [81]

Heteroatom doping is considered a leading avenue to work on the electrochemical action of carbon-based electrode materials for both Li-ion batteries (LIBs) and Na-ion batteries (SIBs) because of the presentation of an unstable electron environment and developed interlayers of carbon materials. Nitrogen and sulfur double-doped flexible carbon (NS-C) film is displayed as an unsupported anode for stable high power and energy LIBs or SIBs. The NS-C film conveys large reversible 965.7mAh g^{-1} capacity in LIBs and 520.1 mAh g^{-1} in SIBs at a current density of 100 mAg^{-1}. Significantly, the film electrodes show brilliant high-paced capacity and momentous long-haul cyclability. For example, as a LIBs anode, the NS-C film stayed at a high capacity of 357.2 mAh g^{-1} at 2.0 Ag^{-1} (~10 min to full charge) after 2000 cycles; even in SIBs, a capacity of 155mAh g^{-1} can likewise be reached at 1.0 Ag^{-1} [82]

Table 5. Some Materials Doped in Carbon Electrode & Its effect to overall battery's working

Materials Doped	Amount of material doped/Synthesis	Discharge capacity	Coulombic efficiency	Capacity Retention	References
Phosphorus	phosphorus-functionalized CNTs (PCNTs) with phosphorus content 1.66%	1106 mAh g^{-1}	High > 96%	75% after 100 cycles	[69]
Nitrogen	Schizochytrium sp. with protein >66% which provides for Carbon and Nitrogen	692.3 mAh g^{-1}	High 92.7%	91% after 100 cycles	[39]
Cobalt decorated Nitrogen	The unattached Co, N-CNFs membrane is trimmed into round discs (6mm radius), and a pre-prepared Li2S6 catholyte is added to make the Co, N-CNFs/Li2S6 composite electrode.	1166 mAh g^{-1}	100 % (Li2S6-based Co, N-CNFs)	71.3% after 100 cycles	[40]
Sulfur	S doped porous Carbon with sulfur content 5.7 %	1380 mAh g^{-1}	High	783 mAh g^{-1} after 100 cycles	[41]

3.3. Material Characterization of Carbon Electrode In-Comparison with other electrodes used in Li-S Battery.

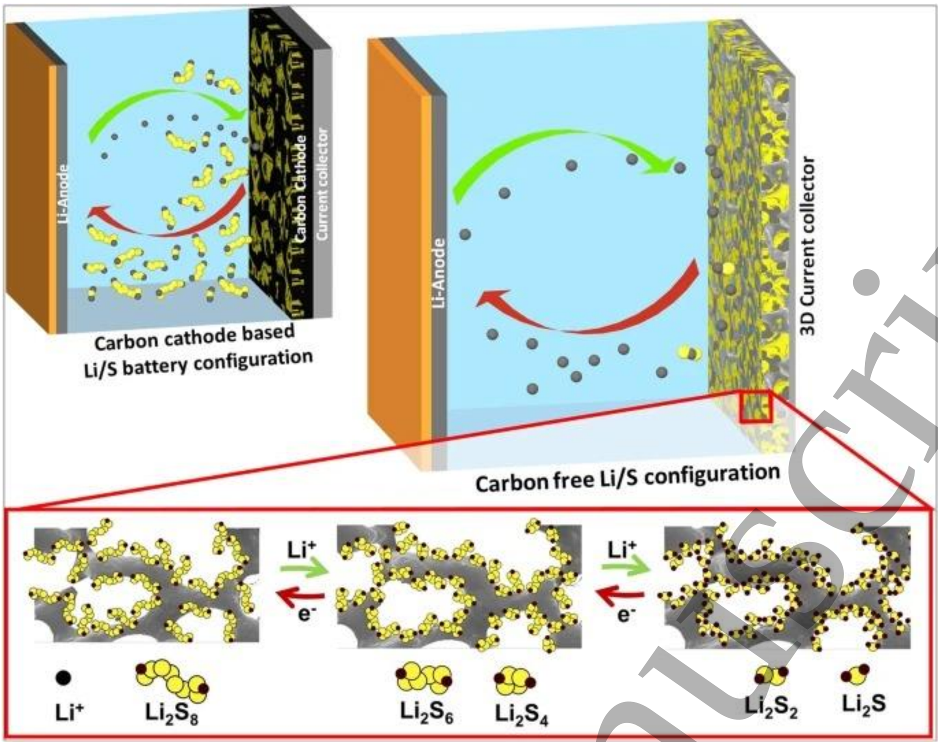

FIGURE 6. Li-S Battery Comparison with Carbon & Carbon-free Configurations [117]

Figure 6 shows the comparison of Li-S battery Configurations: With Carbon Electrode and Without them, alongside representing of conventional carbon cathode-based Li/S battery configuration and novel Metal/PS/Metal battery configuration with majority of PS shuttling mechanism confined on the surface of three-dimensional current collectors [117].

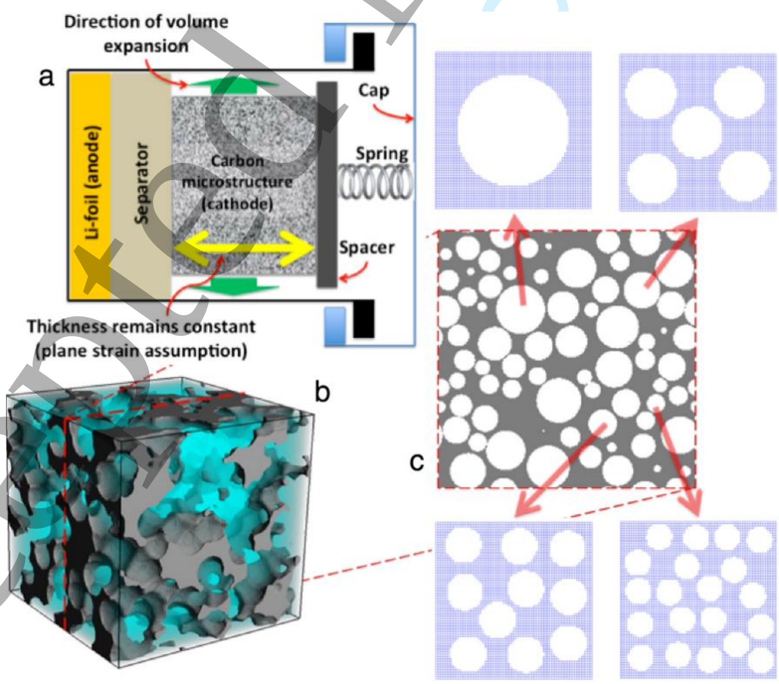

FIGURE 7. (A) Carbon electrode used in Li-S Battery, With (B) 3D view, (C) Cross-sectional view of the cathode microstructure containing spherical pores. [118]

In Figure 7, the zoomed-in images indicate the different pore size distributions possible within the same cathode microstructure [118]. Hierarchical porous Carbon (HPC) consists of a porous conductive media made up of amorphous Carbon, which effectively improves sulfur encapsulation in the electrode. The pores of less than 2nm are very effective against polysulfide dissolution due to their strong adsorption and desolvation of carrier ions leading to a solvent-free environment. The micropores (FIGURE 8) act as a barricade to prevent dissolution and hence ensure full cycling. The HPC structure was formed using ultra-high-speed spray pyrolysis. The micropores on the outer shell were found to be crucial in achieving good electrochemical properties and good cycling stability and inhibition of polysulfide dissolution. [83-85]

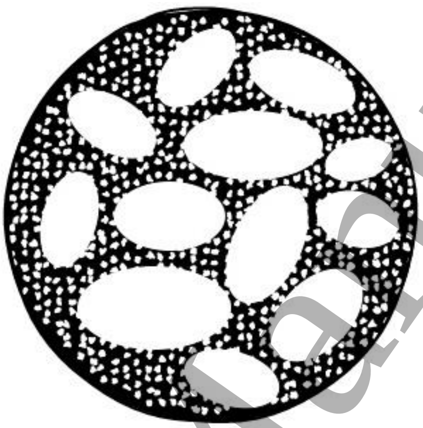

FIGURE 8. HPC structure with micropores on the outer shell

Modifications to the carbon electrode can be done with several materials to improve its electroanalytical behaviour. Usage of multi walled carbon nanotubes (MWCNTs) on the electrode surface have shown reduced impedance upto 95%. Silver-doped titania nanoparticles have also been experimented on in an effort to improve electrochemical performance. Modified electrodes such as these find several applications in industries like pharmaceuticals, textiles as well as in the detection of various hazardous compounds in chemical feeds and finished products.

4. Discussion of Technical Developments in Li-S Batteries

Tang, Q. et al. (2014) reported that Nafion is a copolymer coated on the electrode to boost the overall performance of a Li-S battery. After a series of experiments and measurements, it exhibited a columbic efficiency of 100% and was quite effective in decreasing the shuttle effect and increasing the stability and reversibility of the electrode. However, after a long period of cycling, a crack is observed. Even though this crack exists, it gave an initial discharge capacity of 1084 mAh g^{-1} and a high initial reversible capacity of 1091 mAh g^{-1} [20].

Zheng, S. et al. (2013) studied the Li_2S/MC cathodes were fabricated with a Li metal powder. The Li_2S/MC cathode exhibits stable cycling and a capacity of 510 mAh g^{-1} with a columbic efficiency of 100% and without a visible capacity decline for 800 cycles. A reverse capacity of 650 mAh g^{-1} remained the same even after 900 cycles which displays the best electrochemical performance of Li_2S/MC cathodes. This cathode can also be paired with a Li-free anode like tin, graphite, etc. When paired with graphite, it shows a stable capacity of 600 mAh g^{-1} in 150 cycles. This method will play a significant part in propagating these Li_2S/MC cathodes and developing a Li-S battery [42].

In the research conducted by Zhang, A. et al. (2016) the Cu current collector was modified with a 3D carbon nanofiber network for a dendrite-free Li metal which can be achieved due to its large surface area, high conductivity, and internal capacity of the carbon nanofiber network. This CNF modification can be cycled for more than 300 cycles and exhibits a specific capacity of 1.0 mAh·cm^{-2} with 99.9% columbic efficiency. The 3D structure helps for an even Li growth, dendrite free. Additionally, a stable SEI layer forms that protects the Li metal anode [32].

Liang, X. et al. (2015) noted that MXene nanosheets could function as excellent sulfur cathodes due to their high metallic conductivity and self-functionalized surfaces. They can effectively mitigate the shuttling effect and show long-term cycling stability with a per cycle capacity fade rate of 0.05 % and 80% capacity retention over 400 cycles. They exhibit a specific capacity of about 1200 mAh/g. These results show that they can be promising electrodes for high-performance lithium-sulfur batteries [35].

Jiang, S. et al. (2020) found that the Co/N-C has a micro mesoporous structure and can act as the sulfur host and active material for the modifying separator. It has a coulombic efficiency of close to 100%, which shows that the Co/N-C can stimulate the conversion of polysulfides and confine the shuttling effect. Thus, the results show that it can deliver a high reversible capacity of 1614.5 mAh/g. Moreover, exhibits stable long-term cycling over 1000 cycles with a capacity decay of only 0.04% per cycle. They also have a high area capacity of 5.5 mAh/cm^2, making this method a promising approach [38].

Wang, H. et al. (2016) stated that, PANi is a conducting polymer, and due to its environmental friendliness, economical, good flexibility, exclusive redox properties, and high electrical, proton conductivity, it can be used as an electrode material for Li-S batteries. It exhibits high specific capacitance good cycling stability. PANi can easily couple with other carbonaceous, metal, polymer electrode materials and enhance the battery's performance. PANi can act as a protective network of porous conductive support. Using various techniques to prepare suitable sizes, pores, etc., PANi can be a promising electrode material [34].

Xia, Y. et al. (2017) prepared a low-cost N-doped carbon microsphere using sustainable microalgae as Nitrogen and carbon source. It has a hierarchically porous structure that can help achieve high electronic conductivity and high sulfur content and suppresses the polysulfide shuttling effect. As a result, the cathode exhibited a superior reversible capacity of 1030.7 mAh g^{-1} with an exceptional capacity retention of 91% after 100 cycles and delivered a sufficient discharge capacity of 692.3 mAh g^{-1}. This method is a green and practical biosynthetic approach to design high-performance sulfur cathode and controllable fabrication of lithium-sulfur batteries [39].

Zeng, P. et al. (2017) paired graphite anodes with sulfur composite cathodes in a super-concentrated ether electrolyte. This system makes the Li-S battery safer since replacing the lithium metal anode with graphite is also beneficial in shunning corrosion of Li metal anode. The electrolyte has a peculiar networking structure of Li^+ ions and TFSI anions with Li cations and forms a stable TFSI derived film, which helps suppress continuous electrolyte decomposition and polysulfide shuttling effect. Thus, a high specific capacity of 1031 mAh g-1 with a columbic efficiency of 100% and a reversible capacity of 686 mAh g-1 after 105 cycles. It is a cheap and safe method owing to the substitution of Li metal anode with graphite, making it a promising energy storage device [43].

Zhu, L. et al. (2014) explained that employing CNTs as cathode materials exhibited a high initial discharge capacity of 1288 mAh·gS^{-1} and a high areal discharge capacity of 3.21 mAh·cm-2 and achieved the highest sulfur utilization of 77% in comparison to other cells. These CNTs exhibit conductive scaffolding and provide potent ion channels and electron pathways and a robust electrochemical environment to carry out the electrochemical process of Li-S batteries. It is a productive method to build composite electrode-cathode for Li-S batteries [27].

In the research conducted by Liu, M. et al. (2015), high-surface-area carbon derived from coconut shells and activated by KOH was loaded with Sulfur and used as the electrode for Li-S battery. The microporosity of the activated Carbon and the mesoporosity of the entire system helps in shuttling the polysulfide effect with a high columbic efficiency of 99.9% and exhibited a high initial discharge capacity of 1233 $mAhg^{-1.}$ The capacity retention of 929 mAh g^{-1}, which is capacity retention of 80% after 100 cycles, was achieved due to strong absorption force and high pore volume. Its low cost and easy availability make this electrode quite promising for advanced Li-S batteries [22].

Han, K. et al. (2014) demonstrated and explained that N-doped graphene paper has good electrochemical properties due to its sulfur binding capabilities. The coin cell test confirms its efficiency and specific capacities as a free-standing binder-free electrode. The effects of N-doping were studied using EIS measurements and showed good cycling stability after 100 cycles at 0.2 C. Electrodes with different distributions of N species were compared to confirm that the pyrrolic and pyridinic N sites enhance the battery performance more effectively. (FIGURE 9) shows the cycling performances of both concentrations were found to have almost identical specific capacity and charge-discharge voltages, the only significant difference being in its stabilization period and activation process, which took more cycles for higher concentrations [72].

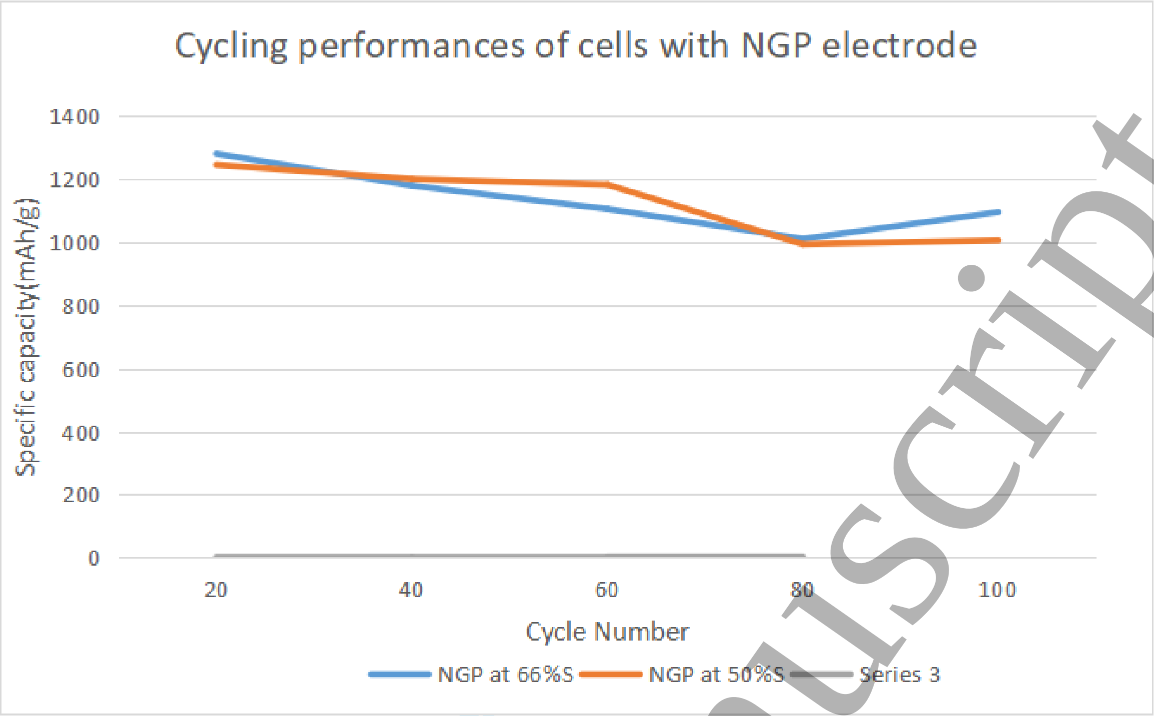

FIGURE 9. Different cycling performances of NGP electrodes with two types of sulfur loadings, namely 66% and 50%

Imtiaz, S. et al. proved biomass-derived porous carbons to be an innovative alternative for sulfur hosts and interlayers as they are cheap, efficient, and show excellent electrochemical performance [24]. Electrochemical tests show that microporous Carbon prevents polysulfide dissolution significantly while mesoporous Carbon improves the sulfur loading and ionic/electronic/electrolyte transmission.

Li, M. et al. (2017) explained that CNT foams infiltrated with Sulfur and other materials had been found to show high gravimetric and areal capacities[75]. This method of vapor infiltrating various materials into pre-formed low-density materials is a cost-effective and scalable way to manufacture high-energy-density cathodes with wide application in a variety of nanostructured composites. In this research, a low-density CNT foam was vapor infiltrated with Sulfur using capillary thermodynamics and tested for its energy density and sulfur utilization. The optimistic results prove the viability of these battery-oriented nano-manufacturing methods in a large-scale industry to manufacture high-energy Li-S batteries with advanced 3D architecture.

Li, S. et al. (2015) found that usage of aerogels in Li-S batteries have recently gathered research momentum mainly due to their ability to achieve high loading of Sulfur and increase sulfur content, which was difficult to achieve simultaneously in traditional electrode designs [74]. The carbon nanoribbon aerogel (Am-CNR) used in this research achieved high specific capacities at high sulfur loadings. This high performance is mainly attributed to the strong retention capability of the gel to the catholyte, high surface area, the microporous structure of the nanoribbon design, and its strong binding to the polysulfides. Additionally, its low-cost and environmentally friendly nature makes them an excellent candidate for future electrode research.

According to the literature review and case studies conducted in [39-41,69], the doping of some materials showed an improvement in discharge capacities, coulombic efficiencies, and capacity retention. For instance, phosphorus functionalized carbon nanotubes (PCNTs) with a phosphorus content of 1.66% showed a high discharge capacity of 1106 $mAhg^{-1}$ and a high coulombic efficiency of more than 96 percent and capacity retention of 75% after 100 cycles. Nitrogen and Carbon were provided by Schizochytrium sp. with protein prepared using low-cost and renewable microalgae. This doping of Nitrogen into Carbon to produce N-containing groups aid in strong chemical adsorption to polysulfides and also, at the same time, keep the polysulfide shuttle effect on the low, and they help in using active materials. They produce an appreciable discharge capacity of 692.3 mAh g^{-1} and a high coulombic efficiency of 92.7%, and high-capacity retention of 91% after 100 cycles. Cobalt decorated Nitrogen has a discharge capacity of 1166 mAh g^{-1} and outstanding superior efficiency of 100 %, and capacity retention of 71.3% after 100 cycles. Sulfur doping with a 5.7% sulfur content and a high discharge capacity of 1380 mAh g^{-1}, a high coulombic efficiency, and capacity retention of 783 mAh g^{-1} after 100 cycles. This shows that doping plays a significant role in an improved electrochemical performance with a maximum reversible specific capacity, superior rate capability, and high cyclic stability.

5. Summary

The available literature and research works show that usage of pure materials for Li-S batteries is not an efficient or industrially viable production method due to an almost certain material degradation by polysulfide dissolution, low conductivity, and various other restricting factors, hence making its electrochemical performance not even in par with top competitors like Li-ion batteries. Thus, the need for different electrode materials and process changes that improve performance is now more than ever.

The construction and design of the Li-S battery system and its electrodes show us the various electrode combinations possible to achieve its high theoretical capacity of 1675 mAh/g and theoretical gravimetric energy density of 2510 Wh/kg at 2.15V discharge voltage. Out of all the scenarios considered, promising results were found using CNT, Graphene, conducting polymers, and activated carbon types as the electrodes. Several types of composite electrodes composed of Sulfur with porous Carbon, CNTs, and Graphene showed us the wide application of these materials in Li-S batteries.

Conducting polymers like PANi and nafion are trending due to their environmental friendliness, economy, good flexibility, exclusive redox properties, and high electrical, proton conductivity. They can be used as an electrode material for Li-S batteries. They display high specific capacitance and good cycling stability. PANi can easily couple with other carbonaceous, metal, polymer electrode materials and enhance the battery's performance. It can act as a protective network of porous conductive support. Using various techniques to prepare suitable sizes, pores, etc., PANi can be a promising electrode material. [127] Nafion can be coated on the electrode to boost the overall performance of a Li-S battery and exhibits a columbic efficiency of 100%. It is effective in lessening the shuttle effect and increasing the stability and reversibility of the electrode. [20]

Carbon nanotubes have powerful mechanical, thermal properties, hierarchical porous structure, excellent electrical conductivity, high surface area, good surface-to-weight ratio, and satisfying storage capacity. CNTs have proven their worth in the industry as a multi-purpose material with exceptional mechanical properties like high Young's modulus (1.2 TPa) and tensile strength (50-200 GPa). They can serve a variety of roles in the battery composition like conductive materials inside the electrodes (binder-free CNT networks and CNT arrays), supporting materials used for efficient loading of active materials for their full utilization, and even as fully active materials storing Li+ ions on the surface as well as playing a catalytic role in the battery process. Thus, enhancing the capacity and stability of many battery groups. CNTs as cathode materials exhibited high discharge capacity and areal discharge capacity and achieved the highest sulfur utilization compared to other cells. These CNTs exhibit conductive scaffolding and provide potent ion channels and electron pathways and a robust electrochemical environment to carry out the electrochemical process of Li-S batteries.[27]

Graphene-based electrodes are emerging because of their robust Van der Waals force of attraction, good electrical conductivity, thermal and mechanical properties. Porosity and large surface area. Graphene is known for its high mechanical stiffness as well as its elasticity and strength (Young's modulus of 1 TPa and 130 GPa intrinsic strength), and its electron mobility at room temperature make it an optimal candidate for use in the electrochemical energy storage device as an electrode material. Regardless of the excellent electrochemical properties of graphene variants like GA and 3D graphene foam like hierarchical architecture, good electrical conductivity, and added benefits like pore rich binder free 3D networks, light weight, and good flexibility during volume expansion make them great for usage in advanced lithium battery systems. Using Graphene exhibited high energy density, high specific capacity, and long cyclability.[43]

The architecture of these composite electrodes proved to have a significant impact on their electrochemical performance. Although individual usage of these components showed promising results, sulfur-carbon hybrid gave even better specific capacity, coulombic efficiency, and rate performance when compared to other composite electrodes.

Flexible lithium batteries are another exciting avenue in the field of advanced wearable electronics like roll-up displays, on-body sensors, touchscreens, and much more. The inclusion of flexible solid-state electrolytes in the batteries resulted in excellent electric and mechanical properties, although achieving good operational safety and cycling stability while maintaining high power density is still a challenge for most flexible electrode materials. Regardless development of flexible LIBs to give low-cost, high-energy-density wearable electronics looks promising for future applications. [57]

In summary, this paper highlights the various advancements in Li-S battery technology and the various materials used for its development in the past years as well as future developments that can be expected which would refine and optimize existing electrode/electrolyte technology in order to produce efficient high energy, environmentally friendly Li-S battery systems that can compete with and even replace traditional energy storage solutions. [89, 90]

6. Conclusion & Future Directions

In this review, the recent progress in the carbon-based electrode in Li-S batteries is discussed. Several papers reveal that slight alterations in the structure can enhance the overall performance of the battery. The various electrode materials used for the different battery setups have shown us the pros and cons of Li-S battery designs. While new and innovative techniques for improvement are always encouraged, it should be noted that these technologies require much refinement before they can be implemented on an industrial scale [91, 92]. Several ground-breaking techniques like C-nanofiber interlayers, biomass-derived carbon sources, solid-state gel-based electrolytes, and flexible electrodes deserve much appreciation and further research. Development of crucial electrode materials like CNT, Graphene, and conducting polymers should be done further to improve their conductivity and retention capabilities [93-95]. In the future, materials with large surface area and good conductivity need to be advanced as they increase cyclability, specific capacity, and rated capacity. Lithium-sulfur batteries are subjected to the polysulfide shuttling effect caused due to the diffusion and dissolution of polysulfides in the electrolyte, resulting in rapid capacity fading, low columbic efficiency, and poor cycling performance of the Li-S battery [96, 97].

Lithium-ion batteries are the leading used battery technology in today's world despite environmental concerns. Lithium-sulfur batteries have drawn massive attention over the past few decades because the energy density of lithium-sulfur batteries is relatively much higher than that of traditional lithium-ion batteries [98]. Even though Li-S batteries are low-cost and eco-friendly, the shuttle phenomena of polysulfide and the low conductivity of Sulfur resulted in the hindrance of economic applications of Li-S batteries. Thus, they are not used for high-power applications [99, 100]. In order to get control of these drawbacks, various research has been conducted. It is found that the vertically aligned carbon nanotube can boost the battery life about ten times and may also increase energy storage and battery life-cycle around fourfold [101].

Electrolyte plays a crucial role in determining the performance of Li-S battery. Selecting a resourceful electrolyte and a compatible electrode-electrolyte for a Li-S battery enables good ionic transportation and achieves high-performance lithium-sulfur batteries. A solid electrolyte interface also knows as SEI, is a conducting passivation layer [102]. This can suppress the shuttling effect, decrease the interfacial resistance, inhibit further reduction of the electrolyte; however, the formation of SEI can also lead to capacity fading, reduces the cycling and rate performance due to the limited ionic conductivity. The absence of a liquid component whose fluidic properties will restrict the size and design of the cell is a significant improvement over conventional electrolyte types. Leakage prevention, short-circuiting, and separator usage are of no concern when using a solid-state electrolyte [103]. An optimal SEI layer should be Li ion-conducting and electronically insulating. Designing methods ranging from electronic to microscopic scale and phenomenological models are crucial and should be synchronized with each other to make predictions in terms of both qualitatively and quantitatively. Electronic, ionic, and mechanical properties of coating materials might change after lithiation; hence, modeling of the SEI chemical compositions should be done after lithiation. Additionally, computational modeling can be combined with experiments to balance one another and lead to the development of an efficient battery system [104].

Developing flexible cathodes opens opportunities for the Li-S battery to be utilized as a high-energy flexible storage device. Developing flexible batteries requires additional research into its different components like flexible cathodes, anodes electrolytes, and separators. Various electrode materials have their strengths and shortcomings. Carbon nanotubes CNTs and Graphene have low columbic efficiency and low reversible capacity, but they have good flexibility and electrical conductivity [105]. Fabricating these electrodes can help in overcoming the above challenges. To develop a practical, flexible energy storage system, both highly flexible cathode and anode should be given due consideration. Carbon-based materials have many advantages in designing flexible electrodes due to their excellent electrical conductivity, superior mechanical flexibility, high chemical stability, lightweight, low cost, and easy availability. Combining other high-capacity electrode materials with carbon-based electrodes will improve their overall electrochemical performance [106]. Flexible solid-state electrolytes have also been researched as their high ionic conductivity plays a vital role in flexible Li-S battery construction. Graphene-foam-based flexible electrodes are a new avenue of research that can be focused on to improve upon existing technology and discover new flexible electrode materials as possible alternatives. This current S-PDMS/GF electrode has proven the viability of these electrodes for industrial usage by showing excellent rate performance with good stability and high areal capacity. In the future, this graphene-based flexible electrode structure can also be used for other materials like lithium titanium oxide, lithium iron phosphate, and several silicon variants. [107] Future emphasis should be given to improving the electrochemical properties and boosting the mechanical properties of the electrode to the total usage of its flexibility. Overall, future development should focus on the progress of materials having good electrochemical properties and stability in the system. Developing these materials will enhance the energy storage stability and capacity of Lithium-sulfur batteries [108-110].

Several papers on the various electrode materials used were discussed to find the optimal one with low cost and excellent electrochemical properties. Porous Carbon is the most commonly used electrode material due to its high electronic conductivity, structural stability, pore-volume, and surface area [111-113]. Mesopores under 10nm are extremely good at sulfur adsorption and trapping polysulfide molecules, enabling fast transport of lithium ions and electrons from the insulating Sulfur [114, 115]. Computational calculations show that different 2D materials exhibit different adsorption features with the Li2Sn species and the atoms of Sulfur in the cluster determine the binding energy. 3D architectures can have higher sulfur loading due to their high pore volumes and unique structures. Sandwich type 3D architecture involving Graphene's, graphene oxides, PAQSs, and graphene CNT hybrids should be researched in the future to develop more practical applications for Li-S batteries, lithium composite anodes, high-performance separators, and current collectors can utilize these porous carbon designs to improve upon existing electrode technology and lead new research directions for Li-S batteries in the future. [116-118]

References

1. Gröger, O., Gasteiger, H. A., & Suchsland, J.-P. (2015). Review—Electromobility: Batteries or Fuel Cells? Journal of The Electrochemical Society, 162(14), A2605–A2622. doi:10.1149/2.0211514jes
2. Guan, Y., Liu, X., Akhtar, N., Wang, A., Wang, W., Zhang, H., … Huang, Y. (2019). Cr2O3 Nanoparticle Decorated Carbon Nanofibers Derived from Solid Leather Wastes for High Performance Lithium-Sulphur Battery Separator Coating. Journal of The Electrochemical Society, 166(8), A1671–A1676. doi:10.1149/2.1181908jes
3. Oschatz, M., Thieme, S., Borchardt, L., Lohe, M. R., Biemelt, T., Brückner, J., … Kaskel, S. (2013). A new route for the preparation of mesoporous carbon materials with high performance in Lithium–sulphur battery cathodes. Chemical Communications, 49(52), 5832. doi:10.1039/c3cc42841a
4. Ou, J., Yang, L., Zhang, Z., & Xi, X. (2016). Honeysuckle-derived hierarchical porous Nitrogen, sulphur, dual-doped Carbon for ultra-high rate lithium ion battery anodes. Journal of Power Sources, 333, 193–202.. doi:10.1016/j.jpowsour.2016.09.163
5. Liu, Y., Li, G., Fu, J., Chen, Z., & Peng, X. (2017). Strings of Porous Carbon Polyhedrons as Self-Standing Cathode Host for High-Energy-Density Lithium-Sulphur Batteries. Angewandte Chemie International Edition, 56(22), 6176–6180. doi:10.1002/anie.201700686
6. Liu, H., Liu, X., Li, W., Guo, X., Wang, Y., Wang, G., & Zhao, D. (2017). Porous Carbon Composites for Next Generation Rechargeable Lithium Batteries. Advanced Energy Materials, 7(24), 1700283. doi:10.1002/aenm.201700283
7. Urbonaite, S., & Novák, P. (2014). Importance of "unimportant" experimental parameters in Li–S battery development. Journal of Power Sources, 249, 497–502. doi:10.1016/j.jpowsour.2013.10.095
8. Manthiram, A., Fu, Y., & Su, Y.-S. (2012). Challenges and Prospects of Lithium–Sulphur Batteries. Accounts of Chemical Research, 46(5), 1125–1134. doi:10.1021/ar300179v
9. Zhao, M., Li, B. Q., Zhang, X. Q., Huang, J. Q., & Zhang, Q. (2020). A perspective toward practical lithium–sulfur batteries. ACS Central Science, 6(7), 1095-1104.DOI: 10.1021/acscentsci.0c00449
10. Zhang, Yongguang. (2011). Development in Lithium/Sulphur Secondary Batteries. The Open Materials Science Journal. 5. 215-221. 10.2174/1874088X01105010215.doi:10.2174/1874088X01105010215
11. Li, Z., Zhang, J., & Lou, X. W. D. (2015). Hollow Carbon Nanofibers Filled with MnO2Nanosheets as Efficient Sulphur Hosts for Lithium-Sulphur Batteries. Angewandte Chemie International Edition, 54(44), 12886–12890. doi:10.1002/anie.201506972
12. Mao, Y., Li, G., Guo, Y., Li, Z., Liang, C., Peng, X., & Lin, Z. (2017). Foldable interpenetrated metal-organic frameworks/carbon nanotubes thin film for Lithium–sulphur batteries. Nature Communications, 8, 14628. doi:10.1038/ncomms14628

13. Dysart, A. D., Burgos, J. C., Mistry, A., Chen, C.-F., Liu, Z., Hong, C. N., … Pol, V. G. (2016). Towards Next Generation Lithium-Sulphur Batteries: Non-Conventional Carbon Compartments/Sulphur Electrodes and Multi-Scale Analysis. Journal of The Electrochemical Society, 163(5), A730–A741. doi:10.1149/2.0481605jes
14. Li, X., Chen, Y., Huang, H., Mai, Y.-W., & Zhou, L. (2016). Electrospun carbon-based nanostructured electrodes for advanced energy storage – A review. Energy Storage Materials, 5, 58–92. doi:10.1016/j.ensm.2016.06.002
15. Pang, Q., Kwok, C. Y., Kundu, D., Liang, X., & Nazar, L. F. (2018). Lightweight Metallic MgB2 Mediates Polysulfide Redox and Promises High-Energy-Density Lithium-Sulphur Batteries. Joule. doi:10.1016/j.joule.2018.09.024
16. Nagao, M., Hayashi, A., & Tatsumisago, M. (2011). Sulphur–carbon composite electrode for all-solid-state Li/S battery with Li2S–P2S5 solid electrolyte. Electrochimica Acta, 56(17), 6055–6059. doi:10.1016/j.electacta.2011.04.084
17. Li, Z., Zhang, J., Guan, B., Wang, D., Liu, L.-M., & Lou, X. W. (David). (2016). A sulphur host based on titanium monoxide@carbon hollow spheres for advanced lithium–sulphur batteries. Nature Communications, 7, 13065. doi:10.1038/ncomms13065
18. ZHANG Qiang, CHENG Xin-bing, HUANG Jia-qi, PENG Hong-jie, WEI Fei. Review of carbon materials for advanced lithium-sulfur batteries[J]. *NEW CARBON MATERIALS*, 2014, 29(4): 241-264
19. Lach, J., Wróbel, K., Wróbel, J., & Czerwiński, A. (2021). Applications of Carbon in Rechargeable Electrochemical Power Sources: A Review. *Energies*, *14*(9), 2649.**https://doi.org/10.3390/en14092649**
20. Tang, Q., Shan, Z., Wang, L., Qin, X., Zhu, K., Tian, J., & Liu, X. (2014). Nafion coated sulphur–carbon electrode for high performance lithium–sulphur batteries. Journal of Power Sources, 246, 253–259. doi:10.1016/j.jpowsour.2013.07.076
21. Yu, Xingwen; Joseph, Jorphin; Manthiram, Arumugam (2015). Polymer lithium–sulphur batteries with a Nafion membrane and an advanced sulphur electrode. J. Mater. Chem. A, 3(30), 15683–15691. doi:10.1039/C5TA04289E
22. Liu, M., Chen, Y., Chen, K., Zhang, N., Zhao, X., Zhao, F., Dou, Z., He, X., and Wang, L. (2015). "Biomass-derived activated carbon for rechargeable lithium-sulphur batteries," *BioRes.* 10(1), 155-168.
23. Zhong, Y., Xia, X., Deng, S., Zhan, J., Fang, R., Xia, Y., … Tu, J. (2017). Popcorn Inspired Porous Macrocellular Carbon: Rapid Puffing Fabrication from Rice and Its Applications in Lithium-Sulphur Batteries. Advanced Energy Materials, 8(1), 1701110. doi:10.1002/aenm.201701110
24. Imtiaz, S., Zhang, J., Zafar, Z. A., Ji, S., Huang, T., Anderson, J. A., … Huang, Y. (2016). Biomass-derived nanostructured porous carbons for lithium-sulphur batteries. Science China Materials, 59(5), 389–407. doi:10.1007/s40843-016-5047-8
25. Liu, P., Wang, Y., & Liu, J. (2018). Biomass-derived porous carbon materials for advanced lithium sulphur batteries. Journal of Energy Chemistry. doi:10.1016/j.jechem.2018.10.005
26. Li, B., Xie, M., Yi, G., & Zhang, C. (2020). Biomass-derived activated carbon/sulfur composites as cathode electrodes for Li–S batteries by reducing the oxygen content. *RSC Advances*, *10*(5), 2823-2829.**https://doi.org/10.1039/C9RA09610H**

27. Zhu, L., Zhu, W., Cheng, X.-B., Huang, J.-Q., Peng, H.-J., Yang, S.-H., & Zhang, Q. (2014). Cathode materials based on carbon nanotubes for high-energy-density lithium–sulphur batteries. Carbon, 75, 161–168. doi:10.1016/j.carbon.2014.03.049
28. Dörfler, S., Hagen, M., Althues, H., Tübke, J., Kaskel, S., & Hoffmann, M. J. (2012). High capacity vertical aligned carbon nanotube/sulphur composite cathodes for Lithium–sulphur batteries. Chemical Communications, 48(34), 4097. doi:10.1039/c2cc17925c
29. Sun, L., Wang, D., Luo, Y., Wang, K., Kong, W., Wu, Y., … Fan, S. (2015). Sulphur Embedded in a Mesoporous Carbon Nanotube Network as a Binder-Free Electrode for High-Performance Lithium–Sulphur Batteries. ACS Nano, 10(1), 1300–1308. doi:10.1021/acsnano.5b06675
30. Fang, R., Li, G., Zhao, S., Yin, L., Du, K., Hou, P., … Li, F. (2017). Single-wall carbon nanotube network enabled ultrahigh sulphur-content electrodes for high-performance lithium-sulphur batteries. Nano Energy, 42, 205–214. doi:10.1016/j.nanoen.2017.10.053
31. Fang, R., Chen, K., Yin, L., Sun, Z., Li, F., & Cheng, H.-M. (2018). The Regulating Role of Carbon Nanotubes and Graphene in Lithium-Ion and Lithium-Sulphur Batteries. Advanced Materials, 1800863. doi:10.1002/adma.201800863
32. Zhang, A., Fang, X., Shen, C., Liu, Y., & Zhou, C. (2016). A carbon nanofiber network for stable lithium metal anodes with high Coulombic efficiency and long cycle life. Nano Research, 9(11), 3428–3436. doi:10.1007/s12274-016-1219-2
33. Chen, X., Yuan, L., Hao, Z., Liu, X., Xiang, J., Zhang, Z., … Xie, J. (2018). Free-Standing Mn3O4@CNF/S Paper Cathodes with High Sulphur Loading for Lithium–Sulphur Batteries. ACS Applied Materials & Interfaces, 10(16), 13406–13412. doi:10.1021/acsami.7b18154
34. Wang, H., Lin, J., & Shen, Z. X. (2016). Polyaniline (PANi) based electrode materials for energy storage and conversion. Journal of Science: Advanced Materials and Devices, 1(3), 225–255. doi:10.1016/j.jsamd.2016.08.001
35. Liang, X., Garsuch, A., & Nazar, L. F. (2015). Sulphur Cathodes Based on Conductive MXene Nanosheets for High-Performance Lithium-Sulphur Batteries. Angewandte Chemie, 127(13), 3979–3983. doi:10.1002/ange.201410174
36. Tang, X., Guo, X., Wu, W., & Wang, G. (2018). 2D Metal Carbides and Nitrides (MXenes) as High-Performance Electrode Materials for Lithium-Based Batteries. Advanced Energy Materials, 1801897. doi:10.1002/aenm.201801897
37. Xiao, Z., Li, Z., Li, P., Meng, X., & Wang, R. (2019). Ultrafine Ti3C2 MXene Nanodots-Interspersed Nanosheet for High-Energy-Density Lithium-Sulphur Batteries. ACS Nano. doi:10.1021/acsnano.9b00177
38. Jiang, S., Huang, S., Yao, M., Zhu, J., Liu, L., & Niu, Z. (2020). Bimetal-organic frameworks derived Co/N-doped carbons for lithium-sulphur batteries. Chinese Chemical Letters. doi:10.1016/j.cclet.2020.04.014
39. Xia, Y., Fang, R., Xiao, Z., Huang, H., Gan, Y., Yan, R., … Zhang, W. (2017). Confining Sulphur in N-Doped Porous Carbon Microspheres Derived from Microalgaes for Advanced Lithium–Sulphur Batteries. ACS Applied Materials & Interfaces, 9(28), 23782–23791. doi:10.1021/acsami.7b05798
40. Yao, S., Guo, R., Xie, F., Wu, Z., Gao, K., Zhang, C., … Qin, S. (2020). Electrospun three-dimensional cobalt decorated nitrogen doped carbon nanofibers network as free-standing

electrode for lithium/sulphur batteries. Electrochimica Acta, 135765. doi:10.1016/j.electacta.2020.135765

41. Yuan, Y., Chen, Z., Yu, H., Zhang, X., Liu, T., Xia, M., … Shu, J. (2020). Heteroatom-doped carbon-based materials for lithium and sodium ion batteries. Energy Storage Materials. doi:10.1016/j.ensm.2020.07.027
42. Zheng, S., Chen, Y., Xu, Y., Yi, F., Zhu, Y., Liu, Y., … Wang, C. (2013). In Situ Formed Lithium Sulfide/Microporous Carbon Cathodes for Lithium-Ion Batteries. ACS Nano, 7(12), 10995–11003. doi:10.1021/nn404601h
43. Zeng, P., Han, Y., Duan, X., Jia, G., Huang, L., & Chen, Y. (2017). A stable graphite electrode in super-concentrated LiTFSI-DME/DOL electrolyte and its application in lithium-sulphur full battery. Materials Research Bulletin, 95, 61–70. doi:10.1016/j.materresbull.2017.07.018
44. Zhou, G., Li, L., Ma, C., Wang, S., Shi, Y., Koratkar, N., … Cheng, H.-M. (2015). A graphene foam electrode with high sulphur loading for flexible and high energy Li-S batteries. Nano Energy, 11, 356–365. doi:10.1016/j.nanoen.2014.11.025
45. Pang, Q., Kundu, D., & Nazar, L. F. (2016). A graphene-like metallic cathode host for long-life and high-loading lithium–sulphur batteries. Materials Horizons, 3(2), 130–136. doi:10.1039/c5mh00246j
46. Kinoshita, S., Okuda, K., Machida, N., Naito, M., & Sigematsu, T. (2014). All-solid-state lithium battery with sulphur/carbon composites as positive electrode materials. Solid State Ionics, 256, 97–102. doi:10.1016/j.ssi.2013.12.045
47. Wang, A., Kadam, S., Li, H., Shi, S., & Qi, Y. (2018). Review on modeling of the anode solid electrolyte interphase (SEI) for lithium-ion batteries. *npj Computational Materials*, *4*(1), 1-26.https://doi.org/10.1038/s41524-018-0064-0
48. Wang, Q., Guo, J., Wu, T., Jin, J., Yang, J., & Wen, Z. (2017). Improved performance of Li-S battery with hybrid electrolyte by interface modification. *Solid State Ionics*, *300*, 67-72.https://doi.org/10.1016/j.ssi.2016.11.001
49. Li, G., Huang, Q., He, X., Gao, Y., Wang, D., Kim, S. H., & Wang, D. (2018). Self-formed hybrid interphase layer on lithium metal for high-performance lithium–sulfur batteries. *ACS nano*, *12*(2), 1500-1507.https://doi.org/10.1021/acsnano.7b08035
50. Liu, R., Liu, Y., Chen, J., Kang, Q., Wang, L., Zhou, W., … Huang, W. (2017). Flexible wire-shaped lithium-sulphur batteries with fibrous cathodes assembled via capillary action. Nano Energy, 33, 325–333. doi:10.1016/j.nanoen.2016.12.049
51. Pang, Quan; Liang, Xiao; Kwok, Chun Yuen; Kulisch, Joern; Nazar, Linda F. (2016). A Comprehensive Approach toward Stable Lithium-Sulphur Batteries with High Volumetric Energy Density. Advanced Energy Materials, (), 1601630–. doi:10.1002/aenm.201601630
52. Ren, J., Xia, L., Zhou, Y., Zheng, Q., Liao, J., & Lin, D. (2018). A reduced graphene oxide/nitrogen, phosphorus doped porous carbon hybrid framework as sulphur host for high performance lithium-sulphur batteries. Carbon. doi:10.1016/j.carbon.2018.08.026
53. Zhao, Y., Yin, F., Zhang, Y., Zhang, C., Mentbayeva, A., Umirov, N., … Bakenov, Z. (2015). A Free-Standing Sulphur/Nitrogen-Doped Carbon Nanotube Electrode for High-Performance Lithium/Sulphur Batteries. Nanoscale Research Letters, 10(1). doi:10.1186/s11671-015-1152-4

54. Tai, Z., Zhang, Q., Liu, Y., Liu, H., & Dou, S. (2017). Activated Carbon from the graphite with increased rate capability for the potassium ion battery. Carbon, 123, 54–61. doi:10.1016/j.carbon.2017.07.041
55. Matsuda, S., Kubo, Y., Uosaki, K., & Nakanishi, S. (2017). Lithium-metal deposition/dissolution within internal space of CNT 3D matrix results in prolonged cycle of lithium-metal negative electrode. Carbon, 119, 119–123. doi:10.1016/j.carbon.2017.04.032
56. Pang, Q., Kundu, D., Cuisinier, M., & Nazar, L. F. (2014). Surface-enhanced redox chemistry of polysulphides on a metallic and polar host for lithium-sulphur batteries. Nature Communications, 5(1). doi:10.1038/ncomms5759
57. Zhou, G., Li, F., & Cheng, H.-M. (2014). Progress in flexible lithium batteries and future prospects. Energy Environ. Sci., 7(4), 1307–1338. doi:10.1039/c3ee43182g
58. Zhuosen Wang, Xijun Xu, Shaomin Ji, Zhengbo Liu, Dechao Zhang, Jiadong Shen, Jun Liu,Recent progress of flexible sulphur cathode based on carbon host for lithium-sulphur batteries,Journal of Materials Science & Technology,Volume 55. doi:10.1016/j.jmst.2019.09.037.
59. Lee, W. Y., Jin, E. M., Cho, J. S., Kang, D.-W., Jin, B., & Jeong, S. M. (2020). Free-standing Flexible Multilayered Sulphur–Carbon Nanotubes for Lithium–Sulphur Battery Cathodes. Energy, 118779. doi:10.1016/j.energy.2020.118779
60. Chen, A., Li, Q., Chen, Z., & Zhi, C. (2021). Carbonaceous and Polymer Materials for Li–S Batteries with an Emphasis on Flexible Devices. *Advanced Energy and Sustainability Research*, *2*(6), 2000096.**https://doi.org/10.1002/aesr.202000096**
61. Xiao, Q., Yang, J., Wang, X., Deng, Y., Han, P., Yuan, N., ... & Liu, R. (2021). Carbon-based flexible self-supporting cathode for lithium-sulfur batteries: Progress and perspective. *Carbon Energy*.**https://doi.org/10.1002/cey2.96**
62. Ponraj, R., Kannan, A. G., Ahn, J. H., & Kim, D.-W. (2016). Improvement of Cycling Performance of Lithium–Sulphur Batteries by Using Magnesium Oxide as a Functional Additive for Trapping Lithium Polysulfide. ACS Applied Materials & Interfaces, 8(6), 4000–4006. doi:10.1021/acsami.5b11327
63. Bieker, G., Küpers, V., Kolek, M., & Winter, M. (2021). Intrinsic differences and realistic perspectives of lithium-sulfur and magnesium-sulfur batteries. *Communications Materials*, *2*(1), 1-12.https://doi.org/10.1038/s43246-021-00143-0
64. Wang, X., Li, G., Hassan, F. M., Li, J., Fan, X., Batmaz, R., … Chen, Z. (2015). Sulphur covalently bonded Graphene with large capacity and high rate for high-performance sodium-ion batteries anodes. Nano Energy, 15, 746–754. doi:10.1016/j.nanoen.2015.05.038
65. Xu, X., Zhou, D., Qin, X., Lin, K., Kang, F., Li, B., ... & Wang, G. (2018). A room-temperature sodium–sulfur battery with high capacity and stable cycling performance. *Nature communications*, *9*(1), 1-12.https://doi.org/10.1038/s41467-018-06443-3
66. Adelhelm, P., Hartmann, P., Bender, C. L., Busche, M., Eufinger, C., & Janek, J. (2015). From lithium to sodium: cell chemistry of room temperature sodium–air and sodium–sulfur batteries. *Beilstein journal of nanotechnology*, *6*(1), 1016-1055. https://doi.org/10.3762/bjnano.6.105

67. Li, Z., Vinayan, B. P., Diemant, T., Behm, R. J., Fichtner, M., & Zhao-Karger, Z. (2020). Rechargeable Calcium–Sulfur Batteries Enabled by an Efficient Borate-Based Electrolyte. *Small*, *16*(39), 2001806. https://doi.org/10.1002/smll.202001806
68. Feng, H., Tang, L., Zeng, G., Tang, J., Deng, Y., Yan, M., … Chen, S. (2018). Carbon-based core–shell nanostructured materials for electrochemical energy storage. Journal of Materials Chemistry A, 6(17), 7310–7337. doi:10.1039/c8ta01257a
69. Ghosh, A., & Lee, Y. H. (2012). Carbon-Based Electrochemical Capacitors. ChemSusChem, 5(3), 480–499. doi:10.1002/cssc.201100645
70. Guo, M., Huang, J., Kong, X., Peng, H., Shui, H., Qian, F., … Zhang, Q. (2016). Hydrothermal synthesis of porous phosphorus-doped carbon nanotubes and their use in the oxygen reduction reaction and lithium-sulphur batteries. New Carbon Materials, 31(3), 352–362. doi:10.1016/s1872-5805(16)60019-7
71. Hu, G., Sun, Z., Shi, C., Fang, R., Chen, J., Hou, P., … Li, F. (2016). A Sulphur-Rich Copolymer@CNT Hybrid Cathode with Dual-Confinement of Polysulfides for High-Performance Lithium-Sulphur Batteries. Advanced Materials, 29(11), 1603835. doi:10.1002/adma.201603835
72. Han, K., Shen, J., Hao, S., Ye, H., Wolverton, C., Kung, M. C., & Kung, H. H. (2014). Free-Standing Nitrogen-doped Graphene Paper as Electrodes for High-Performance Lithium/Dissolved Polysulfide Batteries. ChemSusChem, 7(9), 2545–2553. doi:10.1002/cssc.201402329
73. Jeong, Y. C., Lee, K., Kim, T., Kim, J. H., Park, J., Cho, Y. S., … Park, C. R. (2016). Partially unzipped carbon nanotubes for high-rate and stable Lithium–sulphur batteries. Journal of Materials Chemistry A, 4(3), 819–826. doi:10.1039/c5ta07818k
74. Li, Z., Huang, Y., Yuan, L., Hao, Z., & Huang, Y. (2015). Status and prospects in sulphur–carbon composites as cathode materials for rechargeable lithium–sulphur batteries. Carbon, 92, 41–63. doi:10.1016/j.carbon.2015.03.008
75. Li, M., Carter, R., Douglas, A., Oakes, L., & Pint, C. L. (2017). Sulphur Vapor-Infiltrated 3D Carbon Nanotube Foam for Binder-Free High Areal Capacity Lithium–Sulphur Battery Composite Cathodes. ACS Nano, 11(5), 4877–4884. doi:10.1021/acsnano.7b01437
76. Li, S., Mou, T., Ren, G., Warzywoda, J., Wei, Z., Wang, B., & Fan, Z. (2017). Gel based sulphur cathodes with a high sulphur content and large mass loading for high-performance lithium–sulphur batteries. Journal of Materials Chemistry A, 5(4), 1650–1657. doi:10.1039/c6ta09841j
77. Dicks, A. L. (2006). The role of Carbon in fuel cells. *Journal of Power Sources*, *156*(2), 128-141. https://doi.org/10.1016/j.jpowsour.2006.02.054
78. Suzuki, K., Tateishi, M., Nagao, M., Imade, Y., Yokoi, T., Hirayama, M., … Kanno, R. (2016). Synthesis, Structure, and Electrochemical Properties of a Sulphur-Carbon Replica Composite Electrode for All-Solid-State Li-Sulphur Batteries. Journal of The Electrochemical Society, 164(1), A6178–A6183. doi:10.1149/2.0341701jes
79. Tripathi, B., Martinez, M. L. V., Katiyar, R. K., Sharma, K. B., & Katiyar, R. S. (2017). Scalable Study on Nanostructured Carbon – Sulphur Composite Electrodes for High Energy Lithium Sulphur (Li-S) Battery. ECS Transactions, 77(11), 47–57. doi:10.1149/07711.0047ecst

80. Wu, Q., Yang, L., Wang, X., & Hu, Z. (2017). From Carbon-Based Nanotubes to Nanocages for Advanced Energy Conversion and Storage. Accounts of Chemical Research, 50(2), 435–444. doi:10.1021/acs.accounts.6b00541
81. Song, J., Gordin, M. L., Xu, T., Chen, S., Yu, Z., Sohn, H., … Wang, D. (2015). Strong Lithium Polysulfide Chemisorption on Electroactive Sites of Nitrogen-Doped Carbon Composites For High-Performance Lithium-Sulphur Battery Cathodes. Angewandte Chemie International Edition, 54(14), 4325–4329. doi:10.1002/anie.201411109
82. Wu, Q., Zhou, X., Xu, J., Cao, F., & Li, C. (2019). Carbon-based derivatives from metal-organic frameworks as cathode hosts for Li–S batteries. Journal of Energy Chemistry. doi:10.1016/j.jechem.2019.01.005
83. Ruan, J., Yuan, T., Pang, Y., Luo, S., Peng, C., Yang, J., & Zheng, S. (2018). Nitrogen and sulphur dual-doped carbon films as flexible free-standing anodes for Li-ion and Na-ion batteries. Carbon, 126, 9–16. doi:10.1016/j.carbon.2017.09.099
84. Jung, D. S., Hwang, T. H., Lee, J. H., Koo, H. Y., Shakoor, R. A., Kahraman, R., … Choi, J. W. (2014). Hierarchical Porous Carbon by Ultrasonic Spray Pyrolysis Yields Stable Cycling in Lithium–Sulphur Battery. Nano Letters, 14(8), 4418–4425. doi:10.1021/nl501383g
85. Li, G., Sun, J., Hou, W., Jiang, S., Huang, Y., & Geng, J. (2016). Three-dimensional porous carbon composites containing high sulphur nanoparticle content for high-performance lithium–sulphur batteries. Nature Communications, 7, 10601. doi:10.1038/ncomms1060
86. Li, Z., Guan, B. Y., Zhang, J., & Lou, X. W. (David). (2017). A Compact Nanoconfined Sulphur Cathode for High-Performance Lithium-Sulphur Batteries. Joule, 1(3), 576–587. doi:10.1016/j.joule.2017.06.003
87. Wang, B., Wang, Y., Peng, Y., Wang, X., Wang, J., & Zhao, J. (2018). 3-dimensional interconnected framework of N-doped porous Carbon based on sugarcane bagasse for application in supercapacitors and lithium ion batteries. Journal of Power Sources, 390, 186–196. doi:10.1016/j.jpowsour.2018.04.056
88. Li, S., Leng, D., Li, W., Qie, L., Dong, Z., Cheng, Z., & Fan, Z. (2020). Recent progress in developing Li2S cathodes for Li–S batteries. *Energy Storage Materials*, *27*, 279-296.https://doi.org/10.1016/j.ensm.2020.02.010
89. Wang, S., Guo, J., Guo, R., Sun, X., Li, F., Li, T., ... & Luo, Y. (2021). CoS2 Nanospheres Anchored on 3D N-Doped Carbon Skeleton Derived from Bacterial Cellulose for Lithium-Sulfur Batteries. *Journal of The Electrochemical Society*, *168*(2), 020512. Doi:10.1149/1945-7111/
90. Wu, F., Chen, S., Srot, V., Huang, Y., Sinha, S. K., van Aken, P. A., … Yu, Y. (2018). A Sulphur-Limonene-Based Electrode for Lithium-Sulphur Batteries: High-Performance by Self-Protection. Advanced Materials, 30(13), 1706643. doi:10.1002/adma.201706643
91. Xu, J., Su, D., & Wang, G. (2017). Co3O4-Carbon Cloth free standing cathode for lithium sulphur battery. IOP Conference Series: Materials Science and Engineering, 222, 012013. doi:10.1088/1757-899x/222/1/012013
92. Zhang, S. S., & Tran, D. T. (2012). A proof-of-concept lithium/sulphur liquid battery with exceptionally high capacity density. Journal of Power Sources, 211, 169–172. doi:10.1016/j.jpowsour.2012.04.006

93. Zhang, L., & Du, J. (1999). Comparison of the Performance of Rockfill Dams of Different Heights. In *Waterpower'99: Hydro's Future: Technology, Markets, and Policy* (pp. 1-10)., doi: 10.1016/j.carbon.2018.09.067
94. Saisaban Fahad, Zhen Wei, Akihiro Kushima,In-situ TEM observation of fast and stable reaction of lithium polysulfide infiltrated carbon composite and its application as a lithium sulphur battery electrode for improved cycle lifetime, Journal of Power Sources. doi:10.1016/j.jpowsour.2021.230175
95. Wang, Z., Wang, L., Liu, S., Li, G., & Gao, X. (2019). Conductive CoOOH as Carbon-Free Sulphur Immobilizer to Fabricate Sulphur-Based Composite for Lithium–Sulphur Battery. Advanced Functional Materials, 1901051. doi:10.1002/adfm.201901051
96. Yan, Y., Cheng, C., Zhang, L., Li, Y., & Lu, J. (2019). Deciphering the Reaction Mechanism of Lithium–Sulphur Batteries by In Situ/Operando Synchrotron-Based Characterization Techniques. Advanced Energy Materials, 1900148. doi:10.1002/aenm.201900148
97. Ren, Y. X., Zeng, L., Jiang, H. R., Ruan, W. Q., Chen, Q., & Zhao, T. S. (2019). Rational design of spontaneous reactions for protecting porous lithium electrodes in Lithium–sulphur batteries. Nature Communications, 10(1). doi:10.1038/s41467-019-11168-y
98. Agostini, M., Hassoun, J., Liu, J., Jeong, M., Nara, H., Momma, T., … Scrosati, B. (2014). A Lithium-Ion Sulphur Battery Based on a Carbon-Coated Lithium-Sulfide Cathode and an Electrodeposited Silicon-Based Anode. ACS Applied Materials & Interfaces, 6(14), 10924–10928. doi:10.1021/am4057166
99. Ai, W., Luo, Z., Jiang, J., Zhu, J., Du, Z., Fan, Z., … Yu, T. (2014). Nitrogen and Sulphur Codoped Graphene: Multifunctional Electrode Materials for High-Performance Li-Ion Batteries and Oxygen Reduction Reaction. Advanced Materials, 26(35), 6186–6192. doi:10.1002/adma.201401427
100. Babu, G., Ababtain, K., Ng, K. Y. S., & Arava, L. M. R. (2015). Electrocatalysis of Lithium Polysulfides: Current Collectors as Electrodes in Li/S Battery Configuration. Scientific Reports, 5(1). doi:10.1038/srep08763
101. Barai, P., Mistry, A., & Mukherjee, P. P. (2016). Poromechanical effect in the Lithium–sulphur battery cathode. Extreme Mechanics Letters, 9, 359–370. doi:10.1016/j.eml.2016.05.007
102. Barchasz, C., Mesguich, F., Dijon, J., Leprêtre, J.-C., Patoux, S., & Alloin, F. (2012). Novel positive electrode architecture for rechargeable lithium/sulphur batteries. Journal of Power Sources, 211, 19–26. doi:10.1016/j.jpowsour.2012.03.062
103. Borchardt, L., Oschatz, M., & Kaskel, S. (2016). Carbon Materials for Lithium Sulphur Batteries-Ten Critical Questions. Chemistry - A European Journal, 22(22), 7324–7351. doi:10.1002/chem.201600040
104. Liao, H., Ding, H., Li, B., Ai, X., & Wang, C. (2014). Covalent-organic frameworks: potential host materials for sulphur impregnation in Lithium–sulphur batteries. J. Mater. Chem. A, 2(23), 8854–8858. doi:10.1039/c4ta00523f
105. Eftekhari, A., & Kim, D.-W. (2017). Cathode materials for Lithium–sulphur batteries: a practical perspective. Journal of Materials Chemistry A, 5(34), 17734–17776. doi:10.1039/c7ta00799j

106. Chen, W., Lei, T., Lv, W., Hu, Y., Yan, Y., Jiao, Y., … Xiong, J. (2018). Atomic Interlamellar Ion Path in High Sulphur Content Lithium-Montmorillonite Host Enables High-Rate and Stable Lithium-Sulphur Battery. Advanced Materials, 1804084. doi:10.1002/adma.201804084

107. Cheng, X.-B., Huang, J.-Q., Zhang, Q., Peng, H.-J., Zhao, M.-Q., & Wei, F. (2014). Aligned carbon nanotube/sulphur composite cathodes with high sulphur content for Lithium–sulphur batteries. Nano Energy, 4, 65–72. doi:10.1016/j.nanoen.2013.12.013

108. Cheng, Z., Pan, H., Zhong, H., Xiao, Z., Li, X., & Wang, R. (2018). Porous Organic Polymers for Polysulfide Trapping in Lithium-Sulphur Batteries. Advanced Functional Materials, 1707597. doi:10.1002/adfm.201707597

109. Ghazi, Z. A., Zhu, L., Wang, H., Naeem, A., Khattak, A. M., Liang, B., … Tang, Z. (2016). Efficient Polysulfide Chemisorption in Covalent Organic Frameworks for High-Performance Lithium-Sulphur Batteries. Advanced Energy Materials, 6(24), 1601250. doi:10.1002/aenm.201601250

110. Eroglu, D., Zavadil, K. R., & Gallagher, K. G. (2015). Critical Link between Materials Chemistry and Cell-Level Design for High Energy Density and Low Cost Lithium-Sulphur Transportation Battery. Journal of The Electrochemical Society, 162(6), A982–A990. doi:10.1149/2.0611506jes

111. Fang, X., & Peng, H. (2014). A Revolution in Electrodes: Recent Progress in Rechargeable Lithium-Sulphur Batteries. Small, 11(13), 1488–1511. doi:10.1002/smll.201402354

112. Fang, R., Zhao, S., Sun, Z., Wang, D.-W., Cheng, H.-M., & Li, F. (2017). More Reliable Lithium-Sulphur Batteries: Status, Solutions and Prospects. Advanced Materials, 29(48), 1606823. doi:10.1002/adma.201606823

113. Chadha, U., Bhardwaj, P., Padmanaban, S., Kabra, D., Pareek, G., Naik, S., Singh, M., Banavoth, M., Sonar, P., Singh, S., Latha, S., Ray, A.K., Badoni, B, & Rao, N.S. (2021). Carbon Electrodes in Magnesium Sulphur Batteries: Performance Comparison of Electrodes and Future Directions. Journal of The Electrochemical Society. https://doi.org/10.1149/1945-7111/ac4104

114. Kulkarni, K., Chadha, U., Yadav, S., Tarun, D M, K G, Thenmukilan, Bhardwaj, P., Singh, S., Latha, S., Ray, A.K., Badoni, B., Rao, N.S., Banavoth, M., & Sonar, P. (2021). Review—Latest Trends and Advancement in Porous Carbon for Biowaste Organization and Utilization. ECS Journal of Solid State Science and Technology. https://doi.org/10.1149/2162-8777/ac438a

115. Bhardwaj, P., Singh, S., Kharangarh, P.R. and Grace, A.N., 2020. Surfactant decorated polypyrrole-carbon materials composites electrodes for supercapacitor. Diamond and Related Materials, 108, p.107989.

116. Suriyakumar, S., Bhardwaj, P., Grace, A.N. and Stephan, A.M., 2021. Role of Polymers in Enhancing the Performance of Electrochemical Supercapacitors: A Review. Batteries & Supercaps, 4(4), pp.571-584.

117. Babu, G., Ababtain, K., Ng, K.S. and Arava, L.M.R., 2015. Electrocatalysis of lithium polysulfides: current collectors as electrodes in Li/S battery configuration. Scientific reports, 5(1), pp.1-7.

118. Barai, P., Mistry, A., & Mukherjee, P. P. (2016). Poromechanical effect in the lithium–sulfur battery cathode. Extreme Mechanics Letters, 9, 359-370.