A review on recent advancement in lithium-selenium batteries: Progress and prospects

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Abstract

Li-Se batteries are a new generation of batteries with noticeable benefits over the other Li-based counterparts, especially Li-S batteries owing to Se's greater melting point and better electrical conductivity compared to S, resulting in a battery that is safer at high temperatures. As a result, Li-Se batteries perform better electrochemically and have a substantially higher conductivity. Although selenium has certain issues with sulfur, such as the shuttle effect, which reduces battery efficiency, many researchers have concentrated on Li-Se batteries because of the potential they provide, such as improved performance in common carbonate-based electrolytes. After the rise of Li-Se batteries in the last 10 years, many researchers focused on improving Li-Se batteries in different parts, such as electrode active materials, electrolytes, separators, and binders. In this paper, we review the recent investigations on Li–Se batteries.

Keywords: *Lithium-selenium batteries, Energy conversion, Electrochemical properties, Various battery components*

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1. Introduction

Designing and developing renewable energy systems are crucial in recent years for declining the using of fossil fuels and GHG. Electrochemical energy storage devices such as batteries are effective answers for these issues and now people have higher and higher expectations for battery energy density due to the quick development of power grid applications and automotive electrification. It is widely agreed that grid-level energy storage, which transfers electricity from the electrical energy-producing network into a storable form and back into electrical energy when required, is an attractive technological solution to the problems above-outlined [1]. One of the most widely used methods of energy storage, lithium-ion battery (LIB) technology has recently seen a surge in popularity. However, when the electrochemical performance of the battery approaches its theoretical limit, practical LIB are having trouble keeping up with the rising demands [2]. Because of the increasing need for large-scale energy storage, high-performance secondary batteries have received a lot of research and development attention [3]. LIB have had outstanding success in extremely small electronic devices over the last twenty years. Even when fully developed, the maximum energy capacity that LIB can provide is still far insufficient for requirements [4,5]. For instance, high volumetric and gravimetric energy density are both necessary for electric vehicles [6].

As underdeveloped storage systems, lithium-selenium batteries offer advantages such as good electrochemical performance and high electrical conductivity of Se, making them a viable candidate for electrochemical energy storage (Figure 1). Despite having a similar volumetric energy density to Li-S batteries (2600 WhL^{-1}), Li-Se batteries have a lower specific capacity (675 mAhg^{-1}) than Li-S batteries [7]. In addition, Se has 510-28 Sm^{-1} which is much higher than S conductivity (110-3 Sm^{-1}). Therefore, this secondary battery type may be further improved to accommodate various needs by making use of their own benefits [8]. Notably, Se cathode has a greater capacity density of 3254 mAhcm^{-3}, which is higher than LiCoO$_2$ (700mAhcm^{-3}) and comparable to S (3467 mAhcm^{-3}). Even the specific capacity of Se is less than S but it is still significantly higher than LiCoO$_2$'s (274 mAhg^{-1}). Consequently, selenium and selenide have gained popularity as possible cathode materials for secondary batteries, commonly known as lithium-selenium batteries (LSeB). Basically, Se guarantees that Li batteries have greater energy storage capability. According to a schematic in Figure 1, LSeB have a high energy density of 2528 WhL^{-1}, which is comparable to lithium-sulfure batteries (LSB) (2800 WhL^{-1}) but much higher than LIB (1190WhL^{-1}) [9,10].

The battery's volumetric energy density is important for small devices and electric cars. Intriguingly, LSeB can function in hotter environments than LSB, thus expanding its spectrum of possible uses [10]. However, the battery's energy density per unit volume is also important to think about, particularly when the battery will be used in compact devices or electric vehicles [11-13]. The high inherent electronic conductivity of Se makes it possible to use pure Se as the cathode for LSeB in a variety of morphologies. Up
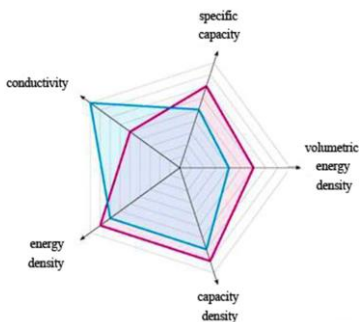
Figure 1. The properties and performances of LSB and LSeB

until now, it has been demonstrated that changing the morphology of Se can decrease the related volume changes (by =98%) while also promoting electrolyte infiltration. However, owing of the bothersome side effects and shuttle effects, performances are typically subpar, therefore, to avoid these problems two requirements should be provided by the ideal host:

I.   the Se species should be shielded from poly selenide diffusion and adverse reaction,

II.   use the conductive and electrolyte-accessible materials with enough sturdy to bear volumetric expansions [10].

In LSeB, lithium ions and electrons move between the anode and the cathode, storing chemical energy through the conversion of electric energy representing as $2\ Se_8 + 16\ Li \rightarrow 8\ Li_2Se$ which is very similar to the corresponding overall chemical reaction during the charge/discharge operation in LSB $16\ Li + S_8 \rightarrow 8\ Li_2S$ [8]. The first studies on Se-based cathodes back to the 1960s, when early metal-Se batteries had intriguing electrochemistry in combination with a metal anode, such as copper or silver, but the low capacity of anodes prevented them from meeting current practical usage standards. Since Li has the highest capacity (3860 mAhg^{-1}) and the most negative electrochemical potential, it is the suitable anode for batteries with high energy. After coupling with Se, LSeB are anticipated to provide adequate energy storage capability that is significantly superior than that of modern LIB. Fused salt electrolytes were employed in the prior research on LSeB, however, their study revealed that they are ineffective below 300°C [10]. Amine

et. al. in 2012, performed groundbreaking research to prove the Se cathode's feasibility in carbonate electrolytes, which helped rechargeable LSeBs reach a significant milestone. After that, LSeB research has attracted growing interest, and in the last few years, outstanding achievements have been made. Despite the fact that there have been a number of great reviews on materials research and technological advancement [10,14]. Newly discovered selenium sulfide (SexSy) compounds for high-energy-density Li-Se$_x$S$_y$ batteries [15], are able to adequately make up for selenium's higher cost and lower gravimetric energy density compared to that of sulfur [16]. They are able to do this by combining the large theoretical capacity of sulfur with the great electrical conductivity that selenium has. Selenium disulfide (SeS$_2$) has drawn the most attention among the different Se$_x$S$_y$ solid solutions [17] because it exhibits electrochemical characteristics that are comparable to those of sulfur and selenium. Recent research has shown that diverse porous carbon materials may function as acceptable hosts for hybrid SeS$_2$ cathodes when paired with various polar nanostructures, including sulfides, and nitrides oxides. Additionally, the regulated shuttle effect of intermediate polysulfides/poly selenides and volume fluctuations might improve the exploitation of active materials and cyclic stability in both ether- and carbonate-based electrolytes [13,15,16,18]. The latest current advancements in Li-Se batteries are discussed in this article.

2. Selenium-based cathode materials

Several important techniques are thoroughly investigated to overcome the difficulties of Se-based cathodes (Figure 2), including chemisorption, physical confinement, conductive structure and catalytic conversion of Se [19]. Modern cathodes based on se are categorized in the following and further described with significant structural and electrochemical properties in Table 1 to help distinguish between various techniques.

2.1 The electrochemical properties of Se-based cathodes

Normal Sulphur-carbon cathodes can only provide reliable performances in ether electrolytes. When used in ether and carbonate electrolytes, Se often exhibits

strong electrochemical properties [20]. In order to investigate how selenium behaves electrochemically in electrolytes containing of carbonate, Amine *et al.* [21] used X-ray near-edge absorption spectroscopy for the first time. During the lithiation/delithiation process, they found no intermediates of poly selenide and just selenium and lithium selenide. Due to the nucleophilic interactions with carbonate electrolytes, the polarization of S cathodes increased quickly, which can cause electrochemical activity to decrease.

porous carbons, and microporous carbons (Figure 2) [24-28].

Three distinct electrolytes, such as ester-based, ether-based, and solvate electrolytes, Bo Lu and colleagues [24] demonstrated the possibility of adjusting the cycle life and rate capacity of the electrochemical performance activity of the Se/C-based cathode for LSeB. Due to a serious polyselenide shuttle issue, the Se/C-based cathode revealed the ether-based solution has seen significant overcharging and demonstrated a
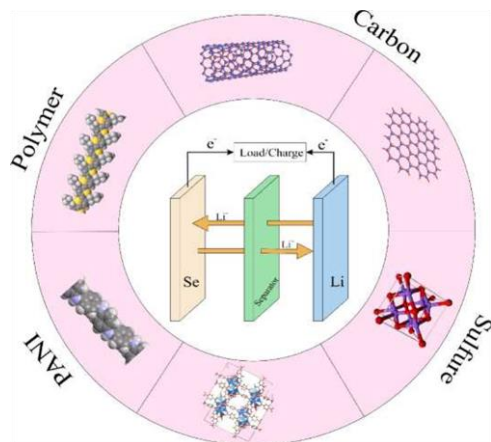

Figure 2. Type of Se-based cathodes [10].

S_8 rings are insulating because Se is in a chain in its thermodynamically steady state, whereas Sen chains have an organized construction that can encourage electrical conductivity. Se with a chain construction also has greater electrocatalytic activity and is more stable during cycling because each chain contains two active terminal atoms [22]. As a result of these two active terminal atoms, substrates can also be more effectively contacted. As an illustration, Li *et al.* [23] created a unique Se-based material that served as the cathode for a Li-Se battery and after 1200 cycles, displayed exceptional cycling stability.

2.2 Se-based electrodes with carbon

At the moment, it has been shown that making composite electrodes from materials like Se and carbon is a quick and efficient way to deal with the aforementioned problems. The parameters of Se hosts can be met by a number of carbon-based compounds, carbon nanotubes, including graphite, hierarchically

mediocre electrochemical performance activity in the ester-based electrolyte solution. With an initial specific capacity of 621 mAhg^{-1} after 200 cycles, the Se-carbon cathode achieved extraordinarily high Se usage, whereas the solvate electrolyte maintained a very low overpotential even when the composite's Se concentration exceeded 80%. When utilizing an ester-based electrolyte solution, the Se/C-based cathode technique has a modest electrochemical performance activity.

The Se-based cathode was produced using a hierarchical structure of porous carbon that was made from soybeans using an activation/carbonization technique for Li-Se batteries, according to research by Amir Hosein Ahmadian and colleagues [29]. In LSeB using a carbonate-based electrolyte, researchers looked at how the porosity structure of activated carbons changed depending on the activation temperature (500, 600, and 700°C). The electrochemical performance of the C-Se cathode composite was linked to this phenomenon. It was

discovered that raising the activation temperature resulted in a larger surface region and a larger pore volume for the porosity of carbon. The C600 Li-Se battery showed remarkable rate capability, good extended cycling stability, and a superb reversible discharge rate of the capacity of 640 mAhg^{-1} at 0.1 C after 100 cycles. Due to the highly porous structure of the C600/Se cathode, which may aid in the effective containment of Se, electrolyte solution wetting, Li-ion transit, and accommodating volume changes so it had higher electrochemical activity than the other samples. Both its pore volume and surface region are substantial. Junwei Hao and coworkers [30] stated that a simple synthesis process using a hydrothermal reaction was used to create a composite with a 3D hierarchical structure covered with CoSe2 nanoparticles and composed of mesoporous carbon nanosheets sitting atop carbon fiber fabric. CFC-C@CoSe$_2$ mesopores can effectively catalyze the conversion of the intermediates to Li$_2$S/Li$_2$ Se by chemically adsorbing the intermediates and physically restraining their movement as a complete substrate. In the soaking experiment, the CFC-C@CoSe$_2$ demonstrates a greater attraction to polysulfides/polyselenides than the comparison sample CFC-C@Co. Additionally, the CFC-C@CoSe$_2$ -SeS$_2$ cathode has a density of exchange current greater than the CFC-C@Co-SeS$_2$ cathode by three times, indicating that the latter has substantially far quicker charge-transfer kinetics. As a consequence, when measured at 1.0 Ag^{-1}, the independent CFC-C@CoSe$_2$SeS$_2$ electrode displays a remarkable initial capacity rate to 943.4 mAhg^{-1} having a remarkable coulomb efficiency.

Hoa Thi Bui and colleagues [31] has been suggested that interlayer MoSe2 may be electrochemically intercalated onto graphene Li$_2$Se-based cathode components. The initial chalcogenide Gr-MoSe$_2$ was produced in a closed system for reflux using diethylene glycol as the solvent, selenoacetamide as a source of selenium precursors and polypropylviologen as a source of carbon precursors. This was then put through calcination to create Gr-layers between the MoSe2 interlayers in an environment of argon and nitrogen. Then, Mo in Gr-MoSe2 nanomaterials is electrochemically decreased (lithiated process) to give selenide molecules and multilayered graphene structures,

which are simultaneously produced within graphene multilayered in Li-Se batteries. At a current density of 1 ag^{-1}, the cell's capacity decreases at a rate of 0.04 percent per cycle over 100 cycles. The active substance doesn't have any conductive carbon black additive., which is in line with the characteristics of Gr-MoSe$_2$, which we are also presenting here as a new class of Li$_2$Se cathode.

2.3 Se-based electrodes with sulfur

The scientific community has recently paid a lot of attention to lithium-sulfur/selenium batteries since they offer a potentially greater energy density than traditional lithium-ion batteries. Researchers are still hampered by the lithium-sulfur/selenium batteries' built-in shuttle effect and the large-volume effect of sulfur/selenium. However, due to their greater specific surface area, better flexibility, and stronger conductivity, metal-free carbon-based materials have emerged as a possible contender [32].

Yin Zhang and associates [33] Introduced an easy-to-engineer ultralight self-standing interlayer made of porous carbon fibers made from organic feed-stock and embellished with cobalt electrocatalysts (CF-Co), and with very little mass loading (0.14 mgcm^{-2}). The resulting Li-SeS$_2$ batteries are then enhanced by the addition of a very permeable hierarchical structure, conductive CF-Co interlayer with exceptional electrocatalytic effects and adsorptive to capture dual-intermediate polysulfides/poly selenides after the low conductivity sulfur (10-28 Sm^{-1}) is swapped out for the Selenium disulfide with a greater conductivity (SeS$_2$, 10-6 Sm^{-1}) is used as the active cathode material. As a result, the coin cells exhibit excellent performance under circumstances of superior SeS2 loading (5.0 mgcm^{-2}), with good cycling stability and extraordinary capacity for high rates (404 mAhg^{-1} at 8 Ag^{-1}). Importantly, by constructing this interlayer with double-side SeS$_2$-loading cathodes, functioning steadily at comparatively lower electrolyte conditions (6.0 mLmg^{-1}), high practical capacity (> 5.5 mAhcm^{-2}) LieSeS$_2$ pouch cells can be produced.

According to Youyi Lei and colleagues [9], Li-Se batteries may be made to operate more efficiently by trapping selenium in porous carbon hosts. It is still unclear how limited Se is structured and what

lithiation mechanism corresponds to it. In this study, a composite material called Se@CISC-58 that has the same amount of mesopores and micropores as CISC-58 hierarchically porous carbon was created and employed as the cathode material for LSeB. Se@CISC-58's loaded selenium assumes the Sex chain structure as opposed to the cyclic Se8 structure. In conclusion, Se@CISC-58 demonstrates good rate performance at a current density of 5 C with a specific capacity of 471.5 (297) mAhg^{-1}.

Chengwei Lu and colleagues [3] stated that two simple synthesis methods—ball milling and direct heating—have been effectively devised to generate pure Li2Se particles by reacting LiHpowerswith Se Powers (2 LiH + Se = Li$_2$Se + H$_2$). The microstructure of Li$_2$Se particles has been analyzed for the very first time using a technique known as cryogenic transmission electron microscopy. When loaded heavily, the Li2Se cathode performs electrochemically superiorly (698 mAhg^{-1} @ 50 mAg^{-1}@10.6 mgcm^{-2}; 333 mAhg^{-1} @ 1000 mAg^{-1} @ 7.1 mgcm^{-2}) is due to the active layer's excellent poly selenides-interception and high conductivity as well as its high polyselenides-trapping and reutilization capability. It is greatly anticipated that the practical use of the secure good energy-density of Li-Se batteries will be facilitated by this creative Li$_2$ Se synthesis approach and the interesting cathodic structure design.

2.4 S/Se-based electrodes with polymer

The polymers primarily used in LiS/Se batteries are polypyrrole (PPy), polythiophene (PTh), and polyaniline (PANI) along with its derivatives, such as poly (3,4-ethylene dioxythiophene) (PEDOT) and poly (3,4-ethylenedioxythiophene)-poly (styrene sulfonate) (PEDOT:PSS) [34]. This section presents the fundamental studies. In addition, some polymers have functional atoms (such as Nitrogen, Sulfide, or Oxygen) that may absorb lithium polyselenides, which makes them popular in Li-S/Se batteries. Additionally, the researchers created composite materials by combining polymers, carbon, and polar substances, and performing Li-S/Se batteries is enhanced by the composite materials' synergy. These polymers are primarily used in Li-S/Se batteries as the coating layers, host sulfur, interlayers, mediators of redox, and binders to prevent lithium poly selenide from

dissolving, reduce volume expansion, and increase the cathode's electrical conductivity, which relatively boosts the batteries' electrochemical performance [8].

The S/Se Elements make up the majority of the cathodes in Li-S/Se batteries. However, due to the insulating properties of S and the low conductivity of Se, S/Se does not have a solid crystal structure that can create a solid cathode electrode and a cage structure that can house lithium ions. This prevents S/Se from functioning as a lithium-ion battery. As a result, S/Se cannot be used to construct the whole cathode [35]. To address the aforementioned problems, researchers have suggested employing S/Se elemental in conjunction with other substances (such as metal-organic frameworks, conductive polymers, carbon, etc.) [8]. Wen-Da Dong and colleagues [36] described how they created S, O, and N co-doped hierarchically porous nanobelts of carbon (HPCNBs) for Li-Se batteries using entire Porous polymer networks (MPNs) based on organic melamine as a precursor. Quick transport routes for ions, electrolytes, and electrons are provided by the N, O, and S co-doping that produces the defect-rich HPCNBs, but it also effectively reduces volume change. With a capacity of 345 mAhg^{-1} after 150 cycles and an excellent rate capacity of 281 mAhg^{-1} even at 2000 mAhg^{-1} when used as a Li-ion battery, it shows an advanced lithium storage capability.

2.5 S/Se-based electrodes with PANI

PANI is speculated to have a total capacity of 294 mAhg^{-1} on a theoretical level and can take part in the electrode's redox process in the same area as the elemental S's S-S bond. Additionally, PANI possesses a potent immobilization ability that allows it to chemically seize evaporating lithium polysulfide (polyselenide) (Figure 2). The trapping process arises from the chemical interaction of the species that are composed of S/Se using the quinonoid imine (-N=) that is located on the quinone ring [8].

Li et al. [37] carbonized the hollow PANI to produce the N-containing HCSs. The depth of reaction was improved by the hollow carbonized PANI's high conductivity when it was used as a cathode storing medium for use. Additionally, the nitrogen atoms in its hollow structure and excellent trapping of Se and Li$_2$Sen. As a direct consequence of this, the HCPS/Se

cathode that had a high Coulombic efficiency was able to exhibit an initial discharge capacity rate of 571.5 mAhg^{-1}. The Se/C composites were coated with PANI using the oxidative polymerization process for LSeB. The PANI@Se/C-G composites were then made by enclosing the composites in sheets of graphene. After 500 cycles at a high rate of 2 C, the PANI@Se/C-G cathode was able to reach a great capacity rate of 528.6 mAhg^{-1} due to the interaction with graphene by the PANI layer may greatly speed up the movement of electrons and ions [8,38].

2.6 Se-based electrodes with MOF

In order to act as a barrier for the capture of LiPSs/ LiPSes in Li-SeS$_2$ batteries, Biao Wang and colleagues [3] reported a Co-N-C@C multifunctional porous membrane made from ZIF-67@PAN. The conductivity of the hierarchical porous network helps facilitate the movement of lithium ions and electrons through the material. The Co-N-C architecture, meanwhile, makes use of chemical interactions to both entrap free-floating LiPSs/ LiPSes and catalyze the LiPSs/ LiPSes conversion process throughout the cycle phase. Incorporating their multipurpose properties, the manufactured Li-SeS$_2$ cells with the aforementioned interlayer show off a remarkable rate capacity of 532 mAhg^{-1} at 3 Ag^{-1}.

3. Summary of selenium-based cathodes electrodes

An overview of important advances in Se-based cathodes is given in the table 1 below.

4. Components

The main components of this type batteries are cathodes, separator and binder. Which will be discussed in the next chapters.

Table 1. briefing on the purported Li-Se battery cathodes made from Se-based materials substances used for the cathode Se.

Sample	Electrolyte	Se Content (wt%)	Capacity (mAhg^{-1})	Life Cycles	Ref
Li-Se	-	-	-	1200 cycles	[23]
Se-based with carbon	ester	80 %	621	200 cycles	[24]
Se-based with porous carbon	-	-	640 at 0.1C	100 cycles	[29]
CFC-C@CoSe$_2$SeS$_2$	-	-	943.4		[30]
Gr-MoSe$_2$				100 cycles	[31]
CF-Co	-	0.14 mgcm^{-2}	404 at 8 Ag^{-1}	good	[33]
Se@CISC-58	-	-	471.5	-	[10]
Li$_2$Se	-	10.6 mgcm^{-2}	698 @50 mAg^{-1}	-	[3]
Li$_2$Se	-	7.1 mgcm^{-2}	333@ 1000mAg^{-1}	-	[3]
organic Melamine-based porous polymer	-	-	345	150 cycles	[36]
S/Se-based with PANI	-	-	294	-	[8]
PANI@Se/C-G	-	-	528.6	500 cycles	[37]
Co-N-C@C multifunctional porous membrane made from ZIF-67@PAN	-	-	532 at 3 Ag^{-1}	-	[3]

4.1 Cathodes

Since there aren't many chemical ways to make selenium, melting diffusion is typically used to create the most of selenium-based cathodes. Commercial Se powders are specifically mixed with host materials (such as porous carbon) before being heated at a temperature of $260°C$ for 12 hr in an Ar environment. Capillary action will help the molten Se spread through the pores of the host material. Cathodes based on Se may be prepared, and after the materials have cooled to room temperature, the Se will be uniformly distributed throughout the host. As a result, there is a significant amount of interest for creating new methods to improve LSeB. Some issues with the Se cathode include the shuttle effect of PSe and the sluggish kinetics of the interaction between Li and PSe, and poor conductivity of Se, which are thoroughly investigated using several key strategies, including chemisorption of Se, conductive skeletons for Se, catalytic conversion of PSe, and physical confinement of Se [19,39-41].

In the recent years development of LSB has focused on the application of several different polymeric materials as cathodes, electrolyte membranes, and interlayers. Regardly, the straightforward electrospinning technique enables creative polymeric structures construction to handle the significant problems presented by chemistry of Li and S. Using polymers that conduct electricity and have nitrogen functionality at the cathode, like polyaniline (PANI) and polypyrrole (PPy), provides a strong affinity toward lithium polysulfides by chemisorption, assisting in enhancing cycle life [42,43]. For instance, Zhu et al. recently synthesized a freestanding 3-D CNF/S/PANI composite architecture using an in-situ polymerization and the electrospinning process. First, the PAN solution was electrospun into free-standing CNF mats, which were then stabilized and carbonized for one hr at $1000°C$. The S/CS_2 solution was then used to inject S into the CNF mats, ensuring a consistent distribution of S throughout the CNF's surface and good electrical contact between the two in the CNF/S electrodes. To obtain the final 3D CNF/S/PANI architecture, in-situ polymerization of PANI was carried out directly on the CNF/S structures using ammonium persulfate, phytic acid, and aniline monomer. The mappings of the elements N, S, and C

according to their elemental properties and the TEM picture of a single CNF/S/PANi showed that S and PANi were distributed uniformly. The electrochemical performance was assessed in an ethereal electrolyte made with 0.1 M lithium nitrate ($LiNO_3$) and 1 M bis(trifluoromethane)sulfonamide lithium (LiTFSI) in a 1,2 dimethoxyethane (DME)/1,3 dimethoxyethane (DOL) mixed solvent (with volume of 1:1). The initial capacities of the conventional slurry-based CNF/S cathode (58 wt%S) and C/S cathode (70 wt% S) were 807 $mAhg^{-1}$ and 909 $mAhg^{-1}$, respectively, at C/5 rate. However, after 300 cycles, only 44.8% and 60.7% of these initial capacities remained, with respective capacity decay rates of 0.36 and 0.13% per cycle. The CNF/S/PANI cathode (52 wt%S) demonstrated an important initial capacity of 1278 $mAhg^{-1}$ at C/5 rate and maintained 74.6 capacity after 300 cycles. After 300 cycles and with an S loading of 2 $mgcm^{-2}$ (67 wt%), the CNF/S/PANI cathode displayed a capacity of 711 $mAhg^{-1}$ while operating at a C/5 rate [44-48].

In a different study, Li *et al.* used electrospun cyclizedPAN-CNF (CP@CNF) interlayers to show better electrochemical performance of LSB. In the beginning of this study, CNF mats were electrospun from a PAN solution in DMF. After 30 seconds in the 5 wt% PAN solution, the CNF mats were dried at $80°C$ for 12 hr. The stabilization of PAN coated CNF mats at $300°C$ for 10 hr in an Ar atmosphere led to the creation of the CP@CNF interlayers in the end. A diagram showing the intermolecular cyclization reaction, the CP@CNF film, the CNF film, the PAN coated CNF film, the PAN chemical structure, and the cyclized-PAN film. Exact numbers show that after 100 and 200 cycles at 0.3C rate, the CP@CNF interlayer-equipped Li-S cell had a reversible capacity of 910 $mAhg^{-1}$ and a coulombic efficiency of 99.5%. The sulfur utilization in the CP@PAN interlayer structure is enhanced thanks to the conductive CNF skeleton acting as an upper current collector. The postmortem FTIR, XPS, and TEM studies demonstrated that the cyclic- PAN layer with abundant polar C=N (i.e., pN (pyridinic)) groups (than CNF interlayer alone) minimized the shuttle effect. This was achieved through the physical (similar to CNF interlayer) and chemical trapping (chemisorption through p-electrons on pN) of polysulfides [49-52].

4.2 Separators

Separator is an essential component of a battery; the separator allows for easy ion migration while protecting the anode and cathode from short circuit. Typically, separators are made of porous polymer membranes, such as commercial polypropylene membranes or glass fibers. However, because they are nonselective, these conventional separators cannot stop intermediates from shuttling. An early investigation of LSeB was described by Fang *et al.* [53], who used a polymer membrane separator covered with graphene. It is widely acknowledged that separator modification is particularly successful in resolving the problems connected to soluble species diffusion. Excellent conductivity in the graphene layer allows it to suppress the migration of polyselenides while increasing redox kinetics. Covalent organic frameworks (COF) with large specific surface area, low weight, and high porosity are also thought to be advantageous for LSeB applications in addition to graphene.

In order to preferentially bind LiTFSI in the electrolyte, Yang *et al.* [54] designed TPB-DMTP-COF (TPB: 1,3,5-tri(4-aminophenyl)benzene; DMTP: 2,5-dimethoxyterephthalaldehyde). The immobilized LiTFSI not only aids in Li-ion transport but also decreases the pore size of TPB-DMTP-COF, hence blocking the activity of the intermediate shuttles. As a result, a high areal loading of 4 mgcm^{-2} was able to produce a long lifespan of 800 cycles. Due to their desirable 2D laminar structure and strong affinities to intermediates, emerging MXenes (Ti$_3$C$_2$Tx) were recently evaluated to functionalize the separator in addition to COF. A self-assembled coating layer made of CNTs, MXenes, and CTAB was created to prevent the movement of polyselenides [10,55,56].

The effective polyselenides adsorption by CTAB/MXenes through Lewis acid-base interactions was proposed by DFT calculations and permeability measurements. While the CNT components support improved ions transport and electrolyte infiltration. With this configuration, the LSeB operated at 1 C for 500 cycles. It is possible to reduce the incidence of PSe shuttle effects by using interlayers between the cathodes and separators to physically inhibit the diffusion of PSe from the cathodes to the Li anode sides. When the functional materials are introduced into the interlayers, it is anticipated that a number of chemical reactions will have a synergistic improvement on the PSe shuttle. Because of the evolution of interlayers to include both free-standing films and films over typical PP separators, rational interlayer design is seen as a promising strategy for fabricating high-performance LSeB [10].

Due to their enormous number of macropores, the conventional Celgard or PP separators are inadequate at preventing the migration of tiny PSe from the Se-based cathode to the Li anode. In order to prevent the shuttle effect of PSe physically and/or chemically, as an alternative, functional materials might be applied to PP flexible separators to serve as the inter-layer. Graphene nanosheets coated over traditional polymer separators ensured clean Se electrodes with a high Se content of 70 wt% and a modest capacity fading rate of 0.048, promising graphene for enhanced LSeB. Better PSes chemisorption and possibly catalytic conversion may be anticipated while using doped graphene nanosheets as the separator's interlayer material. LSeB electrochemical performance was improved by chemically reacting with metal oxides or carbides formed on the separators. It has been observed that 2D MXene nanosheets may typically combine into an MXene-based film interlayer for LSeB. In particular, PSes may be chemically bound to the MXene surfaces through the polar functional groups, 2D structures can physically prevent PSes from diffusing to the Li anode side, and conductive MXene nanosheets can significantly lessen LSeB-related voltage polarization. One common example is the electrostatic assembly and filtration of 2D MXene nanosheets and 1D cetrimonium bromide modified CNTs (CCNT) into an ultrathin hybrid film on PP separator. A lower contact angle of 10.12 degrees was shown by the resultant CCNT/MXene/PP hybrid separator with electrolyte compared to that ofPP (38.49 degrees). In electrochemical impedance spectroscopy, the Li-Se cells with CCNT/MXene/PP separators consequently shown decreased resistance. As an added bonus, a carbon black/Se hybrid cathode was able to reach a remarkable capacity of 554 mAhg^{-1} at the 100th cycle thanks to the use of CCNT/MXene/PP separators [19,57,58].

4.3 Binders

Binders are among the most important auxiliary components in Li-S/Se batteries because they are used in the manufacturing of electrodes, which necessitates a high bonding performance between the active electrode material, the current collector, and the conductive agent. Binder is essential for the Li-S/Se batteries system because it improves sulfur loading and usage, increases cyclic stability, and stabilizes the cathode structure. Currently, polyvinylidene fluoride (PVDF), polyethylene oxide (PEO), polytetrafluoroethylene (PTFE), and others are the most often utilized binders in Li-S/Se batteries. These binders still have a lot of issues, though. Their insulation, for example, has a little effect on increasing the cathode's conductivity, and their affinity for lithium polysulfides is not strong enough to allow them to address the shuttle issue (polyselenides). Not only that, but the interchain connections in linear polymers are weaker, therefore the chains themselves tend to be more brittle, and they are unable to buffer significant volume fluctuations throughout the discharge/charge cycle process, necessitating the addition of additional functional binders. High molecular polarity and excellent conductivity make lithium polysulfides (polyselenides) resistant to diffusion and promote rapid electron transfer [8,59].

5. Mechanism of electrolyte

The battery's essential element, the electrolyte, may have a direct impact on the redox route, which would control the cycle life and capacity [24]. Many studies have confirmed how electrolyte affects the electrochemical behavior of LSeB. LSeB produce a common single-phase change in carbonate electrolytes, however, they are still debatable in terms of mechanics. To clarify the research advancements and spur more effective study, this section offers a thorough review of the redox behavior of LSeB in ether-based and carbonate electrolytes solution [10,60].

Amine *et al.* [61] also investigated the mechanisms underlying reaction in LSeB in ether electrolytes solution and discovered that these electrochemical characteristics were distinct from those in carbonate electrolytes solution, although Se and lithium selenide are insoluble in ether electrolytes solution, poly selenides are quite soluble in them.

5.1 Carbonate electrolytes

The cathode for LSeB was first proposed by Amine and coworkers [62] as a composite of Se and multi-walled carbon nanotubes (MWCNTs). According to their research, the Se-based cathode in carbonate electrolytes has a typical electrochemical behavior that includes charge and discharges plateaus at 2.4 and 2.0 V, respectively (Figure 3). This result differs from the one obtained for S in ether-based electrolytes solution, where the creation of polysulfide intermediates is connected to the appearance of two sets of plateaus [63,64]. Kundu *et al.* [65] and Zhou *et al.* [66] found that the charge/discharge curves for Se nanowire cathodes showed many plateaus. They, therefore, hypothesized that LSeB perform the multi-phase conversion in carbonate electrolytes, similar to what LSB do. Further research by Zhou and colleagues [66] revealed that the lithiation process is significantly influenced by Se's crystal structure, with trigonal Se producing single-phase transformation whereas amorphous Se exhibits multi-step lithiation. Amorphous Se-based cathodes have also been used in other contributions, and same phenomena have been seen there [27,67].

5.2 Ether-Based Electrolytes

In an electrolytes solution that is based on ether, the lithiation/delithiation of Se is surprisingly similar to that of S, with the exception of slightly lower redox potential, as seen in Fig.3. Most of the time, Se is broken down into $Li2Se_n$ ($n \geq 4$) at 2.1 V, Li_2Se_2 at 1.9 V, and finally Li_2Se. $Li2Se$ is immediately oxidized at 2.3V during the charging process, skipping Li_2Se_2, to become Li_2Se_n ($n \geq 4$), and then to Se. The associated charge curve only displays one oxidation plateau as a result of the potential overlap. Similar to LSBs, the synthesis and dissolution of poly selenide intermediates pose the biggest problems for Li-Se batteries when combined with electrolytes that are based on ether. Due to the concurrent shuttle effects, the Li anode eventually corrodes during electrochemical processes, which lowers cycling stability [68,69].

5.3 Ester-Based Electrolytes

Ester-based electrolytes can offer excellent LSeB compatibility since Se is converted directly into Li_2Se without the need for an intermediary poly selenide. According to the findings of a number of investigations, the capacity of the Se/carbon cathode may add more than 400 mAhg^{-1} to the battery after it has been subjected to a long cycle consisting of 100 cycles in an ester-based electrolyte [41,70]. The reaction mechanism of $LieSeS_2$ batteries, which have electrochemical characteristics comparable to those of LSB in ester-based electrolytes, has been explored by Cui and his colleagues [33].

6. Challenges

In contrast to LSB, studies on LSeB frequently focus on the systems' real-world applications; yet, little is known about this system. In order to properly grasp the conversion process, testing the performance of the battery in both ex-situ and in-situ is crucial. As opposed to the multistep conversion in ether-based electrolytes, the process of conversion in carbonate-based electrolytes seems to be a single step, although it should entail numerous sub-steps [71]. There are some challenges with these types of batteries, which include of:

I.   thick electrodes (> 10 mgcm^{-2}) with large energy densities,

II.   selection of appropriate Se species.

In order to ensure that active materials are used to their full potential for high area capacity, high mass electrodes need to have sufficient electron and ion conductivity. Selenium typically requires the use of conductive carbon to supply electron routes due to its poor electron conductivity; nevertheless, these inactive carbons necessarily reduce the energy density of the related electrodes. To resolve the aforementioned conundrum, intelligent selection of particular Se species is crucial. Selenium sulfides (SeSx) may be the best option in this case due to their higher electron conductivity and theoretical energy density than pure selenium. The synthesis and design of enhanced Se hosts with many functions is the second problem. As was already noted, the more advanced Se hosts are anticipated to integrate the beneficial effects of PSes being catalyzed through chemical chemisorption, physical confinement, and chemical chemisorption. Therefore, it is important to properly integrate chemical components and nanostructure design into a single system. SACs coated porous carbons may be one of the best options in this situation since they fully utilize catalysts at the atomic level without significantly compromising energy density [19].

The secret is to create brand-new, inexpensive synthesis techniques for these remarkably stable porous hosts with high SAC concentrations. For a variety of applications, new configurations of host materials are also essential. Some advanced hosts for fiber-shaped LSeB might be found in 1D porous carbon materials. Weak, porous interlayers for dependable LSeB are a natural next step, but their development presents its own set of challenges. While graphene and MXene nanosheets have higher conductivity and a variety of surface chemistries, 2D nanosheets may be quickly and inexpensively constructed into porous membranes. Both of them have
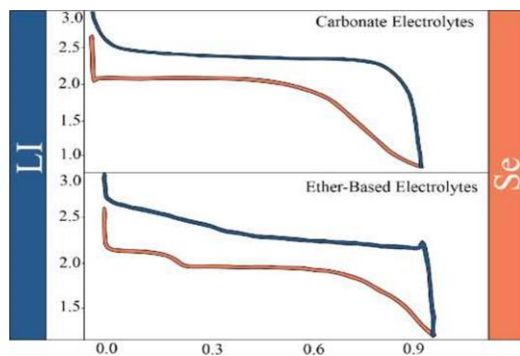

Figure 3: LSeB charge/discharge in ether and carbonate electrolytes [10].

intriguing uses for building interlayers that stand alone or on separators. It is crucial to carefully adjust the correct pore shapes to enable adequate Li^+ conductivity and avoid the diffusion of PSes. According to this viewpoint, creating 2D nanosheets and MOFs/COFs hybrids may be a practical method, allowing for the assurance of both electron conductivity and ion transfer in materials like 2D nanosheets (like MXene) and COFs/MOFs with clearly defined nanoporous structures [6,72]. These cutting-edge methods allow for the revelation and perceptive comprehension of the Li-Se cells' internal energy storage mechanisms. Notably, LSB and LSeB should be explicitly differentiated from one another rather than just using LSB processes. The well-defined processes of Li-Se cells, as well as the minor differences between Li-Se and Li-S cells, will naturally be revealed via the development and implementation of newly de-signed in-situ and operando characterization methods. Then, finally, LSeB are intricate systems that go beyond the cathode sides. LSeB electrolytes and Li anodes, which are not included in this paper, are equally important. Different types of electrolytes, including new ionic liquids and solids, for in-stance, might make it possible for LSeB with new functionality to be made safely (such as wide working temperature). As with other Li metal-based batteries (Li-O_2 and Li-S, for example), LSeB suffer from the same issues with Li anodes, including lithium dendrites and poor coulombic efficiency. In conclusion, we predict that, with the help of further fundamental and applied research, LSeB will become a very viable option in the next generation of energy storage technologies for practical applications [73-76].

7. Conclusion and future perspective

The construction of an appropriate porous carbon matrix to load active material is the primary focus of LSB and LSeB research. Numerous types of porous carbon matrix, including microporous, mesoporous, and micromesoporous carbon matrix, have been produced by researchers. The use of heteroatoms to change S molecules or carbon matrix is still in its early stages. Furthermore, heteroatom doping in combination with a suitable porous car-bon matrix may further enhance the electrochemical performance of LSB and LSeB. Before LSB and LSeB

be used commercially, there is still much work to be done. We think that the battery community's efforts will help LSB and LSeB achieve more exciting accomplishments and have a bright future [77].

In this article, an attempt has been made to review various materials about lithium sulfide batteries, and also its different components have been reviewed, and the challenges and future prospective for this type of batteries have been reviewed. It also reviews the different types of materials that are utilized for these types of batteries especially cathode part.

Unique 1D nanostructures have made steady progress in bringing this technology closer to use, especially for LSB. And it is evident that the focus of this review is on the interior and exterior alterations made to the S/Se cathode employing different 1D nanomaterials. However, it is unavoidable that certain key methods, safety risks from lithium anode dendrites, are impeding their commercialization. The creation of lithium dendrites, which unquestionably manifests when employing lithium metal as the an-ode, might be fully eliminated by the use of 1D nanomaterials as the anode, such as pre-lithiated Li_7B_6 and Si NWs. Additionally, using 1D nanomaterials to shield the lithium anode, such as SCNT, silver nanowires, etc. could effectively stop the growth of lithium dendrites. As was said above, a 3D cathode with a high active material loading and a safe 3D anode may both benefit from the use of 1D nanomaterials. This yields LSB and LSeB with 3D nanostructured electrodes composed of 1D nanomaterials that are safe, reliable, and good for the environment; they have a high energy and power density and a high Coulombie effciecny; their cycle life is lengthy; and they have a low probability of an accident occurring. There is no denying that the great theoretical capacity and energy density of Li-S/Se batteries have increased their profile in recent years. Important progress has been made in developing 1D nanostructured electrodes based on sulfur and selenium. It should be noted, though, that some earlier research sacrificed the electrode's sulfur/selenium content in favor of greater specific capacity and longer cycle life. The Li-S/Se battery's energy density is the primary benefit for practical applications, hence greater emphasis should be placed on raising the overall energy density

of Li-S/Se batteries. The electrolyte/selenium and electrolyte/sulfur ratio, which was typically disregarded in the past, is another significant component that decreases the energy density of Li-S/Se batteries, in addition to the sulfur/selenium concentration, which has a significant impact on the energy density. Although studies in this field are only getting started, the development of novel electrolyte systems such as gel polymers shows promise. From an application viewpoint, high energy/power densities of Li-S/Se batteries need a large sulfur cathode surface area/volume and a little quantity of electrolyte. Finally, developing low-cost and scalable manufacturing methods is necessary before these 1D nanostructures may be used in Li-S/Se batteries in a practical setting [14,78,79].

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