Chinese Chemical Letters 34 (2023) 107783

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Recent advances in cathodes for all-solid-state lithium-sulfur batteries

Shengbo Yang, Bo Wang*, Qiang Lv, Nan Zhang, Zekun Zhang, Yutong Jing, Jinbo Li, Rui Chen, Bochen Wu, Pengfei Xu, Dianlong Wang*

MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, State Key Laboratory of Urban Water Resource and Environment, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

ARTICLE INFO

Article history:
Received 13 July 2022
Revised 8 August 2022
Accepted 24 August 2022
Available online 28 August 2022

Keywords:
All-solid-state Li-S battery
Cathode active material
Cathode host material
Cathode structure
Solid-state electrolyte

ABSTRACT

Lithium-sulfur (Li-S) batteries have been regarded as the candidate for the next-generation energy storage system due to the high theoretical specific capacity (1675 mAh/g), energy density (2600 Wh/kg) and the abundance of elemental sulfur, but the application of Li-S batteries is impeded by a series of problems. Recently, all-solid-state Li-S batteries (ASSLSBs) have drawn great attention because many drawbacks such as safety issues caused by metallic lithium anodes and organic liquid electrolytes can be overcome through the use of solid-state electrolytes (SEs). However, not only the problems brought by sulfur cathodes still exist, but more trouble arouses from the interfaces between SEs and cathodes, hampering the practical application of ASSLSBs. Therefore, in order to deal with the problems, enormous endeavors have been done on ASSLSB cathodes during the past few decades, including engineering of cathode active materials, cathode host materials, cathode binder materials and cathode structures. In this review, the electrochemical mechanism and existing problems of ASSLSBs are briefly introduced. Subsequently, the strategies for developing cathode materials and designing cathode structures are presented. Then there follows a brief discussion of SE problems and expectations, and finally, the challenges and perspectives of ASSLSBs are summarized.

1. Introduction

The increasing depletion of fossil fuels and the application limitations of traditional energy sources have stimulated the development of advanced energy storage technologies [1–3]. Under the situation like this, electrochemical energy storage systems have shown increasing importance in a wide range of applications. After years of development, lithium-ion batteries have replaced many traditional energy storage batteries and are used in portable electronic devices, electric vehicles and other fields, greatly changing the global energy storage market and related industries [4,5]. However, conventional Li ion batteries with liquid electrolytes (LEs) suffer from safety concerns, including flammable organic electrolytes, thermal instability, Li dendrite growth and toxic chemicals [6–9]. Therefore, using solid-state electrolytes (SEs) and assemble all-solid-state batteries without organic LEs is a feasible choice to overcome the shortcomings of traditional liquid batteries [3,6-8]. It was proved by researchers that both safety performance and energy density could be improved by replacing LEs with SEs [10,11].

The demand for energy is increasing nowadays, but the energy density of lithium-ion intercalation reaction energy storage is gradually approaching its theoretical limit, which is difficult to meet the demand for energy in the future. In addition, due to the high cost of manufacturing using lithium-ion batteries, the development of large-scale energy storage will also be hindered [4,12]. Therefore, to meet the growing demand for more efficient and economical energy storage, it has become necessary to explore alternative battery technologies with new chemistries and economic advantages for charge carrier storage. The two-electron redox reaction between S and Li, simplified as $S_8 + 16Li^+ \rightarrow 8Li_2S$, can exhibit specific capacities of the two electrodes (1675 mAh/g for sulfur and 3860 mAh/g for Li) [1–3,13,14], which is about ten times as much as a Li ion battery (170 mAh/g for $LiFePO_4$ and 372 mAh/g for graphite as an example). Although the operating voltage of the battery is about lower compared to conventional Li ion batteries, the theoretical energy output of lithium-sulfur (Li-S) batteries is close to 2600 Wh/kg and the actual specific energy is expected to be greater than 500 Wh/kg, which shows a significant advantage compared with the 380 Wh/kg of intercalation type Li ion battery

* Corresponding authors.
E-mail addresses: wangbo19880804@163.com (B. Wang), wangdianlonghit@163.com (D. Wang).

https://doi.org/10.1016/j.cclet.2022.107783
1001-8417/

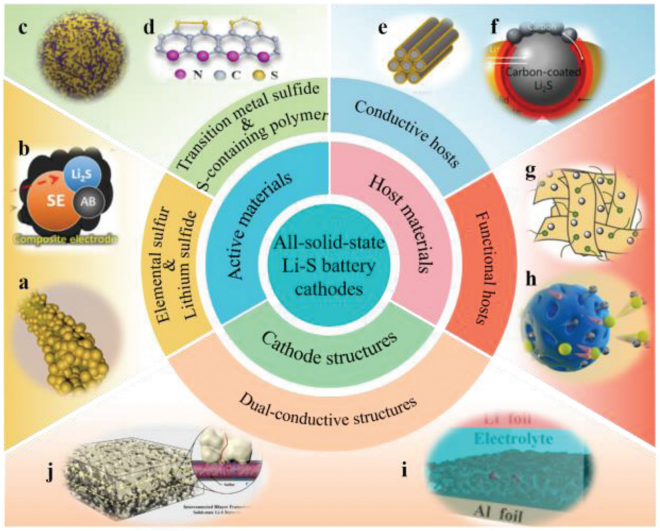

Fig. 1. Schematic illustration of the outline for ASSLSB cathodes. Active materials: (a) elemental sulfur; (b) lithium sulfide; (c) transition metal sulfide; (d) S-containing polymer. Reproduced with permission [20]. Copyright 2020, Elsevier. Reproduced with permission [21]. Copyright 2020, Elsevier. Reproduced with permission [22]. Copyright 2018, American Chemical Society. Reproduced with permission [23]. Copyright 2020, Elsevier. Host materials: (e) porous carbon host for elemental sulfur; (f) carbon coating for lithium sulfide; (g, h) functional hosts for active materials. Reproduced with permission [24]. Copyright 2020, American Chemical Society. Reproduced with permission [25]. Copyright 2018, Elsevier. Reproduced with permission [26]. Copyright 2017, Royal Society of Chemistry. Reproduced with permission [27]. Copyright 2021, American Chemical Society. Dual conductive structures: (i) 3D cathode framework; (j) dual-conductive interlayer. Reproduced with permission [28]. Copyright 2020, American Chemical Society. Reproduced with permission [29]. Copyright 2022, Elsevier.

[1,2,14]. In addition, sulfur which is one of the most abundant elements in the earth's crust, costs low and it is a by-product produced in large quantities in the process of hydrodesulfurization in the refining industry [15]. Therefore, lithium-sulfur batteries are expected to replace lithium-ion batteries as a new generation of energy storage batteries in the future.

Taking safety as well as high capacity into account, to meet the energy demand of the future, there is a need for all-solid-state Li-S batteries (ASSLSBs) [3,16,17]. SEs for ASSLSBs are usually divided into three types: inorganic solid electrolytes (ISEs, *i.e.* ionic conductive glass or ceramic materials), solid polymer electrolytes (SPEs, *i.e.* ionic conductive polymers) and composite polymer electrolytes (CPEs, *i.e.* ionic conductive composites consisting of polymers and inorganic materials) [3,8,18,19]. Recent reviews about ASSLSBs are mostly focused on anodes and SEs, paying little attention on cathodes. However, it cannot be ignored that the research on various cathode active materials (Figs. 1a-d) [20–23], the development of binders and host materials (Figs. 1e-h) [24–27], and the configurations of cathode structures (Figs. 1i and j) [28,29] are driving the development of ASSLSBs. Therefore, this review summarizes the studies on ASSLSB cathodes for the first time, focusing on the measures researchers have taken to overcome the defects of ASSLSB from the cathode aspect. In this review, the reaction mechanism of ASSLSBs and the defects that hampering practical application are introduced at first. Subsequently, the studies in cathode materials including active materials, host materials and binder materials aiming at solve the problems of ASSLSBs are discussed. Then, some efforts in cathode structure designation to improve the performance of ASSLSBs are presented, followed by a brief discussion of SEs. Finally, the challenges and perspectives of ASSLSBs are summarized. This review will provide ideas for future researches on ASSLSB cathodes and solutions to ASSLSB cathode problems from multiple perspectives.

2. Mechanism and main problems of Li-S batteries

The working mechanism of a LE-based lithium-sulfur battery contains a series of reactions, in which Li ions leave from Li anode to sulfur cathode during discharging and return from cathode to anode during reverse charging [17,30]. As shown in Fig. 2a, during discharge process, S_8 first undergoes a ring-opening reaction to form higher-order polysulfides (PSs), as known as lithium polysulfide intermediates. As the reactions go on, the higher-order PSs undergo processes of gradually chain shortening, during which the valence state of S continues to decrease, and subsequently reacts with more Li ions to generate lower-order polysulfides, and finally form Li_2S [1,31,32]. However, the PSs are soluble in electrolytes and likely to migrate from cathode into the electrolyte, losing electrical contact with the cathode body and further shuttling to the anode, where they react with metallic lithium to form a solid precipitate, resulting in irreversible capacity loss, known as the "shuttle effect" [19,32–34].

Using SEs to assemble ASSLSBs is a feasible measure to prohibit shuttle effect (Fig. 2b). In SPE/CPE-based systems, although PSs are soluble in some polymer electrolytes such as polyethylene oxide (PEO) [15,35–37], many solutions can be applied to inhibit the formation of PSs [16] or prohibit PSs from shuttling [38–40]. While in batteries using other polymer electrolytes such as polyvinylidene fluoride (PVDF) in which PSs are insoluble, PSs are mostly restrained in cathode region [41,42]. In ISE-based ASSLSBs, the shuttle effect can be eliminated because there is no PS generated according to the charge-discharge curves in which the plateau regions representing the reactions about PSs are absent [20,43–45].

The advantages of ASSLSBs have attracted many researches on Li anodes and SEs. However, there are still a number of shortcomings in sulfur cathodes which hinder the implementation of ASSLSBs [2,30,47–49]. To begin with, the electronic and ionic conductivity of sulfur is weak, and because of which, a composite cathode is usually fabricated by mixing sulfur, conductive carbon and SE, that contributes to limited loading of active material. Moreover, the charge-discharge cycle of Li-S batteries can cause severe volume changing in sulfur cathodes, which is destructive to cathode structures, separating insulating sulfur from conductive hosts and resulting in irreversible losses of active materials. It is also worth mentioning that replacing a traditional liquid-solid interface with a rigid solid-solid one weakens the transportation of Li ion in electrolyte/cathode interface (Fig. 2c), and is unlikely to make full use of active materials [50]. Therefore, in order to ensure the applicability of ASSLSBs and give full play to the advantages of the high theoretical capacity, many efforts have been done with cathode materials and cathode structures to overcome the drawbacks.

3. Engineering of cathode materials

Much effort on the innovation of cathode materials has been done to overcome the drawbacks of traditional sulfur cathodes. There are many researches on active materials which are regarded as the most promising solutions, including optimizing the preparation method of traditional types of cathodes and developing new types of active materials. Additionally, the developments of host materials and binder materials for cathode active materials also help to improve the performance of all-solid-state lithium-sulfur batteries.

3.1. Engineering of active materials

Being the most significant part of a composite cathode, active material should be carefully selected and designed. To remedy the above shortcomings, a number of measures were developed,

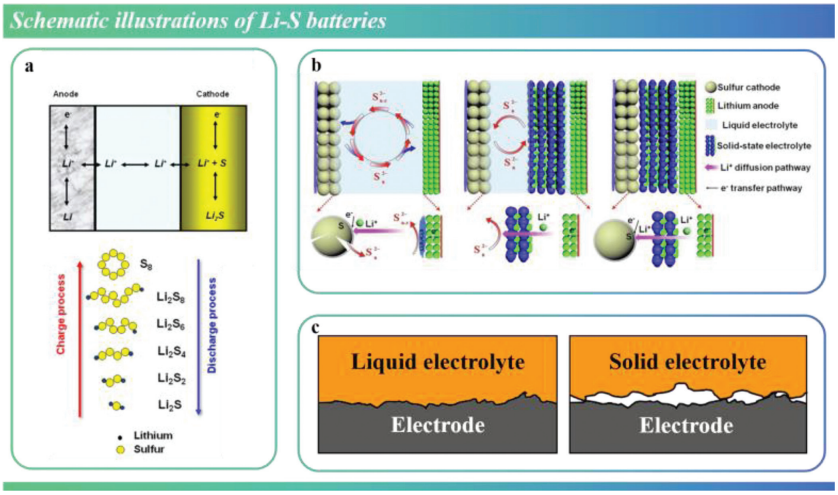

Fig. 2. (a) Schematic illustrations of traditional sulfur cathode performances. Reproduced with permission [33]. Copyright 2021, Springer Nature. (b) Schematic illustrations of LE-based, *quasi*-solid-state and ASSLSBs. Reproduced with permission [46]. Copyright 2020, Elsevier. (c) Different electrolyte/electrode interface of LE-based and ASSLSBs.

which could be simply divided into two dimensions: optimizing the preparation methods of traditional cathodes, and synthesizing novel active materials with better performance than traditional ones. Examples of these materials will be presented in the following sections.

3.1.1. Elemental sulfur

Combining sulfur with carbon materials and SEs is a common way to prepare conductive cathodes. Two-step mechanically mixing, consist of a combination of sulfur with carbon and another combination of S/C with SE, is generally applied to prepare sulfur-carbon-SE composites [51]. According to Nagao and coworkers [52], cathodes prepared by ball-milling method showed better discharge-charge performance than that prepared by mortar grinding, demonstrating that smaller particles are more likely to achieve the intimate contact among sulfur, carbon and SE. Additionally, the impact of ball-milling temperature [53] and time [54] were also studied, indicating that a temperature of 155 °C (Fig. 3a) [53], a time of 20 h (Figs. 3b and c) [54] for the second step were two of the most favorable parameters in ball-milling process. Based on the fact that sulfur melts at 155 °C [13,53,55], another mixing way, known as heating treatment was applied to combine sulfur with carbon materials and replace the first ball-milling step in cathode preparation, in order to achieve a sufficient contact between sulfur and carbon without destroying the structure of carbon material (Fig. 3d) [45,56]. Xu *et al.* [45] reported a composite cathode prepared by heating treatment and ball-milling, where sulfur and reduced graphene oxide (rGO) were mixed at 155 °C for 24 h under argon atmosphere precede ball-milling with $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ electrolyte. Sulfur was loaded on rGO after heating, and a uniform dispersion was also achieved (Fig. 3e). The ASSLSB based on the composite cathode delivered an initial discharge capacity of 969 mAh/g at 0.05 C, and a reversible capacity over 827 mAh/g after 60 cycles.

Hou *et al.* [56] studied the interfacial electronic contact between sulfur and carbon hosts, and demonstrated that heating treatment was able to form more intimate contacts and achieve more effective electron transfer than mechanically milling. The key to solving the poor electron transport in sulfur cathodes is to form intimate contact between sulfur and conductive hosts. In order to obtain homogeneous mixtures and to form conductive percolation construction among sulfur and conducting additives, other methods such as sulfur liquid deposition or sulfur vapor deposition were employed and proved to reach better electrochemical performance than that fabricated through heating treatment [45,57–59].

Sulfur liquid deposition is mainly divided into two forms. Sulfur can be deposited on the host as a reaction product [26,57] or it can be precipitated out of solution as a solute [24,44,60,61]. Unlike mechanically mixing, after the procedure of liquid deposition, the original morphology of the conductive host can be preserved [62]. Zhou *et al.* [57] reported a liquid deposition method, through which sulfur was produced by the reaction of sodium thiosulfate with hydrochloric acid at room temperature and deposited onto Ketjen black (KB). Composites of sulfur and KB prepared by mechanically mixing (S + KB) and heating treatment (S-KB) were used for comparison in the study. The S@KB fabricated by liquid deposition possessed the lowest BET surface area among the three kinds of samples, indicating the most excellent surface coverage and pore-filling of KB. Furthermore, the diameter of particles increased after the sulfur deposition, but the composite preserved the shape as the original KB particles, implying the uniformity of sulfur coating (Fig. 3f).

Through sulfur liquid deposition, nano-scale elemental sulfur can be obtained and sulfur morphology can be controlled. Zhang *et al.* [44] deposited sulfur on carbon nanotubes (CNTs) from a saturated solution in which sulfur was dissolved in tetrahydrofuran. The cell assembled with S-CNT cathode showed no capacity fading for the first 400 cycles and a discharge capacity of 834.3 mAh/g at 0.25 C after 1000 cycles, corresponding to a capacity retention of 85.1%. The electrochemical performance was attributed to the small size of sulfur. Fig. 3g showed sulfur nanoparticles with size of 10-20 nm, and after 50 cycles, nanoparticles of 5-10 nm were obtained, indicating that the size of sulfur particles decreased during the cycling and that the volume expansion was relieved to achieve a better reversible reaction ability. Yao *et al.* [60] reported a cathode consist of $Li_{10}GeP_2S_{12}$ (LGPS) SE, acetylene black (AB), and rGO@S composite, which was fabricated by sulfur liquid deposition onto rGO. The solution for deposition contained a certain amount of sublimed sulfur and anhydrous ethylenediamine. Fig. 3h showed the nanosheet structure of rGO@S composite, where sulfur particles uniformly deposited on both sides of rGO surface and the thickness of sulfur layer was estimated below 2 nm. The ASSLSBs using the composite cathode showed a high initial discharge capacity of 1629 mAh/g at 0.05 C at 60 °C. At 1.0 C, a high discharge capacity of 830 mAh/g was retained after 750 cycles, demonstrating good long-term cycling stability. Zhang *et al.* [61] dissolved sulfur into anhydrous ethylenediamine to form precursor solutions, and subsequently dropped sulfur precursor solution into the CNTs dispersion to yield CNTs@S composite. The cathodes were synthesized by ball-milling CNTs@S, LGPS and AB. The study demonstrated that

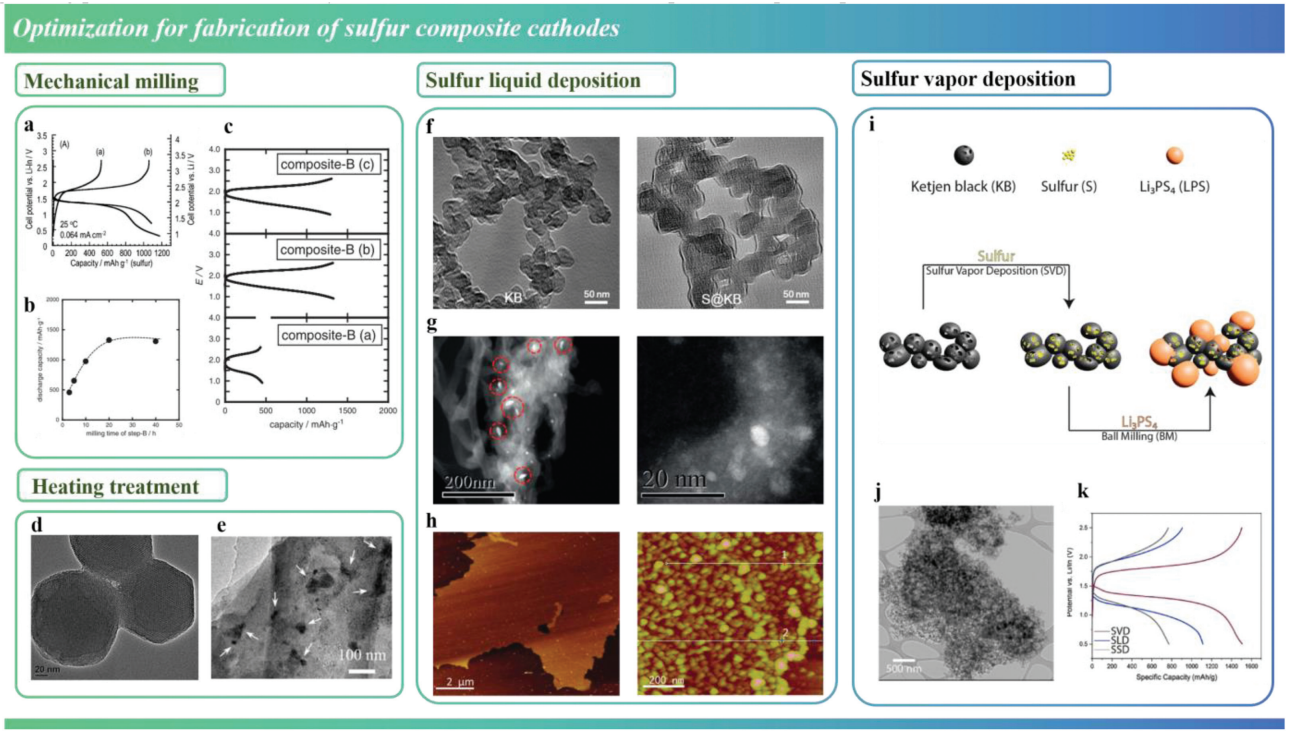

Fig. 3. (a) The first charge-discharge curves of ASSLSBs using S/AB composites prepared by mechanical milling at room temperature (curve a) and 155 °C (curve b) with 0.064 mA/cm^2 at 25 °C. Reproduced with permission [53]. Copyright 2013, Wiley-VCH. (b) The relationship between the first discharge capacity and the milling time in the second milling step of composite cathode. (c) The first discharge–charge cycle curves of ASSLSBs with composite cathodes prepared with the milling time of 3 h (curve a), 20 h (curve b) and 40 h (curve c) in the second milling step. Reproduced with permission [54]. Copyright 2014, Elsevier. (d) TEM images of the ordered mesoporous carbon after the heating treatment with sulfur. Reproduced with permission [55]. Copyright 2011, Elsevier. (e) TEM images of S/rGO composite. Reproduced with permission [45]. Copyright 2017, Wiley-VCH. (f) TEM images of KB (left) and S@KB (right). Reproduced with permission [57]. Copyright 2020, Elsevier. (g) STEM images of the S-CNT composites before cycling with red circles to point out sulfur nanoparticles (left) and the S-CNT composites after 50 cycles (right). Reproduced with permission [44]. Copyright 2018, Royal Society of Chemistry. (h) AFM images of amorphous rGO@S-40 composite on a Si substrate. Reproduced with permission [60]. Copyright 2017, Wiley-VCH. (i) Schematic illustration of synthesis of ASSLSB cathode using sulfur vapor deposition method. (j) TEM images of sulfur-carbon composite prepared by sulfur vapor deposition method. (k) Discharge-charge profiles of samples prepared by sulfur vapor deposition, sulfur liquid deposition, and sulfur solid deposition at 60 °C and 0.5 C. Reproduced with permission [58]. Copyright 2021, American Chemical Society.

a sulfur content of 44% in CNTs@S composite well inherit the tube structure of CNTs, and at 60 °C, the ASSLSBs using CNTs@S-44% cathodes delivered reversible discharge capacities of 1193.3, 959.5, 813.1, 569.6 and 395.5 mAh/g at the rate of 0.1, 0.5, 1, 2 and 5 C, respectively.

Sulfur vapor deposition can be regarded as an improvement of traditional heating treatment, for the heating temperature is enough to sublimate elemental sulfur. The sublimation helps elemental sulfur to adequately cover the surface of the host, which means the huge surface area of porous carbon can be fully utilized. Alzahrani *et al.* [58] reported a sulfur vapor deposition method (Fig. 3i), where sulfur and KB were mixed and heated up to 300 °C to fabricate a composite with homogeneous distribution (Fig. 3j). Mixed with Li_3PS_4 (LPS) electrolyte, the composite cathode showed a capacity retention of 92% after 100 cycles, and delivered a discharge specific capacity of 1792 mAh/g (ascribed to the capacity contribution of LPS electrolyte) at 0.1 C at 60 °C. Compared at 0.5 C and 60 °C, the cathode prepared by sulfur vapor deposition exhibited a higher capacity than cathodes prepared by sulfur solid deposition and sulfur liquid deposition (Fig. 3k). Moreover, it was indicated that composite cathodes prepared by vapor deposition showed more uniform and confined sulfur distribution within the KB carbon than that prepared by liquid deposition, although both methods had similar sulfur content. However, although sulfur cathodes prepared by vapor deposition show better performance, the thickness of sulfur layer and depositing processes cannot be easily controlled, which is a defect compared to liquid deposition.

Electrochemical performance of some rationally designed sulfur cathodes is summarized in Table S1 (Supporting information). The innovation in preparing sulfur/carbon/electrolyte composite cathodes will tighten the connection and improve the conductivity, leading to better electrochemical performance. Some studies also succeeded in increasing the loading of sulfur, achieving composite cathodes with high active material loading. However, according to these reports, the specific capacities of cathodes always decline with the increasing of sulfur loading [44,53,58]. It can be inferred that excess sulfur will impair the conductivity of cathodes and make little contributions to electrochemical performance.

3.1.2. Lithium sulfide

Lithium sulfide (Li_2S) is the final discharge product of Li-S batteries with a theoretical capacity of 1166 mAh/g [13,59,63], and Li_2S is regarded as a pre-lithiated cathode material, which is applicable for assembling Li-S batteries with lithium-free anodes [64], negating the necessity of metallic lithium anode which is likely to cause danger. Compared with sulfur cathodes, Li_2S cathodes suffer no volume expansion problems because Li_2S cathodes undergo a volume shrinkage process in the first charging process, providing voids to buffer the volume expansion during discharge [31]. Additionally, Li_2S can be found in many electrolytes, which means the application of Li_2S cathode in a sulfide electrolyte-based ASSLSB can alleviate the problem of Li ion transport. However, the pre-lithiated material still suffers from poor conductivity as sulfur does, so similar measures should be done to synthesize Li_2S-based cathodes.

Traditionally, Li_2S cathodes are prepared by two-step milling method [65,66], in which the first step is to combine Li_2S with electronic conductive materials while the second is to combine the composites with solid-state electrolytes. Through two-step mechanical milling, compared with artificial grinding, smaller Li_2S particles which are beneficial to the close contact between active materials and conductive materials can be attained [65]. To simplify the traditional method while reserving its advantages, Chang *et al.* [21] integrated the two ball-milling steps and reported a one-step method to prepare Li_2S cathodes. Compared to two-step ball-milling, one-step method could combine Li_2S, solid-state electrolyte and AB more homogeneously.

However, although optimized mechanical milling method can improve the electrochemical performance of Li_2S cathode, some newly developed methods [67–69] such as microwave treatment and liquid deposition were able to product nanostructured Li_2S that was unlikely to be achieved by mechanical milling. Hany *et al.* [67] reported a microwave approach to synthesis nanostructured Li_2S for ASSLSBs. According to their report, nanostructured Li_2S was prepared using a 20-min microwave-assisted heating treatment of a tetraglyme solution containing sulfur and lithium *tert*-butoxide at 200 °C. The composite cathode containing Li_2S, LPS solid-state electrolyte and KB displayed well cycling stability and achieved capacities of 440 mAh/g after 400 cycles at a cycling rate of 100 μA/cm^2.

Spark-plasma sintering (SPS), a process to promote material transfer and produce dense polycrystalline microstructures using microscopic electrical discharge between particles, was applied to prepare a composite of Li_2S and AB with according the report by Takeuchi and coworkers [69]. Li_2S and AB were mingled by ball-milling precede a SPS process at 600 °C to produce Li_2S-C composite, which was then mixed with sulfide SE to form composite cathode. The composite of Li_2S and AB treated by SPS exhibited the initial charge and discharge capacities of 1010 and 920 mAh/g, respectively.

Liquid deposition based on chemical reaction can also be used to prepare nanostructured Li_2S, Lodovico *et al.* [68] synthesized amorphous Li_2S by coprecipitation of the constituents in ethylenediamine. The mechanism of the generation of amorphous Li_2S was also studied, indicating that during the reaction, Li_2S and lithium sulfenamide are formed and co-precipitate to form ethylenediamine-embedded Li_2S (Li_2S-En), hampering the formation of crystalline Li_2S. The material has been tested in ASSLSBs using sulfide electrolyte, and has shown an improved electrochemical performance compared to crystalline Li_2S. This was because of the better contact between amorphous Li_2S and SE, which not only improved the ionic conductivity but also allowed it to cycle reversibly from the first cycle. By comparison, crystalline Li_2S should undergo many cycles to reach a good contact with SE. Moreover, the Li_2S-En can be heated to carbonize ethylenediamine to yield carbon-coated Li_2S, achieving the close contact between Li_2S and conductive carbon host.

Electrochemical performance of some rationally designed Li_2S cathodes is summarized in Table S2 (Supporting information). In ASSLSBs, Li_2S is a potential substitution for sulfur because it prelithiates to alleviate volume expansion and it is thermally stable enough to allow carbon coating. With the optimization of preparation, intimate contact between Li_2S and conductive materials were achieved to relieve the low conductivity of active material thus improving the electrochemical performance of Li_2S-based cathodes. However, other problems of Li_2S such as instability in the air [68] make the preparation more difficult and need tighter controls than sulfur cathodes, which still hinders the further development of Li_2S cathode. Not only high electrochemical performance, but also facile fabrication methods must be considered in the selection of active materials.

3.1.3. Transition metal sulfides

Transition metal sulfides, being electrochemically active in a similar voltage range of sulfur, are known to improve electrochemical performance of ASSLSBs by increasing the electronic conductivity of cathodes, alleviating the volume expansion, and providing additional reactions to increase capacities [70–72]. Additionally, transition metal sulfides will be compatible with sulfide SEs in all-solid-state batteries with sulfide-sulfide interfaces [72], and unleash their full potential that cannot be achieved in LEs-based batteries. These features make transition metal sulfides prospective substitution for traditional active materials for ASSLSB cathodes.

Copper sulfide (CuS) was used as cathode active materials in the early studies of ASSLSB. In 2004, Machida *et al.* [73] reported a CuS/S/C composite cathode synthesized by ball-milling and its electrochemical performance. The same year, Hayashi *et al.* [74] reported a CuS/S/C composite cathode and looked into the influence of S/Cu composition. Fig. S1a (Supporting information) showed the existence of Cu and CuS, which was believed to enhance the electrochemical performance of ASSLSBs by increasing the electronic conductivity of composite cathode as well as acting as active materials (CuS). Hosseini *et al.* [70] reported their study on high CuS-loading CuS/S/C composite cathodes for ASSLSBs in 2020. The research indicated that during discharge, CuS transformed into Cu_2S and finally formed metallic Cu which improved the conductivity. Moreover, as the proportion of CuS in CuS/S/C composite cathode increased, although the initial capacity declined because of the low specific capacity of CuS (590 mAh/g), the cycle performance improved (Figs. S1b and c in Supporting information).

Similar with CuS, when iron disulfide (FeS_2) is applied as cathode active material, metallic Fe can emerge during discharging and disappear after charging [22,71]. In LE-based batteries, FeS_2 can show anchoring/trapping effects on lithium polysulfides, supporting the conversion from sulfur to Li_2S [71]. However, in ether-based systems, the use of FeS_2 leads to the capacity fading due to the dissolution of iron which results in the shuttling and deposition of iron sulfide at anode region. Considering the advantages and disadvantages of FeS_2 active material, Ulissi *et al.* [71] first reported the application of FeS_2 active material in ASSLSB. With LiI-LPS (LPSI) electrolyte to inhibit shuttling, the C-FeS_2-S composite cathode prepared by mechanical milling exhibited a capacity of 1200 mAh/g over 20 cycles at 83.5 mA/g at 20 °C (Fig. S1d in Supporting information). Based on the successful examples of FeS_2, Mwizerwa *et al.* [22] synthesized a thin sulfur layer-embedded FeS_2 (FeS_2@S) microsphere composite as the active material (Fig. S1e in Supporting information). FeS_2 microsphere was fabricated by liquid-phase method, in which sulfur was also deposited to form FeS_2@S composite, enabling the intimate contact between FeS_2 and sulfur. Attribute to the microsphere structure, the FeS_2@S composite can retain a capacity of 430.7 mAh/g for sulfur at 1000 mAh/g after 200 cycles at room temperature (Fig. S1f in Supporting information).

Some transition metal sulfides can irreversibly transform into elemental metal and sulfur during the first discharge process [75,76], providing electronic conductive paths to improve the battery performance. The application molybdenum disulfide (MoS_2) cathode [75] has been studied in LE-based batteries and proved to form elemental sulfur and Mo nanoparticles after full discharge, in which the existence of Mo not only increased conductivity but also restrained shuttle effect. Chen and coworkers [75] studied the performance of MoS_2 active material in Li_6PS_5Br (LPSBr) electrolyte-based cell and found that 3 nm Mo nanoparticles dispersed in cathode after the first full discharge (Fig. S1g in Supporting information). After 700 cycles, the battery delivered a reversible capacity of 270 mAh/g at 0.2 C and a capacity retention of 85% at 1 C at 70 °C (Fig. S1h in Supporting information). Vanadium tetrasulfide (VS_4) is another prospective alternative of sulfur which shows a

similar behavior as MoS_2 does. Zhang *et al.* [76] reported a rGO-VS_4 nanocomposite synthesized through one-pot hydrothermal method and studied the reaction mechanisms (Fig. S1i in Supporting information). Mixed with $Li_7P_3S_{11}$ electrolyte, the composite cathode rGO-VS_4@$Li_7P_3S_{11}$ was attained, exhibiting a reversible capacity of 611 mAh/g at 0.1 A/g at room temperature after 100 cycles. Moreover, it was observed that metallic V nanoparticles emerged and remained chemically inert while after the first discharge process, while amorphous elemental S uniformly distributed on the surface of rGO after the subsequent charging.

Possessed with a higher theoretical capacity (837 mAh/g) than MoS_2 (670 mAh/g), molybdenum trisulfide (MoS_3) was also studied as cathode active material and showed better electrochemical performance (Fig. S1j in Supporting information) [72,77]. Zhang and coworkers [72] synthesized nanostructured MoS_3 *via* liquid-phase reaction that was loaded on rGO to prepare the composite cathode. After the first discharge process, unlike MoS_2, MoS_3 went through an irreversible conversion reaction and transformed into Li_xMoS_2 and Li_2S. The battery using rGO-MoS_3 cathode delivered reversible capacities of 553.4 mAh/g at 0.1 A/g after 100 cycles and 414.1 mAh/g at 1.0 A/g after 500 cycles.

The electrochemical performances of some ASSLSBs using transition metal sulfide cathodes are presented in Table S3 (Supporting information). Transition metal sulfides mentioned above showed higher conductivity than traditional active materials, and improved the electrochemical performance of ASSLSBs with different mechanism. However, the internal mechanism of some transition metal sulfide cathodes is still vague and needs further research and discussion. Additionally, the application of transition metal sulfides in SPE, CPE or other ISE systems has not been discovered, which arouses the question whether transition metal sulfide cathodes can only be applied in sulfide electrolyte-based cells.

3.1.4. S-containing polymers

Organic polymers have gained much attention because of their ability to immobilize sulfur and inhibit the dissolution of polysulfides in liquid-electrolyte-based Li-S batteries [78]. Gracai *et al.* [35] used inverse vulcanized sulfur copolymer as cathode active material for PEO-based Li-S cells in order to mitigate the polysulfide shuttle effect and improve electrochemical performance of ASSLSB. A certain ratio of sulfur and 3,5-divinylbenzene were used to synthesize the copolymer (p(S-DVB)), which was then mixed with KB and PEO electrolyte to form a composite cathode. The discharge/charge performance of p(S-DVB) cathode was comparable that of traditional sulfur cathode, and ASSLSB with p(S-DVB) cathode delivered a capacity of 650 mAh/g at 0.1 C at 70 °C after 50 cycles. Moreover, the post-mortem analysis indicated that S-containing polymer as active material in the cathode could diminish PS shuttle effect in PEO-based cells.

Sulfurized polyacrylonitrile (SPAN) was first reported in 2002 to replace sulfur as cathode active material [79], and has attracted much attention as cathode active material. SPAN composite is a vulcanized polymer that makes use of the interaction between the polymer's nitrile groups and elemental sulfur to destabilize PAN and promote dehydrogenation and cyclization [59]. The lone electron pair present in the nitrile group of PAN can easily interact with Li through coordination bonds [59]. Moreover, SPAN cathode does not form long-chain PS during discharge, where Li_2S can be directly formed [23,78]. These features make SPAN cathode possess high sulfur utilization, high columbic efficiency, as well as cycling stability [78]. Trevey *et al.* [80] first reported the use of SPAN cathode in ASSLSB, which showed an initial reversible capacity of 722 mAh/g (calculated based on the weight of the PAN-S active material) and a reversible capacity of 605 mAh/g after 50 cycles at a current density of 26.5 mA/g.

Sun *et al.* [81] reported a SPAN cathode using Se as eutectic accelerator and synthesized Se_xS_{1-x}@pPAN material, in which when $x = 0.05$ the cathode delivered an initial capacity of 840 mAh/g at 0.1 C and capacity retention of 81% for 150 cycles under 25 °C. The reason why the electrochemical performance of $Se_{0.05}S_{0.95}$@pPAN cathode was better than SPAN cathode without Se (delivered a capacity of 436 mAh/g at 0.1 C) was also studied. According to the report, both the electronic conductivity and ionic conductivity of $Se_{0.05}S_{0.95}$@pPAN cathode are higher than those of SPAN cathode. Moreover, density functional theory (DFT) calculation was used to find the Li ion diffusion barrier of cathodes, indicating that $Se_{0.05}S_{0.95}$@pPAN (0.39 eV) has a smaller diffusion barrier than SPAN (1.33 eV). Zhang *et al.* [82] reported a SPAN cathode using Te as eutectic accelerator and synthesized $Te_{0.05}S_{0.95}$@pPAN material, which delivered specific capacities of 935 mAh/g after 100 cycles and 665.3 mAh/g after 500 cycles at 0.3 C under 60 °C. The use of Te, similar with the use of Se in Sun's study, successfully improved the electronic and ionic conductivity of cathode active material, and the electrolyte coating also increased the Li ion diffusion coefficient ratio from 1.4 to 1.8.

The electrochemical performances of some ASSLSBs using S-containing polymer cathodes are presented in Table S4 (Supporting information). In S-containing polymers, sulfur atoms are usually dispersed in the polymer chains. As for conductive polymer like SPAN, that kind of dispersion can facilitate the battery reactions, resulting in the high utilization of sulfur. However, according to these reports the specific capacity of SPAN still declines with the increase of sulfur content, which is similar to traditional sulfur-carbon based cathodes. Furthermore, the content of active material in SPAN cathodes (including Se or Te doped SPAN) is low [79], as a result, the specific capacity calculated based on the weight of composite cathodes may not be compatible to other kinds of cathodes.

3.2. Engineering of host materials

The conductivity of active materials for ASSLSB cathodes is quite low, and this requires the application of conductive host for ASSLSB cathodes. The ideal host of active materials should be provided with high conductivity, large surface area, electrochemical and mechanical stability [31], so carbon materials are used for loading active materials. Additionally, other problems such as inhomogeneous solid-to-solid contact between active materials and SEs, low utilization of active materials, also demand the application of functional hosts.

3.2.1. Conductive carbon hosts

Conductive host materials were not applied in cathodes during the early researches in ASSLSBs, where cathodes were simply fabricated by mechanically milling active materials and conductive materials. In early studies, because the conductivity of as-prepared S/C composite was far from satisfactory, copper metal was used as a conductive addition in ASSLSB cathodes [73]. With the help of Cu, sulfur and Li_2S cathodes can get the conductivity to work properly in all-solid-state systems [74,83,84]. However, the application of Cu increases the mass of composite cathodes and decreases the content of active materials. Moreover, the low surface area of conductive materials fails to load more active materials, hindering the improvement of cathode performance. Therefore, it is significant to develop conductive host to load active materials instead of simply mixing them with conductive materials [31,85].

Carbon materials, known with high electronic conductivity, facile synthesis, stable structure, are regarded as the ideal host for cathode active materials [31,85–87]. Traditionally, due to the porous structure and high specific surface area, porous carbon materials such as KB and AB are applied in most studies about Li-S batteries.

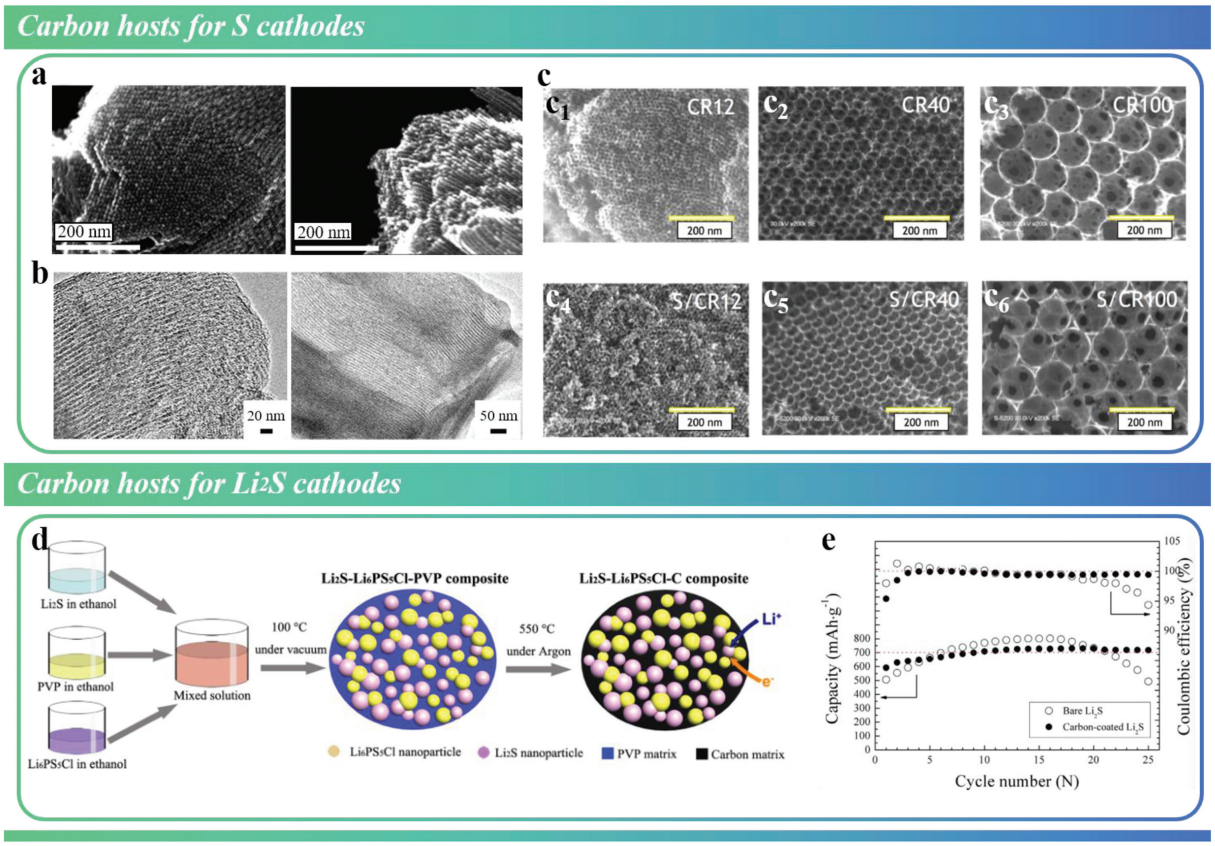

Fig. 4. (a) FE-SEM images of (left) CMK-3 and (right) sulfur/CMK-3 composite. Reproduced with permission [88]. Copyright 2013, Elsevier. (b) HRTEM images of (left) CMK-3 and (right) S/SE/CMK-3 composite. Reproduced with permission [24]. Copyright 2020, American Chemical Society. (c) FE-SEM images of carbon replicas with various pore sizes (c_1-c_3) and the corresponding sulfur/carbon replica composite materials (c_4-c_6). Reproduced with permission [89]. Copyright 2016, Elsevier. (d) Schematic illustration of the fabrication of Li_2S-LPSCl-C nanocomposite. Reproduced with permission [90]. Copyright 2016, American Chemical Society. (e) Cyclic performance and coulombic efficiency of the bare and carbon-coated Li_2S. Reproduced with permission [25]. Copyright 2018, Elsevier.

Mesoporous carbon (CMK-3) acts as an excellent conductive host of sulfur, attracting much attention in studies of ASSLSB cathodes. Nagao and coworkers [88] reported a mesoporous carbon material, CMK-3, synthesized from a templet of SiO_2. The S/C composite was prepared by heating the mixture of sulfur and CMK-3 at 300 °C precede another heating treatment of 170-230 °C to remove any sulfur outside the particles, achieving a thin sulfur layer on CMK-3 surface rather than filling every pore in the carbon matrix. Sulfur was introduced into mesopores between carbon rods and did not change the CMK-3 structure, enabling the contact between sulfur and solid-state electrolyte (Fig. 4a). The composite cathode delivered capacities of 1300 mAh/g and 1000 mAh/g at 25 °C at 0.09 C over 20 and 50 cycles, respectively. In order to achieve better ionic conductivity in S/CMK-3 cathode, Yue and coworkers [24] reported a composite cathode fabricated by infiltrating a solution with Li_3PS_7 (mixture of LPS electrolyte and S) active material into CMK-3, with which the mesoporous structure of S/SE/CMK-3 was successfully retained (Fig. 4b). As a result of the intimate contracts among sulfur, CMK-3 and electrolyte, the ASSLSB cathode benefited from high and balanced mixed conductivity and delivered a capacity of 1025 mAh/g after 50 cycles at 60 °C at 1/8 C.

Had taken it into consideration that the two-dimensional carbon rod structure of CMK-3 resulted in a large carbon ratio in composite cathode, Nagao and coworkers [89] optimized the structure of mesoporous carbon using a carbon replica. Using furfuryl alcohol as carbon source, oxalic acid as catalyst, carbon replicas were synthesized from SiO_2 sphere templets, which were prepared in varying size were to control the pore size. As shown in Fig. 4c, different from CMK-3, the carbon replica showed a highly ordered porous structure uniformly distributed pores, of which the size was successfully controlled by SiO_2 sphere templates. Sulfur-carbon composite was prepared by heating treatment while the composite cathode consisting $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ electrolyte was prepared through ball-milling. Electrochemical experiments indicated that among ASSLSB cathodes prepared in the study, the one with carbon replica synthesized by 12 nm SiO_2 templates delivered the highest first discharge capacity of 1864 mAh/g at a current density of 0.13 mA/cm^2.

As for active materials with high thermal stability such as Li_2S, carbon coating method can be applied to improve the conductivity. This kind of method needs a heating treatment with high temperature to carbonize the carbon precursor coating on active material, so it is not suitable to sulfur-based cathode. Han *et al.* [90] reported a mixed-conductive Li_2S nanocomposite fabricated by carbon coating, using polyvinylpyrrolidone (PVP) as the carbon precursor. Li_2S, PVP and Li_6PS_5Cl (LPSCl) solid-state electrolyte were mingled in ethanol, dried at 100 °C to prepare a Li_2S-LPSCl-PVP composite, which was then heated at 550 °C to carbonize PVP, forming a Li_2S-LPSCl-C composite (Fig. 4d). By contrast, both electronic and ionic conductivity of Li_2S-LPSCl-C composite (2.2×10^{-5} S/cm and 9.6×10^{-6} S/cm, respectively) were higher than those of bare Li_2S ($\sim 10^{-13}$ S/cm and $\sim 10^{-9}$ S/cm, respectively). However, the conductivity is still not high enough so that Li_2S-LPSCl-C composite alone is not capable to be the cathode for an ASSLSB. According to the report, Li_2S-LPSCl-C composite was ball-milled with carbon black and LPSCl to yield ASSLSB cathodes which delivered a reversible capacity of 830 mAh/g for 60 cycles at 50 mA/g. Choi

et al. [25] selected PAN, of which the carbonization yields greater than 50%, as the carbon precursor for carbon coating. Li_2S and PAN were mixed and heated at 600 °C to obtain carbon-coated Li_2S, then were ball-milled with KB and $Li_8P_2S_9$ to prepare composite cathode. According to the comparison between carbon-coated Li_2S and bare Li_2S, the former one showed a lower resistance of 42.2 Ω/cm (318.8 Ω/cm for bare Li_2S) and delivered a higher capacity of 730 mAh/g (490 mAh/g for bare Li_2S) after 25 cycles (Fig. 4e). Carbon coating method can lead to intimate combination of Li_2S and carbon, improve the conductivity, and furthermore, reduce the amount of extra conductive carbon in ASSLSB cathodes.

Besides high electronic conductivity, large specific surface area is also a necessary characteristic of conductive carbon hosts, because the large-area contact of insulated active materials and carbon hosts is essential for high reaction efficiency. However, the low ionic conductivity of carbon materials hinders the improvement in ASSLSB, because active materials and SEs have a different contact area than active materials and carbon hosts. As a result, host materials with high Li ion conductivity or special functions to facilitate reactions of Li ion and active materials are also needed to improve the electrochemical performance of ASSLSBs.

3.2.2. Other functional hosts

Different from LE-based Li-S batteries where cathodes are fully infiltrated with electrolyte, ASSLSBs are faced with a serious interface problem that the inhomogeneous solid-to-solid contact between active materials and SEs severely hinder the transportation of Li ion. To alleviate this problem, Li ion conductive materials can be attached to the electronic conductive materials to reach a dual-conductive host. Zhang *et al.* [26] reported a GO-PEG@C/S dual-conductive cathode for ASSLSB, using PEO-based SE. The GO-PEG host, a structural framework (Fig. S2a in Supporting information) containing Li ion conductive polyethylene glycol (PEG), was synthesized *via* an esterification reaction of carboxyl groups from GO and hydroxyl groups from methoxy polyethylene glycol (mPEG). Subsequently, in the suspension where GO-PEG was achieved, PVP, $Na_2S_2O_3$ and HCl were added to accomplish the depositing of sulfur, precede adding super P to the solution to yield GO-PEG@C/S. The battery using GO-PEG@C/S composite cathode delivered an initial discharge capacity of 1225 mAh/g at 80 °C at 0.2 C, and retained a discharge capacity of 531 mAh/g after 100 cycles at 80 °C at 1 C (Fig. S2b in Supporting information). EIS spectra also indicated that the use of PEG decreased the resistance of cathodes (Fig. S2c in Supporting information). Furthermore, although PSs are soluble in PEO, the highly reactive functional groups of GO and GO-PEG's 3D framework can trap PSs during discharge and charging, inhibiting the shuttle effect of PSs. Besides Li ion conductive polymers, ISEs can also be applied in SPE/CPE-based ASSLSBs and act as functional hosts for cathode active materials. Tao *et al.* [40] reported a Al^{3+}/Nb^{5+} co-doped cubic $Li_7La_3Zr_2O_{12}$ (LLZO) nanoparticle-decorated porous carbon foam (LLZO@C, Figs. S2d and e in Supporting information), used as the host for sulfur. The LLZO@C was synthesized *via* a facile one-step Pechini sol-gel method, and loaded with sulfur through heating treatment to form S@LLZO@C. LLZO, known as an oxide SE, was applied in the sulfur host to improve the ionic conductivity of ASSLSB cathodes. S@LLZO@C, carbon black and LLZO-PEO-$LiClO_4$ electrolyte dispersed in acetonitrile solution were used to formulate the composite cathode, with which the battery delivered specific capacities of 1556, 1210 and 900 mAh/g at 70, 50 and 37 °C, respectively. As shown in Fig. S2f (Supporting information), attributed to the functional LLZO@C host, the battery based on S@LLZO@C exhibited a higher specific capacity than that based on traditional sulfur-carbon composite.

High ionic conductivity and large specific surface area are also demanded in ionic conductive hosts which are similar to conductive carbon hosts, for Li ions should be transported as much as possible to active materials during discharge and to electrolyte during charging. Besides, some other host materials can also help to facilitate Li ion transportation through different paths. Zhao and coworkers [27], inspired by liquid Li-S batteries where intercalation metal oxides were applied in cathodes, reported the application of intercalation host $Nb_{18}W_{16}O_{93}$ (NWO) in sulfur cathodes to relieve the poor transportation of Li ion (Fig. S2g in Supporting information). Possessed with a unique structure to accommodate Li ion with great quantities, NWO is expected to serve as the ionic conductive material in composite cathodes to improve electrochemical performance. $NbCl_5$ and WCl_6 were dissolved in isopropanol, going through a hydrothermal reaction and a heating treatment to fabricate NWO, which was then heated with sulfur and CNTs at 155 °C to yield S/NWO/CNTs composite. S/NWO/CNTs was ball-milled with super P and $Li_7P_3S_{11}$ SE to form composite cathode, which delivered a reversible capacity of 1262 mAh/g after 1000 cycles at room temperature at 0.5 C, higher than composite cathodes without NWO (Fig. S2h in Supporting information). The lithiation/delithiation in S/NWO/CNT during the process of discharge/charge were indicated in XRD images (Fig. S2i in Supporting information), proving that the application of NWO accelerated the redox reactions between Li and sulfur by facilitating the transportation of Li ion.

As mentioned in former chapter, researchers tried to increase the content of cathode active materials to improve electrochemical performance of ASSLSBs, but only to find the decline of specific capacity. Hakari and coworkers [91,92] applied LiI as a host to prepare a Li_2S-LiI solid solution, with which the cell showed high utilization of Li_2S and delivered a reversible capacity of 980 mAh/g at 25 °C at 2 C for 2000 cycles (Figs. S2j and k in Supporting information). The solid solution was synthesized by ball-milling Li_2S and LiI at a ratio of 80:20, and the composite cathode was prepared by ball-milling Li_2S-LiI, LPS SE and vapor grown carbon fiber. The high utilization of Li_2S was ascribed to the extra electrochemical reaction sites provided by LiI. The Li_2S-LiI solid solution also showed a high Li ion conductivity of over 10^{-6} S/cm, but this was not regarded as the main reason for high Li_2S utilization according to the study, for Li_2S-LiCl and Li_2S-LiBr solid solutions were simultaneously synthesized and showed high Li ion conductivity (Fig. S2l in Supporting information) but lower specific capacity than Li_2S-LiI solid solution.

In sulfide electrolyte-based ASSLSBs, high-P/S-ratio SEs used in cathodes can improve the electrochemical performance by enhancing sulfur reactivity [93]. Nagata and coworkers [94] replaced sulfide SE with P_2S_5, increasing the P/S ratio to enhance the activation of sulfur active material. The composite cathodes were synthesized by ball-milling sulfur, activated carbon and P_2S_5 or SE at 60:10:30. Compared with ASSLSBs with cathodes using SE, the battery with a cathode using P_2S_5 delivered a higher discharge capacity of 1042 mAh/g at 1 C (Figs. S2m and n in Supporting information). To further study sulfur cathodes using P_2S_5 and figure out the reason of higher capacity, Tanibata *et al.* [95] synthesized a composite cathode by ball-milling sulfur, KB and P_2S_5 at 50:10:40, with which the cell delivered a discharge capacity of 1288 mAh/g and a charge capacity of 942 mAh/g at 25 °C at 0.1 C. The discharge-charge mechanism of the S-KB-P_2S_5 composite electrode is shown in Fig. S2o (Supporting information), sulfur element in amorphous P_2S_{5+x} which is formed after ball-milling react with electrochemically inserted Li ion to yield LPS and Li_2S in discharge process. The use of P_2S_5 provides more reactive sites for battery reaction and improved the utilization of sulfur. However, the reason why charge capacity is much lower than discharge capacity is not mentioned in the report, neither cyclic performance test of the cell. Apparently, although using P_2S_5 to replace sulfide SEs in cathode could be a prospective measure, there is still much work to be done.

Taking the recent advances in ASSLSB cathode active materials and host materials into account, each kind of active material has its suitable kind of host material. The combination of porous carbon and intercalation materials with high specific surface area can be the promising host for elemental sulfur; carbon hosts prepared by carbonizing are suitable for active material with good heat resistance, such as Li_2S and transition metal sulfides; S-containing polymers may not need host materials because sulfur atoms are immobilized on the polymer chains.

3.3. Engineering of binder materials

Binders are also integral materials in ASSLSB cathodes, even though the contribution of which is often underestimated. In LE-based cells, binders are used for the mere effect to combine active materials and conductive materials. However, in ASSLSBs where the problems of solid-solid interfaces remain unsolved, the existence of conventional binders will decrease the ionic/electronic conduction, leading to the performance loss of SSLMBs [96]. As a result, binders for cathodes should be further studied to improve the performance of ASSLSBs.

PVDF can be regarded as a binder in sulfur cathodes to inhibit shuttle effect. Fang *et al.* [16] employed PVDF binder with low donor number in the sulfur cathode to prohibit the production of PSs. Tested in PEO-based ASSLSBs, the composite cathodes coated with PVDF demonstrated higher capacity retention (77% after 60 cycles) than those coated with PEO electrolyte (49% after 19 cycles), indicating a higher utilization of sulfur.

In ISE-based systems where shuttle effect can be ignored, cathodes designed with low binder content can benefit the construction of electron and Li ion transmission channel. Yuan *et al.* [43] reported a slurry coating method to fabricate composite cathodes with low binder content for ASSLSBs. Silicone rubber (SR) was employed as binder material and n-hexane was selected as the solvent to disperse sulfur and LGPS electrolyte for its weak polarity, low dielectric constant and chemical stability. The ASSLSBs using cathodes with SR content of 2 wt% delivered an initial capacity of 1031.9 mAh/g and a capacity retention of 95.8% after 30 cycles at 0.1 C. The low content of binder showed insignificant influences on charge transfer capability in cathodes.

Polytetrafluoroethylene (PTFE) binder allows a technique known as dry battery electrode (DBE), which creates a 'powder to film' route to fabricate electrodes [96,97]. According to the report of Hu and coworkers [98], PTFE binder in a low content (1 wt%) was applied in composite cathodes containing sulfur, LPS and CNTs, and demonstrated a unique fibrous distribution in cathodes. The electrodes prepared by DBE technique showed higher ionic and electronic conductivity (6.3×10^{-4} S/cm and 0.25 S/cm, respectively) than those prepared by traditional wet coating method (3.9×10^{-4} S/cm and 0.13 S/cm, respectively). In traditional wet coating methods, binders usually infiltrate the voids between the particles, resulting in the indirect contact between active materials and conductive materials. However, DBE technique makes binders exhibit 3D fibrous network connections, which can remain the directly intimate contact between active materials and conductive materials.

4. Engineering of cathode structures

The innovations in cathode materials showed their effect in overcoming the defects of ASSLSBs, but it is inadvisable to ignore the significance of cathode structures while developing new materials. Considering that SEs cannot spontaneously infiltrate cathodes to ensure ionic conductivity as LE does, it is of vital significant to make composite cathode itself an electron/ion dual-conductive one [30,99,100]. Lu *et al.* [101] synthesized Ta-doped garnet $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) electrolyte and employed trace amount of LE while assembling Li-S cells. Although the conductivity of cathodes was improved, the advantage of ASSLSB's high security was also diminished by the application of LE. As a result, designing cathode structures instead of using LEs seems necessary to overcome the drawbacks of SEs.

Compared with ISEs, SPEs and CPEs show advantages in flexibility, malleability, and are more likely to form intimate contact with active materials, reducing the interface resistance [16,102]. Besides, because conductive polymers are usually dispersed in solutions (suspensions) while synthesizing, the formation of SPEs and CPEs requires a vaporing process to eliminate the solvent. Taking these features into consideration, integrating SPE or CPE with an electronic conductive framework loaded with active material is a feasible measure to form a dual-conductive cathode structure [28,103,104]. Through this approach, Yuan *et al.* [104] fabricated a cathode-supported-electrolyte configuration with high mechanical strength and intimate electrolyte/cathode contact which can decrease the interfacial resistance. In this report, high molecular-weight PEO and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) were not only used in polymer electrolyte but also the binder for composite cathode. After casting PEO/PVDF/LiTFSI electrolyte on the cathode glued by ionic conductive binder, compact interface was achieved (Figs. S3a and b in Supporting information) and Li ion transport paths were successfully inserted to realize a dual-conductive structure. As shown in Fig. S3c (Supporting information) the ASSLSB with cathode-supported-electrolyte configuration delivered capacities of 1034 and 387 mAh/g at 55 °C at 0.1 and 1 C, respectively. By contrast, the cell with laminated cathode delivered a lower capacity of 903 mAh/g at 55 °C at 0.1 C, which was attributed to the higher interfacial resistance.

CPEs are possessed with the advantage of SPEs and ISEs [102]. For active filler-reinforced CPEs, the ISE ceramic phase acts as plasticizer, which reduces the polymer crystallinity and increases the portion of amorphous structure thus improving the mobility of Li ions [102]. Zhu and coworkers [103] reported a bilayer electron/ion dual-conductive framework in which a 3D carbon nanofiber/sulfur (CNF/S) cathode and 1D ceramic $Li_{0.33}La_{0.557}TiO_3$ nanofiber-PEO CPE (PEO/LLTO) were integrated to serve as both cathode and electrolyte for an ASSLSB (Fig. S3d in Supporting information). CNF was prepared by the carbonization of PAN nanofibers, and CNF/S was fabricated through liquid deposition in S/CS_2 solution. Facilitated with the bilayer structured cathode, the batteries delivered reversible capacities of 384, 358 and 262 mAh/g at room temperature at current densities of 0.05 C, 0.1 C and 0.2 C, respectively (Fig. S3e in Supporting information). The similar structure can be achieved using other hosts for active materials, and according to the report of Wang and coworkers [28], an electron/ion dual-conductive cathode framework synthesized *via* dropping electrolyte slurry on the surface of rGO/S cathode. The rGO/S cathode showed a porous framework in which one-dimensional CNTs connected with rGO-wrapped sulfur to form a successive electron-transport network, and the PEO/LLZTO electrolyte slurry filled the pores to achieve a dual-conductive configuration (Fig. S3f in Supporting information). Tested at 60 °C, the electrolyte composite cathode demonstrated higher specific capacities and lower resistance (Figs. S3g and h in Supporting information) than the normal sulfur cathode, indicating that dual-conductive structure in cathode was capable to overcome the low conductivity of sulfur.

To overcome the defect and build a dual-conductive structure in ISE-based ASSLSB, Yan and coworkers [29] built an electrolyte-cathode double layer based on $Li_{6.28}La_3Al_{0.24}Zr_2O_{12}$ (LLAZO)-LLAZO@CNF structure (Fig. S3i in Supporting information). On the one hand, through high-voltage electrospinning, the porous sulfur host LLAZO@CNF matrix was fabricated and demonstrated a high conductivity of 218 S/cm; on the other hand, with a precisely controlled structural fabrication, a transition region was created

between LLAZO electrolyte and composite cathode, providing continuous Li ion pathways to improve the ionic conductivity. To compensate for the surface roughness of the garnet network and to reduce the interfacial impedance, thermal-initiated poly (ethylene glycol) diacrylate average (PEGDA) polymer is applied to fill the empty spaces in LLAZO network and form PEGDA(LiTFSI)-LLAZO which demonstrated an ionic conductivity of 0.251 mS/cm at room temperature (Fig. S3j in Supporting information). Assembled with the double layer framework, the ASSLSB delivered a capacity of 1055 mAh/g at 50 °C at 0.2 C and a retained capacity of 939 mAh/g after 50 cycles, corresponding to a capacity retention of 89% (Fig. S3k in Supporting information).

Compared with cells with laminated cathode, those with dual-conductive structures exhibited higher specific capacity and better cycle performance. Different from the innovations in cathode additives, construction of new structures can be achieved through improvements in fabrication methods, which is able to lower the cost in materials. However, the inherently low Li ion conductivity of polymers at room temperature remains. Therefore, exploring for solid polymers with high Li ion conductivity is still necessary for dual-conductive cathodes for ASSLSBs while structural designations such as polymer casting and interlayer introducing are the ways to take full advantage of Li ion conductive polymers.

5. Solid electrolytes

As an essential part of ASSLSBs, SEs should meet the demands such as high ionic conductivity, high Li ion migration number, sufficient chemical and electrochemical stability, sufficient mechanical properties, and good compatibility with electrodes [11,105]. In the researches of LE-based Li-S batteries, the electrolytes are usually liquid solutions including LiTFSI, linear ether, cyclic ether solvents and small amounts of lithium nitrate ($LiNO_3$) [31]. However, in the studies of ASSLSB cathodes, the SEs researchers used were all different, reflecting the fact that there is not an ideal SE for ASSLSBs. ISE, SPE and CPE all have their own advantages and disadvantages (Fig. S4 in Supporting information).

For ISEs, the ionic conductivity is equivalent to LEs and the stability is higher than LEs, but high hardness and low toughness cause weak Li ion transportation in electrolyte/electrode interface and make it difficult to assemble pouch batteries [37,106,107]. For SPEs, the fine flexibility overcomes the defects of ISEs, but the inferior stability, mechanical strength and ionic conductivity show great disadvantages [15].

Compared with others, CPEs are regarded as promising SEs for ASSLSBs and are widely studied recently. The existence of polymer can create homogeneous electrolyte/electrode interface and make SE films more flexible to assemble pouch cells [96]. Oxide electrolytes such as LLZO and LLZTO were usually used to fabricate CPEs for ASSLSBs. Lee *et al.* [108] reported a CPE consisted of PEO, $LiClO_4$ and LLZO, which exhibited an ionic conductivity of 3.8×10^{-4} S/cm at 70 °C. Chen *et al.* [109] reported a CPE containing PEO, LLZO, LATP, LiTFSI and succionitrile, which showed conductivities of 1.16×10^{-4} and 7.26×10^{-4} S/cm at room temperature and 60 °C, respectively. According the recent reports, the conductivity of sulfide electrolytes is generally lower than oxide electrolytes, and sulfide electrolytes are possessed with good deformability and moderate mechanical strength [110–112]. Zhu *et al.* [111] reported a flexible CPE film synthesized by cellulose and LPSCl. The CPE film reached an ionic conductivity of 6.3×10^{-3} S/cm at room temperature and showed good flexibility to assemble pouch cells. However, compared with oxide electrolytes, sulfide electrolytes exhibit lower air conductivity and more complex preparation, which need to be overcome in future studies [110].

In some researches, similar types of SEs were used both in ASSLSBs and Li-ion batteries [28,58,111,113]. In spite of this, it is worth mentioning that compared with batteries using $LiFePO_4$ or NMC cathodes, some indicators should be paid more attention when choosing SEs for ASSLSBs [3,105]. Firstly, SEs should be chemically and electrochemically stable with sulfur, for high SEs content is usually needed in ASSLSB cathodes. Secondly, because sulfur cathodes are low-voltage cathodes, SEs which are not compatible with high-voltage cathodes are still applicable in ASSLSBs. Thirdly, SEs should be able to inhibit the diffusion of sulfur and PSs which can cause capacity fading, which means in ASSLSBs, PEO-based electrolytes will be replaced by others in the future even though they have shown great performance in all-solid-state batteries.

6. Summary and perspectives

In summary, recent advances in cathode materials and cathode structures of ASSLSBs have been reviewed and discussed. To overcome the defects of traditional ASSLSB cathodes, the fabrication methods of traditional active materials are optimized, and new active materials are developed. For the hosts of the active materials which also play important roles, conductive carbon hosts and other functional hosts are studied to improve the electronic conductivity and ionic conductivity of cathodes.

Compared with sulfur carbon composites synthesized through straightforward mixing ways, rationally designed conductive carbon hosts with high surface area enable higher sulfur loading and provide more electron transportation paths in cathodes. Apart from carbon hosts, other functional hosts such as ionic conductive materials and intercalation materials have also been applied in cathodes to facilitate the reactions involving Li ions. The application of host materials with high surface area and conductivity is a feasible solution to the shortcomings such as poor conductivity and low active materials loading which hampers the practical application of Li-S batteries.

As for binder materials, the development of DBE technique brings solutions for the low conductivity and low active substance content of ASSLSB cathodes. However, in cells using PEO-based electrolytes where PSs are soluble, functional binders such as PVDF seems more feasible.

Although many methods have improved the specific capacity, conductivity and stability of cathodes for ASSLSBs, the high utilization of high loading amount of active material is still unable to be achieved both, which may become one of the biggest problems of ASSLSBs in the future. New researches should look into the problem to find out the inherent reason why specific capacities decline with the addition of active materials. Besides, not only smaller particles size of active materials and larger surface area of host materials are needed to solve this problem, but innovations in structures or additives should also be carried out to immobilize active materials as well as control their performance in discharge-charge process, eliminating the drawbacks aroused by high active materials loading amount.

In addition to the developments in new cathode materials, dual-conductive structures have been rationally designed to unleash the full potential of cathode materials. Studies in this field were mostly inspired by LE-based Li-S batteries, in which dual-conductivity was naturally formed by the homogeneous contact of composite cathode and electrolyte. In SPE/CPE-based systems, casting SEs on 3D cathode frameworks can be applied to form a dual-conductive structure because ionic conductive polymer can infiltrate composite cathode before solidification as LE does. Similar method can also be applied in ISE-based systems, but ionic conductive polymer is only used in the composite cathode and the ISE/cathode interface, rather than electrolyte. The dual-

conductivity has always been a vital issue in ASSLSB cathodes. Although the use of conducting polymers can result in a better electrolyte/cathode interface, two kinds of conductive materials are still required in cathode to maintain dual-conductivity, affecting the conduction efficiency. Therefore, it can be a feasible measure to create dual-conductive materials with both desirable ionic conductivity and electronic conductivity, which can replace or partly replace the traditional conductive materials in composite cathodes, contributing to more effective electron/ion transportation and higher percentage of active materials.

Last but not least, now that there is not an ideal electrolyte for ASSLSBs, the research on SEs still needs to be further developed. If the SE does not meet the requirements, no matter how good the cathode performance is, the ASSLSB will not be significantly improved. CPEs have more practical potential than ISEs and SPEs in the future, according to recent advances in SEs. Different polymers and inorganic fillers for CPEs have different applicable fields, so each CPE should give full play to its advantages and avoid the weaknesses. With the developments of materials science and electrochemical research, the problems faced by ASSLSBs will be expected to be solved in the future, and ASSLSBs will be expected to be applied in the future energy system.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Nos. 51874110 and 51604089), Natural Science Foundation of Heilongjiang Province (No. LH2021B011), and Open Project of State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology (No. QA202138).

Supplementary materials

Supplementary materials associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2022.107783.

References

[1] W.P. Wang, J. Zhang, J. Chou, et al., Adv. Energy Mater. 11 (2021) 2000791.
[2] R.P. Fang, J.T. Xu, D.W. Wang, Energy Environ. Sci. 13 (2020) 432–471.
[3] S. Xia, X. Wu, Z. Zhang, et al., Chem 5 (2019) 753–785.
[4] X. Wang, N. Deng, L. Wei, et al., Chem. Asian J. 16 (2021) 2852–2870.
[5] C. Ma, B. Wang, T. Zhang, et al., CrystEngComm 24 (2022) 3189–3198.
[6] R.C. Xu, S.Z. Zhang, X.L. Wang, et al., Chem. Eur. J. 24 (2018) 6007–6018.
[7] P. Bonnick, E. Nagai, J. Muldoon, J. Electrochem. Soc. 165 (2017) A6005–A6007.
[8] E. Umeshbabu, B. Zheng, Y. Yang, Electrochem. Energy Rev. 2 (2019) 199–230.
[9] Q. Lv, Y. Jiang, B. Wang, et al., Cell Rep. Phys. Sci. 3 (2022) 100706.
[10] M. Ge, X. Zhou, Y. Qin, et al., Chin. Chem. Lett. 33 (2022) 3894–3898.
[11] J. Liu, H. Yuan, H. Liu, et al., Adv. Energy Mater. 12 (2021) 2100748.
[12] A.B. Haruna, T.P. Mofokeng, J.J. Ogada, et al., Electrochem. Commun. 136 (2022) 107248.
[13] X. Huang, B. Luo, P. Chen, et al., Coord. Chem. Rev. 422 (2020) 213445.
[14] J. Zhang, G. Zhang, Z. Chen, et al., Energy Stor. Mater. 26 (2020) 513–533.
[15] M. Jiang, Z. Zhang, B. Tang, et al., J. Energy Chem. 58 (2021) 300–317.
[16] R.Y. Fang, H.H. Xu, B.Y. Xu, et al., Adv. Funct. Mater. 31 (2021) 2001812.
[17] X.F. Yang, J. Luo, X.L. Sun, Chem. Soc. Rev. 49 (2020) 2140–2195.
[18] B.B. Wu, S.Y. Wang, W.J. Evans, et al., J. Mater. Chem. A 4 (2016) 15266–15280.
[19] S. Hong, Y. Wang, N. Kim, S.B. Lee, J. Mater. Sci. 56 (2021) 8358–8382.
[20] Q. Wang, Y. Chen, J. Jin, Z. Wen, Solid State Ionics 357 (2020) 115500.
[21] G.H. Chang, Y.S. Oh, S. Kang, et al., Electrochim. Acta 358 (2020) 136884.
[22] J.P. Mwizerwa, Q. Zhang, F. Han, et al., ACS Appl. Mater. Interfaces 12 (2020) 18519–18525.
[23] Y. Wang, G. Wang, P. He, et al., Chem. Eng. J. 393 (2020) 124705.
[24] J. Yue, Y. Huang, S. Liu, et al., ACS Appl. Mater. Interfaces 12 (2020) 36066–36071.
[25] S. Choi, I. Yoon, W.T. Nichols, D. Shin, Ceram. Int. 44 (2018) 7450–7453.
[26] C. Zhang, Y. Lin, Y.W. Zhu, et al., RSC Adv. 7 (2017) 19231–19236.
[27] B.S. Zhao, L. Wang, S. Liu, et al., ACS Appl. Mater. Interfaces 14 (2021) 1212–1221.
[28] J. Wang, X. Yan, Z. Zhang, et al., ACS Appl. Mater. Interfaces 12 (2020) 41323–41332.
[29] C. Yan, Y. Zhou, H. Cheng, et al., Energy Stor. Mater. 44 (2022) 136–144.
[30] M. Yan, W.P. Wang, Y.X. Yin, et al., EnergyChem 1 (2019) 100002.
[31] F. Li, Q. Liu, J. Hu, et al., Nanoscale 11 (2019) 15418–15439.
[32] P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J.M. Tarascon, Nat. Mater. 11 (2012) 19–29.
[33] Y. De Luna, M. Abdullah, S.N. Dimassi, N. Bensalah, Ionics 27 (2021) 4937–4960.
[34] Z. Wang, X. Xu, S. Ji, et al., J. Mater. Sci. Technol. 55 (2020) 56–72.
[35] I. Gracia, H. Ben Youcef, X. Judez, et al., J. Power Sources 390 (2018) 148–152.
[36] X. Li, D.H. Wang, H.C. Wang, et al., ACS Appl. Mater. Interfaces 11 (2019) 22745–22753.
[37] X. Judez, H. Zhang, C.M. Li, et al., J. Electrochem. Soc. 165 (2018) A6008–A6016.
[38] R. Blanga, M. Goor, L. Burstein, et al., J. Solid State Electrochem. 20 (2016) 3393–3404.
[39] Y.X. Song, Y. Shi, J. Wan, et al., Energy Environ. Sci. 12 (2019) 2496–2506.
[40] X.Y. Tao, Y.Y. Liu, W. Liu, et al., Nano Lett. 17 (2017) 2967–2972.
[41] S. Bag, C. Zhou, P.J. Kim, et al., Energy Stor. Mater. 24 (2020) 198–207.
[42] M. Agostini, D.H. Lim, M. Sadd, et al., ChemSusChem 10 (2017) 3490–3496.
[43] H. Yuan, H.X. Nan, C.Z. Zhao, et al., Batteries Supercaps 3 (2020) 596–603.
[44] Y. Zhang, T. Liu, Q. Zhang, et al., J. Mater. Chem. A 6 (2018) 23345–23356.
[45] R.C. Xu, Z. Wu, S.Z. Zhang, et al., Chem. Eur. J. 23 (2017) 13950–13956.
[46] B. Ding, J. Wang, Z. Fan, et al., Mater. Today 40 (2020) 114–131.
[47] Y.Z. Sun, J.Q. Huang, C.Z. Zhao, Q. Zhang, Sci. China Chem. 60 (2017) 1508–1526.
[48] M. Dirican, C.Y. Yan, P. Zhu, X.W. Zhang, Mater. Sci. Eng. R: Rep. 136 (2019) 27–46.
[49] D.N. Lei, K. Shi, H. Ye, et al., Adv. Funct. Mater. 28 (2018) 1707570.
[50] T. Krauskopf, H. Hartmann, W.G. Zeier, J. Janek, ACS Appl. Mater. Interfaces 11 (2019) 14463–14477.
[51] H.U. Choi, J.S. Jin, J.Y. Park, H.T. Lim, J. Alloys Compd. 723 (2017) 787–794.
[52] M. Nagao, A. Hayashi, M. Tatsumisago, Electrochim. Acta 56 (2011) 6055–6059.
[53] M. Nagao, A. Hayashi, M. Tatsumisago, Energy Technol. 1 (2013) 186–192.
[54] S. Kinoshita, K. Okuda, N. Machida, et al., Solid State Ionics 256 (2014) 97–102.
[55] X.A. Liang, Z.Y. Wen, Y. Liu, et al., J. Power Sources 196 (2011) 3655–3658.
[56] L.P. Hou, H. Yuan, C.Z. Zhao, et al., Energy Stor. Mater. 25 (2020) 436–442.
[57] C. Zhou, S. Bag, T. He, et al., Appl. Mater. Today 19 (2020) 100585.
[58] A.S. Alzahrani, M. Otaki, D. Wang, et al., ACS Energy Lett. 6 (2021) 413–418.
[59] R. Kumar, J. Liu, J.Y. Hwang, Y.K. Sun, J. Mater. Chem. A 6 (2018) 11582–11605.
[60] X.Y. Yao, N. Huang, F.D. Han, et al., Adv. Energy Mater. 7 (2017) 1602923.
[61] Q. Zhang, N. Huang, Z. Huang, et al., J. Energy Chem. 40 (2020) 151–155.
[62] Q. Zhao, J.X. Zheng, L. Archer, ACS Energy Lett. 3 (2018) 2104–2113.
[63] Y.J. Liu, P. He, H.S. Zhou, Adv. Energy Mater. 8 (2018) 1701602.
[64] F. Wang, B. Wang, J. Li, et al., ACS Nano 15 (2021) 2197–2218.
[65] M. Nagao, A. Hayashi, M. Tatsumisago, J. Mater. Chem. 22 (2012) 10015–10020.
[66] M. Nagao, A. Hayashi, M. Tatsumisago, et al., J. Power Sources 274 (2015) 471–476.
[67] H. El-Shinawi, E.J. Cussen, S.A. Corr, Nanoscale 11 (2019) 19297–19300.
[68] L. Lodovico, S.M. Hosseini, A. Varzi, S. Passerini, Energy Technol. 7 (2019) 1801013.
[69] T. Takeuchi, H. Kageyama, K. Nakanishi, et al., J. Electrochem. Soc. 157 (2010) A1196–A1201.
[70] S.M. Hosseini, A. Varzi, S. Ito, et al., Energy Stor. Mater. 27 (2020) 61–68.
[71] U. Ulissi, S. Ito, S.M. Hosseini, et al., Adv. Energy Mater. 8 (2018) 1801462.
[72] Q. Zhang, Z.G. Ding, G.Z. Liu, et al., Energy Stor. Mater. 23 (2019) 168–180.
[73] N. Machida, K. Kobayashi, Y. Nishikawa, T. Shigematsu, Solid State Ionics 175 (2004) 247–250.
[74] A. Hayashi, T. Ohtomo, F. Mizuno, et al., Electrochim. Acta 50 (2004) 893–897.
[75] M. Chen, X. Yin, M.V. Reddy, S. Adams, J. Mater. Chem. A 3 (2015) 10698–10702.
[76] Q. Zhang, H.L. Wan, G.Z. Liu, et al., Nano Energy 57 (2019) 771–782.
[77] T. Matsuyama, A. Hayashi, T. Ozaki, et al., J. Mater. Chem. A 3 (2015) 14142–14147.
[78] K. Liu, H. Zhao, D. Ye, J. Zhang, Chem. Eng. J. 417 (2021) 129309.
[79] J.L. Wang, J. Yang, J.Y. Xie, N.X. Xu, Adv. Mater. 14 (2002) 963–965.
[80] J.E. Trevey, J.R. Gilsdorf, C.R. Stoldt, et al., J. Electrochem. Soc. 159 (2012) A1019–A1022.
[81] Y.Y. Zhang, Y.L. Sun, L.F. Peng, et al., Energy Stor. Mater. 21 (2019) 287–296.
[82] W. Zhang, Y. Zhang, L. Peng, et al., Nano Energy 76 (2020) 105083.
[83] A. Hayashi, R. Ohtsubo, M. Nagao, M. Tatsumisago, J. Mater. Sci. 45 (2010) 377–381.
[84] A. Hayashi, R. Ohtsubo, T. Ohtomo, et al., J. Power Sources 183 (2008) 422–426.
[85] M.Y. Wang, X.H. Xia, Y. Zhong, et al., Chem. Eur. J. 25 (2019) 3710–3725.
[86] T. Ould Ely, D. Kamzabek, D. Chakraborty, M.F. Doherty, ACS Appl. Energy Mater. 1 (2018) 1783–1814.
[87] J. Yang, B. Wang, F. Jin, et al., Nanoscale 12 (2020) 4552–4561.
[88] M. Nagao, Y. Imade, H. Narisawa, et al., J. Power Sources 222 (2013) 237–242.
[89] M. Nagao, K. Suzuki, Y. Imade, et al., J. Power Sources 330 (2016) 120–126.

[90] F.D. Han, J. Yue, X.L. Fan, et al., Nano Lett. 16 (2016) 4521–4527.
[91] T. Hakari, A. Hayashi, M. Tatsumisago, Adv. Sustain. Syst. 1 (2017) 1700017.
[92] T. Hakari, A. Hayashi, M. Tatsumisago, Chem. Lett. 44 (2015) 1664–1666.
[93] H. Nagata, Y. Chikusa, J. Power Sources 263 (2014) 141–144.
[94] H. Nagata, Y. Chikusa, Energy Technol. 2 (2014) 753–756.
[95] N. Tanibata, H. Tsukasaki, M. Deguchi, et al., J. Mater. Chem. A 5 (2017) 11224–11228.
[96] L. Xu, Y. Lu, C.Z. Zhao, et al., Adv. Energy Mater. 11 (2020) 2002360.
[97] Y. Lu, C.Z. Zhao, H. Yuan, et al., Matter 5 (2022) 876–898.
[98] J.K. Hu, H. Yuan, S.J. Yang, et al., J. Energy Chem. 71 (2022) 612–618.
[99] S. Gu, X. Huang, Q. Wang, et al., J. Mater. Chem. A 5 (2017) 13971–13975.
[100] M. Liu, X.Y. Qin, Y.B. He, et al., J. Mater. Chem. A 5 (2017) 5222–5234.
[101] Y. Lu, X. Huang, Z. Song, et al., Energy Stor. Mater. 15 (2018) 282–290.
[102] S. Li, S.Q. Zhang, L. Shen, et al., Adv. Sci. 7 (2020) 1903088.
[103] P. Zhu, C. Yan, J. Zhu, et al., Energy Stor. Mater. 17 (2019) 220–225.
[104] L. Wang, X. Yin, C. Jin, et al., ACS Appl. Energy Mater. 3 (2020) 11540–11547.
[105] X. Liang, L. Wang, X. Wu, et al., J. Energy Chem. 73 (2022) 370–386.
[106] R. Xu, B. Xiao, C. Xuan, et al., ACS Appl. Mater. Interfaces 13 (2021) 34274–34281.
[107] W. Kou, J. Wang, W. Li, et al., J. Membr. Sci. 634 (2021) 119432.
[108] J. Lee, K. Heo, Y.W. Song, et al., J. Electrochem. Sci. Technol. 13 (2022) 199–207.
[109] F. Chen, P.M.G. Puente, Y. Zhang, et al., Solid State Ionics 380 (2022) 115926.
[110] Y. Li, D. Zhang, X. Xu, et al., J. Energy Chem. 60 (2021) 32–60.
[111] G.L. Zhu, C.Z. Zhao, H.J. Peng, et al., Adv. Funct. Mater. 31 (2021) 2101985.
[112] X. Huang, C. Liu, Y. Lu, et al., J. Power Sources 382 (2018) 190–197.
[113] H. Tsukasaki, M. Otoyama, Y. Mori, et al., J. Power Sources 367 (2017) 42–48.