Designing principles of advanced sulfur cathodes toward practical lithium-sulfur batteries

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Abstract
As one of the most promising candidates for next-generation energy storage systems, lithium-sulfur (Li-S) batteries have gained wide attention owing to their ultrahigh theoretical energy density and low cost. Nevertheless, their road to commercial application is still full of thorns due to the inherent sluggish redox kinetics and severe polysulfides shuttle. Incorporating sulfur cathodes with adsorbents/catalysts has been proposed to be an effective strategy to address the foregoing challenges, whereas the complexity of sulfur cathodes resulting from the intricate design parameters greatly influences the corresponding energy density, which has been frequently ignored. In this review, the recent progress in design strategies of advanced sulfur cathodes is summarized and the significance of compatible regulation among sulfur active materials, tailored hosts, and elaborate cathode configuration is clarified, aiming to bridge the gap between fundamental research and practical application of Li-S batteries. The representative strategies classified by sulfur encapsulation, host architecture, and cathode configuration are first highlighted to illustrate their synergetic contribution to the electrochemical performance improvement. Feasible integration principles are also proposed to guide the practical design of advanced sulfur cathodes. Finally, prospects and future directions are provided to realize high energy density and long-life Li-S batteries.

KEYWORDS
host materials, Li-S batteries, redox kinetics, shuttle effect, sulfur cathodes

1 | INTRODUCTION

The boomingly increased demands on high-power energy storage devices have motivated vigorous research on the development of novel batteries with high energy density, long service life, and low cost. Of note, the highest energy density that the market-dominated lithium-ion batteries (LIBs) can deliver still could not afford the ever-growing requirements of next-generation electric vehicles and grid-scale energy storage. Among various substitutes for LIBs, lithium-sulfur (Li-S) batteries are generally recognized as one of the most promising candidates for next-generation energy storage systems owing to their superb theoretical capacity (1675 mAh/g) and energy density (2600 Wh/kg).
or 2800 Wh/L. In addition, benefiting from the low cost (~150 $/ton) and environmental benignity of sulfur, Li-S batteries show greatly competitive advantages in practical application. It is foreseen that the well-designed Li-S batteries could potentially achieve the goal of gravimetric energy density of 400–600 Wh/kg and volumetric energy density of 700 Wh/L, respectively. However, certain stubborn challenges still impede the pathway of the practical application of Li-S batteries. In the case of sulfur cathodes, the sluggish redox kinetics and severe lithium polysulfides (LiPSs) shuttle lead to poor rate performance and rapid cycle fading. Over the past decades, strenuous efforts have been exerted to address the aforementioned challenges by designing multifarious architectures for sulfur cathodes with various host materials. More recently, the research focus has been shifted from blocking the dissolution of LiPSs in electrolyte by physical/chemical confinement in early research to promoting the sulfur redox kinetics by various catalytic hosts. Exploration on rational design of adsorption/catalytic host materials is extensively conducted and systematically summarized by numerous reviews, mostly focusing on structure construction and catalyst modulation. However, considering the inseparability of sulfur composite construction and cathode configuration, alongside their synergistic contribution to the performance improvements of Li-S batteries, deeply understanding their intrinsic relationship is highly required. To further guide the integrated design of practical Li-S batteries, a pioneering overview of the state-of-the-art designing strategies of advanced sulfur cathodes is present here.

In this contribution, we not only comprehensively summarize the recent development of catalytic hosts but also systematically discuss two equally important parameters, namely sulfur encapsulation and cathode configuration. The former discloses the correlation between sulfur active materials and host materials, while the latter illustrates the customized relationship between cathode engineering and compositions. We intend to put forward certain integrated design principles of advanced sulfur cathodes for reliable Li-S batteries with high energy density and long-term cycling (Figure 1). In the beginning, the fundamental electrochemistry of Li-S batteries and the accompanied main challenges of sulfur cathodes are elaborately summarized and illustrated. Subsequently, comprehensive summaries of rational sulfur encapsulation methods and applicable design strategies of host materials are expounded, aiming at clarifying the integrated design principles of advanced sulfur composites. Specifically, on the one hand, the sulfur encapsulation methods are illustrated by several representative sulfur and equivalent active materials. On the other hand, the host architectures are introduced mainly through the design guidelines of multifarious architectures alongside modulation principles of adsorbents and electrocatalysts. Remarkably, several typical mechanisms of enhanced sulfur redox kinetics enabled by emerging catalytic materials are clarified. Combining the specificity of the aforementioned sulfur composites and customized fabrication technologies, representative strategies for configuring sulfur cathodes with high energy density, flexibility, and wide temperature range operation are respectively introduced. In the last part, the future perspectives of integrated design principles for advanced sulfur cathodes to achieve high-performance Li-S batteries are proposed.

2 PRINCIPLES AND CHALLENGES OF LI-S BATTERIES

2.1 Principles

Different from traditional LIBs operated through a “rocking-chair” mechanism, Li-S batteries utilizing 16-electron conversion of sulfur cathodes undergo a number of successive reduction steps with complicated phase evolution (solid ↔ liquid ↔ solid) in the whole charge-discharge process. For a typical Li-S battery (Figure 2A), Li metal is directly employed as an anode and active sulfur or derivatives are implemented as the cathode. Meanwhile, aprotic electrolyte, such as 1,3-dioxolane and 1,2-dimethoxyethane with lithium bis (trifluoromethane sulfone) imide as lithium salt, is usually used to ensure the unobstructed ion migration.

During the discharge process, solid cyclic S₈ opens and reacts with lithium-ion (Li⁺) to form liquid Li₂S₈, high-order Li₂Sn (4 < n < 7), low-order Li₂Sn (2 < n ≤4), and solid Li₂S₂/Li₂S in sequence. The Li-S battery usually demonstrates two obvious discharge plateaus at the voltage of approximately 2.3 and 2.1 V (vs. Li/Li⁺), accompanied with multiphase transformation (Figure 2B). The first plateau is generally regarded as the rapid conversion from solid S₈ to liquid Li₂S₄, contributing a theoretical capacity of 419 mAh/g. The second plateau, which provides 75% of the theoretical capacity of sulfur (1256 mAh/g), corresponds to the liquid-solid conversion from Li₂S₄ to Li₂S with relatively slow kinetics. As for the reversible charge process, Li₂S releases Li⁺ into the electrolyte and is reconverted into LiPSs, followed by the formation of S₈. Extensive characterization techniques have been employed to identify the evolution of LiPSs throughout the sulfur redox process. Different from the theoretical “step-by-step” conversion mechanism of sulfur species, the coexistence of S₈⁻, S₆⁻, S₄⁻ dianions produced by electrochemical reduction and S₇⁻, S₅⁻, S₃⁻ anions ascribed to chemical reduction is clearly observed, as verified by UV-visible absorption spectroscopy, Raman spectroscopy, and
For Li-S batteries, the retarded sulfur redox kinetics and notorious long-chain LiPSs shuttle are the major obstacles, which inevitably result in inferior sulfur utilization and cycling stability. Worse still, to realize the practical application of Li-S batteries, a high sulfur loading and lean electrolyte usage with a low electrolyte-to-sulfur (E/S) ratio are essential, which further exacerbate the shuttle effect. In the succeeding subsections, these challenges are separately itemized and discussed.

2.2.1 Sluggish redox kinetics

It is generally recognized that the conversion from liquid Li$_2$S$_4$ to solid Li$_2$S$_2$ requires a much higher activation barrier than the generation of Li$_2$S$_4$ from S$_8$.

Moreover, the final solid-solid conversion from Li$_2$S$_2$ to Li$_2$S, which possesses 50% of theoretical capacity contribution with the highest voltage polarization, further aggravates the
sluggish sulfur reduction kinetics. Because of the insulating nature of Li$_2$S$_2$/Li$_2$S, a detrimental passivation layer is gradually formed on the electrode surface, leading to the premature end of discharge and limited capacity. In addition, the relatively high activation energy of Li$_2$S decomposition in the charge process results in sluggish sulfur oxidation kinetics as well.

2.2.2 Severe shuttle effect

The ether-based electrolyte is frequently used in Li-S batteries, owing to its high mobility for LiPSs and good chemical stability against LiPSs. An appropriate concentration of soluble LiPSs can promote the solid-liquid conversion (S$_8$ → Li$_2$S$_4$) by activating the residual S$^{20}$ and motivate the oxidation of solid Li$_2$S by lowering the electrochemical activation barrier. Nevertheless, highly soluble LiPSs also trigger the inevitable loss of active sulfur. Driven by the concentration gradient, the dissolved LiPSs could diffuse to the anode to irreversibly react with Li, resulting in a severe capacity fading. Meanwhile, the residual LiPSs are chemically reduced to shorter-chain LiPSs, which would subsequently shuttle back to the cathode to be reoxidized upon charging. The unfavorable process occurs repeatedly, namely shuttle effect, bringing serious self-charge process and low coulombic efficiency.

2.2.3 Unstable electrode structure

In addition to a large volume change of Li anode due to its hostless nature, more severe volume expansion (~80%) occurs in sulfur cathode upon discharging because of the apparent different density of S$_8$ (2.07 g/cm$^3$) and Li$_2$S (1.66 g/cm$^3$). With long-term cycling, electrode pulverization is inevitable. The exfoliation of active materials alongside disconnection with conductive substrates leads to a rapid capacity fading and serious safety issues, especially for high sulfur loading cathodes.

2.2.4 Limited practical energy density

It has been pointed out that sulfur loading of more than 4 mg/cm$^2$ with E/S ratio less than 3 μL/mg is the boundary condition for pouch cells with a total gravimetric energy density higher than 500 Wh/kg. However, for most reported Li-S batteries, low sulfur loading (<2 mg/cm$^2$), flooded electrolyte (E/S > 10 μL/mg), and an excess amount of Li anode were employed. It should be mentioned that volumetric energy density is another key factor, which was rarely mentioned in previous reports.

The theoretical density of elemental sulfur is 2.07 g/cm$^3$, which is much lower than the cathode materials of conventional LIBs. To date, the volumetric energy capacity of Li-S pouch cells is still limited within 200–400 Wh/L, in contrast to that of advanced LIBs possessing superior volumetric density beyond 700 Wh/L.

3 SULFUR-BASED CATHODE DESIGN

Sulfur-based cathodes, one of the most critical components of Li-S batteries, provide the reaction sites for sulfur and Li and determine the output discharge capacity. How to improve the cycle stability and achieve maximum sulfur utilization in sulfur cathodes have puzzled researchers in the last few decades. Among tremendous work on inhibiting the shuttle effect and expediting the redox kinetics to improve the electrochemical performance of Li-S batteries, one of the most effective strategies is rationally designing adsorbents and electrocatalysts, as comprehensively introduced in the following sections. In addition, sulfur encapsulation and cathode configuration engineering also play pivotal roles in achieving high-performance cathodes. Thus, the general methods of sulfur encapsulation and cathode configuration are deservedly included as well.

3.1 Encapsulation methods of active materials

Enlightened by the innovative work from Nazar’s group, the strategy of incorporating sulfur with host materials is widely accepted. Various methods have been developed to effectively infiltrate sulfur into host materials. Hence, in the succeeding subsection, several representative sulfur encapsulation methods are introduced and discussed, with emphasis on their respective advantages, disadvantages, and compatibilities to coupled hosts.

3.1.1 Ball-milling method

Physically mixing sulfur particles with conductive carbon, namely ball-milling method, was a simple and cost-effective technique to fabricate composites in the early stage. Utilizing specific processes (i.e., dry or wet milling) with controlled rotation rates, the sulfur particle size and the surface functional group could be modified. Meanwhile, the interfacial resistance of composites could be sharply decreased, strengthening the electron/ion transport rate. By utilizing this method, not only conductive agents but also adsorbents or electrocatalysts could
be attached, greatly broadening its applicability for the fabrication of large-scale practical sulfur-based cathodes. However, the inherent shortcomings of the ball-milling method, such as uneven particle size, limited surface mixing, and fatal structural deterioration, still impede its application for constructing cathodes with elaborate structures.

### 3.1.2 Melting-diffusion method

Different melting temperatures can lead to the obvious viscosity change of sulfur. The most optimal melting temperature was determined to be 155°C, as first employed by Nazar et al. in 2009.\(^{24}\) By impregnating sulfur into specific mesoporous carbon (CMK-3) via the melting-diffusion method, a high reversible capacity of up to 1320 mAh/g was attained, which invigorates the whole development of Li-S batteries. Although molten sulfur could easily diffuse into the tailored porous host materials through the capillary force and be encapsulated into nanosized pores,\(^{10}\) the reaggregation of sulfur followed by surface reaccumulation when drying is still unavoidable, which deteriorates the cycling performance of Li-S batteries, especially under high sulfur loading conditions. To solve this issue, subsequent treatments with higher temperature (300°C) (Figure 3B)\(^ {26}\) or CS\(_2\)\(^ {32}\) to remove the surface sulfur is commonly employed. Alternatively, when vaporized at 500°C, small sulfur molecules (e.g., S\(_6\) or S\(_2\)) were successfully impregnated into the channels of CNTs and the prepared cathodes demonstrated superior cyclability with high coulombic efficiency.\(^ {33}\) However, the sulfur loading is adversely affected by the vapor-infiltration method.

### 3.1.3 Dissolution-recrystallization method

Instead of melting, dissolving sulfur in a specific solvent followed by dropping it into substrates is a suitable method to prepare free-standing cathode.\(^ {34}\) By modulating the sulfur concentration and droplets number, the sulfur loading content could be readily adjusted. CS\(_2\)\(^ {35}\) and toluene\(^ {36}\) are the most common solvents to dissolve sulfur. However,
because of their toxicity, ethanol was also used in certain situations.\textsuperscript{37,38} Notably, melting-diffusion treatment was always conducted after the dissolution-recrystallization process in most reported studies\textsuperscript{39,40}

Evolved from the traditional dissolution-recrystallization route, a nucleation-recrystallization strategy was first introduced in 2018.\textsuperscript{41} The initially dissolved sulfur is adsorbed onto a single-walled CNT to act as a crystal nucleus and induce the subsequent sulfur recrystallization, generating a uniform sulfur layer eventually. Owing to the strong interfacial interaction between sulfur and carbon substrates, the resultant free-standing cathodes showed excellent structural durability and rate performance.

In addition to pristine sulfur, LiPSs, as alternative active materials, possess higher reactivity compared to solid sulfur. They could be directly employed as catholytes\textsuperscript{42} or dropped into the substrates\textsuperscript{27} to form composite cathodes. Notably, by fully taking advan
tages of this strategy, Manthiram’s group prepared the cathodes with extremely high sulfur loading of up to 18.1 mg/cm\textsuperscript{2} and an ultrahigh areal capacity of approximately 20 mAh/cm\textsuperscript{2} was attained in 2016, which was the highest reported areal capacity at that time.\textsuperscript{42}

### 3.1.4 Chemical deposition method

The electrochemical performance is critically dependent on the sulfur particle size, and ultrasmall sulfur nanoparticles usually demonstrate higher capacity compared to larger sulfur particles.\textsuperscript{43} Especially, nanosized sulfur can be easily synthesized by chemical deposition strategy. Customized to the characteristics of host materials, nanosized sulfur could be synthesized by the reaction between certain sulfur-containing salts (e.g., Na\textsubscript{2}S, Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, Na\textsubscript{2}S\textsubscript{x}) and acids in aqueous solution.\textsuperscript{44-46} Followed by the melting-diffusion process, homogeneous carbon/sulfur cathode materials could be obtained.\textsuperscript{29} Back to 2013, Cui and co-workers first synthesized uniform and monodisperse core-shell/yolk-shell S@TiO\textsubscript{2}, where the sulfur core was fabricated by the reaction of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} and hydrochloric acid.\textsuperscript{28} Owing to the unique yolk-shell structure with internal void space, the obtained electrochemical performance of corresponding yolk-shell composites demonstrated an obvious improvement compared to the core-shell counterpart. Associated with systematic experiments, the authors further illustrated the significance of voids and intact shells for accommodating the volume expansion of sulfur and minimizing LiPSs dissolution.

Another typical synthesis route of sulfur is the reduction of metal sulfide, which can avoid the generation of harmful gases (e.g., SO\textsubscript{2} and H\textsubscript{2}S) in above methods. By utilizing ZnS spheres as sulfur and phenol formaldehyde resin as carbon precursors, yolk-shell S@C composites were successfully obtained by the carbonization and oxidation process in sequence (Figure 3C).\textsuperscript{30} During the oxidation process, mild ferric nitrate solution was adopted and the corresponding reaction is described as follows:

\[
2\text{Fe}^{(aq)}^{3+} + \text{ZnS(S)} \rightarrow 2\text{Fe}^{(aq)}^{2+} + \text{Zn}^{(aq)}^{2+} + \text{S(S)}.
\]

Owing to the effective confinement of in-situ generated sulfur particles inside the pores, excellent cycling performance was obtained. More significantly, inheriting the aforementioned advantages of in-situ sulfur oxidation, the case of cathodes with an extremely high sulfur content of 90 wt% by the reaction between Na\textsubscript{2}S and Fe\textsuperscript{3+} was first reported by Geng et al.\textsuperscript{47} Owing to the in-situ homogenous distribution of sulfur nanoparticles and covalent bonding to porous graphitic carbon, the prepared cathodes exhibited excellent performance with a high specific capacity (1115 mAh/g at 2 C) and long-life cycling (small capacity decay of 0.039% per cycle over 1000 cycles at 2 C), shedding light on the general synthesis of carbon-coated sulfur cathodes.

### 3.1.5 Organosulfur copolymers

In parallel with the research on sulfur-based cathodes, organosulfur, an alternative ideal cathode material, also triggers great interest and is treated as a promising candidate of the next-generation high energy/power density cathode materials,\textsuperscript{48-50} owing to its tunable functional groups with strong LiPSs affinity and flexible characteristics with low volume change during cycling.

Sulfurized polyacrylonitrile (SPAN) is a special kind of organosulfur, first reported by Wang et al. in 2002.\textsuperscript{48} During the heating process at 300°C, PAN is dehydrogenated by sulfur, resulting in the formation of organosulfur composites with conductive main chain grafted by sulfur intercalated heterocyclic compounds. Different from routine sulfur cathodes, the synthesized composites demonstrate great potential as cathode materials when coupling with carbonate electrolyte. Along with a total “solid-solid” conversion, the assembled cathodes showed a single sloped voltage plateau at 1.9 V, indicating the absence of the formation of soluble LiPSs. Although relatively low capacity (600 mAh/g after 50 cycles) was attained in this pioneering work, the electrochemical performance of fabricated Li-SPAN cathodes was further improved with persistent endeavors drawn by other researchers.\textsuperscript{51,52} Regrettably, to date, the structural evolution and reaction mechanism of SPAN during the charge-discharge process are still elusive,\textsuperscript{52} which need more in-depth research.
In addition to SPAN, a direct copolymerization strategy for elemental sulfur and vinlyc monomers was proposed in 2013. The sulfur copolymer cathodes demonstrated a high specific capacity (823 mAh/g after 100 cycles) and enhanced capacity retention, showing a new avenue of preparing sulfur-rich copolymer composites for sulfur cathodes. Since then, with unremitting efforts, various sulfur-grafted organosulfur polymer composite cathodes were successfully prepared and all demonstrated remarkable performance improvement.

3.1.6 Lithium sulfide (Li$_2$S)

Li$_2$S cathode enables the use of safer Li-free anode (e.g., graphite, silicon, or alloy) and liberates from the issue of large volume changes existing in sulfur cathode. Manthiram and coworkers claimed that the poor cyclability of Li-S batteries was attributed to the rapid depletion of Li inventory. Thus, Li$_2$S coupled with Li-free anode can slow down the Li inventory loss rate and significantly enhance the cycling stability. Because of its intrinsically high electrical resistance and large energy barrier in the initial charge process, Li$_2$S did not gain many attention until Cui et al. found that a high cutoff charge potential of 4 V (vs. Li/Li$^+$) was necessary to activate the Li$_2$S cathode in the first charge process.

To lower the overpotential of Li$_2$S decomposition, preparing nanosized or amorphous Li$_2$S particles is the common synthetic route. With the aid of high-energy ball milling under Ar atmosphere, nanosized Li$_2$S with the size of 200–500 nm was produced. Admittedly, ball milling is a common and effective strategy to produce nanosized Li$_2$S in large scale, but these nonuniform agglomerates are still ineludible. To solve this problem, Yushin et al. proposed an ethanol-Li$_2$S solution method to induce the self-assembling of Li$_2$S and polyvinylpyrroli-done in anhydrous ethanol, followed by carbonization at 700°C. The derived C-Li$_2$S nanocomposites, composed of nanosized Li$_2$S core (5–20 nm) and rigid carbon shell, sharply decreased the activation barrier of Li$_2$S to 3.2 V (vs. Li/Li$^+$). After that, reported by Yang’s group, they first developed a low-cost carbothermal method to prepare nanosized Li$_2$S by annealing Li$_2$SO$_4$ under high temperature (600–1000°C). Inspired by this work, Qiu’s group successfully fabricated in-situ generated Li$_2$S-ZnS@NC derived from Li$_2$SO$_4$@ZIF-8 composites (Figure 3D). By utilizing the confinement/separation effect of metal-organic molecular cage on ionic clusters, Li$_2$SO$_4$ ionic clusters were homogenously restricted in ZnN$_4$-imidazole molecular cages. Followed by the thermal reduction in H$_2$/Ar, Li$_2$S-ZnS@NC was obtained. A more facile method to prepare Li$_2$S@graphene nanocapsules was developed by Ji and coworkers. By burning Li foils in CS$_2$ vapor at 650°C, one-step generated core-shell Li$_2$S@graphene was synthesized according to the following reaction:

$$4\text{Li}(l) + \text{CS}_2(g) \rightarrow 2\text{Li}_2\text{S}(s) + \text{C}(s).$$

Notably, even at a high Li$_2$S loading of 10 mg/cm$^2$, the resultant cathodes still exhibited a low activation barrier of approximately 2.8 V (vs. Li/Li$^+$) and an areal capacity of 8.1 mAh/cm$^2$. They further broadened this strategy to a series of Li$_2$S/transition metal nanocomposites via lithiothermic reduction reaction. With systematical investigation of the corresponding electrochemical behaviors, the rate capability and cyclability were dramatically improved for Li$_2$S/W, Li$_2$S/Mo, and Li$_2$S/Ti cathodes compared to pure Li$_2$S. Coincidentally, our previous work also illustrated the irreversible conversion of MoS$_2$ into Li$_2$S after lithiation with the assistance of in-situ/operando XAS, further corroborating that it could serve as a substituted high-performance cathode material for Li-S batteries.

3.1.7 Metal sulfides

Metal sulfides are another sulfur-equivalent cathode materials for Li-S batteries. For example, amorphous chain-like MoS$_3$ prepared by the acid precipitation method in aqueous solution was a representative case. During the discharge process, only a plateau at approximately 1.9 V (vs. Li/Li$^+$) was observed when tested in the carbonate-based electrolyte. The MoS$_3$ cathodes displayed a large reversible specific capacity and impressive cycling stability for over 1000 cycles. Interestingly, during the lithiation/delithiation of MoS$_3$, no Mo-S bond breaking and formation of LiPS$_3$s intermediates were observed. With the assistance of theoretical calculation, it was revealed that Li$^+$ was only adsorbed at the bridging sites of two adjacent sulfur atoms, largely preserving the chain-like structure of MoS$_3$ during cycling.

3.1.8 Selenium (Se)/tellurium (Te)-sulfur composites

Taking full advantage of the fast reaction kinetics of selenium and high reversible capacity of sulfur, Se$_x$S$_y$$_2$ composites are promising cathodes for Li-S batteries. Since the pioneering work reported by Amine and coworkers in 2012, a series of Se$_x$S$_y$$_2$-based cathodes for Li-Se$_x$S$_y$$_2$ batteries were reported. For example, the $S_{22.2}$Se/KB cathodes presented an excellent electrochemical performance under a solid-state conversion with an
excellent rate capability of 700 mAh/g at 5 C together with minimal shuttle effect.\textsuperscript{66} Meanwhile, Te\textsubscript{2}S\textsubscript{3} composites were also synthesized and showed great potential as high-performance Li-S cathodes.\textsuperscript{67}

In short, each method mentioned above has its own advantages and disadvantages. Considering the specificity of various host materials, how to select the most suitable method to fabricate sulfur composites plays a vital role. Herein, we summarize the characteristics of each method and list their preferable utilization condition, as shown below:

1. The ball-milling method with incomparable advantages on facile large-scale preparation of materials is more suitable for random hosts without elaborate structure. However, uneven particle size distribution and limited surface mixing are still inevitable.

2. The melting-diffusion method is one of the most frequently used methods. Those host materials with extremely high pore volume are promising candidates for realizing a high sulfur loading target. Nevertheless, the high diffusion resistance could inescapably result in uncontrollable aggregation and surface redistribution of sulfur when drying.

3. The dissolution-recrystallization method is an effective strategy to lower the diffusion resistance of sulfur. Especially, by optimizing the dropping condition and subsequent melting treatment, self-supporting electrodes with high sulfur loading could be easily realized. Nonetheless, surface redistribution when drying is unavoidable.

4. Chemical deposition method with high adjustability to various reducing agents could realize the in-situ deposition of sulfur in the substrate. However, multistep treatments under acid condition and involvement of impurity ion should be taken into account.

5. Organosulfur copolymers provide an alternative avenue for preparing sulfur-equivalent cathodes. Because of their wide origins and tunable characteristics, more in-depth studies on exploring high-performance materials are meaningful. To date, SPAN, as one of the most promising organosulfur cathode materials for practical application, is not satisfactory for realizing high energy density because of the low sulfur content (<40 wt%) and voltage plateau (~1.9 V). Predictably, by taking advantages of electrospinning technique, fabricating self-supporting SPAN derived from PAN might be a practical avenue on realizing high-performance cathodes.

6. Li\textsubscript{2}S, coupling with Li-free anode, presents a feasible approach to circumvent the safety issue of Li anode. But the necessary activation process and sensitivity of Li\textsubscript{2}S toward water/air still impede its practical application. Therefore, developing more economic and facile technologies for Li\textsubscript{2}S synthesis is imperative.

7. Metal sulfides, another sulfur-equivalent cathode material with appreciable theoretical capacity, are limited by the low discharge cutoff voltage. Coupling metal sulfides with all-solid-electrolyte is a better choice compared to conventional liquid electrolyte.

8. Selenium/tellurium-sulfur composites, whose reaction kinetics are promoted at the cost of decreased theoretical capacity, are promising cathode materials by optimizing the content of replaceable selenium or tellurium to realize the highest energy density.

It should be emphasized here that we should choose the most appropriate method according to the experimental purpose and characteristics of host materials. Meanwhile, a combination of more than one of these methods to fabricate cathode composites is more efficient and realistic.

### 3.2 Sulfur cathode host design

An ideal cathode host should be customized by the characteristics of host materials and endowed with specific functions according to the requirements. The specificity of host materials determines the corresponding suitable encapsulation methods of active materials. Because of the severe shuttle effect and sluggish sulfur redox kinetics, conductive substrates that are capable of physically confining LiPSs and accelerating redox kinetics were extensively explored over the past decade.\textsuperscript{5,6} Classified by the morphological structure, composite modification principles, and corresponding host design strategies, they will be respectively introduced in the following sections.

#### 3.2.1 Structural variety

Because of the merits of accommodating high sulfur content, facilitating rapid ion migration, and physically confining LiPSs, multidimensional conductive materials with specific channels/pores are proved to be ideal hosts. The design principles of pore size and structure are addressed in sequence in the next sections.

**Pore structure optimization**

It is well known that the porous materials are mainly classified into three kinds according to the distance between two opposite walls of the pore, namely micropore (<2 nm), mesopore (2-50 nm), and macropore (>50 nm). Among them, mesopore is frequently employed in sulfur host design.\textsuperscript{68,69} This is because the high specific surface area of
the mesopore could induce the uniform distribution of sulfur and regulate the length of ion migration path. In addition, mesopore can also strongly inhibit the LiPSs shuttle via physical confinement at the cost of decreased sulfur loading compared to macropore. Various mesoporous carbon/68,70/metal-based hosts alongside a tailored degree of pore ordering71,72 were synthesized by different methods (hard/soft template), and the resultant composite cathodes demonstrated significant performance improvements.

Conversely, some groups focused on small enough microporous carbonaceous hosts (<0.7 nm) to confine metastable small sulfur (S_{2-4}) molecules inside (Figure 4A).73 The results indicated that no long-chain LiPSs were generated and the shuttle effect was eliminated over cycles, which presented a single-plateau electrochemical behavior with stable cycling. Thanks to the quasi-solid-solid conversion of S_{2-4} molecules, decent applicability toward carbonaceous substrates was realized, guaranteeing a safer working environment. Remarkably, microporous carbon derived from metal-organic frameworks (MOFs) demonstrates a more convenient route,74 which inspires great interest in various MOFs-derived microporous carbon.

Small-angle X-ray scattering (SAXS) is an efficient technique to identify the location of sulfur species in porous substrates and ascertain whether the solid S_8 and Li_2S are resting in the pores or on the surface of the composite. With the aid of operando SAXS and N_2 adsorption-desorption analysis, Kim and coworkers deciphered the migration mechanism of sulfur species into micro-/mesoporous carbon materials: S_8 prefers to locate in micropores when micropores and mesopores coexist in the material. The LiPSs migrate from the micropores to the mesopores during the discharge process, and reduce to Li_2S/Li_2S. Reversely, after charging, the S_8 formed by the oxidation of LiPSs is restored in micropores.80 These unconventional results emphasize the significance of rationally designing cathode materials through the comprehensive understanding of the bisected role of nanopores.

**Morphological design**

Because of the inferior ionic conductivity and electrolyte wettability of sulfur, Li^+ shows large energy barrier for migrating throughout the cathodes. To promote the sulfur redox kinetics, enhancing the Li^+ migration rate in cathodes by altering corresponding morphological structure is necessary. In the following subsection, zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) cathode hosts are introduced in turn.
0D materials, such as quantum dots and clusters, cannot be directly used as host materials because of their serious self-agglomeration effect. Implanting them into carbonaceous substrates to prepare hybrid hosts is a well-recognized strategy. Thanks to their nearly 100% exposed active sites, the assembled Li-S batteries with quantum dots display remarkable performance improvement.\(^{31,82}\) For example, Xiong et al. designed composite cathodes modified by polyethyleneimine functionalized carbon quantum dots (PEI-CDots),\(^{81}\) which demonstrated remarkable cycling stability with high areal sulfur loading. As confirmed by detailed electrochemical impedance spectra and cyclic voltammetry (CV) studies, the involved PEI-CDots improved ionic conductivity around the solid-electrolyte interface, which was the rooted reason for the performance enhancement.

1D materials, dominating preferential electron/ion transport in radial direction, have been widely utilized in Li-S batteries.\(^{83-86}\) For instance, CNTs and fibers, initially used as conductive agents,\(^{83}\) have been regarded as effective sulfur-immobilization hosts owing to their strong physical confinement ability toward LiPSs. Associated with different surface functionalization methods, works with effective sulfur-chemical inhibition effect under high sulfur loading conditions were reported.\(^{84}\) Meanwhile, thanks to their high aspect ratio and good mechanical strength, flexible freestanding substrates with a crosslinked conductive network can be easily fabricated by simple filtration or directly woven by electrospinning.\(^{85,86}\) Compared to conventional vapor/liquid phase growth, electrospinning shows a broad application prospect in preparing 1D inorganic compounds with tunable porosity and structure. For example, Yu and coworkers prepared a flexible free-standing TiN-VN embedded carbon nanofiber as an advanced host via simple electrospinning.\(^{85}\) Because of their synergistic adsorption and catalysis, a high areal capacity of 5.5 mAh/cm\(^2\) at 0.1 C was attained. To date, along with consistent progress in 1D materials design, precisely adjusting the pore structure or fabricating coaxial multichannel structure can further optimize the Li\(^+\) migration rate in axial/radial direction.

2D materials, possessing atomic or near-atomic thickness with infinite lateral dimensions, are demonstrated to be meritorious as emerging cathode hosts.\(^{4}\) Thanks to their anisotropic transport properties, surface exposure of polar active sites, and different edge/basal sites, 2D hosts, such as carbon materials,\(^{50}\) layered metal oxides,\(^{38}\) sulfides,\(^{85}\) carbynes,\(^{88}\) layered double hydroxides (LDHs),\(^{45}\) and MOFs,\(^{89}\) have been extensively investigated. On the one hand, due to the weak van der Waals interaction of atomic interlayers, the interlayer spacing can be tuned to accelerate Li\(^+\) migration.\(^{75,90}\) For instance, a phyllosilicate material with a large interlamellar distance that can lower the Li\(^+\) diffusion barrier was discovered by Xiong et al.\(^{90}\) Density functional theory (DFT) calculation of Li\(^+\) diffusion barrier and corresponding electrochemical investigations revealed that the significant enhancement of Li\(^+\) migration should be responsible for the improved electrochemical performance. On the other hand, due to the strong in-plane bonding of NbS\(_2\) that can efficiently entrap LiPSs in the interlayer during the whole reaction, the fabricated NbS\(_2@S@IG\) delivered ultrahigh rates (20–40 C) with excellent cycling stability (2000 cycles) (Figure 4B).\(^{75}\) In addition, edge engineering is another powerful strategy to promote Li-S performance, owing to the specificity of edge and basal sites.\(^{76,91}\) For example, it was proposed that preferential adsorption of higher-order liquid LiPSs with subsequent conversion to lower-order solid species occurred on the edge sites of sulfides (Figure 4C).\(^{76}\) Remarkably, with the assistance of in-situ detections, the distinct sulfur growth behaviors on 2D materials were reported by Cui’s group.\(^{91}\) With simultaneous sulfur growth visualization and electrochemical measurements, they successfully identified a correlation between sulfur states (liquid vs. solid) and electrochemical performance, which held promise for the design of flow and fast charge batteries.

Ranging from composites consisting of 1D/2D materials to complicated hierarchical structure (e.g., hollow, core-shell, yolk-shell, and multishell structure), various 3D materials are endowed with diverse properties on sulfur accommodation, electrolyte infiltration, ion migration, and sulfur immobilization.\(^{77-79,92}\) For instance, a novel composite host composed of hollow carbon tubes and MnO\(_2\) nanosheets was constructed by Lou’s group (Figure 4D).\(^{77}\) Benefiting from the inimitable 3D conductive network, rapid electron/ion transport during the redox reaction was realized. Moreover, constructing integrated hierarchical hosts (Figure 4E),\(^{78}\) stacked layer by layer macrostructure (Figure 4F),\(^{79}\) or binder-free cathodes by in-situ growing materials on commercial substrates\(^{92}\) are considerable strategies to fabricate cathodes with high sulfur loading.

In short, structural regulation is an essential strategy for optimizing sulfur accommodation, ion migration rate, and physical LiPSs confinement ability. The characteristics of the component and synthetic technology should be preferentially considered in tailoring the structure of sulfur composite cathodes.

### 3.2.2 Component modification principles

Because of the strong chemical adsorption between soluble LiPSs and polar hosts, the LiPSs would be immobilized to effectively suppress their shuttle. Moreover, such
chemical interaction will enhance the charge transferability and LiPSs redox kinetics. To date, it has been widely accepted that the adsorption-catalysis synergy can greatly promote sulfur utilization. Given that nonpolar carbon materials, functional polymers, and heteroatom-doped/molecules grafted carbon substrates only exhibit relatively low binding energy toward LiPSs (0.1–2.6 eV), multifarious metal-based hosts draw more attention because of their stronger LiPSs affinity in recent years. Although some nonmetal-based materials, such as black phosphorus, siloxane, or boron carbide, occasionally demonstrate equivalent affinity, the universal LiPSs affinity, and tunable components bestow metal-based materials wider application prospects. Therefore, this part mainly presents a comprehensive retrospect of the emerging metal-based catalytic materials applied in Li-S batteries.

Adsorption regulation principles

Various metals and metal-based compounds, such as single atoms, metals, oxides, sulfides, selenides, tellurides, hydroxides, nitrides, phosphides, carbides, fluorides, tellurides, borides, iodides, bismuth oxychlorides, MOFs, covalent-organic frameworks, and polyoxometalates, exhibit quite different LiPSs affinity. Moreover, modulating the exposed crystal faces can further regulate the adsorption ability. It is worth noting that only appropriate affinity with LiPSs can alleviate their shuttle, whereas too high binding energy will impede or destroy the subsequent conversion of LiPSs. Table 1 summarizes the binding energy of typical polar host materials with S and different LiPSs.

Note that the theoretical calculation is the most frequently used method to evaluate the LiPSs affinity of host materials, but the complicacy of geometric configurations makes it challenging to directly compare the results from different works. Thus, systematical DFT calculation investigation of the relationship between component modification and corresponding binding energy is extremely important to guide the future screening and rational design of Li-S host materials. To date, some related works, such as atom electronegativity, single-atom doped graphene, surface-functionalized Ti3C2 MXenes, transition metal oxides, sulfides, tellurides, and MOFs, have been reported. Based on the theoretical calculation and experimental results, it has been proposed that the Li-X (X represents nonmetals, such as B, N, O, and S) bonds exhibit “lithiophilic” and “sulfiphilic” interaction, respectively. Accordingly, composite hosts with dual lithiophilic-sulfiphilic sites demonstrate wider application prospects in high-loading cathode design. In addition, quantitative investigation of LiPSs adsorption capability by visual adsorption experiments is another generic method to determine the suitable material and appropriate amount to employ for adequate LiPSs adsorption.

Catalysis regulation principles

Though blocking the dissolution of LiPSs by physicochemical adsorption can restrain their shuttle, the sluggish redox kinetics still cannot be addressed. In contrast, promoting the LiPSs conversion to enhance the sulfur utilization and decrease their dissolution in electrolyte might fundamentally solve the shuttle effect. A pioneering review by Yang and coworkers summarized the catalytic capacity of polar materials in increasing the conversion kinetics from soluble long-chain LiPSs to insoluble Li2S2/Li2S, and vice versa. Recently, advanced strategies, such as heterogeneous/homogeneous structure design, interfacial engineering, and defect engineering, have been widely applied to improve the catalytic capacity of host materials to enhance sulfur redox kinetics. However, the intrinsic role of electrocatalysts in promoting the LiPSs conversion was rarely concluded in previous reviews. Hence, four main catalytic processes are respectively clarified here.

First, Arava and coworkers demonstrated that graphene decorated with uniform dispersed Pt nanoparticles showed a 40% enhancement in the specific capacity of sulfur cathodes compared to the pristine one. Based on the results of Tafel plots and corresponding exchange current density values (i0), it indicated that the involved Pt could promote the conversion kinetics of LiPSs. Meanwhile, postmortem analysis of electrodes at various electrochemical conditions further confirmed the complete conversion of LiPSs without precipitation on the electrodes. Later on, Zhang’s group proposed the underlying conversion mechanism. Because of the strong interrelation between polar hosts and LiPSs, CoS2 could serve as active sites to accelerate the LiPSs redox kinetics. With in-depth theoretical calculation, it is clearly revealed that the energy gap of nonmetallic p-band and metallic d-band center plays a vital role in affecting sulfur conversion. Decreasing the distance of p-band or d-band center toward the Fermi level could promote the electron transfer from hosts to LiPSs and lead to the highest filling fraction of the lowest occupied molecular orbital of LiPSs for facilitating the break of S-S bond with less energy consumption.

By combining p-d band theory with systematic experiments, an in-depth study on unraveling the catalytic capacity of a series of hosts was first introduced by Qian’s group. They deciphered the intrinsic modulation essence of the anions by investigating the kinetics behaviors of sulfur redox on Co-based compounds. Based on comprehensive experiments and DFT calculation, the underlying reason for improved electrochemical
TABLE 1: Binding energy between sulfur species and polar host materials

| Host materials | $S_8$(eV) | $Li_2S_8$(eV) | $Li_2S_6$(eV) | $Li_2S_4$(eV) | $Li_2S_2$(eV) | $Li_2S$(eV) | Refs. |
|----------------|-----------|---------------|---------------|---------------|---------------|------------|-------|
| Fe/C$_2$N      | 8.69      | 9.92          | 8.85          | 6.9           | 6.69          | 5.78       | [98]  |
| Ni-N$_3$/C     | $\sim$2   | $\sim$3       | $\sim$2.8     | $\sim$2.1     | $\sim$2.5     | $\sim$2.8  | [116] |
| Ni-N$_2$/C     | $\sim$0.8 | $\sim$1       | $\sim$1       | $\sim$0.7     | $\sim$0.8     | $\sim$0.7  | [116] |
| Ni-N$_1$/C     | $\sim$0.8 | $\sim$1.05    | $\sim$1       | $\sim$0.7     | $\sim$1       | $\sim$1.3  | [116] |
| SA-Zn-MXene    | $\sim$0.9 | $\sim$1.3     | $\sim$1.1     | $\sim$1.3     | $\sim$1.7     | $\sim$3.2  | [117] |
| Mo-N$_2$/C     | /         | $\sim$3.4     | /             | $\sim$3.3     | /             | $\sim$4.2  | [118] |
| Co (111)       | 2.43      | 4.62          | 5.09          | 5.46          | 6.05          | 4.67       | [99]  |
| V$_2$O$_5$(104)| /         | 1.18          | 3.28          | 2.32          | 2.36          | 2.28       | [100] |
| Mn$_3$O$_4$ (211) | 0.08 | 2.37          | 2.42          | 4.07          | 2.49          | 3.85       | [119] |
| WO$_3$ (100)   | /         | $\sim$7.1     | $\sim$9.3     | $\sim$9.6     | $\sim$5.2     | $\sim$8.8  | [120] |
| ZrO$_2$ (101)  | /         | $\sim$5.3     | $\sim$5.3     | $\sim$5.3     | $\sim$5.8     | $\sim$5.6  | [120] |
| TiO$_2$ (110)  | /         | $\sim$3.5     | $\sim$2.2     | $\sim$3.2     | $\sim$3.6     | $\sim$3.4  | [121] |
| TiO$_2$x (110) | /         | $\sim$6.4     | $\sim$4.4     | $\sim$4.9     | $\sim$6.6     | $\sim$5.3  | [121] |
| MoS$_2$ (001)  | /         | $\sim$0.4     | $\sim$0.8     | $\sim$1.2     | /             | /          | [92]  |
| MoS$_2$ (100)  | /         | $\sim$2.4     | $\sim$3.0     | $\sim$3.2     | /             | /          | [92]  |
| ZnS (110)      | /         | 1.76          | 1.81          | 2.03          | 2.66          | 3.05       | [101] |
| SnS$_2$ (110)  | /         | 2.16          | 2.12          | 2.25          | 3             | 4.43       | [101] |
| SnS (110)      | /         | 3.43          | 2.25          | 2.93          | 3.33          | 5.66       | [101] |
| VS$_2$ (101)   | /         | 1.57          | 1.32          | 0.88          | /             | /          | [122] |
| Co$_2$S$_2$ (100) | /     | $\sim$1.9     | $\sim$2.2     | $\sim$2.4     | /             | /          | [92]  |
| CoSe (110)     | 7.52      | 8.83          | 7.75          | 7.68          | 10.06         | 8.1        | [102] |
| Co-LDH (009)   | 2.57      | 3.84          | 2.93          | 3.43          | 3.0           | 3.94       | [103] |
| NiCo-LDH (009) | 3.09      | 3.91          | 3.43          | 3.77          | 3.6           | 4.3        | [103] |
| Co$_{2+}$N$_{3+}$ (III) | 2.51 | 5.67         | 6.91          | 5.35          | 5.85          | 3.96       | [104] |
| TVN-3 (200)    | /         | 1.81          | 1.37          | 2.78          | 3.32          | 2.54       | [123] |
| CoP (211)      | 1.63      | 1.93          | 2.05          | 2.81          | 3.73          | 4.11       | [99]  |
| CoFeP (001)    | /         | 8.39          | 7.29          | 10.19         | 5.2           | /          | [105] |
| GO-CNT-CoP(A)  | /         | /             | 3.95          | 2.43          | /             | 2.57       | [35]  |
| V$_4$C$_4$ (400) | /     | 0.63          | 2.01          | 1.23          | 1.67          | 1.18       | [100] |
| Co-Bi (001)    | 1.25      | 2.11          | 3.13          | 4.12          | 4.28          | 4.43       | [108] |

Performance was attributed to the rational modulation of interfacial electron transfer dynamics by optimizing p-band center in Co-based compounds. Among the contrastive Co-based compounds, S@rGO/CoP exhibited the best electrochemical performance (417.3 mAh/g at 40 C), endowing the Li-S batteries with an unprecedented power density of 137.3 kW/kg. Similarly, systematic studies on Fe-based compounds, heteroatom-doped graphene, and single-atom metal catalysts (SACs) were also reported. Remarkably, different from traditional catalysts, phase transformation or surface reconstitution was observed for certain electrocatalysts used in Li-S batteries, suggesting the strong interrelation between LiPSs and hosts. Especially, in some cases, the reconstructed electrocatalysts demonstrated higher catalytic capability than the pristine hosts. Such electrochemical activation-derived catalysts are called pre-catalysts. Associated with sufficiently theoretical and experimental perspectives, tracking the real catalytic center to disclose the origin of sulfur redox reaction activity is of significance. For instance, Huang and coworkers revealed an exothermic irreversible electrochemical phase evolution from pristine single-crystalline Co$_4$N to polycrystalline CoS$_x$, and the latter was proved to be the real active electrocatalysts for propelling the sulfur redox kinetics at a high current rate (Figure 5D). Furthermore, Chen and coworkers demonstrated the reversible transformation between CoS$_4$ tetrahedra and CoS$_6$ octahedra on Co$_9$S$_8$ during the charge-discharge process, and they proposed that the gradually increased sulfur vacancies on the octahedral sites further magnified the adsorption capability and enhanced the LiPS redox kinetics (Figure 5E).
Because of the reaction between long-chain LiPSs and MnO$_2$, thiosulfate is in-situ generated on the surface of MnO$_2$ at the beginning of discharge. The newly generated thiosulfate catenates with more Li$_2$S$_n$ (4 ≤ n ≤ 8) to immediately form intermediate polythionate complexes and shorter-chain LiPSs till the full conversion to Li$_2$S$_2$/Li$_2$S is achieved. During the whole discharge process, the polythionate intermediate with high active sites serves as an anchor and transfer mediator to inhibit the dissolution of LiPSs into the electrolyte and control the deposition of Li$_2$S$_2$/Li$_2$S. Furthermore, closely following this discovery, they systematically investigated the effect of redox potential of a series of transition metal oxides on thiosulfate formation and proposed a generic principle, namely the “Goldilocks” principle (Figure 5E). For the metal oxides with a redox potential in a target window (2.4 V < E ≤ 3.05 V), such as VO$_2$ and MnO$_2$, they could oxidize LiPSs to form active surface-bound thiosulfate/polythionate mediators and trigger effective LiPSs conversion. On the contrary, the materials with much higher redox potential (>3.05 V) (e.g., V$_2$O$_5$) may oxidize LiPSs to electrochemically inactive sulfate groups, resulting in poor cycling performance. However, with the rapid development of metal derivatives (e.g., sulfides and phosphides), whether the “Goldilocks” principle can also work is still elusive.

It should be mentioned that the aforementioned catalysts are redox inactive during the whole sulfur reaction. In the following section, two types of catalysts that participate in the lithiation/delithiation process will be shown.

Li et al. proposed intercalation-conversion hybrid cathodes composed of intercalation-type Mo$_6$S$_8$ with conversion-type sulfur. Due to the excellent electronic conductivity and high tap density of Mo$_6$S$_8$, the uniformly dispersed Mo$_6$S$_8$ could greatly decrease the carbon content to approximately 10 wt% and increase the packing density...
to obtain crack-free cathodes with high sulfur loading. The new-generated Li$_1$Mo$_6$S$_8$/Li$_3$Mo$_9$S$_8$ dominates the adsorption of LiPSs and demonstrates higher adsorption capacity compared to pristine Mo$_6$S$_8$, further strengthening the sulfur immobilization. The resultant cathodes displayed excellent stability under realistic conditions, that is, low carbon content of approximately 10 wt%, low electrolyte/active material ratio of approximately 1.2 μL/mg, and high-loading content of >10 mg/cm$^2$, further displaying the great potential of Mo$_6$S$_8$ for practical Li-S batteries. Since then, those high-tap density hosts which can provide extra capacity by Li intercalation reaction and afford strong LiPSs affinity were constantly reported.$^{152,153}$

Another example is the use of a lithium-transfer bridging agent to facilitate the effective conversion of both sulfur and LiPSs to the final Li$_2$S product (Figure 5G).$^{139}$ In that work, two pseudocapacitive oxides, namely orthorhombic Nb$_2$O$_5$ and birnessite MnO$_2$, were devised as desirable electron-ion source and drain, respectively. During the discharge process, Li$^+$ is first stored in Nb$_2$O$_5$ and spontaneously transfers to LiPSs, alongside reversible reaction of Nb$_2$O$_5$-LiNb$_2$O$_5$-Nb$_2$O$_4$. Similarly, during the charge process, MnO$_2$ is treated as electron-ion drain, inducing the rapid reaction from Li$_2$S to sulfur. The electron-ion reservoirs incorporated within cathodes not only rapidly store and release electron and Li$^+$ but also spontaneously react with LiPSs during the charge-discharge process.

To date, various characterization methods (e.g., symmetrical CV measurement, $i_0$ test, and Tafel plot) and theoretical calculations have been adopted to evaluate the catalytic capacity of host materials,$^{136,140}$ which play important roles for the further rational design of desirable catalysts. However, ion migration in substrates, the role of intermediates, morphological evolution of LiPSs absorbed on reaction surface, and electron transfer at the triple-phase interface still need further in-depth investigation to better understand the electrocatalytic process.

**Li$_2$S deposition/decomposition regulation principles**

The sluggish kinetics of the solid-solid conversion from Li$_2$S$_2$ to Li$_2$S (corresponding to 50% of the theoretical capacity) could lead to the premature end of discharge, resulting in low discharge capacity and low sulfur utilization.$^{19}$ Decreasing the dissociation energy of Li$_2$S$_2$ to facilitate Li$_2$S deposition is one of the main research emphases in Li-S batteries. As verified by kinetics analyses and scanning electron microscopy, the Li$_2$S precipitation mechanism was investigated by Chiang and coworkers in detail.$^{154}$ They proposed that the precipitation of Li$_2$S occurred at the triple-phase interface between the solid electrode, solid electrolyte, and solid conductive additive via nucleation by 2D growth mode. Thus, to precisely control the growth of Li$_2$S, advanced morphological characterization techniques emerge to investigate the corresponding mechanism. For example, XRM$^{16}$ and optical observation$^{155}$ were employed to observe the deposition morphology of Li$_2$S on specific substrates. Notably, Kang et al. utilized liquid in-situ TEM to probe the detailed nucleation and growth of Li$_2$S.$^{156}$ Based on their results, it is elucidated that the nucleation and growth of Li$_2$S on polar substrates (TiO$_2$-TiN) exhibit a kinetic transition from a diffusion-controlled process to a reaction-limited process, simultaneously involving a phase change from crystalline to amorphous Li$_2$S (Figure 6A and B). The visual liquid TEM study broadens the understanding of the electrochemistry of Li$_2$S deposition and clarifies the fundamental effect of hosts on shaping Li$_2$S growth.

In parallel with in-depth explorations of the Li$_2$S deposition mechanism, the progress on spatial control of LiPSs deposition on substrates to improve the electrochemical performance has been made.$^{159}$ Inducing the spatial precipitation (3D growth) of Li$_2$S to replace 2D growth seems to be a promising strategy to improve the deposition capacity by modulating the heterointerfaces, which has been frequently reported (Figure 6C).$^{157,160}$ More encouragingly, Liu et al. used a low-surface area and open carbon fiber architecture to control the nucleation and growth of the sulfur species by manipulating the carbon surface chemistry and the solvent property.$^{161}$ The fabricated 3D “flower-like” S/Li$_2$S agglomerates facilitate rapid electron/ion transport and prevent the production of an undesired insulating sulfur-containing layer. Owing to the unique nonencapsulation advantages, the resultant cathodes demonstrated nearly 100% sulfur utilization, over 99% coulombic efficiency, and high energy density (1835 Wh/kg and 2317 Wh/L).

In the inverse process of Li$_2$S deposition, where Li$^+$ diffusion in Li$_2$S dominates its reversibility,$^{162}$ catalyzing the decomposition of Li$_2$S is also vital to retain the cycling stability and achieve high sulfur utilization. In this regard, Cui and coworkers revealed the catalytic oxidation mechanism of Li$_2$S with systematically comparative analysis of a series of metal sulfides (e.g., Ni$_3$S$_2$, FeS, CoS$_2$, VS$_2$, SnS$_2$, and TiS$_2$).$^{163}$ It has been found that the Li$_2$S decomposition barrier is positively correlated with the overpotential in the charge process, and the strong interaction between the escaped Li$^+$ and sulfur in sulfides is the dominant driving force to promote the decomposition of Li$_2$S.

Coincidentally, Li$_2$S incorporated cathodes face the similar predicament. Considering that the pristine Li$_2$S cathodes demonstrate a huge activation barrier in direct conversion from Li$_2$S to sulfur in the initial charge process,$^{164}$ incorporating Li$_2$S with high-conductive catalysts, such as Te$^{165}$ single Fe atoms,$^{166}$ and a series of transition phosphides/sulfides (Figure 6D),$^{158,167}$ is regarded
as an effective strategy to lower the Li$_2$S decomposition barrier and promote the corresponding performance.

In brief, how to effectively improve the intrinsic ionic conductivity of composites or construct multidimensional ion migration channels is the key step for lowering the Li$_2$S deposition/decomposition barrier. In addition, morphological regulation of Li$_2$S deposition is an alternative effective strategy to suppress the generation of dead passivation layer on the surface of cycled cathodes.

3.2.3 | Component modification strategies

Comprehensive reviews have systematically summarized the application of high-conductive, strong LiPSs affinity, and effective catalytic materials in constructing cathode hosts, as classified by different components. Herein, based on previous works, the component modification strategies are mainly discussed.

**Single-atom catalysts**

Owing to their maximized atom utilization efficiency, single-atom materials demonstrate great competitiveness in accelerating the conversion kinetics of active materials. Especially, since the first attempt of single-atom cobalt implanted graphene as sulfur host devoted by Wan’s group, SACs have been extensively employed as sulfur hosts. Precisely selecting the species of metal center and tuning their coordination environment are regarded as two effective ways to modulate the corresponding catalytic ability.

Cheng and coworkers prepared a series of SACs (Metal = Mn, Cu, Cr, and Ti) embedded in 3D carbon foams to elucidate the role of metal center on improving the reaction kinetics of LiPSs. Guided by the systematic theoretical calculation, they found that d-p orbital hybridization between SACs and LiPSs could be used as a descriptor for describing the catalytic capability of SACs in Li-S cathodes. To be specific, transition metals with a lower atomic number are found to have fewer filled antibonding states, which effectively bind LiPSs and catalyze their electrochemical reaction.

Alternatively, the catalytic activities of SACs can also be tuned by modulating their distinct coordination structures. Yang and coworkers systematically explored the interrelationship between as-prepared Co SACs with different N coordination numbers and the corresponding catalytic capacity toward LiPSs. Associated with DFT calculation, the rooted reason for superior catalysis of Co-N$_2$ is attributed to the upshifting of the d-band center of Co atoms, which leads to stronger chemical interaction with LiPSs, resulting in more efficient LiPSs redox kinetics than Co-N$_4$.

Though various transition-metal/metal-free-based SACs implanted carbonaceous matrix or polar compounds demonstrate superior electrocatalytic activity, how to improve the SACs content and precisely tune the inserting position in substrates still need more efforts.

**Multicomponents incorporation**

Metal alloys are representative hosts with synergistic adsorption and catalysis toward LiPSs. For instance, Co-Te alloys where Te was coordinated to Co atoms were successfully synthesized as host materials of Li-S batteries. Compared to pristine Co particles, the Co-Te alloys demonstrated stronger LiPSs affinity, faster redox kinetics, and higher Li$_2$S deposition capacity. As a consequence, the resultant Co-Te/NC/S cathodes maintained a high reversible capacity of 1062 mAh/g after 100 cycles while the discharge capacity of the Co/NC/S cathodes
faded to 770 mAh/g. Meanwhile, multimetal compounds, such as Co₃Mo₃N, La₀.56Li₁₃.33TiO₅, and high-entropy metal oxides, were reported as catalytic hosts to boost the sulfur redox kinetics. For example, a sea urchin-like Co₃Mo₃N in the absence of additional nitrogen sources was prepared by a facile synthesis route, and the excellent structural stability and enhanced catalysis of Co₃Mo₃N should be responsible for the improved sulfur utilization. In contrast to synergetic adsorption and catalysis by multicomponents, the “binary active sites” concept via the application of Co₃V₂O₈ was first reported by Niu et al. The active V sites anchor the LiPSs through the chemical adsorption while the active Co sites enable an accelerated sulfur redox kinetics.

Hence, integrating different components into one compound bestows synergistic or multifunctional effects on adsorption and catalysis of LiPSs, and therefore, how to effectively select suitable components and develop synthetic routes should be further enriched.

Heterostructure

By incorporating the advantages of adsorbents with strong adsorption and catalyst with effective catalysis, the derived heterostructure hosts could greatly improve the sulfur stability and utilization. Given that the application of heterostructure has already been reviewed in previous work, we here mainly introduce the presentative works on selective catalysis encompassing stepwise and bidirectional catalysts in the following subsections.

Stepwise catalysis, as first introduced by Lee and coworkers in 2019, was implemented to sequentially catalyze the reversible conversion of S₈(solid) ↔ Li₂S₄(liquid) ↔ Li₂S₅(solid). A dual-catalyst layer composed of Fe-N@C and Co-N@C was prepared by collocating them in different regions of the sulfur cathodes. During the cycling, the LiPSs migrate to the Co-N@C layer first when discharging and go back to Fe-N@C after charging, where Fe-N and Co-N codoped carbon layers selectively catalyze the long-chain LiPSs conversion (S₈ ↔ Li₂S₅) and the short-chain LiPSs conversion (Li₂S₄ ↔ Li₂S). Then, the stepwise catalytic characteristics were further endowed to heterostructure composed of defective p-type Co₃O₄ and n-type TiO₂. The Co₃O₄ sheets physiochemically immobilize the pristine sulfur and ensure the rapid reduction of S₈ to Li₂S₄, while the TiO₂ dots realize the effective precipitation of Li₂S, bridged by the directional migration of polysulfides from p-type Co₃O₄ to n-type TiO₂ as a consequence of interfacial built-in electric field. The concept of stepwise catalysis provides an alternative avenue on design of selectively catalytic hosts in subsequence.

Bidirectional catalyst, as first proposed by Yang and coworkers in 2020, was recognized to accelerate both the reduction of soluble LiPSs and oxidation of insoluble Li₂S by utilizing in-situ grown TiO₂-Ni₃S₂ heterostructure (Figure 7A). Attributed to the synergetic effect of TiO₂ and Ni₃S₂, high sulfur utilization and good cycling stability were attained, revealing the effective shuttle suppression and refreshment of the catalyst surface. Notably, the bidirectional catalyst was also extended to a single component host. With spectroscopic investigations and theoretical calculations, it was revealed that an in-built Janus crystal facet self-mediation was onsite constructed by the exposed B and Zr atoms for selective S/Li₂S conversion in ZrB₂.

Briefly, the smooth “adsorption-conversion” process could be conducted by coupling with enhanced interfacial charge transfer rate when heterostructure is involved. It is more necessary to ingeniously correlate the specificity of components and multistep phase transformation of LiPSs for future heterostructure design.

Doping strategies

Doping has been proved to be an effective strategy to modify the electric conductivity, electronic configuration, and surface property of host materials. Carbon materials doped with various elements (e.g., B, N, P, and S) have been widely developed and reported. In contrast, the exploration of heteroatom-doped metal compounds is still in its infancy. Hence, anion-/cation-doped metal compounds are extensively covered in what follows.

On the one hand, doping anions can regulate the d-band center of doped metal compounds to enhance the LiPSs affinity and improve the sulfur utilization efficiency. As a representative example of anion doping, N-doped compounds were widely reported. However, few attentions were paid to decipher the bonding ways between LiPSs and compounds in detail. Impressively, enlightened by orbital engineering strategy, Zhang and coworkers demonstrated that the rooted reason for the superior catalytic activity of B-doped MoS₂ is the preferable orbital orientation of B, which has a vacant σ orbital perpendicular to the basal plane to maximize the head-on orbital overlap with sulfur. As a result, the basal plane is fully activated, which can facilitate the kinetics of Li₂S formation and dissolution. Consequently, the as-prepared composite cathode delivered superb cycling performance (capacity fading rate of 0.02% during 1300 cycles). However, the underlying effect of doping concentration was not discussed, mostly attributed to the uncontrollable heteroatom doping content. In contrast, in view that doping content is a significant parameter in shaping the catalytic properties, precisely doping S²⁻ in Ni-Fe LDHs was realized by electrochemical-assisted anionic regulation process, as first proposed by Zhang’s group. Moreover, they discussed the influence of doping content on sulfur utilization enhancement.
On the other hand, attributed to the diversity of cations, more possibilities are endowed to cation-doped compounds. For example, Zhang and coworkers proposed the replacement of Ni with Co for Ni$_2$P by forming Ni$_2$Co$_4$P$_3$ nanowires to modify the d-band center (Figure 7C). Compared to Ni$_2$P, Ni$_2$Co$_4$P$_3$ possesses a higher d-band level, which could strengthen the adsorption to LiPSs and lower the activation barrier of S-S bond breakage and, thus, effectively propel the subsequent lithiation progress. In addition, similar representative works, including V-doped TiN (V was doped into TiN Lattice), Sn doped-MnO$_3$ (Sn was intercalated into the interlayer of MoO$_3$), and P/Co co-doped MoS$_2$ were also reported.

Doping strategies are facile methods to regulate the electronic architecture of host materials. But the accurate characterization of doping sites/concentration and disclosing the electronic variation of doped host materials are worth more efforts to reveal the electrocatalytic mechanism that involves complicated conversion processes still.

**Vacancy engineering**

Similar to doping, the presence of vacancy can also adjust the geometrical and chemical configuration of the compounds. Note that doping and vacancy were commensal in some cases, which are not involved in the following discussion.

**Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ perovskite nanoparticles (PrNPs) were proposed to immobilize LiPSs and guide Li$_2$S deposition in Li-S batteries. Owing to the naturally generated oxygen vacancies in PrNPs, the interaction between LiPSs and PrNPs is enhanced, and accelerated sulfur redox kinetics are boosted.** Besides naturally generated vacancies, artificial vacancies are obtained by different treatments. For example, various vacancies, such as oxygen, sulfur, selenide, nitride, and metal cation, were introduced into host materials of Li-S batteries. Notably, in parallel with prefabricated defective host materials, in-situ generated vacancies in pristine host materials were attained by LiPSs etching during the cycling (Figure 7B). It was speculated that the acquired Fe vacancies could activate the inert Ni$_3$N to promote the kinetics of LiPSs-involving surface reaction. This exploration not only deciphers the true active sites under aprotic condition but also deepens the understanding of vacancy-mediated sulfur redox.

Equally important to the vacancy, the corresponding vacancy concentration could also greatly influence the resulting catalytic capacity of host materials. By adjusting the treatment condition, their vacancy concentration could be adjusted. However, the actual catalytic capacity is not positively correlated with the vacancy concentration. For instance, HNb$_2$O$_8$ (HNO-v) nanobelts with excessive...
oxygen vacancies demonstrated lower electric conductivity and weaker sulfur adsorption ability compared to pristine HNO, leading to inferior performance of Li-S batteries. This study innovatively revisits the paradoxical role of oxygen vacancies and stresses the significance of appropriate vacancies in modulating sulfur redox.

**Surface modification**

To enhance the sulfur adsorption ability and catalytic capacity of host materials, surface modification, such as encompassing modulating the surface lattice distortion, electronic states, and chemical groups, were successfully realized by straining engineering, amorphization, and surface chemistry, respectively. For example, Chen and coworkers fabricated tensile-strained Mxene/CNT porous microspheres by facile spray-drying process. The in-situ generated oxidation layer induces the surface lattice distortion and enlarged Ti-Ti bond, regulating the upshift of the d-band center of Ti atoms toward the Fermi level. The derived Mxene nanosheets with abundant active sites strengthen the sulfur adsorption ability and further accelerate the catalytic conversion.

Wang et al. proposed an amorphization-induced surface electronic states modulation strategy to improve the LiPSs affinity of CoO. It showed that the symmetry of ligand field around Co atoms was notably changed and more coordinatively unsaturated metal sites were generated after amorphization. The DFT results further indicated that amorphization-induced redistribution of d orbitals of Co could strengthen the binding energy of LiPSs, resulting in improved rate performance.

Considering that chemical adsorption usually occurs on the surface, surface modification is, therefore, also an effective route to regulate the adsorption capacity. For instance, Wanget al. revealed the oxidation layer generated on the CoP nanoparticle surface under ambient condition could induce abundant Co-O-P species and, thus, activate the Co sites to chemically bind with the negatively charged sulfur sites of LiPSs (Figure 7D). Owing to the confined LiPSs by surface oxidation layer and the facilitated electron transfer by inner core, a high capacity sulfur cathode with stable cycling was attained.

### 3.3 Cathode engineering

Although many encouraging achievements on suppressing the LiPSs shuttle and promoting the sulfur redox kinetics have been attained by unremitting efforts, the related works were almost based on low areal sulfur loading (<2 mg/cm²) and high E/S ratio (E/S > 10 μL/mg), which cannot meet the requirements of practical Li-S batteries. Therefore, preparing high-loading sulfur cathodes coupled with lean electrolyte is momentous to realize high energy density Li-S batteries. Meanwhile, to endow practical Li-S batteries with exceptional portability and applicability for all-condition and all-environment usage, explorations of flexible sulfur cathodes and stable operations in a wide temperature range were performed as well. In this following section, several representative fabrication technologies for preparing high-loading sulfur cathodes are introduced at first, followed by the breakthroughs on lean electrolyte and high energy density sulfur cathodes, with special attention paid to the practical application in flexible and wide temperature range operation.

#### 3.3.1 High-loading cathode fabrication

The traditional tape-casting method could lead to thickening of electrode coating, which results in the cracking and sluggish electron transfer of the cathodes, and thus, the poor structural stability and inferior sulfur utilization. Therefore, 3D architectures, including binder-free cathodes, growing on 3D current collectors and self-supporting cathodes attracted many attentions, owing to their unique 3D conductive network and advantages of high sulfur loading capability.

##### 3D collectors

Various 3D current collectors, such as carbon cloth, melamine/graphene/nickel foam, aerogel, and biomass materials, have been adopted to fabricate high sulfur loading cathodes. In-situ growth of host materials on 3D conductive current collectors ensures their tight contact to facilitate rapid electron transfer while the self-contained 3D network is beneficial for ion migration. Yu and coworkers utilized 3D melamine foam to fabricate a high-conductive N, P co-doped carbon framework decorated with well-dispersed MOFs (Figure 8A). Owing to its hierarchical 3D network and integrated MOF nanodomains, enhanced electron/ion transport rate and strong inhibition of shuttle effect are simultaneously realized, contributing to the performance improvement. Therefore, a high areal capacity of >16 mAh/cm² and volumetric capacity of 1230.8 mAh/cm³ were achieved. However, considering the nonignorable mass of the substrate, it only delivered a relatively low gravimetric energy density.

##### Filtration

Without binder and metallic current collector, self-supporting cathodes could be easily fabricated via simple filtration utilizing 1D or 2D materials, and conductive carbon is one of the most frequently used host materials. Peng and coworkers prepared a MOFs/CNTs thin film
with a unique hierarchical porous structure and interpenetrated 3D conductive network through a confinement conversion.\textsuperscript{111} Dense CNTs contribute great conductivity and well-dispersed MOFs exhibit synergistically enhanced sulfur immobilization. The resultant Li-S batteries exhibited a high capacity of approximately 7.5 mAh/cm\textsuperscript{2} when sulfur loading reached 11.3 mg/cm\textsuperscript{2}. However, a high E/S ratio of 50 µL/mg was used in the assembled batteries, implying the weak electrolyte-affinity of carbonaceous substrates.

Electrospinning
Electrospinning followed by carbonization process is facile to manufacture freestanding nanofiber with controllable porous architectures and outstanding electric conductivity. With tunable treatment, nanofibers with controllable phases (e.g., polymers, carbon, metal-based derivatives, and their composites) and morphologies (e.g., porous, hollow, and multichannel) can be easily constructed. Considering their unique advantages of flexible and large-scale synthesis, the electrospinning technique has been widely used in cathode and separator modification, which was systematically summarized by Cheng and coworkers.\textsuperscript{214} For instance, a flexible and conductive TiN-Ti\textsubscript{4}O\textsubscript{7} core-shell nanofiber membrane reactor fabricated by simple electrospinning followed with carbonization was devised to electrocatalytically mediate the LiPSSs conversion.\textsuperscript{215} Because of the effective chemical confinement and catalysis of TiN-Ti\textsubscript{4}O\textsubscript{7}, the resultant composite cathodes delivered an areal capacity of 9.3 mAh/cm\textsuperscript{2} at 1.3 mA/cm\textsuperscript{2}. Note that although high sulfur loading can be easily realized with a combination of Li\textsubscript{2}S\textsubscript{x} solution, the nanofiber host materials still suffer from a relatively high E/S ratio resulting from the large porosity. Meanwhile, the low yield of electrospinning nanofiber materials is a prime bottleneck for its application in Li-S batteries.

Spray-drying
Hu and coworkers introduced a brand new one-step spray-drying method to fabricate woolball-like nanocomposites of carbon/sulfur microspheres in 2015.\textsuperscript{216} The spray-drying process is a facile and effective approach, demonstrating great potential in the large-scale synthesis of sulfur-loaded spherical composites for Li-S batteries. Another merit of this technique is improving the whole structural integration for further enhancing the long-range electron/ion transport rate and decreasing internal porosity.\textsuperscript{103} To date, the spray-drying method has been widely used in Li-S cathode hosts fabrication.\textsuperscript{193,202}

3D printing
3D printing is a powerful technique that is capable of fabricating electrodes with high active material loading to improve the energy density of cathodes. By adjusting the number of printed electrode layers, the thickness and active material loading can be precisely controlled.\textsuperscript{217} For example, Yang et al. reported thick sulfur cathodes of 600 µm by 3D printing technique using an ink composed of sulfur particles, 1,3-diisopropenylbenzene, and condensed graphene oxides.\textsuperscript{218} Though the poor performance was attained due to the low electric conductivity of sulfur copolymer, this work indeed motivated tremendous efforts on regulating the employed ink and architecture for realizing sulfur loading cathodes with 3D printing.
Subsequent works such as improving the conductivity of ink\textsuperscript{217} or tailoring thickness and pores\textsuperscript{219} were also reported. Impressively, a versatile 3D printed N-doped porous Ti$_3$C$_2$ MXene framework was fabricated by Sun and coworkers\textsuperscript{88}. When coupled with 3DP N-pTi$_3$C$_2$Tx@Li anode, the resultant batteries demonstrated a high areal capacity of 8.5 mAh/cm$^2$ after 60 cycles with a sulfur loading of 12 mg/cm$^2$. However, the investigation of 3D printing is still in its infancy. Wide exploration of suitable inks to print favorable architectures for Li-S host materials is urgently needed. The specific values of recent works fabricated with different technologies are listed in Table 2.

### 3.3.2 Lean electrolyte cathode fabrication

E/S ratio is tightly bound up with the energy density. According to estimated results by Huang’s group, the E/S ratio should be lower than 5.0 µL/mg, and the areal sulfur loading should be higher than 4 mg/cm$^2$ to achieve high energy density Li-S batteries with 500 Wh/kg.\textsuperscript{22} As the E/S ratio decreases, slow electron/ion transport occurs, resulting in aggravated polarization alongside sluggish sulfur redox kinetics.\textsuperscript{232} Inadequate infiltration and partially high-concentrated LiPSs could induce the spatially uneven electrochemical reaction. Therefore, how to enhance the liquid-solid conversion kinetics and improve the electrolyte utilization rate under low E/S ratio condition is of great significance.

On the one hand, to address the challenges under lean electrolyte condition, constructing high-conductive cross-linked substrates with catalytic capacities to enhance the sulfur redox kinetics is one feasible direction.\textsuperscript{233} Manthiram’s group reported a coaxial-graphene-coated cotton-carbon host material for sulfur cathodes.\textsuperscript{233} Owing to the high conductivity, low nanoporosity, and open macroporous electrolyte channels, the cathodes displayed a high areal capacity of 31 mAh/cm$^2$ with an ultrahigh sulfur loading of 57.6 mg/cm$^2$ and low E/S ratio of 4.2 µL/mg, which was highly competitive to state-of-the-art LIBs.

On the other hand, rationally designing the pore structure of sulfur hosts and cathodes is equally important. Compared to most carbonaceous materials with high porosity, employing metal-based hosts with high tap density is an effective strategy to decrease the E/S ratio.\textsuperscript{234} For instance, S/LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ composites with a lower

### Table 2 Performance comparison with different host materials fabricated with different technologies

| Host materials   | Sulfur loading (mg/cm$^2$) | Areal capacity (mAh/cm$^2$) | Synthetic route | E/S ratio (µL/mg) | Refs. |
|------------------|----------------------------|-----------------------------|----------------|------------------|-------|
| MoS$_2$-MoN      | 12.2                       | 13.3 (0.1 C)                | 3D collector   | 8.3              | [34]  |
| CC@CS@HPP        | 8.1                        | 8.1 (0.01 C)                | 3D collector   | 7                | [102] |
| CNT aerogel      | 20                         | 22.9 (0.2 C)                | 3D collector   | 7.8              | [211] |
| CNTs@TiN-TiO$_2$-5 | 15                      | 12.2 (2 C)                  | 3D collector   | 10               | [220] |
| WLC-CNTs         | 52.4                       | 58 (0.1 C)                  | 3D collector   | 6                | [221] |
| eGF||Li@eGF       | 22                         | 25 (1.6 mA/cm$^2$)          | 3D collector   | 3.5              | [222] |
| PGCNF            | 15.8                       | 21.5 (0.1 C)                | 3D collector   | 10               | [223] |
| CCC@TiO$_2$-TiN  | 13                         | 9.1 (0.2 mA/cm$^2$)         | 3D collector   | 4.6              | [224] |
| TVN-4            | 6                          | 6.11 (0.1 A/g)              | Electrospinning| 6.5              | [123] |
| CCF-TiNOC        | 12                         | 14.4 (2.3 mA)               | Electrospinning|                  | [215] |
| CNF@V$_3$S$_8$   | 7.8                        | 8.2 (0.1 C)                 | Electrospinning|                  | [225] |
| VG/TiC           | 8                          | 9.1 (0.1 C)                 | Electrospinning| 6                | [226] |
| TiO$_2$@TiN/CNFs | 8                          | 8.6 (3 mA/cm$^2$)           | Electrospinning|                  | [227] |
| NPCN-1.8-1000    | 14.3                       | 10.4 (4.8 mA/cm$^2$)        | Electrospinning|                  | [228] |
| GRO              | 8.4                        | 10.3 (0.2 C)                | Filtration     | 12               | [152] |
| EBP/EGr          | 6.1                        | 5.57 (0.1 C)                | Filtration     | 5.7              | [229] |
| NiCo-LDH@rGo     | 5.5                        | 4.3 (0.1 C)                 | Spray-drying   |                  | [103] |
| TVN-4            | 6                          | 6.11 (0.1 A/g)              | Spray-drying   |                  | [123] |
| TS-Ti$_3$C$_2$/CNT| 7                         | 4.9 (0.05 C)                | Spray-drying   |                  | [201] |
| ePCNTM           | 6.5                        | 3.2 (0.1 C)                 | Spray-drying   |                  | [202] |
| N-pTi$_3$C$_2$Tx | 12.0                       | 8.5 (0.1 C)                 | 3D printing    |                  | [88]  |
| VO$_2$-V$_2$C    | 10.8                       | 9.7 (0.05 C)                | 3D printing    |                  | [219] |
| 3DP-C/CoS$_x$    | 8                          | 9 (3 mA/cm$^2$)             | 3D printing    | 10               | [230] |
| 3DPV$_8$C$_7$-VO$_2$||3DP-V$_8$C$_7$-VO$_2$@Li | 9.2                        | 7.4 (0.1 C)    | 3D printing      | 5.2   | [231] |
TABLE 3 Performance comparison with different host materials under lean electrolyte condition

| Host materials          | Sulfur loading (mg/cm²) | Areal capacity (mAh/cm²) | E/S ratio (μL/mg) | Refs. |
|-------------------------|-------------------------|--------------------------|-------------------|-------|
| OVs-TiO₂-X@NC          | 9.5                     | 8.0 (0.05 C)             | 5                 | [121] |
| Mo₉S₈                  | 6.2                     | 7.8 (0.05 C)             | 1.2               | [138] |
| CGCC                   | 57.6                    | 31.3 (0.1 C)             | 4.2               | [233] |
| NG-CN                  | 5.2                     | 5.2 (0.06 C)             | 5                 | [236] |
| HCF                    | 10.8                    | 14.6 (0.05 C)            | 4.9               | [237] |
| NMO                    | 8.2                     | 7.4 (1 mA/cm²)           | 4                 | [238] |
| C₆₀                    | 4                       | 3.2 (0.2 C)              | 5                 | [239] |
| Co-MoSe₂/MXene         | 9.9                     | 8 (0.1 C)                | 3.5               | [240] |
| CoZn-Se@N-MX           | 7.8                     | 6.6 (0.01 C)             | 5                 | [241] |
| Co-NCNT@CF             | 7                       | 7.4 (0.1 C)              | 5                 | [242] |
| Mn-NOPC                | 3.8                     | 4.7 (0.1 C)              | 5                 | [243] |
| Co₃N/NC                | 4.8                     | /                        | 4.7               | [244] |
| Fe-Ni                  | 4.1                     | /                        | 4.5               | [247] |
| ZrB₂                   | 7.8                     | /                        | 2.5               | [180] |
| FDS-C                  | 6                       | /                        | 2.5               | [253] |
| MoB                    | 3.5                     | /                        | 4.5               | [244] |
| SDHPC                  | 8                       | /                        | 2.8               | [245] |
| CoSe@C||CoSe@C/Li       | 6.2                     | /                        | 4.5               | [246] |
| Ni-CF                  | 5                       | /                        | 5                 | [247] |

porosity of 15.9% were employed as cathode materials. Because of their stacked channels, the fraction of inactive electrolyte was greatly decreased, and the resultant cathodes displayed a decent capacity of 1047.5 mAh/g at 0.1 C with a low E/S ratio of 4 μL/mg.

As for cathode engineering, macrocracks and closed pores are usually generated during the thermal drying process, resulting in a higher E/S ratio. Thus, a unique canal-capillary pore structure prepared by the freeze-dried method was proposed by Li and coworkers. Because of the tailored end-to-end highways, facile ion migration, fast electrolyte impregnation, and dispersed distribution of LiPSs were realized simultaneously, resulting in superior performance with an ultralow E/S ratio of 2.5 μL/mg. In addition, employing host materials with controlled morphology or calendering technique to increase the cathodes’ tap density is also constructive. The specific values of recent works under lean electrolyte condition are listed in Table 3.

3.3.3 | High energy density cathode fabrication

To realize the goal of gravimetric energy density of 400–600 Wh/kg and volumetric energy density of 700 Wh/L of Li-S batteries, plentiful efforts have been devoted to improve the practical energy density. Though it is hard to achieve high gravimetric and volumetric energy density simultaneously under current technologies, they are equally significant for practical applications based on the primary requirements of our ever-increasing demands. For instance, high gravimetric energy density is suitable for large-scale stationary electrical energy storage while high volumetric energy density is more appropriate for 3C electronics or electric vehicles. Hence, in the following part, the two parameters are discussed individually.

High gravimetric energy density

Given that sulfur possesses an extremely high theoretical gravimetric energy density of 2600 Wh/kg, increasing sulfur loading content and incorporating light-weight substrates can improve the practical gravimetric energy density. Moreover, free-standing cathodes and lean electrolyte usage could further contribute to the gravimetric energy density increase. Ordered macroporous materials, which can accommodate high sulfur loading and facilitate electrolyte impregnation, are considered as desired hosts to achieve competitive Li-S pouch cell performance. By incorporating 3D ordered macroporous carbonaceous hosts with double-catalytic-site materials (ZnS and Co-N-C), an Ah-level Li-S pouch cell with a specific energy density of over 300 Wh/kg was successfully fabricated. Owing to the
interconnected channels and well-dispersed active sites, the resultant pouch cells still could stably operate for 80 cycles with high coulombic efficiency (>95%) even under lean electrolyte (4 μL/mg) and high sulfur loading (1.2 g) condition. This work represented a significant advancement in fabricating practical Li-S pouch cells.

High volumetric energy density
Considering the low tap density of sulfur (1 mg/cm²) and commercial carbon (0.1 mg/cm²), it is an effective strategy to obtain cathodes with high volumetric energy density by cooperating hosts with high tap density or stacked configuration. Gao’s group has proposed a series of desired hosts using metal-based materials with high tap density to obtain high volumetric energy density cathodes. Besides, developing sulfur-equivalent cathode materials (e.g., SeS, TeS₃, and TiS₃) with higher tap density is also feasible.

Decreasing the electrode porosity is another strategy to realize high volumetric energy density, where calendaring is the most useful technique. The cathode density could be easily enhanced alongside lower porosity, leading to higher volumetric energy density and less electrolyte dosage. Notably, poor electrolyte wettability and blocked diffusion pathway under low porosity condition always induce higher polarization and worse sulfur utilization. Given this, Qi and coworkers systematically investigated the relationship between cathode porosity and corresponding energy density, which showed that the electrode with the porosity of 50–60% was most suitable for practical high energy density Li-S batteries.

3.3.4 Flexible application

To develop wearable devices, flexible batteries with high energy density are urgently needed. Fabricating self-supporting cathodes composed of 1D/2D materials or direct coating materials on flexible substrates (e.g., carbon cloth) are the most frequently used strategies to fabricate flexible sulfur cathodes. In addition, owing to the high controllability of 3D printing, it might be another preferred choice for electrode fabrication.

Though the “flexible” features could be easily realized by the aforementioned methods, more attention should be paid to the cycling stability under bending condition. As shown by Zheng and coworkers, a stable charge/discharge operation under 200 cycles of repeated bends was maintained by tailored tandem batteries, which were composed of Li-deposited CuCFs anodes and S-deposited NiCFs cathodes (Figure 8B).

3.3.5 Wide temperature range application

Although most of the reported Li-S batteries worked at room temperature, some pioneering works on exploring the application of sulfur cathodes in a wide temperature range have been performed. It is acknowledged that high temperature usually aggravates the shuttle effect while low temperature would severely slow down the sulfur redox kinetics. Given that higher temperature can decrease the reaction energy barrier to promote sulfur conversion, investigating the applicability of Li-S batteries at a lower temperature is more challenging. Dong and coworkers demonstrated that BN incorporated graphene could maintain the synergistic adsorption and kinetic enhancement in a wide temperature range, and the resultant cathodes retained high discharge capacities of 738, 669, and 401 mAh/g, when the temperature dropped to 0, −20, and −40°C, respectively. Besides, Sun et al. revealed a new mechanism of direct solid-solid conversion from S₈ to Li₂S in carbonate electrolyte and presented its high reversibility in a wide temperature window of −20 to 55°C.

In parallel with studies on how to maintain the cycle stability affected by accelerated LiPSs shuttle at an elevated temperature, the ever-increasing safety risk needs to be considered as well. Flame-retardant hosts with a hierarchical cellular architecture composed of boron nitride nanosheets and functional CNTs were devised to enhance the safety of Li-S batteries (Figure 8C and D). Because of the homogeneous thermal field with smooth and ultrafast heat-conduction channels that could effectively regulate the heat inside the batteries, the as-fabricated cathodes could cycle over 300 times even at a high temperature of 60°C without suffering thermal runaway.

4 SUMMARY AND OUTLOOKS

The inherent shortages, such as low sulfur utilization and inferior cyclability, still impede the commercial application of Li-S batteries. With countless efforts devoted by researchers, a booming development of elaborate sulfur cathodes has been witnessed in the past decades. Inspired by the pioneering work from Nazar’s group, incorporating sulfur with adsorbents/catalysts to fabricate composites is a widely adopted strategy. In this review, we systematically introduce the impressive progress of cathode fabrication with respect to sulfur encapsulation, host architecture, and cathode configuration. In view of the intimate relationship among these components, integrated design principles for reliable Li-S batteries are proposed. The main conclusions are as follows:
1. To realize Li-S batteries with high sulfur content, the rational structure design of host materials is of great significance. Catalytic sites implanted macroporous substrate is regarded as one of the desired host materials. Although some studies have demonstrated that confining sulfur in pores is unnecessary, designing light-weight materials with effective adsorption-catalysis synergistic effect to ensure the in-situ conversion of sulfur is the key.

2. To realize Li-S batteries with high areal capacity, high sulfur loading and utilization should be taken into account first and foremost. Given the inevitable cracking and sluggish electron transfer existing in conventional thick cathodes, high-conductive catalytic hosts or sulfur-equivalent active materials should be preferentially considered. Meanwhile, constructing 3D conductive frameworks also contributes to the improvement of electron/ion transport rate. The fabrication of 3D frameworks is not restricted to commercial 3D substrates or current collectors, and more attention should be paid to the ordered electrode structure design itself (e.g., stacked electrode or ordered pathway inside the electrode).

3. To realize Li-S batteries with high gravimetric energy density, decreasing the mass proportion of inactive materials (i.e., conductive agent, current collector, and binder) in cathodes is most resultful. Binder-free cathode composed of high-conductive catalytic composites is a promising trend. Meanwhile, investigating more light-weight noncarbon-based catalytic materials is another effective strategy. Considering their high porosity, optimizing the cathode porosity to decrease the electrolyte dosage is also required.

4. To realize Li-S batteries with high volumetric energy density, decreasing the porosity of active material, host substrate and cathode is effective. Exploring composites with higher tap density and optimizing cathode porosity need in-depth studies.

5. To satisfy the ever-growing demands in various application scenarios, endowing Li-S batteries with flexible, wide temperature range operation, and high safety is highly urgent. Associated with collaborative research on electrolyte and anode, the multifunctional Li-S batteries can be realized in the near future.

Though Li-S batteries show great potential to serve as the high energy density storage system beyond LIBs, there are still considerable challenges for the practical application of Li-S batteries. To fulfill the original goal and make full use of the intrinsic advantages of Li-S batteries, more concerns should be paid to the following research directions:

1. Melting-diffusion is a widely applicable sulfur loading method. However, the reaccumulation of sulfur when drying still causes unexpected loss of active sulfur. Coating layer on the cathode surface is treated as an effective strategy. Developing in-situ polymerization or advanced coating strategy such as atomic layer deposition to fabricate self-healing protective interlayer during cycling is a promising route. Besides, though in-situ chemical deposition method is widely used in carbonaceous hosts, exploring in-situ generated sulfur loading methods which are suitable for metal-based substrates is equally important. Moreover, alternative sulfur materials, such as sulfides or organosulfur, which demonstrate bright prospects in high energy density cathodes, need more investigation.

2. Structure design should serve the improvement of volumetric energy density. A stacked structure with ordered pores derived from low-dimension materials is recognized as a prospective candidate.

3. To deepen the understanding of the origin of enhanced LiPSs conversion, studies on dynamically monitoring the electronic and structural evolution of the cathode materials (including active materials and catalytic hosts) during cycling are meaningful. Therefore, in-situ/operando characterization techniques with high temporal/spatial and energy resolution should be greatly beneficial.

4. DFT calculation has been widely used for guiding the cathode design. However, considering the complicated multielectron conversion, the detailed catalysis mechanism for \( S_8(solid) \leftrightarrow Li_2S_4(liquid) \leftrightarrow Li_2S_2(solid) \leftrightarrow Li_2S(solid) \) is not clear. Associated with advanced characterization techniques and theoretical calculation of kinetics, quantitatively clarifying the underlying mechanism of rate-limited steps is required, which can further guide the precise catalysis. Besides, more attention should be paid to the charge process, where the shuttle effect also exists. In view that sulfur oxidation is the reversible process for sulfur reduction, the current catalytic mechanisms for \( Li_2S \) deposition might be no longer appropriate for \( Li_2S \) decomposition. The catalytic interaction between the metal-based host and \( Li_2S_x \) in charge process should be reconsidered.

5. Given sulfur redox occurring at the triple-phase interface, interfacial ion migration and \( Li_2S \) nucleation behaviors should be explored with in-depth and detailed analyses. How to regulate the interfacial adsorption-diffusion-conversion process based on surface modification and structural specificity (e.g., edge site, interlayer, and orientation) needs more endeavors as well. In addition, exploration on illustrating the morphological evolution and spatial distribution of LiPSs during the entire charge-discharge process is another
important issue for future research, which can inspire the following studies on shaping the Li$_2$S growth and S$_8$ recrystallization.

6. Compared to conventional solid-liquid-solid conversion in Li-S cathodes, persistent development on high safety cathodes dominated by solid-solid conversion and high-rate cathodes relying on liquid-liquid conversion is of practical significance.

Overall, we wish this review can arouse the researchers’ attentions to the closely linked relationship among sulfur encapsulation, host architecture, and cathode configuration. Meanwhile, we believe the presented integrated principles could guide the subsequent high-performance cathode design.

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CONFLICT OF INTEREST
The authors declare no conflict of interest.

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Hongtai Li: formal analysis, conceptualization, data curation, and writing-original draft. Yanguang Li: formal analysis and data curation. Liang Zhang: formal analysis and data curation.

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