Exploration of the Unique Structural Chemistry of Sulfur Cathode for High-Energy Rechargeable Beyond-Li Batteries

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The increased demand for energy has prompted users to seek alternative energy storage devices. Post-Li-ion battery chemistries have been considered potential contenders for the development of next-generation battery technologies. The high specific capacity (~1675 mAh g⁻¹) and high natural abundance (~953 ppm) of sulfur provide opportunities to meet the rigorous requirements of the market's demands, such as high energy density and low cost. When combined with a high capacity metal anode (e.g., Na ≈ 1165 mAh g⁻¹, Mg ≈ 2205 mAh g⁻¹, and Al ≈ 2980 mAh g⁻¹), it leads to high energy density that can outperform the existing battery technologies, including high-energy Li-ion batteries. Despite the unique attributes of the sulfur-based battery system, it remains in infancy owing to the complex reaction chemistry of sulfur cathode, and the level of complexity increases with an increase in valency of metal ions. This review summarizes the unique aspects of a sulfur cathode essential to stabilizing sulfur cathode-based high-energy rechargeable batteries. Furthermore, deeper insight into the electrochemical performance of various metal–sulfur-based systems has been provided. This review may pave the path for the researchers to accelerate the development of sulfur cathode for post-Li-ion batteries.

1. Introduction

Increased demand for high-energy storage technologies has resulted in a substantial rise in high-energy rechargeable batteries.¹–⁴ Among various rechargeable battery chemistries, the Li-ion system currently dominates the consumer market. It is part of stationary storage due to its appreciably high energy density and long cycle life.⁵–⁹ However, their viability has been severely impacted by the high cost of cathode materials and limited energy density that inherently limits its applications in large-scale grid storage applications and long-range electric mobility applications.¹⁰,¹¹ There has been a quest for a high-energy cathode with substantial storage capacity. In pursuit of the prerequisites above, realizing an alternate solution toward feasible battery chemistry is imperative to leapfrog the existing Li-ion chemistries.¹²–¹⁴

Post-Li-ion battery technologies, for instance, metal–sulfur batteries, represent one of the most promising chemistries for high-energy rechargeable batteries.¹⁵,¹⁶ Lithium–sulfur (Li/S) battery chemistry was initially investigated in the 1960s.¹⁷ Lithium metal anode with a high theoretical capacity of 3860 mAh g⁻¹, when coupled with the sulfur cathode, brings out a high theoretical specific energy of about 2500 Wh kg⁻¹.¹⁸–²¹ These merits are further strengthened by its low-temperature operation and low cost of the electrode material ($0.02 g⁻¹).²²,²³ Sulfur with relatively low redox potential is ideally configured with different metals to achieve state-of-the-art cascaded sulfur-based battery technologies.²⁴ As schematically illustrated in Figure 1, a metal–sulfur battery comprising a sulfur cathode, a metal anode, and a separator soaked in the liquid electrolyte. The mechanistic aspect of metal–sulfur chemistries shares a similar fundamental understanding. The complexity and viability of a metal–sulfur battery strongly depend on the nature of the metal anode. Though the nature of the charge/discharge products strongly depends on the metal anode used, the reversibility and stability of the sulfur cathode can be tuned by altering the physical structure of cathode materials (see Figure 1).²⁵,²⁶

This review explicitly gives a holistic overview of various cathodes used in metal–sulfur batteries (metal—Na, Mg, and Al). Notably, we aim to unveil the unique aspects of sulfur chemistry dictating the electrochemical reversibility of various metal anodes.

2. Overview of the Elemental Sulfur

In contrast to traditional insertion-type cathodes, sulfur as a conversion cathode reacts in bulk to be reduced to metal sulfides, resulting in its lowest oxidation state (i.e., S²⁻).²⁷ Based on the anionic redox mechanism, sulfur delivers a remarkably high...
theoretical specific capacity of 1675 mAh g⁻¹, which is orders of magnitude higher than other insertion cathodes.[28–30] Sulfur, with various oxidation states and polyatomic structures, octasulfur (cyclo-S₈), is considered a thermodynamically stable allotrope of sulfur at room temperature (RT).[31] Some of the critical properties of sulfur are tabulated in Table 1. Despite its function as an electrical and thermal insulator with low electrochemical potential, sulfur yields a high specific energy density when paired with other metals.[32–35] Thus, sulfur has been revitalized as a potential candidate for use as a cathode in high-energy rechargeable batteries.

3. Progress toward Cathode System in a metal–sulfur Interacted Battery System

While particular attention is given to Li/S battery systems, recent efforts focused on developing other chemistries with high-performance, low-cost, and long-term sustainability.[19] The reaction chemistry of sulfur is complex, and it heavily depends on the nature of the metal anode.[16–18] Each system requires a sulfur cathode with unique physical and chemical properties.

In contrary to the monovalent ions (e.g., Li or Na), which have been explored up to some extent, the appeal toward divalent (Mg) and trivalent ions (Al) has been overwhelming owing to their remarkable theoretical specific capacities.[39–43] Despite their alluring attributes, the system becomes more complicated and sluggish with increased charge and ionic size.[11] As the viable applications of these metal–sulfur batteries are impeded with severe challenges, sulfur-based technology still needs innovative efforts and in-depth understanding. Though considerable progress has been made toward RT Na/S, Mg/S, and Al/S batteries, their development remains in infancy. The significant milestones achieved in developing sulfur cathode in various metal–sulfur systems are schematically illustrated in Figure 2.

Based on the two-electron redox mechanism of sulfur at the cathode, sulfur undergoes a series of discharge reactions (see Table 2)

The overall electrochemical reaction occurring in a metal–sulfur battery during a discharge reaction can be expressed as

Anode: \( nM \rightarrow nM^{n+} + ne^- \) (1)

Cathode: \( S_8 + nM \rightarrow M_xS \) (2)

Overall: \( S_8 + nM \rightarrow M_xS \) (3)

Reduction of sulfur occurs at the cathode during discharge cycles, resulting in a multistep transformation into a series of complicated intermediate metal polysulfides.[44] During metal ion insertion, polysulfides are formed by accepting metal ions and electrons via electrolyte and external circuits.[23,45] The metal–sulfur battery systems result in different voltage profiles and storage capacity; however, a similar reaction mechanism occurs in all metal–sulfur systems with a phase transition from solid to liquid to solid during the discharge process.[45,46]

Steady progress has been made hitherto on the development of a suitable host for S-cathode. Different conductive hosts have been engineered to mitigate the shuttling phenomena and achieve a high energy density battery system in various practical applications.[47–50] The classification of different hosts has been categorized based on their capability to entrap sulfur and its reduction species, such as 1) physical entrapment using porous carbonaceous-based composites or coating a composite layer as a barrier,[51,52] for example, micro/meso/macro/ultramicroporous interconnected structures,[53] hollow carbon spheres,[54] layered carbon nanotube,[55] carbon nanofibers,[56] and graphene[57]; 2) chemical immobilization of reduction products of sulfur via chemical adsorption, such as chemical dopants[58–60] single-atom crystals,[61,62] metal oxides,[63] and metal sulfides,[64,65]; and 3) polymer-based composites based on covalent bonding, for instance, polyacrylonitrile, copolymer mixtures, and others.[44,46] In this regard, various mechanistic investigations have been made to unveil sulfur’s unique properties for RT metal–sulfur battery chemistries.

### Table 1. Important properties of the elemental sulfur.

| Sulfur | Atomic weight [amu] | Electronegativity | Oxidation states | Conductivity [S cm⁻¹ @ 25 °C] | Potential (vs SHE) | Theoretical capacity [mAh g⁻¹] | Boiling point [°C] | Melting point [°C] | Density [g cm⁻³ @ 20 °C] |
|--------|---------------------|-------------------|------------------|-----------------------------|------------------|-----------------------------|-----------------|-----------------|---------------------|
| Sulfur | 32.065              | 2.58 eV           | −2, +4, +6       | 5 × 10⁻³⁰                  | −0.340           | 1675                        | 444.6           | 112.8 (n-S)     | 2.07 (n-S)         |
|        |                     |                   |                  |                             |                  |                            |                 | 118.7 (li-S)    | 1.96 (li-S)       |

Figure 1. Schematic illustration of a metal–sulfur battery system (M = Li, Na, Mg, and Al) with different physical structures of sulfur cathodes.
3.1. RT-Na/S Battery System

As an alternative to Li/S batteries, there has been a surge of interest in developing sodium–sulfur batteries due to their high theoretical capacity, cycle life, and a low cost per cycle.[67,68] However, the high-temperature sodium-sulfur batteries (HT-Na/S) have been used for stationary storage applications since the early 2000s.[69–72] As a cutting-edge technology, HT-Na/S has progressed significantly over the years and found its use in various applications, including space and other large-scale stationary storage applications.[73–75] Despite their unique attributes with a theoretical specific energy density of about 760 Wh kg\(^{-1}\), the HT-Na/S battery is severely compromised due to its HT operation, which poses safety challenges.[76,77] This cell chemistry is expected to meet inevitable roadblocks: 1) HT operations (>300 °C), 2) corrosivity of molten electrodes, 3) high reaction enthalpy of 420 kJ mol\(^{-1}\), and 4) scale and cost requirements.[78,79] In contrast, RT-Na/S delivers a high theoretical specific energy density of 1230 Wh kg\(^{-1}\) with long-term sustainability and safety besides low cost and abundance.[80–83] The viability of RT-Na/S batteries is severely challenged by the highly corrosive nature of its discharge products, which are identified to be more alkaline than their Li counterparts.[84] In addition to that, the shuttle phenomena are exacerbated in RT-Na/S battery, resulting in higher volumetric fluctuations, i.e., about 170% (in contrast to 70% of volumetric changes in the Li/S system).[68,85] Besides the formidable challenges, the system experiences overall degradation in performance and low utilization of sulfur cathode.[86] Therefore, extensive research has been put forward with a rational combination of matrices for the S-host to surmount the drawbacks mentioned above. Recently, significant progress in engineering the cathode structure has been made. The researchers have focused on exploring structured electrode materials with enhanced sulfur loading and higher catalytic absorption sites.[87,88] The following architectures of the sulfur host have been developed to stabilize RT-Na/S battery operation.

![Figure 2. Overview of the physical and chemical aspects of the sulfur cathodes used in various metal–sulfur batteries.](image)

**Table 2. Redox kinetic reactions at sulfur cathode for different metal–sulfur batteries.**

| Battery | Scheme I | Reaction | Potential (V) |
|---------|----------|----------|--------------|
| Li/S    | S + 2 Li\(^+\) + 2 e\(^-\) → Li\(_2\)S | 2.40 V |
| Na/S    | S + 2 Na\(^+\) + 2 e\(^-\) → Na\(_2\)S | 2.20 V |
| Mg/S    | S + Mg\(^2+\) + 2 e\(^-\) → MgS | 2.50–1.50 V |
| Al/S    | S + 2 Al\(^3+\) + 3 e\(^-\) → Al\(_2\)S | 0.80–0.60 V |
3.1.1. Physically Adsorbed S-Host

Considering the insulating nature of sulfur and discharge moieties, carbon scaffolds with good electronic conductivity and mechanical stability may boost active material’s effective utilization besides mitigating the migration of polysulfides via physisorption.[89,90] Due to the availability of various adsorption sites, the cotton textile was utilized as a precursor to fabricate carbon fiber cloth (CFC) as a host for the sulfur cathode in the RT-Na/S battery. A binder-free CFC/S composite was synthesized via a solution impregnation strategy followed by a melt-diffusion technique with an S-loading varying from 1 to 3 mg cm$^{-2}$.[91] The open architecture of CFC provides pathways for electrolyte uptake and space to buffer volumetric changes with an alleviated diffusion length for sodium ions. The cotton textile host with intermediate sulfur loading (i.e., 2 mg cm$^{-2}$) depicted the best performance with an initial discharge capacity of 486 and 148 mAh g$^{-1}$ at the end of 300 cycles. A modified morphology of the carbon felt through a thin (≈6 nm) coating of inorganic–organic hybrid nanoparticles resulted in improved performance and Coulombic efficiency of 99.9%.[92] Hu et al.[93] reported a novel design of commercial sulfur particles that offered high tap density and delivered a higher practical volumetric energy density. However, the capacity of such bulk-sized sulfur particles is known to tail off shortly due to the sluggishness of the charge-transfer kinetics. As a result, carbon materials were added into the host to elevate the intrinsic properties of sulfur and enhance the reversibility of the electrochemical reactions. Due to a higher defect density and binding affinity, the processed nanocarbon leads to deliver a specific capacity of 713 mAh g$^{-1}$ at 0.2 C. The increased binding energy can be credited to the adsorption between sulfur and processed nanocarbon surface. As depicted in Figure 3a, the adsorption energy reaches to $-0.628$ eV, compared to lower energies without carbon defects ($-0.523$ eV). The deformation charge density of sulfur molecule and carbon with different carbon defect sizes is depicted in Figure 3b, resulting in the high binding energies toward sodium polysulfide.

Microporous carbon is considered a potential host for its homogeneously distributed small pore sizes and high surface area. Despite the essential attributes of microporous carbon ($<2$ nm), it is intrigued by the limited confinement of sulfur, which tends to lower the specific capacity of the electrode materials.[94] Carter and co-workers developed a microporous carbon template based on sucrose and infused the sulfur particles to design a sulfur cathode.[95] The composite cathode delivered a

![Figure 3](https://www.advancedsciencenews.com)
high 300 mAh g\(^{-1}\) at 1 C after 1500 cycles with Coulombic efficiency of about 98%. Another group contributed to enhancing the microporous carbon-based sulfur system by choosing a metal–organic framework (ZIF-8) for the synthesis of "microporous carbon polyhedron–sulfur composite (MPCS)."\(^{[96]}\) MPCS showed the morphology of rhombic dodecahedra, retaining the structure of the ZIF-8 template. The cell delivered a high first discharge capacity of 1614 mAh g\(^{-1}\) at 0.1 C with a reversible capacity of 800 mAh g\(^{-1}\) after 50 cycles. The development of a high sulfur-loading cathode is essential to be realized for achieving a high practical energy density. Inspired by the high structural integrity of carbon backbone with high tap density and hollow nanospheres, Wang et al.\(^{[97]}\) developed an interconnected matrix of mesoporous carbon hollow nanospheres (iMCHS) with an S-loading of 3.2–4.1 mg cm\(^{-2}\). At a current density of 100 mA g\(^{-1}\), the cell displayed retention of \(\approx\)292 mAh g\(^{-1}\) after 200 cycles. Ultramicroporous carbon (\(d < 0.7 \text{ nm}\)) with narrow pore size was studied in the subsequent years.\(^{[98]}\) In these studies, the cathode was often plagued with rapid attenuation rates and limited cycle life, severely hindering the viability of Na/S battery systems. Guo et al.\(^{[99]}\) reported a unique strategy of using slit-type ultramicroporous to alleviate polysulfide dissolution and the shuttle effect.\(^{[99]}\) An activated ultramicroporous coffee carbon (ACC) based on coffee residue constituting a small chain of sulfur molecules was considered the host for the sulfur cathode in the RT-Na/S battery. The ultrastable performance was attained via a one-step reaction process without the formation of intermediate polysulfides. The only resultant discharge product, i.e., Na\(_2\)S, was obtained after complete discharge of the cell (see UV/vis analysis in Figure 3c). At an S-content of 40 w%, the cathode (ACC-40S) could maintain a remarkably high capacity of 1492 mAh g\(^{-1}\) at 0.1 C. Furthermore, even at higher mass loading of 3 mg cm\(^{-2}\), the ultramicroporous carbon loaded with sulfur could deliver overwhelming reversible capacity of 960 mAh g\(^{-1}\) after 200 cycles at 0.1 C. When cycled for around 2000 cycles at 1 C, ACC-40S cathode showed negligible attenuation rate with almost 100% Coulombic efficiency (Figure 3d).

Zhang and co-workers proposed a sulfur-filled porous carbon microsphere protected with double-shell carbonaceous materials as an efficient host for the cathode.\(^{[100]}\) Scanning electron microscope (SEM) micrographs in Figure 3e,f display a porous morphology with the interconnected structure of carbon beads. The composite cathode resulted in cycling stability for over 350 cycles with a capacity of 290 mAh g\(^{-1}\) at 100 mA g\(^{-1}\). It was observed that the intermediate polysulfides were well-sealed inside the spheres, reducing their direct contact with the electrolyte. The beads’ structure allowed sufficient space for volume fluctuations during charge/discharge reactions. 1D structured carbon nanofibers (CNFs) have been extensively used as a host in Li/S systems. Xia et al.\(^{[101]}\) synthesized carbon hollow nanobubbles on porous carbon nanofibers (CHNBs@PCNFs). The uniform morphology of carbon nanobubbles with thin shells (thickness \(\approx 2 \text{ nm}\)) could be observed in Figure 3g. In addition, CHNBs@PCNFs maintain a continuous network of long fibrous structures where the CHNBs behave as the anchoring site for many particles (see Figure 3h). The as-synthesized composite displayed a long-term cycling stability at a high rate of 2 C, retaining discharge capacity of 256 mAh g\(^{-1}\) after 400 cycles. A high S-content of 71.2% could be accommodated within the porous matrix, suggesting strong absorption of sulfur by the composite materials. Physical confinement of sulfur particles within carbon hosts occurs through a weak interaction, rendering low adsorption to sustain repeated charge/discharge cycles. In addition to that, due to the limited availability of adsorption sites and polar groups, it is often realized with low sulfur loadings and low binding energies.

### 3.1.2. Chemisorbed S-Host

An approach to chemically bind the sulfur species with the host structure through heteroatoms is one of the promising strategies to enhance sulfur loading and simultaneously minimize polysulfide dissolution.\(^{[102,103]}\) The heteroatoms, such as nitrogen,\(^{[104,105]}\) phosphorus,\(^{[106–108]}\) and boron,\(^{[109,110]}\) have widely been explored to boost sulfur loading. For example, Qiang et al.\(^{[111]}\) reported N and S (\(\approx 40 \text{ at}\%\)) doped nanoporous carbon to boost the stability of RT-Na/S batteries. Due to the high polarity of N and nanoporous structure of carbon, side reactions could be inhibited besides effective entrapment of polysulfides, leading to an ultralarge cycle life for over 8000 cycles. Recently, metal–organic frameworks (MOFs) have gained interest as an excellent host to render long-term stability. MOFs are a group of crystalline compounds that consist of metal ions and organic ligands. Owing to remarkably high surface area and 3D interconnected porous matrix, MOFs provide ordered coordination among the components to exhibit unique chemical features and stable architectures. For instance, Chen et al.\(^{[112]}\) reported a nitrogen-doped carbonized ZIF-8/S (sodalite-type structure) as the cathode for the RT-Na/S battery. The cell could deliver an initial discharge capacity of 873 and 500 mAh g\(^{-1}\) after 250 cycles. N-doped carbonized MOF promotes improved interaction of sulfur species with the host structure. Despite the advantages, the cathode still suffered from low S-loadings (0.7–0.9 mg cm\(^{-2}\)) that impede its use in practical applications. Xiao and co-workers fabricated a porous carbon host doped with S, N to encapsulate sulfur (see Figure 4a), guaranteeing homogenous distribution of sulfur into the matrix but with a mass loading of only 0.9–1.5 mg cm\(^{-2}\).\(^{[113]}\) The nitrogen-doped carbon, wrapped with polydopamine (PDA), displayed a long cycle life of 1000 cycles with a high reversible capacity of 270 mAh g\(^{-1}\) at a current density of 1 A g\(^{-1}\) Coulombic efficiency of \(\approx\)100%. Nitrogen-doped graphene nanosheets/sulfur nanocomposites (NGNS/S) displayed a 3D voile-like hierarchical morphology with minimum agglomeration and a high S-content of 86 w%.\(^{[114]}\) In contrast, NGNS/S with the lowest S-loading exhibited the best performance upon testing for 300 cycles, delivering a discharge capacity of 48 mAh g\(^{-1}\) at 0.1 C. However, polar hosts, such as heteroatom doping, have demonstrated effective confinement of sodium polysulfides due to strong chemical polar interactions. Yet, the results were still far from expectations due to slow reaction mechanisms. Nonmetal dopant’s adsorption capability for polysulfides is still lacking and generally holds weaker polarity than metal components; thus, the shuttle phenomena in metal–sulfur batteries persist.\(^{[115]}\)

The affinity toward polysulfides can be enhanced through a single metal atom, or clusters, demonstrated recently.\(^{[116,117]}\) Due to high electrical conductivity, single metal atoms expedite
the electrokinetics of polysulfides conversion from long-chain to short-chain polysulfides.[118] It is identified that the metal atoms can lower the decomposition energy barrier of polysulfides due to higher polar–polar interactions and physical/chemical adsorption that speed up the redox kinetics of the battery.[119] In recent years, nanoclusters of various transition metals, for instance, iron, copper, vanadium, and nickel, have been reported to attenuate the dissolution of sodium polysulfides.[120] Among these, the composite with iron metal nanocluster exhibits unprecedented results with efficient immobilization of sulfur and catalytically enhanced kinetic process of soluble polysulfides. Zhang and co-workers examined atomic cobalt due to its high electrocatalytic reactivity in hollow carbon nanospheres (S@Co_{n}-HC) (see Figure 4b).[121] The sulfur cathode with an S-loading of about 5 mg cm\(^{-2}\) delivered a remarkably high initial discharge capacity of 1081 mAh g\(^{-1}\) at 100 mA g\(^{-1}\) and retained 508 mAh g\(^{-1}\) after 600 cycles. As depicted graphically (Figure 4c), the high negative energy of \(\sim10.67\) eV suggests a fast kinetic conversion from intermediates to Na\(_2\)S that could obviate the shuttling effect, resulting in an outstanding enhancement of sulfur loading. Due to multiple adsorption sites and stable structural architecture, a hybrid 3D network of nickel hollow spheres (Ni-NCFs) was synthesized to entrap the soluble polysulfides effectively.[122] Field emission scanning electron microscope (FESEM) images in Figure 4d reveal the cathode’s morphology after incorporating sulfur, which is well affirmed by energy dispersive X-ray analysis (EDS) elemental mapping (see Figure 4e). As depicted in Figure 4f, the transmission electron microscopy (TEM) image clearly shows the darker inner wall of nickel spheres, which illustrates the effective encapsulation of sulfur within the inner shells. Ni-NCFs@S exhibited high rate capability at various C-rates of 0.2, 0.3, 0.5, 1, 2, 3, and 5 C. Additionally, first discharge capacity of 431 mAh g\(^{-1}\) at 1 C and \(\sim233\) mAh g\(^{-1}\) after 270 cycles with a decay rate of 0.17% per cycle was observed for the composite cathode.

Recently, Zhu et al.[123] reported carbon nanospheres doped with nitrogen and a fractional amount of iron (0.14 atomic wt%). Strong interaction with the sulfur moieties provided by an excellent electrocatalytic activity of iron resulted in retaining a reversible capacity of 180 mAh g\(^{-1}\) after 200 cycles. To effectively harness the attributes of metal clusters, Ma et al. reported a sulfur-containing flexible architecture of graphene aerogel wrapped with cobalt nanoparticles (S@Co/C/rGO).[124] Graphene aerogel could provide a stable framework for anchoring sulfur particles, while cobalt atoms facilitate long cycling performance. Owing to the high reversibility, fast conversion reactions, and strong adsorption capability of gold atomic clusters on sulfur, the gold cluster, along with hierarchical structured nitrogen-doped carbon microspheres, was examined recently. The cathode could attain a prolonged cycle life with a capacity of 369 mAh g\(^{-1}\) at 10 A g\(^{-1}\) after 2000 cycles.[125] In addition to that, the cathode could observe a high S-content of about 56.5 wt%.

A weak interaction between the carbonaceous compounds and polysulfides has failed to restrain the long-chain polysulfides that lead to sluggish kinetics and eventually quick capacity fade.[126,127] Besides using highly effective chemical dopants (e.g., metal and nonmetal dopants), metal-based composites such as metal oxides, metal sulfo-des, metal phosphides, and others have been explored.[128–131]

**Figure 4.** a) Schematic representation of the synthesis process of Zn-MOF, MOF-C/S, MOF-C/PDAc, and MOF-C/S/PDAc composites. Reproduced with permission.[113] Copyright 2020, Wiley-VCH GmbH. b) Schematic illustrations of the reaction mechanism of an atomic cobalt-decorated hollow carbon-sulfur host (S@Co_{n}-HC). c) Energy profiles of Na\(_2\)S\(_4\) adsorption on carbon-supported Co\(_6\) cluster (in blue) and carbon support (in red). Reproduced with permission.[121] Copyright 2018, Springer Nature. d) FESEM, e) TEM, and f) EDS elemental mapping of Ni-NCFs@S electrode. Reproduced with permission.[122] Copyright 2019, Wiley-VCH GmbH.
Ma et al.\textsuperscript{[132]} reported a flexible freestanding cathode (see Figure 5a) comprising sulfur in a porous carbon scaffold with BaTiO$_3$ coated with amorphous titanium dioxide (TiO$_2$). While BaTiO$_3$ developed a spontaneous polarization, TiO$_2$ on the matrix resulted in high encapsulation of sulfur. The sulfur loading could be reached to $\approx 3.5 \text{ mg cm}^{-2}$. The as-modified matrix exhibited a stable interface with ultralong cycling performance and retained a specific capacity of 524.8 mAh g$^{-1}$ at 1 A g$^{-1}$ after 1400 cycles. Similarly, a judicious combination of heterostructured TiN-TiO$_2$ embodied in multichannel CNFs was reported recently to exhibit high electronic conductivity and high adsorption energies toward sodium polysulfides (see Figure 5b).\textsuperscript{[133]} Due to the improved electrocatalytic activity of the scaffold, a rated capacity of 490.5 mAh g$^{-1}$ at 1 A g$^{-1}$ after 100 cycles could be achieved. However, the electrode was plagued with a low S-loading of 1.08 mg cm$^{-2}$.

With the assistance of metal sulfides as the hosts for a sulfur cathode, there has been considerable progress in enhancing sulfur loading and the specific capacity of the cell.\textsuperscript{[134,135]} Ye et al.\textsuperscript{[136]} studied a layered MoS$_3$ to enhance the sulphilic property of the sulfur cathode. A chain-like amorphous structure of MoS$_3$ with an exceedingly high loading of 7.1 mg cm$^{-2}$ was achieved to deliver an initial capacity of $\approx 248$ mAh g$^{-1}$ and a stable cycle life of about 200 cycles. Besides that, the cathode could also exhibit an extended cycle life of 1000 cycles with a retained capacity value of $\approx 180$ mAh g$^{-1}$ at 0.45 A g$^{-1}$. Exploiting the advantages of sulfur-rich amorphous molybdenum sulfide, Meyerson and co-workers introduced Mo$_x$S$_y$ with different sulfur to molybdenum ratios as an equivalent host for S-cathode in RT-Na/S battery.\textsuperscript{[137]} Compared to MoS$_{3.5}$, amorphous MoS$_{5.6}$ displayed better electrochemical properties, yielding a reversible capacity of over 300 mAh g$^{-1}$ at a current density of 0.2 A g$^{-1}$.

More recently, the unique architecture of cobalt sulfide bipyramidal prisms with interwoven carbon is demonstrated as an effective S-host with a higher S-loading of 4.4 mg cm$^{-2}$.\textsuperscript{[138]} Due to the high electrical conductivity and catalytic activity, CoS$_2$ could facilitate the conversion process of long-chain polysulfides to insoluble short-chain sodium polysulfides (see Figure 5c). In addition to that, the high affinity of Co toward sodium polysulfides suppresses the dissolution of polysulfides, thus avoiding any parasitic side reactions on the anode surface. The FESEM micrographs (see Figure 5d,e) depict the wide hollow spaces ($\approx 376$ nm) of CoS$_2$/C along with the bipyramidal hollow architectures. The cathode could deliver an initial discharge capacity of $\approx 1300$ mAh g$^{-1}$ and a capacity of 701 mAh g$^{-1}$ after 350 cycles. Besides, cathodes with high S-loading (e.g., 7.3 and 9.1 mg cm$^{-2}$) were tested for cycling performance and delivered an initial areal capacity of 6.24 and 8 mAh cm$^{-2}$, respectively (see Figure 5f,g).
Yan et al. [139] introduced “a multi-region Janus featured CoP-Co structure” based on heteroseed MOFs. The heterostructured cathode was constituted with a CoP-Co network and a conductive carbon scaffold of carbon hollow nanocages doped with nitrogen. Considering the optimized redox reaction and strong polarity toward polysulfides, S@CoP-Co/NCNHC cathode exhibited a high reversible capacity of 448 mAh g\(^{-1}\) for 700 cycles. Despite the improved stability, the heterostructure cathode was realized with low mass loadings of only 1.7 mg cm\(^{-2}\), which is a significant roadblock toward the feasibility of a practical Na/S battery.

### 3.1.3. Covalently Bonded S-Host

Due to weak physical adsorption of sulfur with carbonaceous materials and underutilizing of carbon scaffold, the material systems with large functional groups have been researched in recent years. [44] Covalent bonding of materials reinforces strong binding interactions among sulfur moieties without compromising the electrode materials’ specific capacity. [140] For instance, a covalently fixed sulfur–carbon composite with complex benzene sulfonic acid (BDSA) was developed with a high sulfur concentration of about 40.1 wt%. [141] Instead of the elemental sulfur, —SO\(_3\)H and SO\(_4\)^{2−} were served as the source of sulfur, delivering a high mass loading of \(\approx 3\) mg cm\(^{-2}\). The studies have shown that forming a mediator-like insoluble RS\(_2\)O\(_2\)^{2−} on the surface of covalent-bonded composite facilitates the anchoring of soluble sodium polysulfides.

Chen et al. [142] formed a thioether bond with functionalized carbon (SC) using a sulfur-rich precursor of thiophene monomer. A functionalized structure of C—S—C thioether bond in SC cathode could be untied via voltage scissors in the range of 0.01–0.50 V versus Na/Na\(^+\). Furthermore, sulfur-doped carbon formed the interaction of carbon defects to trap the insolvable polysulfides (Na\(_2\)S\(_2\)/Na\(_2\)S) (Figure 6a), promoting reversibility for sodium storage. However, their practical implementation is limited by the low mass loadings (0.9–1.1 mg cm\(^{-2}\)), which severely affects the overall energy density.

Polymer-based compounds such as polyacrylonitrile have also been investigated for metal–sulfur batteries. The high mechanical strength and flexibility enable polycrylonitrile cathode to withstand the deformation related to volume changes. [66,143] Kim et al. prepared a flexible cathode of sulfurized polyacrylonitrile (SPAN) with high bendability up to 180°. [144] During cycling, the electrode demonstrated an initial discharge capacity of 604 mAh g\(^{-1}\), retaining over 266 mAh g\(^{-1}\) after 200 cycles.

Li and co-workers reported a pyrolyzed polyacrylonitrile combined with selenium dioxide (pPAN/SeS\(_2\)).[145] A 1D framework of pPAN/SeS\(_2\) exhibited the first discharge capacity of 1043 mAh g\(^{-1}\) with a capacity retention of 800 mAh g\(^{-1}\) after 400 cycles.

Li et al. [146] designed polymer-bound sulfurized polyacrylonitrile (S@pPAN), and altered S@pPAN with 4 mol% of tellurium dopant, resulting in a composite of Te\(_{0.04}\)S\(_{0.96} @ pPAN\). Tellurium demonstrated high reversibility with enhanced kinetics, as schematically depicted in Figure 6b, and induced a high conductivity in the electrode (\(\approx 1.6\) times of pPAN). Owing to the high sodium ion diffusion coefficient, Te\(_{0.04}\)S\(_{0.96} @ pPAN\) composite cathode exhibited a reversible capacity of...

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**Figure 6.** a) Illustration of carbon defects induced by the sulfur dopant to confine the insolvable sulfides. Reproduced with permission. [278] Copyright 2019, Royal Society of Chemistry. b) Reaction pathway for Te\(_{0.04}\)S\(_{0.96} @ pPAN\) and S@pPAN composites. Reproduced with permission. [146] Copyright 2019, American Chemical Society. c) Scheme presenting the confined electrocatalytic polysulfide conversion during sodiation. Reproduced with permission. [147] Copyright 2021, Wiley-VCH GmbH. d) Schematic of the possible surface redox reaction between Na\(_2\)S\(_6\) and Mn\(_x\)O\(_y\). Reproduced with permission. [148] Copyright 2019, American Chemical Society.
1236 mAh g\(^{-1}\)). It attained a cycle life of 600 cycles with a low attenuation rate of 0.015% per cycle.

Different covalent-bonded composites have made a breakthrough in monovalent metal–sulfur battery development. Despite their advantages, covalently bonded materials are limited due to their swelling tendency, which disrupts the architecture of the electrode with cycling. While in contact with the solvent, their interconnected structures tend to unbound themselves and align, resulting in inevitable structural changes, e.g., swelling or dissolution. Furthermore, their inability to confines more sulfur and low discharge potential results in attenuated cyclic performance. Nevertheless, it is anticipated that numerous pathways will be created to open up new opportunities to enhance the bonding among the materials to achieve energy-dense cathode composites.

### 3.1.4. Hybrid S-Host

Although many researchers have put forward novel ideas to expedite the development activities of RT-Na/S battery technology, yet the sulfur loading is not satisfactory to meet the desired goal of 10 mg cm\(^{-2}\). In pursuit of improving S-loading, Hwang and co-workers proposed a 3D interconnected network with carbon fiber (CFC) with a high S-loading of 6.4 mg cm\(^{-2}\). A “redox-active polar shell” consisting of a bifunctional sheath of Fe(CN)\(_6\)\(^{3-}\) doped with polypyrrole (FC-PPy) was coated on the carbon fibers. The hybrid host was able to diffuse the polysulfides via multimode interactions, i.e., physical, chemical, and covalent. A schematic illustration of sulfur confinement and immobilization of sulfur can be seen in Figure 6c, enabling the full reduction of polysulfides. When cycled for 200 cycles, the cathode maintained a remarkably high reversible capacity of 1071 mAh g\(^{-1}\) with a retention rate of 72.8%.

More recently, a hybrid 3D reinforced structure of reduced graphene oxide (rGO) with mixed-valence manganese oxide (Mn\(_3\)O\(_4\)) in combination with a hybrid sodium alginate/polyaniline (SA/PANI) adhesive matrix was developed as a host for S-cathode with S-loading of 2.05 mg cm\(^{-2}\). During sodiation, manganese oxide serves as a reducing agent as the oxidation state of manganese reduces from Mn\(^{4+}\) to Mn\(^{3+}\) on interaction with polysulfides; the redox reaction between Mn\(_3\)O\(_4\) and Na\(_2\)S\(_6\) is schematically shown in Figure 6d. The freestanding rGO/S/Mn\(_3\)O\(_4\)@SA–PANI cathode exhibited a storage capacity of 631 at the second cycle, retaining a reversible capacity of 535 mAh g\(^{-1}\) after 50 cycles.

Tremendous progress has been made in the past few years to propel the high S-loading and subsequent utilization. Yet, there are still many scientific and engineering challenges that need to be addressed to access the full potential of Na/S battery technology.

### 3.2. RT-Mg/S Battery System

An increasing interest in magnesium sulfur battery technology has been revived owing to its distinctive aspects and electrochemistry. Rechargeable Mg/S batteries promise a high theoretical energy density of \(\approx 1722\) Wh kg\(^{-1}\), owing to the divalent nature of magnesium ions. Magnesium has a specific capacity of 2205 mAh g\(^{-1}\), which is inferior to Li but superior to Na metal. The system also experiences extraordinary stability toward liquid electrolytes due to the low negative potential of \(-2.37\) versus SHE of magnesium. Considering the availability of magnesium (fifth most abundant element on earth’s crust), the Mg/S battery is considered emerging battery chemistry to leapfrog the energy requirements.

Another important aspect is the intrinsic benefits of dendrite-free electroplating of magnesium ions on the surface of anode that allows it to outperform the currently developed Li/S batteries, resulting in safe operability. Aurbach and co-workers were among the first to demonstrate RT-Ma/S working cell back in 2000, where they reported Mo\(_6\)S\(_8\) for sulfur cathode instead of the elemental sulfur cathode. The first proof-of-concept Mg/S battery system was reported in 2011. The magnesium anode coupled with various other cathodes achieved a milestone in the evolution of rechargeable magnesium-based batteries. Some cathode systems include Mo\(_2\)S\(_2/\)Graphene, H\(_2\)V\(_3\)O\(_8\), Ti\(_3\)C\(_2\)T\(_x\), Ni-MnO\(_2/\)CNTs, FeS\(_2\), and TiS\(_2\). Attempts were made to expedite the progress in the rechargeable magnesium-ion batteries; however, the traditional insertion-type cathodes were found to suffer numerous challenges. For example, there is limited availability of cathode materials compatible with Mg metal and electrolyte systems, sluggish reaction kinetics, and a high diffusion barrier for Mg\(^{2+}\) ions. Additionally, one of the major setbacks of the Mg/S battery is the formation of complex intermediate magnesium polysulfides, which impede the system with low reversibility and poor cyclic performance.

Despite the issues highlighted above, tremendous breakthroughs in rechargeable Mg/S batteries have been made in recent years. The quest for chemically compatible cathode systems offering high performance and practical energy density has been explored over the past few years.

### 3.2.1. Physically Adsorbed S-Host

The carbon-based materials with physically or chemically trapped sulfur particles have widely been investigated as the potential sulfur cathode. Several groups have reported on a porous, stable, high surface area and conductive carbon host to physically accommodate the elemental sulfur and its reduction species. Yu et al. proposed a 1D preactivated CNFs as the host for S-cathode for effective facilitation of ions and electrons. The assembled Mg/S cell exhibited a remarkable first discharge capacity of about 1200 mAh g\(^{-1}\) based on the active mass of sulfur. Furthermore, when tested for 20 cycles, the cell suffered minimal decay in capacity, and the discharge/charge profiles were also examined at different C-rates (0.02, 0.05, and 0.1 C). However, the S-loading in the CNF matrix was limited to a small range of over 1 mg cm\(^{-2}\), and the cell showed poor cycle performance.

Microporous carbon-infused sulfur with high S- utilization was demonstrated as an effective sulfur host for Mg/S batteries. The microporous carbon host with sulfur exhibited an initial discharge capacity of 979 mAh g\(^{-1}\) at 0.1 C and stable cycling of 200 cycles with capacity retention of 368.8 mAh g\(^{-1}\).

Vinayan et al. reported using graphene/sulfur composite as a representative candidate for rechargeable Mg/S battery.
Graphene/S nanocomposites exhibited an initial discharge/charge capacity of 1024/548 mAh g⁻¹, retaining 219/236 mAh g⁻¹ after 50 cycles at a current density of 20 mA g⁻¹. The high rate of rechargeability was credited to a well-dispersed uniform layer of sulfur species over graphene flakes (see Figure 7a,b). The graphene flakes behave as a buffer layer, and the oxygen functional groups over its surface help buffer the volume change upon cycling, as depicted in Figure 7c,d. Besides that, the high binding affinity of the functional groups toward the discharge products helps minimize polysulfide dissolution.

Another possible way to mitigate polysulfides dissolution is through a unique structure of porous graphdiyne-filled active sulfur (SGDY); the structure is schematically depicted in Figure 7e.[174] The unique attributes of the layered-structured host for S-cathode (see Figure 7f) lead to a discharge/charge capacity of 1124.9/539.3 mAh g⁻¹ at a current density of 50 mA g⁻¹, retaining a capacity of 77.3% after 36 cycles. Despite all these efforts to physically trap the sulfur particles, Mg/S cell showed a loading of about 1 mg cm⁻² and an attenuated rate of decline in capacity with an increase in current density, which may be due to the formation of a resistive cathode interphase layer over the electrode.

3.2.2. Chemisorbed S-Host

During the discharge reaction of the Mg/S cell, the shuttle effect becomes dominant due to the poor affinity of the host toward discharge products. The chemisorption of the polysulfides is a prominent strategy for alleviating the polysulfide dissolution and shuttling effect.[175,176] Zeng et al.[177] proposed a metal-stabilized S-cathode for Mg/S batteries. A composite of S/C coated onto the current collectors, where copper chemically stabilizes the sulfur particles, resulting in copper sulfides which shows a higher binding affinity toward polysulfides. The Mg/S cell with the first discharge capacity of about 659 mAh g⁻¹ retained 113 mAh g⁻¹ after 20 cycles at 10 mA g⁻¹. Inspired by the high catalytic activity and strong chemical interactions offered by copper, He and co-workers studied the effect of copper nanoparticles on CNFs as an additive for S-cathode (see Figure 8a).[178] The S-cathode with Cu@CNF delivered a specific capacity of about 452 mAh g⁻¹ at 1 C after 100 cycles. Though Cu nanoparticle coating leads to attaining a higher initial discharge capacity, shuttling of polysulfides could not be alleviated. Besides, the sulfur loading was limited to 0.06–0.12 mg cm⁻². They further studied the cathode with the addition of a higher amount of copper content, a slightly higher S-loadings could be achieved (0.35–0.42 mg cm⁻²). The development is, however, barred with a relatively high cost of copper metal. Zhou and co-workers reported intriguing studies on MOF-derived carbon frameworks codoped with nonmetal nitrogen and a metal dopant of cobalt particles as the host for sulfur particles (see Figure 8b).[179] The composite cathode based on ZIF–C precursor attained a high S-content of about 47%. The Mg/S cell could deliver an initial discharge capacity of ≈700 mAh g⁻¹ at 0.1 C. A capacity of ≈400 mAh g⁻¹ could still be preserved after 150–250 cycles at 1 C. A carbon framework with heterogeneous doping resulted in a superior Mg/S battery performance.

Vinayan and co-workers examined a hybrid nanostructure of nitrogen-doped graphene and MWCNT as the cathode (S/NC)
for Mg/S batteries. The electrochemistry of the cell was investigated with different amounts of S-loadings varying from 0.5 and 3 mg cm\(^{-2}\). During the discharge/charge cycle, operando Raman analysis were carried out to comprehend the transformation of bulk sulfur (S\(_8\)) to intermediate discharge products and finally to its end product (i.e., MgS) and studied the reverse kinetics upon charging (i.e., from MgS to short- and long-chain to elemental sulfur) (Figure 8c). The spectral measurements further confirmed the generation of a nanocrystalline phase of magnesium sulfide as the end product during discharge reaction. Theory calculations were performed to understand the charge/discharge characteristics further. An increase in resistance and overpotential was also considered as the consequence of the migration of polysulfides. The composite cathode with an S-loading of about 3 mg cm\(^{-2}\) was cycled at 0.02 C, delivering an initial discharge capacity of 431 mAh g\(^{-1}\) while retaining 53% of its capacity after 50 cycles. More recently, Zhao et al.\[^{181}\] developed a heterostructure of Co\(_3\)S\(_4\)@MXene-S cathode composite. Co\(_3\)S\(_4\)@MXene-S cathode delivered a specific capacity of about 1220 mAh g\(^{-1}\) at 0.2 C. After 100 cycles, the cathode could maintain a specific capacity of \(\approx\)528 mAh g\(^{-1}\). They have observed that the MXene framework provides a suitable structure for promoting ion transfer; meanwhile, Co\(_3\)S\(_4\) as an electrocatalyst creates a strong chemical interaction between the host and polysulfides species, attenuating the shuttle effect.

3.2.3. Covalent-Bonded S-Host

Covalently fixed composites with the ability to confine sulfur are also adopted for rechargeable Mg/S batteries. Itaoa et al.\[^{184}\] constructed Mg/S cell with a cathode comprising elemental sulfur and bis[alkenyl]compound. The electrochemical performance of two types of sulfur-containing composites, viz., 1) a crown-like cyclic ether unit of bis(undec-10-enoyloxymethylbenzo)-18-crown-6-ether (BUMB18C6) and 2) a liner ether unit of undecenoic acid, oxybis(2,1-ethanediyl-2,1-ethane-diyl) ester (UOEE), were investigated. The cell containing sulfur composite with BUMB18C6 and UOEE exhibited an initial discharge capacity of 460 and 495 Ah kg\(^{-1}\), respectively. At the tenth cycle, the cell, however, delivered a capacity of 68.1 and 0.18 Ah kg\(^{-1}\) for BUMB18C6-S and UOEE-S-based electrodes, respectively. The better performance of the sulfur-based BUMB18C6...
electrode was credited to the cyclic ether unit, which promoted the formation of conduction paths for magnesium ions. Polyacrylonitrile (PAN) composites have also been examined and widely used as a cathode owing to their high conductivity and infusion of sulfur products.\[185\] Wang and co-workers tailored a sulfurated PAN cathode of 0.6 mg cm\(^{-2}\) S-content.\[186\] Figure 9a schematically shows the redox mechanism of the SPAN cathode in the ambiance of Mg\(^{2+}\) ions, and it is believed that Mg\(^{2+}\) ions are well confined into the cathode’s matrix. Furthermore, Wang and co-workers analyzed Mg/S battery based on SPAN composite S-cathode.\[187\] Based on high-resolution X-ray photoelectron spectroscopy (XPS) data (see Figure 9b), peaks were observed when the pristine SPAN cathode was discharged to 1.5 and 0.1 V. A peak at 161.9 eV corresponds to C\(\equiv\)S in the SPAN cathode, assigned to sulfur species, and thus, confirms the continuous formation of polysulfides on reduction. The SPAN cathode and Mg powder cell could deliver a higher discharge capacity of 500 mAh g\(^{-1}\) and an energy density of 422 mWh g\(^{-1}\). Given that the interactions among the particles can easily be disconnected upon vigorous volume changes, it has become challenging to maintain a high S-loading in a cathode composite under a continuous cycling process.\[188\] Zhang et al.\[189\] recently analyzed an amorphous sodium polyacrylate (PAAS)-based SPAN cathode which delivered good electrochemical performance with a higher retention rate and cycling stability and formed a 3D network upon cross-linking. A high cohesion and adhesion force could be maintained to provide a crack-free and uniform electrode surface even after cycling, as depicted in SEM images (Figure 9c-e). PAAS-based SPAN cathode delivered lower voltage polarizations and thus, improving the rate capability of the Mg/S battery systems.

### 3.2.4. Hybrid S-Host

In the quest for rechargeable Mg/S batteries, Muthuraj et al. introduced the concept of magnesium sulfide catholyte for the first time for an Mg/S battery.\[190\] A freestanding cathode with a liquid phase of Mg\(_x\)S\(_y\) infiltrated into polyaniline-coated carbon cloth (CC@PANI@Mg\(_x\)S\(_y\)) was fabricated. Attributing to the low energy, the stable stoichiometry of magnesium polysulfides and polyaniline as an immobilizer, Mg/S cell with CC@PANI@Mg\(_x\)S\(_y\) cathode maintained a specific capacity of...
514 mAh g⁻¹ with a stable performance up to 25 cycles at a current density of 20 mA g⁻¹ (see Figure 9f.g). High reversibility with a reasonable S-utilization was observed for the cell with CC@PANI@MgSₓ cathode. Nevertheless, the Mg/S cell with CC@PANI@MgSₓ cathode was unable to show improved performance beyond 25 cycles. Therefore, it is necessary to construct an effective electrode with more substantial adsorption capability toward sulfur and its discharge species to achieve an energy-rich option for practical applications.

3.3. RT-Al/S Battery System

The demand for high-energy and low-cost batteries has brought aluminum-based batteries to the researchers’ attention.[191–193] The redox coupling between aluminum and sulfur provides an energy-dense and safer option than the other metal–sulfur system.[194] A three electron transfer reaction makes the anode exhibit a very high specific capacity of about 2988 mAh g⁻¹. The reduction potential of Al is sufficiently negative (−1.7 V vs SHE) to exhibit a high energy density.[195,196] Besides that, a theoretically high energy density of 1340 Wh kg⁻¹ can be achieved with the Al/S system, which is multifold compared to that of commercial LiCoO₂-graphite cells.[197]

The aluminum-based chemistry has long been researched; however, Tao and co-workers recently demonstrated the first rechargeable Al/S.[197] With burgeoning growth toward rechargeable Al/S technology, significant progress is made to extend the cycle life and enhance the Coulombic efficiency, yet the commercial implementation of such systems is way far. Some of the critical issues, such as, formation of a passivation layer over Al metal anode, sluggish reaction kinetics, and hydrolysis of discharge products on the electrodes’ surface, cause a massive gap in the feasibility of this system.[194,198] Unlike the monovalent alkali metals, aluminum-based electrochemistry is comparably stable toward aqueous and non-aqueous based electrolytes.[199–201]

3.3.1. Physically Adsorbed S-Host

Besides forming a passivation layer over the Al metal anode, the development of the Al/S system is critically impeded due to the lack of a suitable sulfur cathode. Constant efforts have been laid down to overcome the obstructions mentioned above associated with the sulfur cathode, including the physical confinement of sulfur and polysulfide species using carbonaceous-based components.[202–204] Cohn et al.[205] studied the electrochemical reduction kinetics of the discharge products of the sulfur cathode (i.e., S/C cathode). The as-fabricated Al/S cell displayed a remarkably high specific capacity of about 1500 mAh g⁻¹ based on the weight of sulfur. An energy density as high as 1.7 Wh g⁻¹ could be achieved through this approach. Despite the competitive value of the energy density and specific capacity, the Al/S system lacks cycling stability. Xia et al.[206] developed an ionic-based Al/S battery with an S/C cathode, which exhibited an initial capacity of about 113.0 mAh g⁻¹ and maintained a discharge capacity of 104.0 mAh g⁻¹ after 40 cycles. Gao and co-workers designed an activated carbon cloth/S composite as the cathode to demonstrate a stable cycling performance of 20 cycles with a specific capacity of about 1000 mAh g⁻¹. The improved reversibility can be attributed to the increased oxidation kinetics of AlSₓ upon charging, which physically confines the aluminum sulfide species within the microporous (<2 nm) structure, resulting in shortened diffusion path for aluminum ions and a more prominent reaction area.

A reversible RT-Al/S battery based on a nonaqueous system with a strategically well-designed CNF/S matrix was demonstrated by Xu et al.[207] During charge/discharge reactions, a reversible transformation between Sₓ²⁻ and Sₓ²⁻ (1 ≤ x ≤ 6) species was observed during charge/discharge reactions. The CNF matrix on S-cathode could mitigate the dissolution of polysulfides and minimize the electrode polarization. The persistence of the voltage plateau suggests the occurrence of solid-state conversion reactions in Al/S cells.[208] The diffusion barrier calculation supported by theory calculation predicts a 15-fold faster rate of reaction in addition to a lower energy barrier per molecule. The formation of a passivation layer on the surface of the Al anode and the hydrolysis AlSₓ in the cathode has become significant roadblocks in the development of the Al/S battery. Traditionally used organic electrolytes delivered appealing yet inherently unsafe applications due to their high flammability and corrosiveness with toxicity and air sensitivity impediments. Comparatively, discovering aqueous-based electrolytes has shown favorable insights toward developing a safe and cost-effective battery system. The battery system for stationary storage applications must exhibit a high long cycle life, a low cost per cycle, and high safety, which could be achieved through a battery technology that relies on earth-abundant electrode materials and aqueous electrolytes.[209,210] As a result, a water-in-salt electrolyte with carbonized MOF precursor was demonstrated to restrain the hydrolysis of discharge products (AlSₓ) while maintaining a high open-circuit voltage of about 3.0 V.[211] The battery exhibited an initial specific capacity of 1410 mAh g⁻¹ and reversible capacity retention of 420 mAh g⁻¹ after 30 charge/discharge cycles at 200 mA g⁻¹ while delivering a high Coulombic efficiency 97%. In addition to MOF-based cathode composites, CNT-based S-host has also been examined for Al/S batteries. For instance, S-cathode comprises a self-woven CNF paper that delivered a specific capacity of ≈1000 mAh g⁻¹ for the initial discharge cycle and retained up to 600 mAh g⁻¹ after 50 charge/discharge cycles.

Smajic et al.[212] investigated cathode composed of sulfur and a single-walled CNTs (SWCNTs) for nonaqueous Al/S battery. The electrochemical characteristics of the SWCNT/S cathode deliver a high discharge capacity of 1024 mAh g⁻¹ with a high S-utilization of about 61%. The Coulombic efficiency was observed to approach close to 89%. Despite an excellent conductive pathway and E/S ratio (17 μL mg⁻¹), the decay in capacity could be controlled marginally. The SWCNT/S cathode provided good physical support. However, the charge transfer kinetic reactions were inhibited due to poor interaction between the host and sulfur species (i.e., discharge products). It was evident from the studies that the synergy between sulfur and carbon-based composites offers a limited physical contact (i.e., bound together by weak van der Waals forces) and a slow charge transfer process. The electrochemistry of Al/S batteries is intriguing. The underlying role of carbon-based materials and storage mechanisms needs to be further studied.
Jiang and co-workers recently demonstrated an Al/S cell using an S-cathode comprising multiwalled CNT and sulfur particles.\textsuperscript{213} Al/S battery delivered the first discharge capacity of 453 mAh g\textsuperscript{-1} while retaining a specific capacity of 358 mAh g\textsuperscript{-1} after 200 cycles, as shown in Figure 10a. Despite the improved mechanical stability, the battery performance degrades sharply upon increasing sulfur content from 15 to 50 wt%. Recently, Zhang et al.\textsuperscript{214} synthesized a sulfur cathode for an Al/S battery composed of hollow carbon nanospheres (HC) as a potential host for the sulfur cathode. A hollow carbon matrix with a highly porous network is believed to provide great diffusion sites for ions, besides a high specific surface area (1344.87 m\textsuperscript{2} g\textsuperscript{-1}) for adsorption and change in volume accommodation. TEM images in Figure 10b,c revealed a cave-like porous morphology, which leads to well dispersion of sulfur particles and effective entrapment of sulfur discharge products. The electrochemical performance was conducted for the HC/S cathode that could be cycled for at least 28 cycles, and retaining a capacity of 378 mAh g\textsuperscript{-1}.

It is apparent from the studies that the high irreversibility of AlS\textsubscript{2} could not be fully controlled, resulting in limited stability and inefficient cycling performance.

3.3.2. Chemisorbed S-Host

Dharmasena and co-workers initially demonstrated an Al/S battery based on a concentrated polysulfide catholyte to demonstrate an energy-dense system.\textsuperscript{215} An open-circuit voltage of about 1.3 V could be maintained; the energy density encountered was remarkably low. Similarly, Litch et al. put forward an Al/S cell with an Al metal and molten sulfur and studied the polysulfide redox kinetics of the cell.\textsuperscript{216} Despite the relatively high operating temperature, the system was severely obstructed with lower energy density values (170 Wh kg\textsuperscript{-1} based on dry materials and 110 Wh kg\textsuperscript{-1} based on total battery materials) and limited cycle life.

The nonpolar nature of carbon-based composites shows a weak interaction with sulfur and its discharge species, causing sluggish reaction kinetics and polysulfide shuttling. To promote the interaction, transition metal sulfides with a high sulfphilic property can open up pathways to confine sulfur and its species, along with higher reaction kinetics.\textsuperscript{217–219}

Geng and co-workers attempted to achieve reversible intercalation and extraction of aluminum ions in Mo\textsubscript{6}S\textsubscript{8} cathode with good electrochemical performance.\textsuperscript{220} The as-synthesized cell resulted in a discharge capacity of 148 mAh g\textsuperscript{-1} in the initial cycle while stabilizing at 70 mAh g\textsuperscript{-1} after 50 cycles. A Coulombic efficiency of \approx 100 % suggests gradual entrapment of ions in the Mo\textsubscript{6}S\textsubscript{8} morphology. In addition, the electrode was investigated for its rate capabilities at different current densities ranging from 6 to 120 mA g\textsuperscript{-1}. Another group designed a hybrid composite of graphene, CoS\textsubscript{2}, and sulfur as the cathode for the Al/S battery with an S-loading of 0.2–0.4 mg cm\textsuperscript{-2}.\textsuperscript{221} Homogenous distribution of sulfur was achieved on the matrix with an improved S-content of 60 wt% as determined by SEM images and EDS elemental mapping (see Figure 11a). With enhanced suppression of polysulfides and decreased polarization effect, the Al/S cell could deliver a first discharge capacity of 680 mAh g\textsuperscript{-1} and remain at 1145 mAh g\textsuperscript{-1} after 38 stable cycles at 50 mA g\textsuperscript{-1}. Based on the critical issue of limited capacity and poor cycle span, one strategy is to develop an S-host with nonmetal dopants such as nitrogen. As such, Wang et al.\textsuperscript{222} reported an S-cathode composed of nitrogen-doped in a 3D network of multistage porous carbon. The pore structure of macropores and mesopores were nested in order, as demonstrated in SEM images (Figure 11b,c). The 3D hierarchical carbon matrix could effectively provide space to load the active material up to 51 wt% and the nitrogen dopant could enhance sulfur chemisorption. The N-C/S composite cathode delivered a high initial discharge capacity of 1800 mAh g\textsuperscript{-1} while retaining a capacity of 700 mAh g\textsuperscript{-1} after 20 cycles.

Recently, single-atom catalysts have been introduced into cathode engineering for metal–sulfur battery systems due to their high catalytic efficiency for improving redox conversion reactions.\textsuperscript{219} In contrast to the adsorption capability of nonmetal dopants, single metal atoms or clusters provide a dual mechanistic effect of adsorption and catalytic effect. For instance, Guo et al.\textsuperscript{223} implanted a stabilized copper within the skeleton of a well-known carbonized MOF (HKUST-1), which improved reversibility for the Al/S battery. Dark-field TEM images in Figure 11d,e indicate the well-intact microbelt-like morphology of carbonized HKUST-1 even after successfully incorporating S-loading within the matrix. Attributing to the conductivity of copper ionic clusters, the kinetic barrier for the conversion reactions of sulfur was significantly decreased and resulted in a lower
charge transfer resistance with 34 wt% S-content. At a current density of 1 A g\(^{-1}\), the cathode could be met with a high initial discharge capacity of 1200 mAh g\(^{-1}\). A reversible capacity of 460 mAh g\(^{-1}\) could be retained for 500 stable cycles with 95% Coulombic efficiency. Guo et al.\[224\] demonstrated the electrochemical catalytic effect of cobalt (II, III) decorated on a carbon skeleton as the host for S-cathode. The successful catalysis of Co (II, III) on the electrochemical conversion reaction of sulfur yielded a lower voltage hysteresis of 0.5 V and improved S-utilization in the cathode. XPS analysis suggests high chemical binding and catalytic effect provided by the cobalt cluster in S-cathode, which may be due to the formation of strong chemically bonded Co\(_x\)S\(_y\) and shift in valence states of cobalt during the charge/discharge cycles. With resultant improved kinetics of S-cathode, the rechargeable Al/S battery could deliver a capacity retention of 500 mAh g\(^{-1}\) at a current density of 1 A g\(^{-1}\) after 300 cycles in addition to a specific capacity of 300 mAh g\(^{-1}\) even when the cell was cycled at 3 A g\(^{-1}\).

However, the utilization of cobalt in batteries sets off several challenges such as its scarcity, sever dissolution effect, deterioration, expensive mining strategies, and others.\[225\] Due to price fluctuations and constraints in the supply of cobalt, the momentum of using electric vehicles and grid-storage applications has come to a standstill which has prompted the researchers to seek alternative cost-efficient metals.\[226,227\] As a result, Bhauriyal et al.\[228\] employed "a 2D Cu-benzenehexathial (Cu-BHT) MOF (Figure 11f)" as a potential anchoring host for S-cathode in Al/S battery. The conductive nature of Cu-BHT-MOF could successfully compensate for the intrinsic insulating nature of sulfur-based products. A critical study was conducted further to analyze the affinity of Cu-BHT-MOF toward Al polysulfides, as illustrated in Figure 11g. Based on the calculations, Cu-BHT-MOF binding energies increased from S\(_8\) to Al\(_2\)S\(_3\) in the range 1.11 to 3.56 eV. They showed a remarkably higher binding affinity toward low-order polysulfides, which can be credited to the optimized formation of Al─SCu-BHT and Cu─SM bonds. Following the charge density distribution between aluminum polysulfides and Cu-BHT-MOF, an extent of charge transfer increment from Al\(_2\)S\(_{18}\) to Al\(_2\)S\(_3\) and the lowest for Al\(_2\)S\(_{12}\) could be observed. As represented in Figure 11h, a network of agglomerated Cu-BHT monolayer could be demonstrated, delivering a synergistic dual function of Al─SCu-BHT and Cu─SM bonds, which results in minimized kinetic barrier for polysulfide redox reactions due to high chemisorption and high S incorporation of 45.81 wt% in the host framework.

A thoroughgoing demonstration of a 2D layered composite of MoS\(_2\), WS\(_2\), and boron nitride (BN) was comprehensively studied for their immobilization effect on sulfur species.\[229\] Due to their exposed sites and large surface area, transition metal dichalcogenides sulfides (MoS\(_2\), WS\(_2\)) and nonsulfides (BN) were studied as the sulfur fixers for a high-performance Al/S battery.
Consequently, the highest capacity with 532 mAh g\(^{-1}\) was delivered by BN/S/C cathode at 100 mA g\(^{-1}\). Furthermore, a resultant apparent discharge plateau at \(\approx1.15\) V versus AlCl\(_4^+\)/Al and unparalleled long-term stability of about 300 cycles with 94.3% Coulombic efficiency could be demonstrated for the Al/S battery system.

### 3.3.3. Covalent-Bonded S-Host

As a new emerging class of hosts for a sulfur cathode, covalently fixing sulfur in various polymer composites provides strong bonding to entrap sulfur at the molecular level effectively. Up to date, a variety of covalent-bonded materials have been addressed in Li/S battery systems to enable stable immobilization of sulfur moieties.\(^{[230–232]}\) Sulfurized polyacrylonitrile (SPAN) is a polymeric compound that constitutes a typical nitrile group bonded with sulfur, and the molecular structure is composed of pyrroline rings.\(^{[113,233–236]}\) Owing to good conductivity of \(\approx10^{-4}\) S cm\(^{-1}\), Wang and co-workers investigated the stability of SPAN as a cathode for Al/S batteries.\(^{[100]}\) Based on the cyclic voltammogram technique (Figure 12a), different anodic and cathodic peaks were shown and an activation process in the initial few cycling tests. As a result, an activation process was detected in the initial few cycles at \(\approx0.3\) V versus Al/Al\(^{+}\). An initial discharge capacity of 320 mAh g\(^{-1}\) was observed, with its highest peak observed at 605 mAh g\(^{-1}\) and subsequently retaining a capacity of 201 mAh g\(^{-1}\) after 20 cycles (see Figure 12b). At different current densities of 0.025, 0.05, 0.1, 0.2, and 0.5 A g\(^{-1}\), the Al/S cell demonstrated a superior rate capability of 343, 258, 160, 93, and 54 mAh g\(^{-1}\), respectively (Figure 12c).

### 3.4. RT-Zn/S Battery System

Attempts have been made to study various metal–sulfur systems, for instance, Li/S, Na/S, Mg/S, and Al/S. However, Zn/S chemistry has seldom been investigated. Based on the two valence electrons, Zn possesses a theoretical specific capacity of \(\approx824\) mAh g\(^{-1}\), making it an attractive contender for achieving an energy-dense battery system.\(^{[237,238]}\) Besides that, a reductive potential of \(-0.76\) V versus SHE makes it suitable for both aqueous- and nonaqueous-based electrolytes.\(^{[239–241]}\)

There is a dearth of studies on Zn–S battery chemistry, which could be due to the challenge in constructing a Zn anode system, besides slow or sluggish kinetics of the sulfur cathode. Recently, aqueous-based electrolyte systems have been examined for Zn/S battery systems. In 2020, Zhao and co-workers reported a reliable Zn/S system based on a polysulfide system and an optimized aqueous electrolyte.\(^{[242]}\) A liquid film that comprises CF\(_3\)SO\(_3^−\) in 4-(3-butyl-1-imidazolio)-1-butanesulfonate ionic liquid facilitates Zn\(^{2+}\) ions. At a current density of 0.3 A g\(^{-1}\), the Zn/S battery delivered a high capacity of 1148 mAh g\(^{-1}\) with a specific density of 724.7 Wh kg\(^{-1}\). The Zn/polySulfide system exhibited a cyclic performance of 700 cycles at 1 A g\(^{-1}\), retaining a capacity of \(>235\) mAh g\(^{-1}\). A reduced transformation from S\(_{6}^−\) \(\rightarrow\) S\(^{2−}\) was obtained through ZnS during discharging. Further concentrating the salt solution, reversibility of the Zn/S system could be enhanced and resulted in extended cycle life of 1600 at a current density of 1 A g\(^{-1}\) with retained capacity values of 204 mAh g\(^{-1}\).

In addition to the liquid electrolytes, a solid electrolyte acted as a shield to prevent the shuttling of polysulfides, maintaining a reversible capacity of 822 mAh g\(^{-1}\) after 50 cycles with a Coulombic efficiency of \(\approx100\%\).\(^{[243]}\) Li et al.\(^{[244]}\) stabilized the plating/stripping of Zn\(^{2+}\) using an aqueous electrolyte of Zn(CH\(_3\)COO)\(_2\) with 0.05 wt\% I\(_2\). I\(_2\), as an additive, served as a channel for Zn ions to travel, thus allowing reduced voltage hysteresis of S-cathode with CNT-50 as the host. A high energy density of 502 Wh kg\(^{-1}\) and an overwhelming capacity of 1105 mAh g\(^{-1}\) with a relatively flat discharge voltage of 0.5 V could be demonstrated. The development of the Zn/S battery system can be carried forward more comprehensively. However, this technology’s viability still has a long way and requires better understanding to reach its practicality.

A detailed comparison of different cathode composites with their summarized performance data for Na/S, Mg/S, and Al/S is illustrated in Table 3.

### 4. Outlook and Future Perspective

It is evident from the studies that the host should meet some basic requirements, for instance, guaranteed facilitation of electronic/ionic transportation, large porous matrix to ensure high sulfur confinement, and polysulfide entrapment to alleviate the shuttling mechanism and buffer the volume changes.\(^{[245–248]}\) The structural modification of sulfur cathode has been experimented with to improve both S-loading and its utilization to boost the electrochemical performance of metal sulfur.

Numerous attempts have been devoted to designing a novel...
Table 3. Performance data for different matrices of sulfur cathode for RT-Na/S battery that is reported in the literature.

| Metal–Sulfur system | Cathode composite | Synthesis route | Electrolyte | The unique contribution of S-host |
|---------------------|-------------------|----------------|-------------|----------------------------------|
| Na/S                | Carbon fiber cloth/S & CaS | Solution impregnation strategy | 1.5 M NaClO₄ and 1.0 M NaNO₃ in tetraethylene glycol dimethyl ether | The 3D host structure demonstrated good conductivity and flexibility. Due to their highly interconnected network, the cathode allowed high uptake of electrolytes and thus, facilitated ions/electrons transfer and good absorption of polysulfides. |
|                    | Nanocarbon-promoted comm- S & CaS | Ball milling process | Gel polymer electrolyte: 1 M NaPF₆/diglyme | The processed nanocarbon enhanced the binding affinity of the host toward sulfur and its moieties, resulting in mitigation of the polysulfide shuttling effect, which simultaneously accelerates the conversion kinetics of the sulfur. |
|                    | Sugar-derived microporous carbon/S & CaS | Isothermal vapor phase infiltration | 1 M NaPF₆ and 0.25 M NaNO₃ in TEGDME | Low-cost sucrose-derived composite alleviated the reactivity of electrode and electrolyte and, thus, the loss of discharge intermediates into the electrolyte. |
|                    | Mesoporous carbon hollow nanospheres/S & CaS | Sol–gel method | 1.0 M NaClO₄ | Interconnected and interlaced mesoporous carbon scaffold as the host showed high tap density and good structural stability even with enhanced loading, and the conductive network could supply active diffusion pathways. In addition, the hollow spaces allowed encapsulation of a high amount of sulfur. |
|                    | Ultramicroporous carbon/S & CaS | Single-step polymer carbonization | 1 M NaClO₄ in EC/DEC | Due to ultramicroporous carbon’s high specific surface area, the host could successfully confine sulfur and its intermediate polysulfides. |
|                    | Activated ultramicroporous coffee carbon/S & CaS | Annealing strategy | 1.0 M NaClO₄ | Space confinement of coffee-derived composite with small sulfur molecules (S₂–S₄) confined in slit ultramicroporous network provided effective suppression of shuttling effect and allowed tuning of sulfur content. |
|                    | Porous carbon microspheres/S & CaS | Chemical vapor deposition | 1.0 M NaClO₄ | Unique double-shell carbon: microsized carbon shells allowed shuttling of sulfur products, and hollow carbon nanobeads inside provided buffer spaces to accommodate sulfur and volume expansion during cycling. |
|                    | Carbon hollow nanobubbles@Porous carbon nanoﬁbers/S & CaS | Electrospinning technique | 1.0 M NaClO₄ | Owing to the high electrical conductivity and adsorption capability, the structurally integrated 3D host delivered good entrapment of polysulfides during cycling. |
| Mg/S                | CNF/S | Dispersion and peeling-off techniques | [((HMDS)₂ Mg] in TEGDME based non-nucleophilic electrolyte | The CNF coating interlayer behaved as an adsorbing layer to restrain the diffusion of MgPS and enhance its reversibility. |
|                    | Microporous carbon/S & CaS | Ball milling and heat treatment | (PhMgCl₂–AlCl₃)/tetrahydrofuran-based nucleophilic electrolytes | A rational combination of small sulfur species (S₂–S₄) and large S₈ molecules allowed a high dispersion inside the microporous carbon matrix. A strong interaction exists within the electrode to protect sulfur species from the electrolyte. |
|                    | rGO/S & CaS | Hummer’s method and thermal exfoliation | [((HMDS)₂ Mg] in tetraglyme | The composite cathode consists of certain oxygen functional groups that enabled a robust binding effect with sulfur and its discharge products, resulting in immobilization of sulfur moieties. |
|                    | Sulfide graphdiyne & CaS | Thermal synthesis | All-phenyl complex (APC)-based nucleophilic electrolyte with LiCl | Unique architecture of a conductive carbon network with short S₈ energy-storing units along with a high ionic pathway has been found to suppress polysulfide dissolution. |
| A/S                | Carbon/S & CaS | Solution-processed slurry based method | AlCl₃/EMICl based ionic electrolyte | A sulfur cathode with varied molar ratios of electrolyte has been investigated, resulting in high material utilization and high energy density. |
Table 3. Continued.

| Metal–Sulfur system            | Cathode composite    | Synthesis route                  | Electrolyte                          | The unique contribution of S-host                                                                 |
|-------------------------------|----------------------|----------------------------------|--------------------------------------|---------------------------------------------------------------------------------------------------|
| Activated carbon cloth/S       | Melt-diffusion technique | AlCl_3/EMICl based ionic electrolyte | AlS_n, sulfur products were well-confined into the microporous carbon matrix, delivering a substantially improved reversibility. |
| CNF/S                          | Vacuum filtration   | AlCl_3/EMICl based ionic electrolyte | SWCNT-coated separator minimizes the polarization effects, which results in the suppression of polysulfides dissolution and diffusion. |
| Mesoporous carbon/S            | Melt-diffusion technique | AlCl_3/NBMPBr | Al_3Cl_6Br^- in a mesoporous carbon host accelerates the kinetic reaction rate up to 15-fold, increasing sulfur-S utilization. |
| Carbonized-ZIF/S               | Carbonization process | LiTFSI in Al[EMIm]Cl-based ionic electrolyte | Water-in-salt electrolyte with special qualities impedes the hydrolysis of polysulfides and deliver repeated redox reaction in MOF-based S-cathode. |
| CNF/S                          | Vacuum filtration and activation process | LiTFSI in Al[EMIm]Cl-based ionic electrolyte | A unique approach of the CNF cathode matrix enhanced the reversibility through chemical reactivation of AIPS. |
| SWCNT/S                        | Nondestructive sublimation–deposition Method | AlCl_3/[EMIm]Cl | SWCNT/S cathode exhibited improved interaction, and their underlying mechanisms of charge-storage kinetics were investigated. |
| MWCNT/S                        | Heat treatment      | AlCl_3/acetamide | Owing to the unique nanostructure and good electrical conductivity, MWCNT showed high mechanical and chemical stability, thus exhibiting a higher performance battery. |
| Hollow carbon spheres/S        | Annealing process   | AlCl_3/[EMIm]Cl | The cave-like porous structure provides sufficient space to encapsulate sulfur, confining AIPS. |

Chemisorbed sulfur composite

Na/S

N-cZIF–8/S                       | Carbonization technique | 1 M NaClO_4 in TEGDME | A high concentration of nitrogen (~18 at%) and synergetic effect of nanoporous carbon could effectively entrap the polysulfides. |

N,S-doped hierarchical porous carbon[111] | Customized roll-to-line strategies | Na_2S in TEGDME | A highly doped carbon matrix demonstrated a robust route to inhibit electrode-electrolyte reactions and suppress the dissolution of sulfur moieties. |

Nitrogen-doped graphene nanosheets/sulfur[114] | Chemical reaction deposition strategy and low-temperature heat treatment | 0.8 M NaClO_4 in EC/DMC | Owing to highly conductive network of the host, the sulfur could be easily intercalated into the expanded graphene layers, establishing a high amount of sulfur content within the matrix. |

MOF-derived S,N-doped porous carbon[115] | Vapor-infiltration method | 1 M NaClO_4 in PC with 5 wt% FEC | Doped S and N allowed increased polarization of carbonaceous products to provide high chemical affinity toward diffused polysulfides, and the 3D matrix provides a large surface area for sulfur. |

Fe-hollow carbon nanospheres/S       | Sol–gel process | 1 M NaClO_4 in PC/EC with wt% FEC | Due to the high chemical adsorption of doped atomic iron, they served as an electrocatalyst to reduce long-chain to short-chain polysulfides during the charge/discharge process. |

Atomic cobalt-hollow carbon nanospheres/S | Sol–gel process | 1 M NaClO_4 in PC/EC with 5 wt% FEC | Synergistic reduction of polysulfides to Na_2S with enhanced conversion mechanisms owing to electrocatalytically active atomic cobalt on hollow spheres. |

Nickel–nitrogen-doped carbon fibers/S | Electrostatic spinning process | 1 M NaClO_4 in TEGDME | The Ni hollow unit allows buffer spaces for volumetric fluctuations and speeds up sulfur’s conversion reaction kinetics from long-chain polysulfides to Na_2S. The nickel atoms act as catalytic centers to provide a high physical and chemical adsorption effect toward NaPS. |
Table 3. Continued.

| Metal–Sulfur system | Cathode composite | Synthesis route | Electrolyte | The unique contribution of S-host |
|---------------------|-------------------|----------------|-------------|----------------------------------|
| Nitrogen-doped carbon nanospheres loaded with Fe[123] | Carbothermal reduction followed by calcination process | 2 M NaTFSI in PC/FEC | The meager amount of iron (≈0.14 at%) in the N-doped carbon matrix provided enhanced chemical interaction with polysulfides to avoid its further dissolution into the electrolyte. |
| Carbon wrapped cobalt nanoparticles on graphene aerogel/S[124] | Thermal treatment | 1 M NaClO₄ in TEGDME | The dual synergistic function of conductive/flexible graphene and electrocatalytic effect of transition metal nanocobalt resolved the issue of low reactivity of sulfur and large volume expansion/contraction during the cycling process. |
| Gold nanodots on hierarchical N-doped carbon microspheres/S[125] | HCl etching process | 1 M NaClO₄ in PC with 5 wt% FEC | Gold nanodots wrapped on hierarchical structures of nitrogen-doped spheres delivered complete reversible reactions in the cathode by allowing electrocatalization of low kinetics reduction of Na₂Sₓ to Na₂S or Sₓ. |
| CNF-L@Co/S[281] | Electrospinning and solution method | 1 M NaClO₄ in EC/DEC | A 3D branch-leaf-like network with a highly conductive pathway could provide large voids and multiple active sites. Furthermore, cobalt nanodots could ensure the formation of a unique layer of Co–S–Na on the cobalt surface to ensure enhanced reduction reactions of NaPS. |
| Ni-MOF-2D/S[282] | Hydrothermal strategy | Na₂S and S in EC/PC | Electron-state Ni-centered entrapment of NaPS could be achieved via 2D MOF structured matrix. The dynamic state of Ni centered in the carbon framework allowed tuning of sodium and sulfur discharge products. |
| C/S/BaTiO₃@ titanium dioxide[132] | Electrospinning technique and atomic layer deposition | 1 M NaClO₄ in EC/DEC | Synergetic structure of BaTiO₃ nanoparticles with firm polar surface and ferroelectric effect can provide spontaneous polarization effect to produce sizeable electric dipole moments and exhibit stabilized ions transport interface. |
| TiN-TiO₂@MCCFs/S[133] | Electrospinning and nitridation process | 1 M NaClO₄ in EC/PC with 5 wt% FEC | Dual function of high electrocatalytically active TiN and strong polar chemisorbed transition TiO₂ provides a well-stabilized sulfur cathode through rapid electrocatalysis to insoluble NaPS. |
| Molybdenum sulfide[137] | Chemical oxidation | 1 M NaPF₆ in DEC/FEC | Sulphilic rich component MoSₓ with relatively low-cost depicted a distinct chemical-bonded environment with bridged-sulfide bonds that enabled high sulfur content inside the matrix. |
| Core–shell ZnS and CoSₓ/S[283] | Carbonization and sol–gel process | 1 M NaClO₄ in DEC/EC with 5 wt% FEC | Besides the flexible nature of conductive carbon architecture to provide abundant enclosed spaces for storing Sₓ, multisulphilic sites of ZnS and CoSₓ augment the catalysis reaction toward the complex sulfur conversion process. |
| CoSₓC/S[134] | Simple reflux method | 1 M NaClO₄ in TEGDME | Unique hierarchical architecture of a polar, catalytic, and hollow bipyrimal prism-structured cobalt sulfide showed interwoven network with wide spaces to accommodate a high amount of sulfur, lock up dissolved polysulfides and buffer the volumetric fluctuations. |
| CoSₓ/N-carbon/S[284] | Dropwise technique and heat treatment | 1 M NaSO₄CF₃ in diethylene glycol dimethyl ether | As a catalyst, CoSₓ serves to enfeeble the S–S bond of the Sₓ-ring structure that enhances the kinetics of short-chain insoluble NaPS. By further tuning the size of the CoSₓ-based composite, the generation of soluble NaPS can be fully suppressed. |
| Metal–Sulfur system | Cathode composite | Synthesis route | Electrolyte | The unique contribution of S-host |
|---------------------|------------------|----------------|------------|----------------------------------|
| CoP/Co–N-porous carbon nanotube hollow cages/S | Sequential carbonization–oxidation–phosphidation | 1 M NaClO$_4$ in EC/PC with 3 wt% FEC | A heterostructured “multi-region Janus-featured” cathode allowed optimization of sulfur conversion reactions. Besides, the conductive hollow cages of carbon scaffold endowed superior affinity toward long-short NaPS. The dual mechanistic function of electrocatalyst and conductive network enhanced strong chemisorption and facilitated charge transfer kinetics, respectively. |
| Mg/S | Cu-CN/S | Hydrolysis process | 0.5 M Mg(TFSI)$_2$ and 1 M MgCl$_2$ in DME | Copper, as an additive, contributed to high reversibility with the formation of more dispersed and smaller reduction products on cycling. |
| N,Co-codoped ZIF-67/S | Pyrolysis and carbonization strategy | [(HMDS)$_2$Mg], AlCl$_3$ and MgCl$_2$ in diglyme with LiTFSI as mediator | Heterogeneous doping of N and Co and modification of separator and cutoff potential suppressed the formation of the passivation layer and loss of sulfur species. |
| N-MWCNT-graphene/S | Hummer’s metho and chemical vapor deposition | Mg[B(hfip)$_4$]$_2$ in DME | In situ characterization techniques with DFT calculations were employed to investigate the mechanism of sulfur conversion reactions during the cycling process. |
| Co$_3$S$_4$/MXene | Etching and heat treatment | 0.4 M (MgPhCl)$_2$/ AlCl$_3$ in THF | Co$_3$S$_4$ promoted catalytically high chemical adsorption toward polysulfides in addition to the MXene skeleton, enhancing the ion diffusion pathway dynamically. |
| Al/S | Graphene/CoS$_2$/S | Hydrothermal strategy | AlCl$_3$/[EMIm]Cl | A sandwich structure based on the cathode and rGO-coated separator with multiple active sites and strong adsorption capability enabled effective confinement of diffused NaPS with decreased polarization effect. |
| N-porous carbon/S | Oil-bath heating reaction and heat treatment | AlCl$_3$/acetamide | A 3D hierarchical porous carbon architecture could successfully provide sufficient buffer spaces in addition to nitrogen dopant enabling high chemisorption of sulfur products. |
| Cu-microporous carbon/S | Hydrothermal method | AlCl$_3$/[EMIm]Cl | Decorated Cu nanorods (10 at%) on microporous carbon-based MOF with S anchored on its architecture provided strong S–Cu ionic clusters to enhance reversibility. |
| Co(II, III)@carbon/S | Heat treatment | AlCl$_3$/[EMIm]Cl | Co’s catalytic effect with different valence states improved kinetic reactions, high sulfur utilization, and decreased voltage hysteresis values. |
| Boron nitride@carbon/S | Ball milling | AlCl$_3$/[EMIm]Cl | A 2D layered BN material could behave as a sulfur fixer during a continuous reaction process via strong chemical bonding with sulfur moieties to deliver low decay rate. |

**Covalent-fixed sulfur composite**

| Metal–Sulfur system | Cathode composite | Synthesis route | Electrolyte | The unique contribution of S-host |
|---------------------|------------------|----------------|------------|----------------------------------|
| Na/S | Covalent sulfur–carbon complex (SC-BDSA) | Calcination and thermal treatment | 1 M NaClO$_4$ in EC/PC | A composite as the host with sulfur existing in bridge bonds (O–S/C–S) ensures high conductivities and interfacial contact. |
| Covalent sulfur into carbon matrix (SC) | In situ wet chemical solvothermal | 1 M NaClO$_4$ in EC/DEC with 5 wt% FEC | Covalent bond formation of S–C allows homogenous distribution of sulfur among the interior and exterior of the carbon architecture. |
| Thioether bond functionalized carbon/S | Carbonized cross-linked polymerization | NaClO$_4$ in PC with 5 vol% C$_3$H$_3$FO$_3$ | The thioether covalently bonded host contains small sulfur moieties, which on reduction forms nonsolvable sulfides. These are eventually confined within the carbon defects. |
| SPAN webs | Electrospinning process | 1 M NaPF$_6$ in EC/DEC | A web-like SPAN was synthesized to deliver a reversible bond formation between S–S and C–S bonds. |
microporous scaffold for RT-Na/S battery systems. Due to the homogeneous distribution of fine pores, microporous carbon behaves like a suitable container to accommodate and immobilize small-sized sulfur particles, thus mitigating the diffusion of polysulfides. However, due to limited S-loading in micropores, the performance of the RT-Na/S battery remained low.

In contrast to the alkali metal-based battery system, the Mg/S battery system’s studies have focused on conductive layered materials as the host for a sulfur cathode. Due to high voltage hysteresis during the cycling process, the Mg/S battery often suffers from poor efficiency. Layered host composites can minimize the electrostatic force between Mg\(^{2+}\) ions and polysulfides; however, it enlarges the reaction overpotential. The polysulfides formed are well confined within the layered matrix and thus, resulting in enhanced cycling performance of the battery. As most layered sulfides are poor electronic conductors, the cycling performance of Mg/S batteries is limited to a few tens of cycles.

On the other hand, Al/S battery systems have shown escalated performance with the chemisorbed matrix of atomic metal dopants in hollow structures. The strong chemisorption among the transition metal nanodots and polysulfides provides a strong binding affinity toward aluminum polysulfides and suppresses the polysulfide dissolution effect in the battery system. As a result, the formation of the passivation layer in the anode is significantly reduced, and the stripping/plating is further enhanced.

The studies show that the structure of sulfur cathode plays a vital role in controlling the electrochemical process. Its response...
in various metal–sulfur systems is compassionate toward the choice of metal ions, i.e., Na\(^{+}\), Mg\(^{2+}\), or Al\(^{3+}\).

Theoretical investigations through computational tools, such as density functional theory (DFT) calculations, have been formulated to investigate the thermodynamic behavior of composites in metal batteries.\(^\text{249–252}\) DFT calculations have been used to study the diffusion kinetics of Na ions through the electrode, demonstration of electronic and structural properties of both anode and cathode, unveiling charge/discharge reactions, and developing new materials for high-performance rechargeable batteries.\(^\text{1253,254}\) In addition, theory calculations have also been used to understand the reactivity of electrolytes at the electrode/electrolyte interface. The computational tools may provide a deeper insight to study the electrolytes’ degradation or chemistry of electrodes.\(^\text{255,256}\) Under the premise of achieving a stable metal–sulfur battery system with high energy density, these theoretical studies can be formulated to understand electrochemistry.

The host materials must possess the basic properties to achieve high storage performance, for instance, enhanced electronic/ionic transport, high porosity/polarity to ensure improved sulfur confinement (either physical or chemical), and polysulfide entrainment to alleviate the shuttling effect and buffer the volume changes.\(^\text{245–248}\) Pope et al.\(^\text{257}\) reported the importance of high sulfur loading to achieve high specific capacity. They observed that the S-loading should be greater than 2 mg cm\(^{-2}\) to achieve high specific energy of \(\approx 400 \text{ Wh kg}^{-1}\) in a Li/S battery. Furthermore, Liu and co-workers facilitated the fundamental understanding to increase the specific capacity by tailoring the amount of sulfur in the composite cathode.\(^\text{258}\) They have put forward the following principles to achieve a desirable S-cathode with a high energy density: 1) the S-content to be high, preferably \(>80\text{ wt}\%\), and 2) the S-loading to be in the range of 4–5 mg cm\(^{-2}\). Although improving sulfur loading is of unprecedented importance to reach the theoretical values of energy densities, as a consequence, the system is met with formidable challenges with an increase in thickness of the electrode.\(^\text{259–261}\)

For instance, with an increased thickness or S-loading, the active material losses its contact electrically and affects electrochemical reactions, thus experiencing cracks and peeling off issues from the electrode surface. As the sulfur loadings are further enhanced, the IR drop is augmented, hindering the uptake of electrolyte ions.\(^\text{265}\) In-depth mechanistic studies need to be conducted to develop new chemistries to enhance the S-loadings without compromising the reaction kinetics and cycle life of the cell.

Electrolyte plays an essential role in the kinetic reaction of metal–sulfur electrochemistry.\(^\text{262–265}\) The ionic conductivity of the electrolyte enhances the facilitation of ions and electrons, with influence on the dissolution of soluble polysulfides into the electrolyte.\(^\text{266,267}\) However, the degradation of electrolytes in a cell is inevitable due to the formation of insoluble polysulfides and solid electrolyte interface (SEI).\(^\text{268}\) The interaction between the electrolyte and the conventional cathode determines the amount of sulfur confinement and distribution within the composite’s matrix. Of late, importance has been laid on the electrolyte/sulfur (E/S) ratio as it predominantly affects the specific energy density.\(^\text{269}\) An increase in the E/S ratio can hinder the electrolyte from accessing the electrode sites.\(^\text{270}\) It is considered that the electrolyte permeates through the pores of the scaffold and then continues to fill the voids between the components of the cell. Therefore, a composite host with a high surface area and high porous structure would take up a large volume of electrolytes. Additionally, to achieve high power density, the requirement of a flooded electrolyte comes into the picture. It occupies extra spaces in the cell due to repeated dissolution of intermediate polysulfides, thus sacrificing the energy density of the metal–sulfur battery.\(^\text{271}\) According to the literature, an E/S ratio of 10 μL g\(^{-1}\) is typically maintained to extract the maximum capacity out of the cathode due to continuous degradation of the cathode.\(^\text{272}\) Nevertheless, with such high values of electrolyte (μL) content per gram of sulfur, the practical energy density achieved for metal–sulfur batteries can be reduced due to the

![Figure 13. Indirect approaches to achieve a high-performance metal–sulfur battery technology.](image-url)
high weight and volume of electrolyte.\textsuperscript{[273]} On that account, a higher energy density is determined by maintaining a lower amount of E/S ratio.\textsuperscript{[274–276]} However, this ratio varies with different cell chemistries and electrolyte systems. An E/S ratio as low as 2:1, 3:1 in Li/S batteries has been reported to circumvent the aforementioned formidable challenge.\textsuperscript{[276,277]}

However, achieving all the required properties in a single cathode system can be tedious. Therefore, different groups have put together different strategies to design a high-performance RT-metal–sulfur battery technology. New approaches have come to light from groundbreaking innovations made in Li/S batteries. Based on some of the successful reports made by researchers, it is likely that the following approaches, as illustrated in Figure 13, can contribute to positive results in the RT-metal–sulfur battery system.

5. Conclusion

Although the kinetic reaction mechanisms of sulfur-based battery systems are complex, metal–sulfur batteries have demonstrated outstanding advantages over Li-ion chemistries. Development in alkali metal-sulfur systems has escalated more comprehensively. Critical analysis of monovalent, divalent, and trivalent metal–sulfur battery systems with different cathode systems was incorporated in this review structure, along with their performance and capability. Despite the hurdles in the current investigations of Na/S, Mg/S, and Al/S batteries, this technology still provides a base for more sustainable integration of grid-storage applications.

Metal–sulfur batteries are still in the nascent phase. Numerous problems are yet to be addressed to reflect practical use to compete with commercial Li-ion batteries in every aspect. Notably, particular focus needs to be put forward toward finding a compatible host or rational combination of hosts for cathodes to tackle challenges concerning polysulfide moieties and low amount of sulfur loading. Notably, in-depth research into the chemical bonding of sulfur-hosts and configurational innovations with unique architectures must be unveiled—the computational studies required to develop a database for sulfur cathodes and their compatible metal anodes. A more comprehensive study needs to be conducted in formulating new strategies to 1) enhance S-loading, 2) increase utilization of sulfur content, 3) lower the E/S ratio, and 4) build a mechanically and chemically robust matrix. In addition, state-of-the-art in situ or operando characterization techniques must be developed/explored to understand the storage and conversion kinetics of the sulfur host and intermediate sulfur species. Now, even more in-depth research needs to be carried out to meet the proliferated demands of the energy market.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

aluminum, conversion, magnesium, metal–sulfur, sodium, sulfur

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