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Rational designing and prospecting iron-based compounds as efficient host materials for lithium–sulfur batteries

Dongjiu Xie[1], Qingping Wu[1,2], Meltem Karaismailoglu Elibol[1,3], Lihong Jiang[1] and Yan Lu[1,4,5]

Abstract

Known for its high theoretical capacity and low cost, the commercialization of Li–S batteries is hindered by the notorious shuttle behavior of the intermediate lithium polysulfides in liquid electrolyte and the sluggish kinetics of the liquid-to-solid reaction. Recently, to improve the electrochemical performance, iron-based compounds with well-designed nanostructures have been developed and applied as host material for sulfur because they have strong chemisorption of polar polysulfide molecules and could reduce the nucleation energy of solid Li_2S. Here, we have reviewed the latest research progresses (in the last three years) of various iron-based compounds as sulfur host materials and prospected the designing principles of efficient host materials with multiple functionalities to address the issues in sulfur cathode.

Addresses

[1] Institute of Electrochemical Energy Storage, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, Berlin 14109, Germany

[2] Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, China

[3] Department for Energy Science and Technology, Turkish-German University, Şahinkaya Cad 106, İstanbul 34820, Turkey

[4] Institute for Technical and Environmental Chemistry, Friedrich-Schiller-Universität Jena, Philosophenweg 7a, Jena 07743, Germany

[5] Helmholtz Institute for Polymers in Energy Applications Jena (HIPOLE Jena), Lessingstraße 12-14, Jena 07743, Germany

Corresponding author: Lu, Yan (yan.lu@helmholtz-berlin.de)

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Keywords

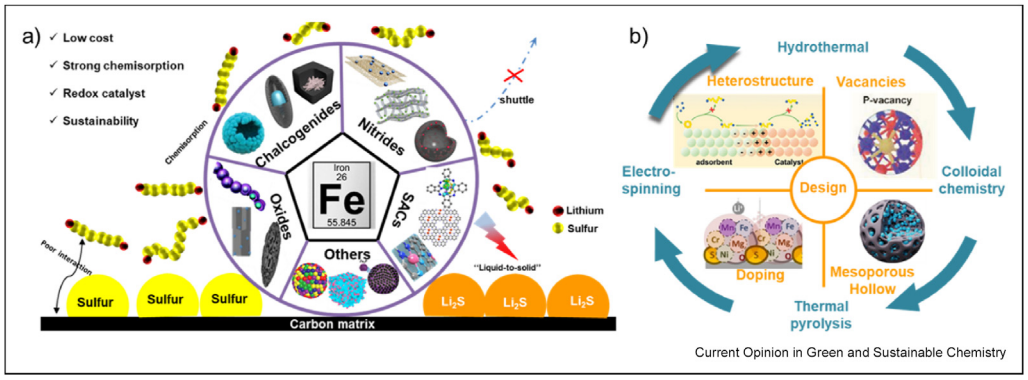
Host materials, Cathode, Nanostructure, Iron-based compounds, Lithium-sulfur batteries.

Introduction

Nowadays, lithium-ion (Li-ion) batteries are dominant as power supply devices for portable devices and electric vehicles. However, Li-ion batteries are approaching to their theoretical capacities. Among different types of energy storage systems, lithium-sulfur (Li–S) batteries have attracted a lot of attention since sulfur as cathode shows a high theoretical capacity of 1675 mAh g^{-1} and an energy density of 2600 Wh kg^{-1} [1]. Unlike the intercalation mechanism, the electrochemical reaction of sulfur during the discharging process is a multiple-step conversion reaction from sulfur to lithium polysulfides (LiPSs, Li_2S_n, $4 \leq n \leq 8$) and then to Li_2S. It is worth mentioning that the soluble Li_2S_n molecules tend to shuttle between two electrodes and react with the metallic Li anode, leading to the loss of active material with a fast capacity decay along cycling [2]. Theoretically, ~75% of the theoretical capacity of sulfur is contributed by the conversion reaction from liquid Li_2S_4 to solid Li_2S [3]. However, the LiPSs in liquid electrolyte cause a high energy barrier for solid Li_2S nucleation, leading to sluggish kinetics during the discharging step. Thus, boosting the liquid-to-solid reaction is crucial for improving the sulfur utilization efficiency and rate capability of Li–S batteries [3]. Moreover, both sulfur and Li_2S are poor conductors for electrons and lithium ions, resulting in an inferior rate capability. Additionally, the density difference between sulfur and Li_2S contributes to significant volume changes during cycling.

To address the above issues, using rationally designed nanostructured materials as sulfur host has been proven to be an efficient way to improve the electrochemical performance of Li–S batteries [4]. Firstly, the pores or voids in the nanostructured host materials can mediate the volume change in sulfur cathode and physically confine LiPSs, suppressing the shuttle effect. Simultaneously, the sulfur host materials designed with catalytic properties could lower the nucleation barrier of Li_2S, facilitating the liquid-to-solid conversion to improve the discharging capacity and rate capability. Recently, polar transition metal-based compounds have been explored as sulfur host materials because of their higher bonding strength with polar LiPSs compared to that of non-polar

Figure 1



(**a**) Overview of the iron-based compounds (*e.g.* oxides [6–8], chalcogenides [9–11], nitrides [12–14], single-atom catalysts (SACs) [15,16], and others (alloy [17], phosphide [18], and carbide [19])) used as sulfur host materials for Li–S batteries; (**b**) the summarized synthesis methods and designed strategies (heterostructure [20], doping [21], vacancies [22], and mesoporous or hollow [23]) for efficient iron-based compounds in Li–S batteries.

carbon materials. Due to the low cost, sustainability, strong adsorption ability to LiPSs, and low lithiation voltage, iron-based compounds including oxides, chalcogenide, nitrides, and single iron atom catalysts, etc, as shown in Figure 1, have been investigated as sulfur host material for Li–S batteries [5]. Iron atom with the electron configuration of $[Ar]3d^6 4s^2$ is easily oxidized into Fe^{2+} and Fe^{3+}, because its *3d* and *4s* electrons are relatively close in energy. Fe-based materials exhibit unique physicochemical properties, including high electrical conductivity, diverse crystal structures (such as cubic and hexagonal), magnetic properties, and polar surfaces. The unique *d* orbital structure of the iron atom has a low field splitting energy, endowing a possible catalytic effect on sulfur reduction reaction in Li–S batteries [24]. Importantly, iron-based compounds could be easily synthesized in a large scale to be used in Li–S pouch cells, showing good electrochemical performance with great potential for commercial application. Through introducing heterostructures [20,25], active sites (alien atom doping or vacancies) [26], or mesoporous structures in iron-based compounds, as shown in Figure 1(**b**), their catalytic effects and adsorption capability to LiPSs could be further improved to achieve better electrochemical performance. To shed light on the rational design of sulfur host materials, this mini-review aims to provide a brief overview of the iron-based compounds as sulfur host material with corresponding electrochemical performances in the last three years, and summarize the applied synthesis approaches to obtain highly efficient host materials for sulfur.

Iron-based compounds as sulfur host materials

Iron-based oxides

Iron-based oxides are regarded as attractive candidates for sulfur host materials in Li–S batteries (as listed in Table 1) because of their sustainability, non-flammability, and defect adjustability [27,28]. Besides, different electronegativities between iron and oxygen atoms lead to a strong polarity on the surface of iron oxide particles, which could chemically anchor the polar LiPS molecules and suppress the shuttle effect. Importantly, iron-based oxide nanoparticles could be synthesized in a large scale through a one-step precipitation method, allowing for the potential commercialization of Li–S batteries. Among different types of iron-based oxides, magnetite Fe_3O_4 is more widely applied as sulfur host material in Li–S batteries than the others due to its high chemical stability and electrical conductivity [24].

Guided by the ideology of the combination of chemical adsorption and physical confinement of LiPSs to suppress the shuttle effect in Li–S batteries, most of the efforts have been devoted to designing and synthesizing nanostructured carbon materials composited with iron oxide particles [27,28]. For instance, Deng et al. reported a nitrogen-doped hollow carbon structure embedded with Fe_3O_4 nanoparticles as sulfur host for Li–S batteries, in which the hollow carbon can both provide sufficient space for loading sulfur and accommodate the volume change during the cycling, while the polar Fe_3O_4 particles could accelerate the kinetics of sulfur reduction reactions and enhance the polysulfide adsorption [29]. Besides nanoparticles, iron oxides with pores or voids can more efficiently immobilize LiPSs through the combination of chemisorption and physical confinement [6].

Based on the current studies on iron oxide-based sulfur host, increasing multiple metal elements (such as Co, Ni, Zn, Mg, and Mn) into the iron oxide with an increased entropy could exhibit a synergistic effect on boosting the diffusion and conversion of LiPSs and offer

Table 1

Comparison of various iron-based compounds as sulfur host materials for Li–S batteries.

Iron-based compounds	Synthetic method	Sulfur content (wt.%)	Areal sulfur loading (mg cm^{-2})	E/S ratio (μL mg^{-1})	Electrochemical performance	Ref.
Fe_3O_4@C nanochain	Wet chemistry	66.7	0.95	20	1204 mAh g^{-1} at 0.2C; 51.9% after 500 cycles at 0.2C	[7]
Fe_3O_4/nitrogen-doped carbon nanosheet	Colloidal chemistry	61.2	1	40	1256 mAh g^{-1} at 0.1C; 70% after 100 cycles at 0.2C	[28]
Carbon@ mesoporous Fe_3O_4	Colloidal chemistry	~70	1.5	17.3	1618 mAh g^{-1} at 0.1C; 66.5% after 100 cycles at 0.2C	[6]
$CoFe_2O_4$ nanorods	Solvothermal	~75	2	8	1535 mAh g^{-1} at 0.1C; 89% after 100 cycles at 1C	[42]
$CoFe_2O_4$@ nitrogen-doped carbon nanofibers	Electrospinning	81~87	3.29	5.2	1096 mAh g^{-1} at 0.2C; 62.1% after 500 cycles at 0.2 C	[43]
$(Mg_{0.2}Mn_{0.2}Co_{0.2}Ni_{0.2}Zn_{0.2})Fe_2O_4$ nanofiber	Electrospinning	77.4	1.4	20	1368.7 mAh g^{-1} at 0.1C 632.1 mAh g^{-1} at 5C	[30]
Yolk–shell Fe_3O_4/FeP@C	Colloidal chemistry	70	4.15	8	833 mAh g^{-1} after 50 cycles at 0.1C	[20]
Fe_3O_4–FeTe@porous carbon microspheres	Colloidal chemistry	N/A	9.73	5.5	~600 mAh g^{-1} after 50 cycles	[23]
Fe_3O_{4-x}/FeP@carbon nanotube	Hydrothermal	80	4	7	338 mAh g^{-1} at 0.1C after 50 cycles	[8]
Yolk–shell FeS_2-Carbon	Colloidal chemistry	~60	~1.1	40	877.6 mAh g^{-1} at 0.5C with a retention ratio of 86.7% after 300 cycles	[10]
FeS_2@porous carbon	Pyrolysis	83.3	7.1	4	372 Wh kg^{-1} at 0.1C	[44][a]
FeS/N–C	Pyrolysis	~80	3.2	N/A	729 mAh g^{-1} at 0.5 C after 500 cycles	[45]
$Fe_{0.34}Co_{0.33}Ni_{0.33}S_2$	Hydrothermal	70	2	2–2.5	1350 mAh g^{-1} at 0.7C, 879 mAh g^{-1} after 300 cycles	[32]
FeSe@Carbon	Hydrothermal	75	1.5	15	1057.4 mAh g^{-1} at 1 C, discharge capacity of 630 mAh g^{-1} after 400 cycles	[46]
$FeSe_2$@Carbon nanoboxes	Hydrothermal	83.3	1.5	15	1281 mAh g^{-1} at 1 C, capacity retention of 81% after 200 cycles	[9]
FeSe–MnSe/carbon microsphere	Hydrothermal	~80	1.5	18	1334 mAh g^{-1} at 0.2C, capacity decay of 0.029% at 1C for 1000 cycles	[11]
Fe_2CoSe_4@Carbon skeleton	Wet chemistry	70	1.5–2.0	20	1406 mAh g^{-1} at 0.1C, capacity retention of 82.3% after 300 cycles at 0.2C	[47]
$Co_{5.47}N/Fe_3N$ heterostructure-carbon nanotube	Pyrolysis	~80	~2.7	~7	1293 mAh g^{-1} at 0.1C and 791 mAh g^{-1} at 2C	[14]
Fe_2N-VN@carbon nanofiber	Electrospinning	~71	10	5	952.5 mAh g^{-1} after 200 cycles at 0.1C	[48]
Phosphorus-modified Fe_4N@ N,P co-doped graphene	Hydrothermal	73	1.1–1.4	20	1386.1 mAh g^{-1} at 0.1C 417.4 mAh g^{-1} at 1 C after 1000 cycles	[13]
Fe_xN@carbon nanocapsules	Colloidal chemistry	~70	1.5	17.3	1085 mAh g^{-1} at 0.5C and 930 mAh g^{-1} after 200 cycles	[12]
Deficient Single-atom Fe–N–C catalyst	Wet chemistry	~75	5.0	5.3	4.5 mAh cm^{-2} at 1C	[16]
Fe–Co diatomic catalyst@hollow carbon nanospheres	Wet chemistry	~80	4.6	5	~1120 mAh g^{-1} at 0.1C	[41]
Single N_2–Fe–B_2 catalyst	Wet chemistry	~70	~11.6	3	359 Wh kg^{-1} at 2.0 mA cm^{-2}	[15][a]
Fe–N_5–C	Wet chemistry	~75	1	19.1	1224 mAh g^{-1} at 0.2C and 662 mAh g^{-1} at 1 C after 500 cycles	[49][a]

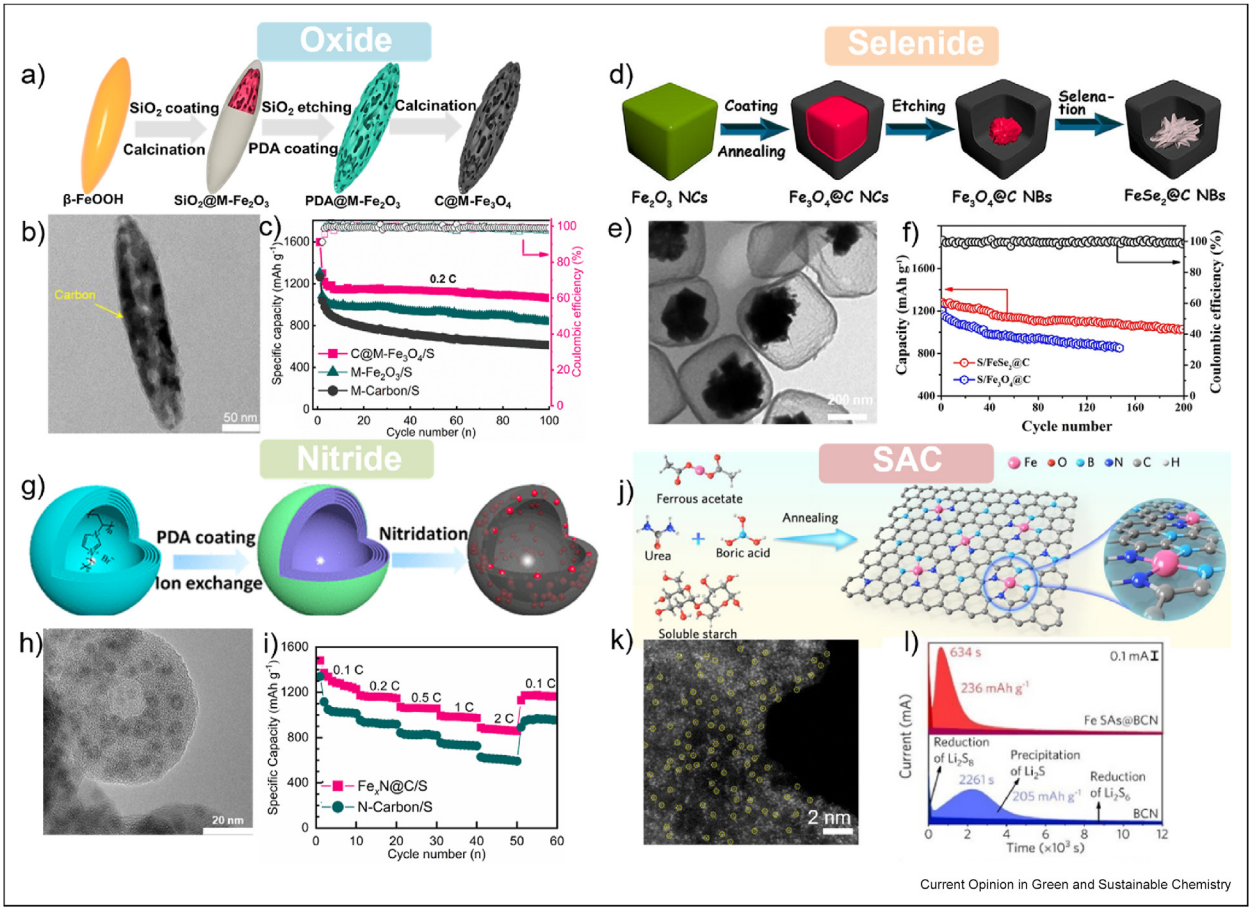
[a] Obtained from Li–S pouch cells.

sufficient binding sites for the chemical entrapment of LiPSs [21,30]. Meanwhile, designing the heterostructures of Fe_3O_4 nanoparticles with metal sulfides or phosphides by sulfidation or phosphidation reaction could enhance the sulfur reduction reactions through the balance of the adsorption and catalysis process of LiPSs.

Iron-based chalcogenides

Compared with oxides, iron-based chalcogenides (FeS, FeS_2, and $FeSe_2$) generally exhibit higher electrical conductivity and stronger electrocatalytic effect in the Li−S batteries [9,10,31]. Since the Fe-X (X = S, Se) bond is weaker than the Fe−O bond in oxides, electrons of LiPSs could transfer to iron atoms in chalcogenides, contributing to a better adsorption capability than the Fe_3O_4 counterpart [31]. According to the Hard and Soft Acid and Base theory, the interactions between chalcogenide anions (soft-base) and iron cations (soft-acid) endow iron atoms with a high valence electron density in chalcogenides, allowing iron atoms as active sites to catalyze the sulfur reduction reactions. For instance, catalytic $FeSe_2$ nanoparticles (Figure 2(**e**)), derived from the selenide reaction with Fe_3O_4 particles (Figure 2(**d**)), were encapsulated with carbon shell and used as a multifunctional sulfur host to restrain the polysulfide shuttle effect with improved cycling stability (Figure 2(**f**)). To further enhance the electrocatalytic activity, doping with different metal ions into iron chalcogenides has been also applied because the incorporation of heteroatoms could change the local electronic structure of iron atom [32]. Lu et al. synthesized a novel ternary sulfide ($Fe_{0.34}Co_{0.33}Ni_{0.33}S_2$) to improve the binding of polysulfides through Lewis acid−base interaction [32]. Using this ternary metal sulfide as sulfur host material, the constructed 3Ah-level pouch cells achieved energy densities of 267 and 394 Wh kg^{-1} at the current density of 4 and 1.5 mA cm^{-2}, respectively [32]. Besides doping, nanoengineering the adsorbent and catalyst of LiPSs with a heterostructure, as shown in Figure 1(**b**), can also improve the whole electrocatalytic activity of sulfur host material by synergizing the merits of each component together [11,33]. For instance, Hu et al. rationally designed

Figure 2



Schematic illustration of the synthetic procedures for various nanostructured iron-based compounds (oxide (**a**, **b**, and **c**) [6], selenide (**d**, **e**, and **f**) [9], nitride (**g**, **h**, and **i**) [12], and SAC (**j**, **k**, and **l**) [15]) with the corresponding TEM images and electrochemical performance.

FeSe−MnSe heterostructures with rich Se vacancies to lower the interfacial energy barrier of Li_2S and facilitate its nucleation and growth during cycling [11]. The signal of polysulfides in the cell with FeSe−MnSe was not detected by *in-situ* Raman spectroscopy, indicating the heterostructured FeSe−MnSe could efficiently anchor LiPSs [11]. Although iron-based chalcogenides as electrocatalysts show great potential in Li−S batteries, their synthetic procedures towards sulfur host materials are usually more complicated than those of iron-based oxides. In addition, nanosized iron-based chalcogenide particles are easily oxidized when exposed to air, which may decrease their electrocatalytic activity.

Iron-based nitrides

In the case of iron-based nitrides, in addition to their excellent electrical conductivity, N atoms could shrink the *d* band of iron atoms with an increased electron density, which allows the N atoms in iron-based nitrides (Fe_2N, Fe_3N, and Fe_4N) to act as conductive Lewis bases to capture positively charged particles, favoring iron-based nitrides as the most promising catalysts for sulfur redox reaction [34]. Beyond that, the electronegativities of nitrogen and sulfur are almost equal and can form covalent bonds, thereby reducing the shuttle effect of LiPSs and improving the cycle stability of Li−S batteries [35]. Iron-based nitride nanoparticles as electrocatalyst are usually loaded or embedded into nanostructured carbon materials due to their poor chemical stability in air. Using poly(ionic liquids) nanovesicles as soft template and melamine as ammonia source (Figure 2(**g**)), Xie et al. prepared hollow carbon nanocapsules embedded with fine iron nitride nanoparticles(3−5 nm, see in Figure 2(**h**)), which have been used as sulfur host material for Li−S batteries [12]. Benefiting from this nanostructure, as shown in Figure 2(**i**), the constructed cathode showed a high discharge capacity of 858 mAh g^{-1} at 2C, which is much better than that of its counterpart.

Besides, engineering heterostructure has also been reported to further improve the electrocatalytic activity of iron nitrides. Through DFT calculation, it was found by Nguyen et al. that the $Co_{5.47}N/Fe_3N$ heterostructures improved the state density at the Fermi level, contributing to a better adsorption ability to LiPSs [14]. Consequently, the combination of high catalytic activity Fe_3N and adsorptive $Co_{5.47}N$ in the sulfur host materials could efficiently suppress the shuttle effect of LiPSs and improve the capacity of Li−S batteries [14]. Although iron-based nitride nanoparticles could improve the electrochemical performance, they may suffer from poor catalytic stability along cycling since metal nitride may react with LiPSs in electrolyte, forming the corresponding sulfides.

Single iron atom catalyst

Very recently, porphyrin-based metal compounds with a single metal atom center have demonstrated unique electrocatalytic properties in improving the electrochemical performance of lithium-sulfur batteries. Porphyrin rings often play the role of catalytic centers to improve the conversion rate of LiPSs. Among them, metal chelating sites serve as catalytic sites, while strongly polar π-conjugated porphyrin rings can not only act as transport networks to accelerate charge transfer, but also provide polar adsorption sites to fix LiPSs through strong chemical adsorption interactions (N−Li bonds) [36]. Compared with porphyrin-based metal compounds, isolated metal single atoms (as shown in Figure 2(**j,k**)) on a carbon matrix endow an adjustable electronic environment, good chemical stability, excellent reversibility, and more importantly, extremely high atom utilization [37]. Among various single-atom catalysts, Fe-based SACs (Fe-SACs) are potential candidates for enhancing polysulfide conversion reaction kinetics (as demonstrated in Figure 2(**l**)) in Li−S batteries due to the unique electronic structure and catalytic behavior of iron, coupled with the widespread and low cost of the corresponding precursors (as shown in Figure 2(**j**)) [38]. In addition, the chemical stability, electronic properties, and catalytic activity of Fe-SACs for polysulfide conversion can be controlled by coordination structures and adjacent heteroatoms (*e.g.*, N, B, and S) [39].

There may also be a synergistic effect by introducing additional metal centers into Fe-SAC to generate dual active sites, forming a bidirectional or continuous polysulfide redox process, to further enhance the conversion reaction kinetics [40]. The presence of Fe atomic centers facilitates the acceleration of discharge process, while the Co atomic centers are conducive to the charging process [41]. Although a variety of Fe-SACs with different coordination environments have been designed to facilitate the polysulfide conversion reactions in Li−S batteries, systematic research is rarely reported to elucidate the evolution of individual Fe metal atoms and their interactions with carriers and other molecules (such as LiPSs) during cycling. A unified catalysis mechanism for the polysulfide conversion reaction at the molecular level has not been established yet.

Conclusions and perspectives

In summary, we present an overview of the latest research progress of iron-based compounds as sulfur host materials for Li−S batteries. The excellent electrochemical results in the literature (Table 1) demonstrate that rationally designed iron-based compounds with novel nanostructures can efficiently anchor LiPSs and boost the Li_2S nucleation process. However, the following issues still need to be addressed before the massive application of iron-based compounds as sulfur host material:

1) Advanced *in-situ* and *operando* characterization techniques have played an important role in promoting the understanding of the mechanism of Li−S batteries, enabling real-time observation of the interaction between catalysts and LiPSs during sulfur reduction reactions. The catalytic stability of iron-based compounds and their catalytic mechanism in Li−S batteries are rarely investigated in depth by *operando* or *in-situ* methods (such as X-ray absorption spectroscopy). Iron-based compounds as redox catalyst may be deactivated since the accumulated non-conductive sulfur/Li_2S particles on the catalyst surface will decrease the catalytic active sites along cycling, especially under high sulfur loading with lean electrolyte conditions. Moreover, iron-based compounds, especially Fe-SACs, may react with LiPSs, poisoning the catalyst with low efficiency.
2) Few research has been conducted on the Li−S pouch cells with iron-based compounds as sulfur host materials because the synthesis and preparation of high-performance iron-based compounds may involve intricate methods, potentially leading to a poor yield and elevated synthesis costs. It is necessary to explore a simple, low-cost, green, and sustainable method to synthesize iron-based compounds with defined nanostructures in a large scale.
3) Standard parameters for the preparation of sulfur cathode and testing of the electrochemical performance should be established since it is still a great challenge to compare the electrochemical results from different research groups, leading to a low efficiency in discovering high-performance iron-based compounds for Li−S batteries.

Overall, this review attempts to stimulate researchers' continued design and in-depth exploration of high-performance Li−S batteries inspired by iron-based compounds. We believe that the summarized design principles can potentially guide subsequent research on sulfur cathodes for practical Li−S batteries.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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* of special interest
** of outstanding interest

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