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Review

Recent advances in rare earth compounds for lithium–sulfur batteries

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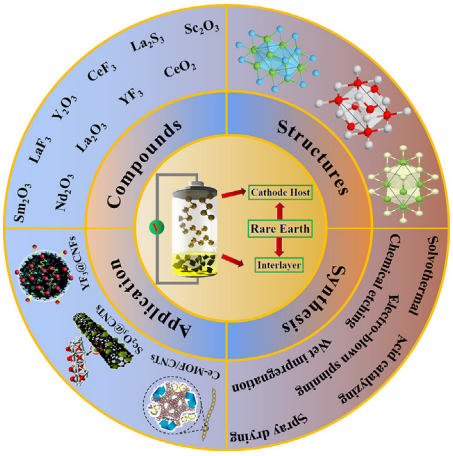
HIGHLIGHTS

- Applications of rare earth compounds as cathode hosts and interlayers in lithium–sulfur batteries are introduced.
- Rare earth compounds are shown to have obvious advantages for tuning polysulfide retention and conversion.
- Challenges and future prospects for using RE elements in lithium–sulfur batteries are outlined.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium–sulfur batteries are considered potential high-energy-density candidates to replace current lithium-ion batteries. However, several problems remain to be solved, including low conductivity, huge volume change, and a severe shuttle effect on the cathode side, as well as inevitable lithium dendrites on the anode side. Rare earth compounds, which play vital roles in various industries, show latent capacity as cathode hosts or interlayers to tackle the inherent problems of lithium–sulfur batteries. However, the application of rare earth compounds in lithium–sulfur batteries has not been reviewed so far, despite they showing obvious advantages for tuning polysulfide retention and conversion. In this mini-review, we start by introducing the concept of lithium–sulfur batteries and providing background information on rare earth-based materials. In the main body, we explore rare earth compounds as cathode hosts or interlayers, then discuss various types of each. Finally, we offer an outlook on the existing challenges and possible opportunities for using rare earth compounds as cathode hosts or interlayers for lithium–sulfur batteries.

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1. Introduction

Although lithium-ion batteries (LIBs) have been a big success in portable electronics and electric vehicles, higher energy density is being demanded [1–5]. However, LIBs over the last three decades have almost reached their limit of theoretical energy density, which is intrinsically determined by their topological intercalation chemistry [6]. Based on their cathodic conversion reaction and anodic deposition/depletion process, lithium–sulfur (Li–S) batteries are potential replacement candidates, as they possess about six times the energy density of LIBs [7]. In addition, the non-toxicity, low cost, and environmental friendliness of sulfur as a cathode material reinforce the superiority of Li–S batteries [8–10].

The concept of Li–S batteries was first put forward in a patent form by Herbert Danuta and Ulam Juliusz in 1962 [10]. Since their advent, Li–S batteries have long been plagued by low capacity and rapid capacity fading. Worse, the successful commercialization of LIBs in 1991 by Sony Corporation was a setback for Li–S batteries [11]. In spite of new vitality injected by the discovery that 1,3-dioxolane (DOL) and dimethoxyethane (DME) form a suitable co-solvent, research on Li–S batteries remained a low priority for a long time [12]. The great breakthrough came from Nazar *et al.* in 2009 [13], who found that a rather high capacity of over 1000 mAh/g with stable battery life was obtained when sulfur was hosted within a mesoporous CMK-3 carbon by a melt-diffusion method. This kickstarted additional research on Li–S batteries, and research on cathode hosts, lithium metal protection, solvent optimization, interlayers, separators, electrolyte additives, binders, and other related topics entered the fast lane [14–20]. So far, more than 12,000 publications on Li–S batteries are available.

Li–S batteries are composed of a lithium metal anode, an electrolyte, a separator, and a sulfur cathode. In the discharge process, lithium metal is directly oxidized into Li^+, while sulfur in the form of a ring-shaped rhombic S_8 molecule is initially reduced to S_8^{2-} via ring cleaving. Subsequently, S_8^{2-} is reduced to S_4^{2-} and then S_2^{2-}/S^{2-}, as shown by the galvanostatic charge/discharge curve in Fig. 1a. During the charging process, S^{2-} is reversibly oxidized into S_2^{2-}, S_4^{2-}, S_8^{2-}, and S_8 on the cathode side, with Li metal deposition on the anode side. The half-reaction and total reaction of a Li–S battery during the discharge process are as follows [21]:

$$\text{Cathode}: S_8 + 16Li^+ + 16e^- \rightarrow 8Li_2S$$

$$\text{Anode}: 16Li \rightarrow 16Li^+ + 16e^-$$

$$\text{Total Reaction}: 16Li + S_8 \rightarrow 8Li_2S$$

Though Li–S batteries are regarded as candidates for high-energy-density batteries, their commercialization cannot be realized in the short term due to several serious problems [22,23]. First of all, the low conductivity of the discharge product Li_2S and the charge product S leads to low active material utilization and poor rate capability [24,25]. Second, volume changes during cycling cause pulverization. The densities of sulfur and lithium sulfide are 2.07 g cm^{-3} and 1.66 g cm^{-3}, respectively. Volume expansion/contraction is up to 79% during the charging and discharging process, and this dramatic size change destroys the electrode morphology and structure, resulting in detachment of the electrode materials from the current collector [26]. A third serious problem for the S cathode is polysulfide dissolution and shuttling [27,28], which lead to low Coulombic efficiency, fast capacity fading, and Li metal anode corrosion.

From the cathode host and interlayer perspectives, numerous attempts have been made to tackle the dissolution and shuttling of polysulfide by physical adsorption or chemical anchoring. Specifically, porous materials, especially porous carbons, are widely used as physical adsorption hosts to alleviate polysulfide dissolution [13]. However, the low affinity between the nonpolar carbon host and the polar polysulfide means the polysulfide is not retained effectively, so chemical anchoring has been proposed based on interactions between the polar polysulfide and polar metal compounds [29,30], including metal oxides [31–34], metal sulfides [35–38], metal nitrides [39–42], and metal–organic frameworks (MOFs) [43–46], among others. Currently, polar metal compounds used as sulfur hosts or interlayers primarily center on main group metal compounds and transition metal compounds, but research attention has begun to shift toward rare earth (RE) compounds. For main group metal-based and transition metal-based cathode hosts or interlayers, p valence or d valence electrons are involved in electron transfer, lithium-ion diffusion, polysulfide adsorption, catalytic polysulfide conversion, and lithium sulfide deposition. When RE compounds are used, f valence electrons may instead play the dominant role in those electrochemical processes.

To better understand the unique role of RE compounds in lithium–sulfur batteries, it is first necessary to introduce the properties of rare earth elements. The first RE element, yttrium, was isolated and confirmed by Gadolin Johan in 1794. From 1803 to 1945, the remaining 16 RE elements were discovered [47]. As shown in Fig. 2, they are located in group IIIB of the periodic table [48,49]. Scandium displays an electronic structure of $[Ar]3d^14s^2$ and yttrium of $[Kr]4d^15s^2$, while other lanthanides, from lanthanum to lutetium, display electronic structures of $[Xe]4f^n5d^{0\text{-}1}6s^2$ (n = 0–14). With their large atomic radii, the valence electrons of RE elements are easily lost, indicating high reducibility. In the lanthanide elements, the electrons are lost in the order 6s→5d→4f, so

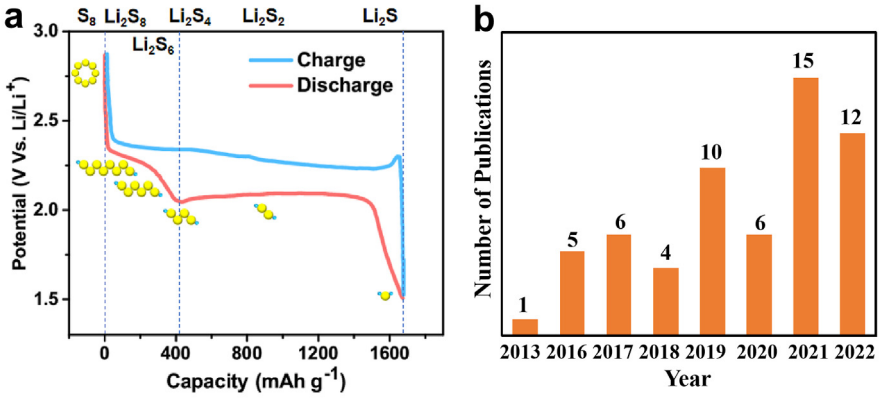

Fig. 1. (a) Galvanostatic charge–discharge profiles of Li–S batteries. (b) The number of publications on RE compounds as cathode hosts or interlayers in Li–S batteries from 2013 to 2022.

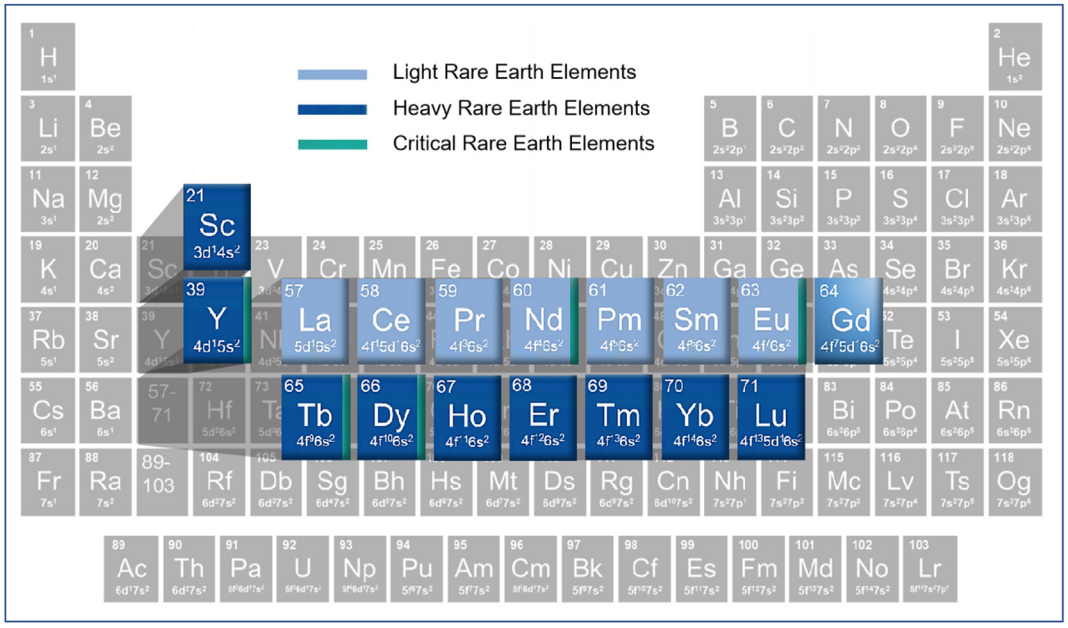

Fig. 2. Valence electron configurations of RE elements. Modified based on a source from the National Energy Technology Laboratory.

these elements are commonly trivalent (RE^{3+}). In addition, the 4f electrons of lanthanide can undergo various f–f and f–d transitions [50].

Given their adaptable coordination numbers, from 6 to 12, doping with RE elements can be very effective for many purposes, such as adjusting crystal structure [51,52], tuning spectra [53,54], enhancing magnetic properties [55], and improving catalytic performance [56]. Recently, battery materials have also benefited from the progress brought by RE elements. For example, the fineness of anode materials in lead acid batteries has been improved after doping with RE elements, which contributes to the formation of PdO_2 thin film [57]. In addition, the low ionic conductivity of solid-state electrolytes has been substantially improved by RE element doping due to the resulting expansion in ion transportation channels, indicating the potential for using RE elements in battery electrolytes [58,59].

Compared with research on transition metal compounds such as oxides and fluorides, the study of RE compounds is still in its infancy, but they hold great promise due to their unique structures and properties (Fig. 3). First, RE compounds possess much higher acidity and lower electronegativity than transition metal compounds, resulting in much stronger chemical adsorption towards Lewis basic polysulfides. As well, the larger ionic radii of RE elements result in less steric hindrance and diverse coordination numbers, providing more polysulfide adsorption sites. In terms of electrochemical reaction kinetics, the partially filled 4f and 5d orbitals of RE elements and their variable valence states contribute to electron transfer during the polysulfide conversion reaction, promoting the reaction kinetics and decreasing the polysulfide's detention time in the electrolyte. Most importantly, the characteristic 4f electrons of RE elements are highly delocalized with respect to the 5d and 6s electrons, resulting in chemical inertness, especially after coordination. However, the 3d-4f-5d orbitals are strongly coupled due to the quantum characteristic of d–f exchange interactions. In particular, the 4f electrons of RE oxides are strongly localized, but hybridization with the

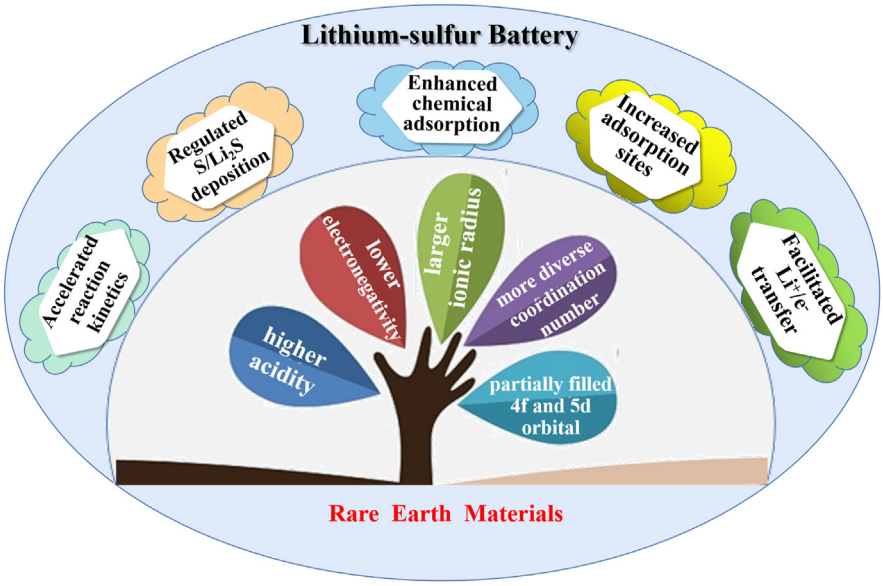

Fig. 3. The unique roles of RE compounds in the lithium–sulfur battery.

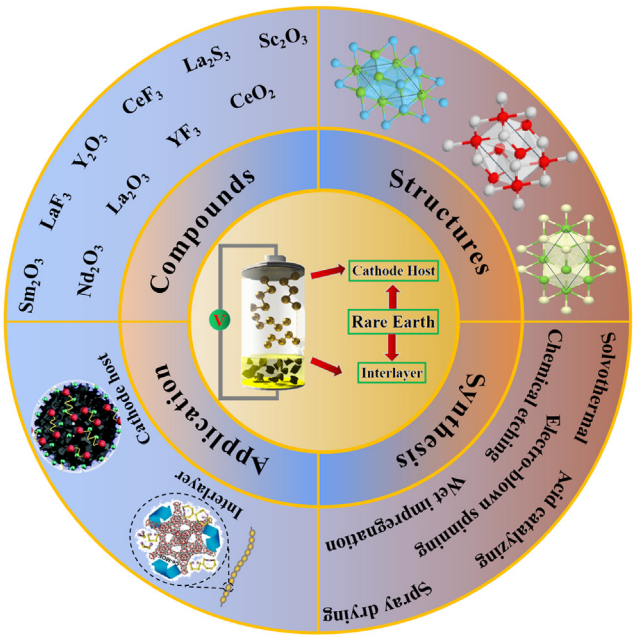

Fig. 4. The application of RE compounds in lithium–sulfur batteries.

2p orbitals of oxygen promotes delocalization, leading to covalent interactions. For example, the band structure of lanthanide oxides reveals that 4f orbitals form sub-bands in the valence region, allowing overlap with the p band of oxygen and confirming the ability to activate 4f electrons via combination with light elements. Because 5d orbitals are polarized by 4f orbitals, interaction with 3d orbitals is enhanced. The coupling of 4f electrons with s electrons and d electrons leads to optimization of the geometric and electronic structures of RE compounds. In particular, delocalized 4f electrons are able to undergo selective Mott transitions, proving the possibility of optimizing the density of states close to EF and ε_d and facilitating electron transfer from the valence band to the conduction band. This unique electronic structure of RE compounds can have a special effect when it comes to catalyzing polysulfide conversion. In contrast, the 3d electrons of transition metals lack the special properties of the 4f and 5d electrons in RE compounds.

Hence, some RE compounds have been reported as advanced electrochemical catalysts for Li–S batteries [60]. RE compounds also show unique roles in regulating Li_2S deposition during the discharge process or S deposition during the charge process, with uniform morphologies attainable if appropriate oxygen vacancies (OVs) can be created. Well-regulated S/Li_2S deposition not only preserves the electron transfer network but also retains the original chemical adsorption sites or catalytic sites. From this perspective, S/Li_2S deposition is one of the most important strategies for achieving a stable cycling life. As shown in Fig. 1b, the number of publications about RE compounds as cathode hosts or interlayers in Li–S batteries increased from 2013 to 2022. However, there have been few systematic summaries on the application of RE compounds in lithium–sulfur batteries.

Herein, recent research progress on the use of RE compounds in lithium–sulfur batteries is reviewed (Fig. 4). First, the concept of using rare earth materials for lithium–sulfur batteries will be introduced. Then, recent highlights in applying rare earth compounds as cathode hosts and interlayers will be discussed. Finally, we will offer our outlook on the existing challenges and possible opportunities for rare earth compounds as cathode hosts or interlayers for lithium–sulfur batteries.

2. Application of RE compounds in Li–S batteries

2.1. RE compounds as cathode hosts

In Table 1 and Fig. 5, we summarize recent research exploring RE compounds as cathode hosts for Li–S batteries [61–71]. To date, work has mainly centered on La-based, Sm-based, Nd-based, Y-based, and Ce-based compounds. In terms of electrochemical performance, sulfur impregnated with these RE compounds shows initial capacities beyond 1100 mAh/g and relatively stable cyclability. Specifically, most of the investigated RE compounds can retain a capacity fading rate below 0.2% for 200 cycles. In one study, the fading rate was as low as 0.05% across 1000 cycles. Such stable cyclability is attributable to constrained polysulfide dissolution and accelerated redox kinetics [72,73]. With respect to rate capability, the capacity can reach 800 mAh/g, even under a current density of 1C. Important factors besides the high conductivity provided by the sulfur host are the accelerated electrochemical reactions catalyzed by RE compounds.

Metal oxides are promising sulfur host materials because of their superior adsorption ability [74]. When it comes to a RE metal oxide, its chemical adsorption of polysulfides and its catalytic polysulfide conversion greatly depress the shuttle effect. With this in mind, nitrogen-enriched mesoporous carbon (NMC) decorated by La_2O_3

Table 1
Summary of RE compounds as cathode host for Li–S batteries.

Materials	Preparation method	Rate (C)	Initial capacity (mAh/g)	nth capacity (mAh/g)	Ref.
La_2O_3/NMC	Wet impregnation	1	1043	100th 799	[61]
$La(OH)_3$/rGO	Spray drying	0.2;	1160	100th 902	[62]
		1		600th 541	
Sm_2O_3/CA	Sol-gel	0.5;	1175	300th 861	[63]
		0.2	1322	300th 866	[64]
Nd_2O_3/CA	Acid catalyzing	0.2;	1327	100th 1082	[65]
		0.5	1143	300th 907	
Y_2O_3/CNTs	Solvothermal	0.5	912	200th 842	[66]
YF_3/CNF	Electro-blown spinning	1	954	600th 709	[67]
CeO_2/KB	Wet impregnation	1	905	300th 710	[68]
CeO_2/MMNC	Ultrasonic degradation	1	1352	500th 835	[69]
CeO_2/CNTs	Solvothermal	0.2	1157	100th 723	[70]
CeF_3/PCNF	Electrospinning	0.5	1395	500th 901	[71]

NMC : nitrogen-enriched mesoporous carbons.
rGO : reduced graphene oxide.
PCNF : porous carbon nanofiber.
CA : carbon aerogel.
CNTs : carbon nanotubes.
CNF : carbon nanofiber.
KB : Ketjen black.
MMNC : micromesoporous N-doped carbon spheres.

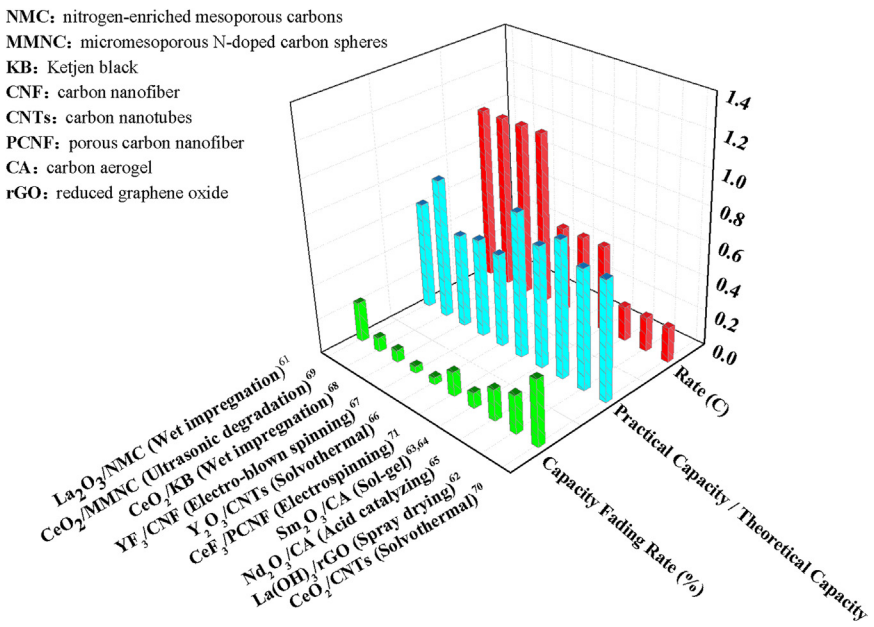

Fig. 5. Electrochemical performance of Li–S batteries with RE compounds as cathode host [61–71].

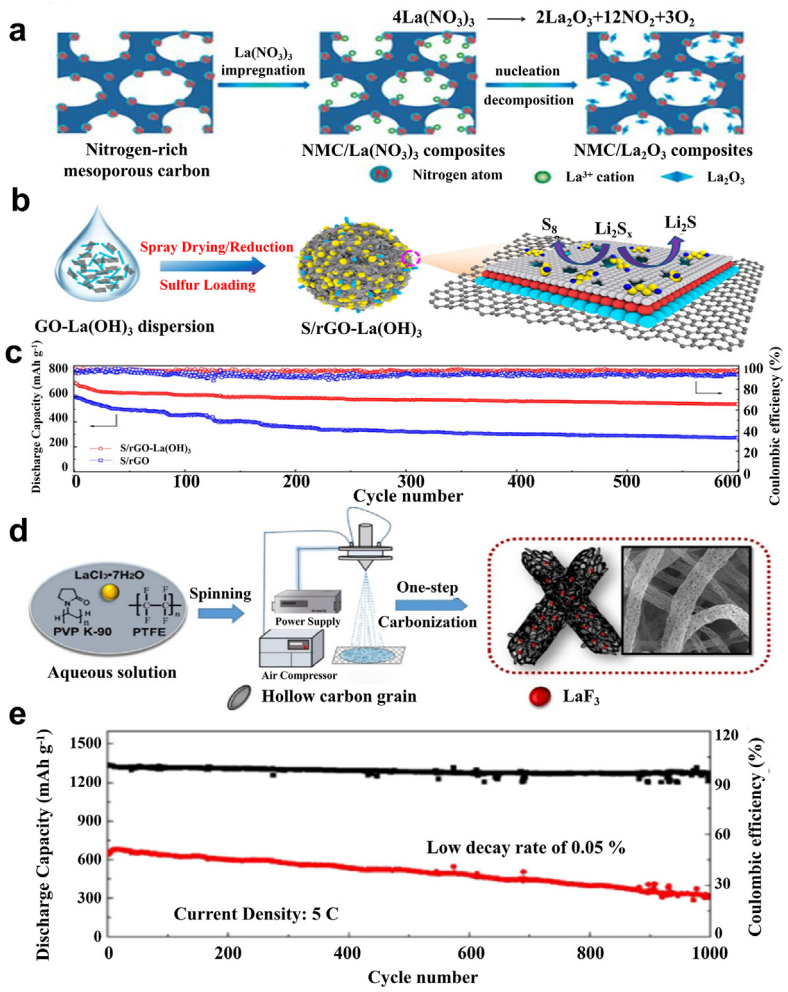

Fig. 6. Application of La-based compound in lithium–sulfur batteries. (a) Schematic representation of the uniform deposition of La_2O_3 within the NMC matrix. Reproduced with permission from Ref. [61]. Copyright © 2013 Royal Society of Chemistry. (b) Schematic illustration of the synthesis of S/rGO–$La(OH)_3$ microspheres and the conversion of Li_2S_x on the S/rGO–$La(OH)_3$ surface. (c) Long-term cycling performances of electrodes at 1.0C. Reproduced with permission from Ref. [62]. Copyright © 2019 American Chemical Society. (d) Synthesis process of LaF_3/PCNF material. (e) Long-term cycling performance of LaF_3/PCNF at 5C. Reproduced with permission from Ref. [75]. Copyright © 2021 Elsevier.

nanoparticles was reported as a cathode host for Li–S batteries in 2013 (Fig. 6a) [61]. The La_2O_3 nanoparticles not only showed strong on-site trapping of polysulfides but also contributed to decreasing the reaction overpotential and improving the reaction kinetics. As a result, the La_2O_3-decorated S cathode delivered a capacity of 1043 mAh/g at 1C and 475 mAh/g at 5C. After 100 cycles, the capacity retention was around 80%. Hydroxides have also been proven to improve battery performance effectively. For example, a $La(OH)_3$/reduced graphene oxide (rGO) sulfur host was prepared by a spray-drying method (Fig. 6b) [62]. Hydroxyl groups offered strong chemical adsorption for lithium polysulfide, as confirmed by density functional theory calculations. Moreover, oxygen defects promoted the polysulfide conversion kinetics, decreasing polysulfide detention time in the electrolyte. $La(OH)_3$ with oxygen vacancies thus has the dual effects of polysulfide chemisorption and catalytic conversion. In electrochemical testing, a sulfur cathode with $La(OH)_3$/rGO exhibited a high initial capacity of 1160.4 mAh/g at 0.2C, and a capacity of 541.7 mAh/g after 600 cycles at 1C (Fig. 6c). Compared with oxides and hydroxides, fluorides may show stronger adsorption of polysulfides, given fluorine's higher electronegativity. LaF_3/porous carbon nanofiber (PCNF) prepared by an electro-blowing spinning technique showed a high discharge capacity of 640 mAh/g at 5C (Figs. 6d and e). At the same current density, the capacity decay rate was as low as 0.05% during 1000 cycles. Such stable cycling performance was attributed to a synergic effect arising from the physical adsorption of porous carbon and the chemical binding of LaF_3 [75].

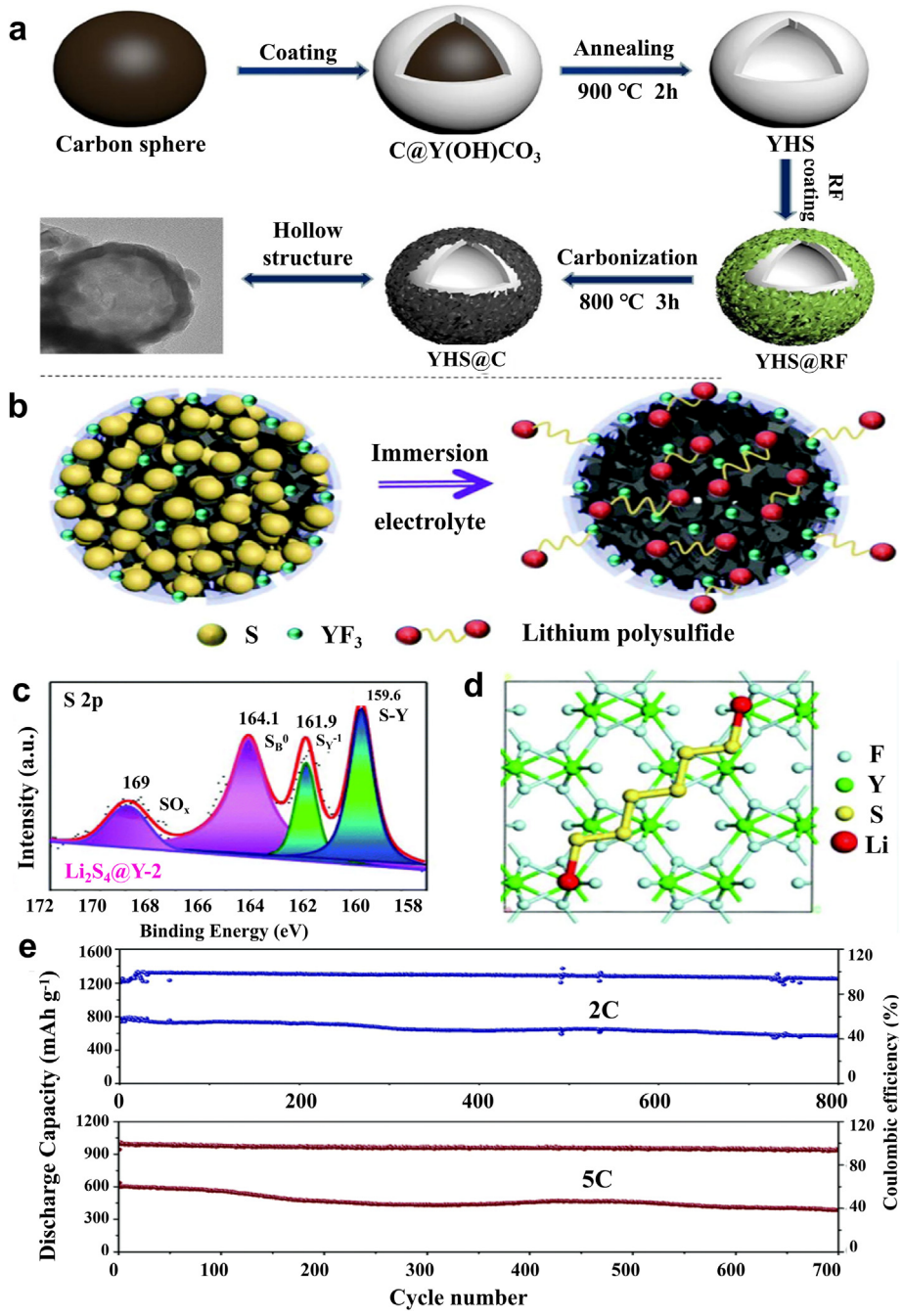

Fig. 7. Application of Y-based compounds in lithium–sulfur batteries. (a) Schematic illustration of the preparation process for YHS@C. Reproduced with permission From Ref. [66]. Copyright © 2019 American Chemical Society. (b) Schematic diagram showing how SC-YF_3-doped 3D in 1D CNFs inhibit the shuttle effect during lithiation. (c) Corresponding XPS spectra of Li_2S_4@Y-2. (d) Spatial adsorption model of Li_xS_y on YF_3 prototype surface. (e) Long-term cycling performances of YF_3/CNF cathode at 2C and 5C. Reproduced with permission from Ref. [67]. Copyright © The Royal Society of Chemistry 2019.

Besides La_2O_3 and $La(OH)_3$, Sm_2O_3 was also reported as an electrochemical catalyst in Li–S batteries. When Sm_2O_3/carbon aerogel was used as the sulfur cathode host, the battery presented a high initial discharge capacity of 1347 mAh/g at 0.2C. In addition, a capacity of 861 mAh/g at 0.5C was maintained after 300 cycles. The authors ascribed these outstanding performance results to the high adsorption ability and facile electron/ion transport pathway provided by Sm_2O_3 and the porous structure of the carbon aerogel [67]. Compared with Sm_2O_3 formation by hydrolysis during a sol-gel process, the preparation of Sm_2O_3 by carbonizing a Sm-containing MOF is more subtle. The resulting smaller Sm_2O_3 nanoparticles thus were distributed more uniformly over the carbon substrate. Subsequently, a cathode host impregnated with sulfur delivered a discharge capacity of 1322 mAh/g in the first cycle at 0.2C. After 300 cycles, the capacity was 866 mAh/g [64].

A representative Nd-based compound used as a Li–S battery host is Nd_2O_3. As reported by He *et al.*, well-dispersed Nd_2O_3 over a carbon aerogel showed an initial discharge capacity of 1327 mAh/g at 0.2C. The capacity remained around 907 mAh/g at 0.5C after 300 cycles. Coupled with the carbon aerogel, well-dispersed Nd_2O_3 not only adsorbed polysulfide by chemical anchoring but also promoted the lithium polysulfide conversion reaction [65].

Currently, the only Y-based compounds explored as sulfur cathode hosts are Y_2O_3 and YF_3. Y_2O_3/carbon nanotubes (CNTs) delivered a capacity of 912.5 mAh/g at 0.5C (Fig. 7a), and the capacity could be kept as high as 842.3 mAh/g, with a decay rate of 0.038% per cycle. Even under a high mass loading of 4.24 mg/cm^2, a considerable areal capacity of 3.79 mAh/cm^2 remained [66]. Similar to its oxide analog, YF_3/carbon nanofiber (CNF) synthesized via electro-blown spinning technology also showed outstanding electrochemical performance (Figs. 7b–e). Besides physical adsorption from the semi-closed carbon nanofiber layer, chemical anchoring to the polysulfide prevented polysulfide dissolution more effectively [67].

Among RE compounds thus far explored as sulfur hosts, Ce-based compounds are the most investigated [76–79]. A simple wet impregnation method was reported for decorating Ketjen black (KB) with CeO_2 nanodots. As-prepared KB/CeO_2 nanodots provided numerous polysulfide fixation spots and catalytic sites, as proved by a rate capability of 800 mAh/g at 2C and a high capacity retention of 710 mAh/g after 300 cycles [68]. The polar metal oxide CeO_2 enhanced cathode chemisorption to LiPSs, promoted the cathode redox reaction through catalysis properties, adsorbed polysulfide, and effectively inhibited the shuttle effect. As a result, CeO_2 has become popular as a sulfur host. CeO_2/micromesoporous N-doped carbon spheres (MMNC) were also investigated as a sulfur host, showing a high reversible capacity of 1066 mAh/g at 0.2C, a good rate capability of 737 mAh/g at 2.0C, and a high cycling stability of 0.024% capacity decay per cycle (Figs. 8a and b). Such outstanding battery performance arose from the synergic effect of N-doping and catalytic CeO_2, which inhibited polysulfide dissolution and accelerated the polysulfide conversion process [69]. Subsequently, CeO_2-webbed carbon nanotubes (CNTs) prepared by a solvothermal reaction were used as a sulfur host. By chemically binding with the polysulfide, CeO_2 suppressed polysulfide dissolution. In addition to fast electron paths provided by the CNTs, a sulfur cathode with CeO_2-webbed CNTs exhibited high specific capacity, superior cycling stability, and good rate capability [70]. Elsewhere, bare CeO_2 hollow spheres used as a sulfur host have shown good battery performance, without physical adsorption from a carbon host. For example, sulfur/CeO_2 hollow spheres exhibited a high rate performance of 876, 761, and 644 mAh/g at 1, 2, and 5C, respectively. During long-cycling testing, the spheres presented a capacity decay as low as 0.073% per cycle (Figs. 8c and d) [80].

Defect chemistry has received substantial attention not only in catalyst research but also with respect to battery cathodes, including RE compounds as sulfur hosts. A heterostructure comprising hollow oxygen-deficient CeO_2 (H–CeO_2-x)/Co nanocrystals@N-doped carbon (NC) nanospheres was developed as a multifunctional sulfur host for Li–S batteries [81]. The resulting H–CeO_2-x/Co@NC-sulfur cathode exhibited outstanding rate performance (626 mAh/g at 5C), superior cycling stability (a capacity retention of 81.6% after 1000 cycles at 2C), and a high areal capacity of 5.3 mAh/cm^2 at 0.1C. This work provided insights that are helpful for the rational design of heterostructures for high-performance Li–S batteries through defect chemistry.

As an analog of Ce oxide, Ce fluoride in the form of CeF_3 was also studied as a sulfur cathode host with PCNF. A sulfur cathode containing

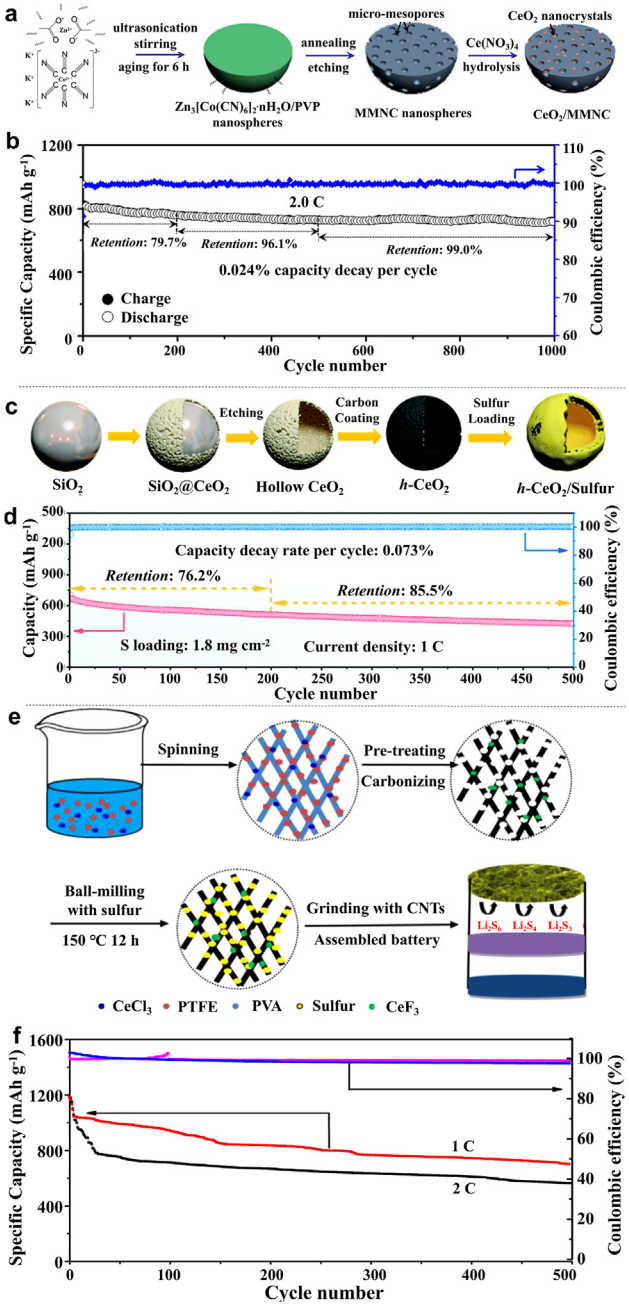

Fig. 8. Application of Ce-based compounds in lithium–sulfur batteries. (a) Synthesis process of CeO_2/MMNC. (b) Rate capabilities of CeO_2/MMNC-S-*x* cathodes. Reproduced with permission from Ref. [67]. Copyright © 2017 American Chemical Society. (c) Illustration of synthetic procedures for an h-CeO_2/sulfur cathode and a CNT/h-CeO_2 interlayer for Li–S batteries. (d) Long-term cycling properties at 1C for 500 cycles. Reproduced with permission from Ref. [80]. Copyright © 2019 Royal Society of Chemistry. (e) Synthesis processes of a CeF_3-doped PCNF–CNT–S composite electrode and battery assembled with the electrode. (f) Battery cycling performance of Ce–PCNF-2–CNT–S at various rates of 1 and 2C. Reproduced with permission from Ref. [71]. Copyright © 2018 American Chemical Society.

CeF_3/PCNF delivered a high initial discharge capacity of 1395 mAh/g and retained a capacity of 901.2 mAh/g after 500 cycles at 1C (Figs. 8e and f). In addition, a capacity of 819.3 mAh/g at 2C could be maintained, indicating outstanding rate capability [71].

2.2. RE compounds as interlayers

During the cycling process of Li–S batteries, problems such as active material loss, volume change, polysulfide dissolution, and shuttling cannot be entirely resolved by the cathode host. The concept of an interlayer was therefore first proposed in 2012 by Manthiram *et al.* [82]. Different from the function of the sulfur host inside the cathode, an interlayer aims to depress polysulfide shuttling outside the cathode. To some extent, the interlayer can be defined as a vice-electrode [83]. Since 2012, various materials have been studied as interlayers in Li–S batteries, including a carbon material [84], a metal compound [85], and a polymer [86]. Unlike the physical adsorption exhibited by carbon materials and the weak chemical adsorption engaged in by polymers, metal compounds show strong chemical anchoring with polysulfides due to a polar–polar interaction. Furthermore, some interlayers based on metal compounds even show a catalytic effect toward polysulfide conversion [87]. As summarized in Table 2, RE compounds used as interlayers in Li–S batteries mainly consist of oxides, sulfides, fluorides, and MOFs. A sulfur cathode delivers an initial capacity of over 800 mAh/g when RE compounds are applied as interlayers, and the high capacity can persist after hundreds of cycles. The corresponding capacity fading rate is analyzed in Fig. 9. In most cases, the capacity fading rate is below 0.1%, with the lowest reaching 0.022% across 800 cycles. With respect to rate capability, the specific capacity at 1C can reach 800 mAh/g for Y-based, Sc-based, and Ce-based compounds.

To date, RE metal oxides, including CeO_2, Y_2O_3, and Sc_2O_3, have been studied as interlayers in Li–S batteries. A CeO_2/multiwalled carbon nanotubes (MWCNTs) interlayer maintained a capacity of 520.7 mAh/g after 300 cycles, benefiting from the chemical adsorption of CeO_2 [88]. Ceric dioxide particle-incorporated carbon nanofibers (CO@CNF) were also used to form a functional interlayer [95]. Not only did the CO@CNF interlayer work as a physical barrier to the soluble polysulfide, but the presence of ceric dioxide particles also provided chemical adsorption for the polysulfide. Owing to these advantages, Li–S batteries with the CO@CNF interlayer delivered a high discharge specific capacity of 1086 mAh/g at 0.1C. In addition to the above chemical adsorption, CeO_2 even showed a catalytic effect toward polysulfide conversion. As a result, the battery exhibited not only stable cycling performance but also outstanding rate capability, even under a high mass loading of 6 mg/cm^2 [89]. Elsewhere, research on using Y_2O_3/KB as an interlayer for Li–S batteries was conducted. With this physical shield to restrain polysulfide shuttling, a capacity of 816 mAh/g remained after 200 cycles. Moreover, electrochemical impedance spectroscopy showed a low charge transfer resistance that indicated fast electrochemical kinetics as well as superior rate capability [90]. Unlike other RE oxides, Sc_2O_3 used as a catalyst even outperforms

Table 2
Summary of RE compounds as interlayer for Li–S battery.

Materials	Preparation method	Rate (C)	Initial capacity (mAh/g)	nth capacity (mAh/g)	Ref.
CeO_2/MWCNTs	Precipitation	0.2	898	300th 520	[88]
S/KB-CeO_2	Dealloying	0.2	830	1000th 225	[89]
Y_2O_3/KB	Wet impregnation	1	1054	200th 816	[90]
Sc_2O_3/CNTs	Solvothermal	1	1037	500th 788	[91]
La_2S_3	Precipitation	0.2	1280	100th 863	[92]
CeF_3/CNTs	Solvothermal and annealing	0.2	1015	100th 950 300th 705	[93]
Ce-MOF-808/CNTs	Solvothermal	1	1021	800th 838	[94]

MWCNTs：multiwalled carbon nanotubes.
KB：Ketjen black.
CNTs：carbon nanotubes.
MOF：metal-organic frameworks.

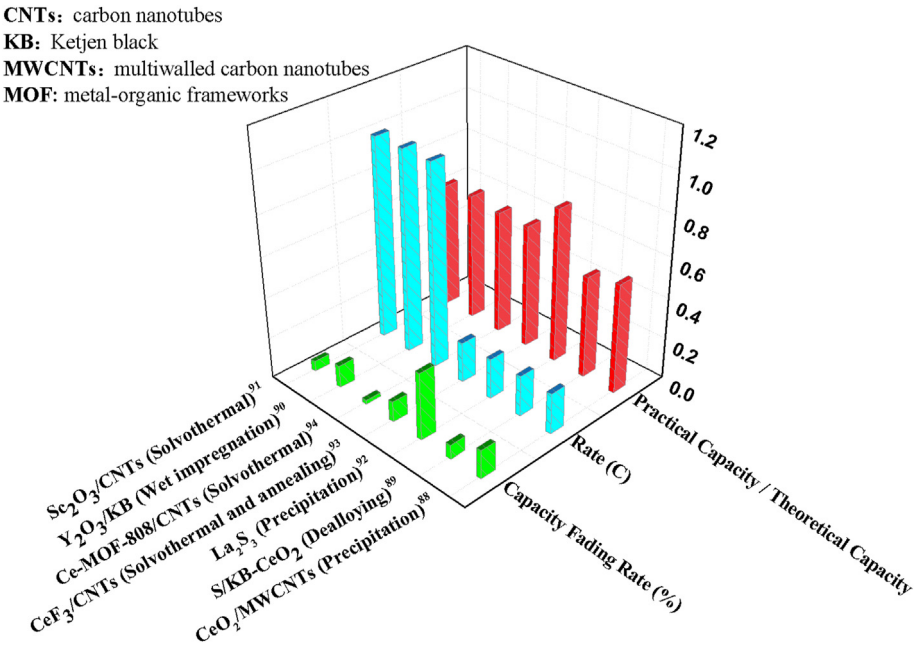

Fig. 9. Electrochemical performance of Li–S batteries with RE compounds as interlayers [88–94].

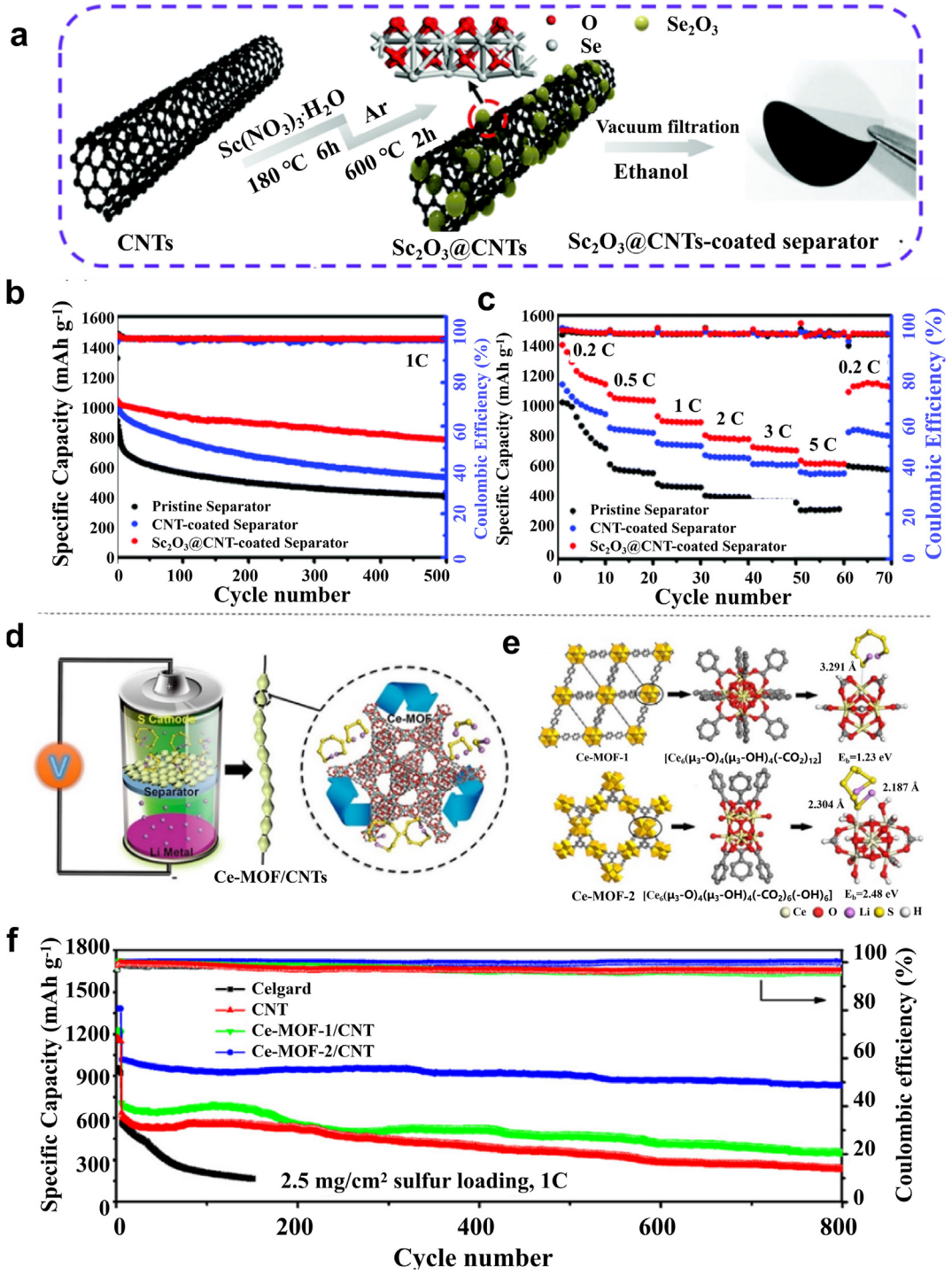

Fig. 10. RE compounds as interlayers for Li–S batteries. (a) Schematic illustration of the preparation of the Sc_2O_3/CNTs composite. (b) Cycling performance and (c) rate capabilities of cells with Sc_2O_3/CNTs-coated separators. Reproduced with permission from Ref. [91]. Copyright © The Royal Society of Chemistry 2020. (d) Scheme of Ce-MOF/CNTs as the separator coating material for a Li–S battery. (e) Structure, metal nodes, and Li_2S_6 adsorption sites in two different Ce-MOF materials. (f) Cycling performances of cells with different Ce-MOF/CNTs separators at 1C for 800 cycles (2.5 mg/cm^2 sulfur loading). Reproduced with permission from Ref. [94]. Copyright © 2019 American Chemical Society.

some noble metals, but its catalytic capability towards polysulfide conversion remains unknown. In one study, carbon nanotubes decorated by Sc_2O_3 were tested as an interlayer, yielding high capacity, outstanding rate capability, and stable cyclability (Figs. 10a–c). Low self-discharge and the mitigation of anode corrosion were also demonstrated [91].

RE metal sulfides were not studied as an interlayer in Li–S batteries until 2017, when Zheng *et al.* investigated La_2S_3. An ultralow decay rate of 0.055% was obtained during their cycling test. The stable cycling performance resulted from the strong interaction between the La–S bond and S–S bond, which effectively adsorbed polysulfide and slowed down polysulfide dissolution, therefore significantly improving the cycling performance [92]. As a representative RE metal fluoride, CeF_3 mixed with CNTs was studied as an interlayer. As with other RE compounds, porous carbon modified by CeF_3 catalytically accelerated the redox reaction, in addition to improving the physical adsorption and chemical binding. With such strong depression of polysulfide dissolution, the

battery showed quite stable cycling performance, with only 0.063% decay per cycle [93].

Besides RE metal oxides, sulfides, and fluorides, a RE-based MOF was studied as an interlayer by Wang *et al.* (Figs. 10d and f). At a mass loading of 2.5 mg/cm^2, the cell delivered an initial specific capacity of 1021.8 mAh/g at 1C. The capacity decay rate was only 0.022%, with 838.8 mAh/g remaining after 800 cycles. Even at a mass loading of 6 mg/cm^2, high capacity and stable cycling were preserved. Such excellent battery performance is attributable to the material's appropriate pore structure and high surface area, which physically depressed polysulfide dissolution substantially. The Ce-based MOF also resulted in the chemical anchoring of polysulfide and accelerated polysulfide conversion, contributing to better cycling performance [94]. In 2021, a mixed-valence cerium MOF named CSUST-1 was reported. Benefiting from the synergism between Ce(IV, III) arrays, abundant oxygen vacancies, and open Ce sites within CSUST-1, the CSUST-1/CNT composite used as a separator coating material in a Li–S battery accelerated the polysulfide redox kinetics and Li transportation to a remarkable extent [96]. Consequently, a Li–S cell with the CSUST-1/CNT-coated separator exhibited a high initial specific capacity of 1468 mA h/g at 0.1C and maintained long-term stability, resulting in a capacity of 538 mA h/g after 1200 cycles at 2C for a decay rate of only 0.037% per cycle.

3. Conclusions and perspectives

To sum up, cathode hosts and interlayers based on RE compounds have gained increasing attention due to the superiority of RE compounds over carbon-based materials and other metal compounds. After providing a general background on RE elements and the working mechanism of Li–S batteries, we have summarized the great improvements in capacity, rate capability, and cycling stability achieved when various RE compounds are used as cathode hosts or interlayers. The improved electrochemical performance is attributed mainly to the strong chemical anchoring of polysulfides, acceleration of the polysulfide conversion process, and controlled S/Li_2S deposition.

Despite this progress in using rare earth compounds for Li–S batteries, most work has centered on the cathode host and interlayer, with only a small portion covering lithium anode protection and electrolyte modification. In addition, the range of RE compounds selected as cathode hosts or interlayers remains quite narrow. Only La-based, Sm-based, Nd-based, Y-based, and Ce-based compounds have been investigated as hosts, and only Ce-based, Y-based, La-based, and Sc-based compounds have been studied for interlayers. In terms of REs used as compound species rather than element species, most research has focused on oxides, with only a scattering of studies on sulfides, hydroxides, fluorides, and MOFs. So RE materials explored to date for Li–S batteries are limited to light RE oxide, CeO_2, and La_2O_3 as representatives. Other as yet unexplored RE element-based compounds may possess higher conductivity, stronger polysulfide anchoring, and better catalytic effects towards the conversion between polysulfide and S/Li_2S. Further exploration should therefore be dedicated to other RE element-based compounds, such as Nd, Sm, Pr, *etc.*, or other compound species, such as nitrides, carbides, and so forth. In addition, our understanding of how RE compounds influence the lithiation of sulfur, the shuttle effect, and the reaction kinetics remains in its infancy, so *in situ* characterization techniques and theoretical calculations should be comprehensively applied to explore the relevant reaction intermediates and electrode/electrolyte interfaces.

Structure and property regulation is another avenue of exploration for RE compounds as cathode hosts or interlayers. For example, more active sites are required as polysulfide anchoring sites or electrochemical catalysis positions. Material nanonization is one way to increase the electrochemical active surface area, while defect engineering has also been proven capable of tuning chemically inert surfaces into catalytically effective interfaces. Researchers should also bear in mind that material design differs for cathode hosts and interlayers. For example, the sulfur cathode must be thick enough to accommodate high mass loading to achieve higher energy density, whereas the interlayer should be thin enough to decrease the weight of inactive components. The surface property of a cathode host should therefore be carefully tuned for strong adhesion to the current collector, thus preventing electrode materials from peeling off, but there is no need to consider surface adhesion when designing an interlayer material.

Although Li–S batteries have been studied intensively, the use of RE compounds as cathode hosts or interlayers remains under-investigated. Compared with carbon materials or transition metal compounds, we do not have a good understanding of the unique roles RE compounds play in polysulfide adsorption, polysulfide conversion, and S/Li_2S deposition, especially in terms of special 4f electrons. Advanced characterization methods, such as *in situ* spectroscopy, should therefore be applied to gain critical and detailed insights into the dynamic processes and interface changes that occur during the charge/discharge process. It is equally important to use theoretical calculations, evaluate the binding energies between polysulfides and RE compounds, and analyze the energy barriers in each elementary reaction.

The traditional view has voiced anxiety about the scarcity and cost of RE compounds. While it is true that some RE compounds, especially heavy ones, are indeed costly due to their rarity and complex production processes — terbium, for example, is worth as much as silver — the light RE compounds widely explored in this review are much cheaper due to their relative abundance and simple preparation. CeO_2 and La_2O_3 cost less than two dollars per kilogram, making them even cheaper than topsoil used to grow flowers. Further, the high energy density of commercial battery packages demands low usage of inactive components; in that context, this review has demonstrated that applying RE compounds as cathode hosts or interlayers is acceptable. Furthermore, the amount of a RE compound used can be further lowered if its catalytic function is brought into full play. Based on the above cost-effectiveness analysis, the application of RE compounds as cathode hosts or interlayers, especially from a financial perspective, is beyond question.

Last but not least, we hope this mini-review will become the starting point for researchers who want to extend the application of RE compounds to Li–S batteries or who are working on understanding the different effects that the d electrons of transition metal compounds and the f electrons of RE compounds have on electrochemical reactions. Continued efforts are required to further advance this booming area.

Author contributions

Bixia Lin completed the manuscript and revisions. Yuanyuan Zhang, Weifeng Li, and Junkang Huang participated in the Writing & Editing. Yong Yang and Siu Wing Or participated in Writing-Review. Zhenyu Xing and Shaojun Guo conceived and designed this work.

Conflict of interest

The authors declare no conflict of interest.

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