Advanced design of cathodes and interlayers for high-performance lithium-selenium batteries

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Abstract
Lithium-selenium (Li-Se) batteries have attracted ever-increasing attention owing to high volumetric capacity comparable to lithium-sulfur batteries and excellent electronic conductivity of Se. However, unsatisfactory energy density and cycling life of Li-Se batteries mainly caused by low utilization of Se and shuttle effect of polyselenides (PSES) seriously prevent their commercial applications. Herein, this work systematically reviews the recent advances of the state-of-the-art cathodes and interlayers in high-performance Li-Se batteries. First, the fundamental chemistries of Li-Se batteries are introduced in terms of various Se precursors and electrochemical behaviors. Second, the main strategies in cathodes and interlayers for addressing poor conductivity of Se and shuttle effects of PSES are summarized as three-dimensional conductive skeletons for Se, physical confinement of Se, chemisorption and catalytic conversion of PSES, and free-standing interlayers and interlayers on separators. Further, the synthesis strategies and enhanced electrochemical performance are especially exemplified to highlight the possible enlightenments for constructing advanced cathodes and interlayers. Finally, the future challenges and perspectives of advanced cathodes and interlayers in high-performance Li-Se batteries are briefly discussed.

KEYWORDS
cathodes, energy storage, high energy density, interlayers, lithium-selenium batteries
With the rapid development of our society, lithium-ion batteries (LIBs) have been widely applied in various aspects such as cell phones, laptops, and electric vehicles (EVs).\(^1\) However, current LIBs based on conventional graphite anodes could not meet the requirement of high energy density (e.g., >400 Wh/kg) in long-range EVs, therefore, advanced batteries based on lithium metal anodes with ultra-high capacity of 3860 mAh/g and cathodes with multielectron reactions have attracted considerable attention for next-generation energy storage technologies. Among them, lithium-selenium (Li-Se) batteries are regarded as a promising candidate,\(^{2,3}\) and intensively studied during the past several years (Figure 1A).

The great research enthusiasm of Li-Se batteries mainly originates from several following features of selenium (Se).\(^4\) Se, as a congener of sulfur (S), possesses a higher density (\(\rho\)) of 4.81 g/cm\(^3\) than S (2.07 g/cm\(^3\)), thus, its theoretical gravimetric capacity (\(C_m\)) and energy density (\(E_m\)) based on the reaction of Se + 2Li\(^{++}\) + 2e\(^-\) = Li\(_2\)Se are 675 mAh/g and 1155 Wh/kg, which are 40.4 and 44.4% of the values of S (Figure 1B), respectively. However, high volumetric capacity (\(C_v\)) of 3254 mAh/cm\(^3\) and energy density (\(E_v\)) of 2528 Wh/L can be achieved for Li-Se batteries, which are 93.9 and 90.3% of the corresponding values of Li-S batteries. Notably, the volumetric parameters of batteries seem to be more important than gravimetric counterparts for practical applications, therefore, Li-Se batteries appeal extensive interest after the rising of Li-S batteries. Moreover, the Se shows high conductivity of 1x10\(^{-3}\) S/cm (vs. 5x10\(^{-30}\) S/cm for S) and low Se-Se bond energy (BE) of 172 kJ/mol (vs. 240 kJ/mol for S-S bond) (Figure 1B). Further, compared with polysulfides (PSs), polyselenides (PSes) exhibit weak shuttle effects,\(^5\) therefore, Li-Se batteries possess the potential to perform superior rate capability and cycling life to Li-S batteries.\(^{h}\)

Besides the unsolved issues of lithium metal anodes (e.g., lithium dendrites) in Li-based batteries, three main challenges of Se cathodes seriously prevent their commercialization process of Li-Se batteries.\(^3,6,7\) First, the insufficient conductivity of Se can not ensure excellent electron transfer in cathodes, especially in thick electrodes, which will lead to low utilization of Se and sluggish reaction kinetics with high voltage polarization (Figure 1C). Second, the soluble nature of intermediate PSes in electrolytes will cause notorious shuttle effect. In this case, the Se in cathodes firstly reacts with lithium ions, and thus, the intermediate PSes will diffuse into the electrolyte, and ultimately form solid Li\(_2\)Se on the surface of Li anode (Figure 1D). As a result, such undesired side-reactions of Li anode and the loss of active Se-based species in cathodes comprehensively result in battery failure within a short service time. Lastly, the volume

![Figure 1](https://example.com/figure1.png)

**Figure 1** (A) A statistic of articles on Li-Se batteries published in the past 10 years. (B) Comparison between Se and S in terms of properties and corresponding battery performance, in which \(\sigma\) and \(mp\) represent conductivity and melting point, respectively. (C-E) The main challenges of Li-Se batteries, including (C) poor conductivity of solid Se or Li\(_2\)Se with low utilization, (D) shuttle effect of PSes, and (E) serious pulverization of electrodes during charge/discharge processes.
Figure 2: Schematic of advanced cathodes and interlayers for high-performance Li-Se batteries, including conductive skeletons for Se, physical confinement of Se, chemisorption of PSe₅, catalytic conversion of PSe₅ in cathodes, free-standing interlayers and interlayers on the separators.

2 | SE CHEMISTRIES IN LI-SE BATTERIES

Before the discussion of cathodes and interlayers in Li-Se batteries, the fundamental Se chemistries are firstly clarified to better understand the following various cathodes and corresponding work principles of Li-Se batteries. Typically, one traditional Li-Se cell consists of a Se-based cathode, a Li metal anode, a polypropylene (PP) separator, and electrolyte. It is noted that different electrolytes seriously influence the reaction behaviors between Se and Li. In general, the ether-based electrolyte consists of 1 M lithium bis(trifluoromethylsulfonyl) imide (LiTFSI) salt in 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane solvents with a volume ratio of 1:1, and typical charge/discharge profiles involving multiphase mechanism are usually recorded in such electrolytes. However, the cycling performance tends to be unsatisfied due to the serious shuttle effect caused by high PSe₅ solubility in ether-based electrolytes. For instance, microporous carbon spheres/seleoniun hybrid cathode (MPCS/Se) showed three reduction peaks at 2.06, 1.95, and 1.53 V in the first cycle, which corresponded to the reductions of Se to Li₂Seₙ (4 < n < 8), Li₂Se₂, and final solid Li₂Se (Figure 3A and C), respectively. Meanwhile, two oxidative peaks were recorded at 1.90 and 2.32 V corresponding to the oxidation of Li₂Se to Li₂Seₙ and Se, respectively. However, when carbonate-based electrolyte of 1.0 M LiPF₆ in mixed solvents of dimethyl carbonate and ethylene carbonate (EC) with a volume ratio of 1:1 was used, one reduction peak at 1.57 V and one oxidation peak at 1.96 V were only observed as one-step electrochemical reaction between Se and Li₂Se without the involvement of liquid PSe₅ (Figure 3B and C), thus, shuttle effect was basically avoided to achieve excellent cycling life.

The Se chemistries in Li-Se batteries are closely relative to Se molecular structures. Due to similar physicochemical properties of S and Se, both S₈ and Se₈ possess similar ring-like structure, when Se is substituted with S, the resulting SeₙS₈₋ₙ ring may integrate their advantages. As shown in Figure 3D, electron cloud around Se in Se₂S₈ ring tends to migrate to S due to the higher electronegativity of S. Therefore, in contrast to S₈, superior conductivity of Se₂S₈ could be achieved. And the calculated bond breaking and lithiation energy (ΔU) of S-Se (−614.04 kJ/mol) was in the middle of S-S (−663.85 kJ/mol) and Se-Se (−607.115 kJ/mol) (Figure 3E). Accordingly, an ordered mesoporous carbon/Se₂S₈ hybrid cathode (CMK-3/Se₂S₈) showed two oxidative peaks at 2.4 and 2.5 V in cyclic voltammetry (CV) curve (Figure 3F), while the compared CMK-3/S and CMK-3/Se cathodes presented one oxidative peak at 2.35 and 2.6 V, respectively.
FIGURE 3  The fundamental chemistries in Li-Se batteries. (A, B) CV curves of MPCS/Se cathode in (A) ether-based electrolyte and (B) carbonate-based electrolyte, and (C) corresponding charge/discharge profiles in both electrolytes. Reproduced with permission from Ref. [11]. Copyright 2020, Elsevier. (D) Electron cloud distributions of S₈ and Se₂S₆ around Se in Se₂S₆ ring, and (E) calculated bond breaking and lithiation energies of Se₂S₆. Reproduced with permission from Ref. [13]. Copyright 2019, Wiley-VCH. (F) CV curves of CMK-3/SeS₂, CMK-3/Se, and CMK-3/S electrodes. Reproduced with permission from Ref. [14]. Copyright 2017, Wiley-VCH. (G) The schematic of Se/PAN and possible molecular structure of Se/PAN, and (H) possible energy storage mechanism. (I) The charge/discharge profiles and (J) cycling performance of Se/PAN cathodes obtained at various current densities. Reproduced with permission from Ref. [15]. Copyright 2015, Royal Society of Chemistry

The Se can also exist as chain-like Se in polymer matrix, which is chemically bonded with polymer backbones with molecular level mixture.¹⁷ Owing to the strong interaction between Se species and polymer matrix, unique electrochemical behaviors with single one charge/discharge voltage plateau are usually recorded, and the shuttle effects of PSees are greatly suppressed. As a typical example, black selenized polyacrylonitrile (Se/PAN) was synthesized via heat treatment of Se and PAN mixture at 500°C in Ar atmosphere (Figure 3G), during which C≡N bonds in PAN were cyclized to generate heterocyclic structures with C=C and C=N bonds. Meanwhile, chain-like Se₉ linked two adjacent polymer backbones, and the length of Se₉ could be roughly adjusted by varying the weight ratio of Se and PAN precursor.¹⁵ Notably, the nitrogen groups in Se/PAN possibly involved the electrochemical process, in which the hexatomic rings in the polymer main chains were opened at the nitrogen groups in the initial discharge stage, and the nitrogen groups would dissociate from and chemically bond with the main chains during discharge/charge processes (Figure 3H), respectively. Interestingly, a pair of discharge/charge voltage plateaus was observed mainly in the range of 1.6-2 V (Figure 3I), and the voltage polarizations slightly increased with the rise of current density from 0.05 to 5 mA/cm², demonstrative of excellent rate capability of Se/PAN.¹⁵ Moreover, the as-fabricated Se/PAN cathodes showed superior cycling performance over 200 times without any capacity fading (Figure 3J).¹⁸

Based on the above understanding of the main Se chemistries in Li-Se batteries, it is highlighted that the Se-based cathodes are one of the key aspects to determine the final performance of Li-Se batteries. Therefore, advanced design and protection of Se-based cathodes have been paid much attention recently, such as the inhibition of shut-
tle effects of PSes via physical or chemical effects in Se-based hosts, interlayers, and modified separators of Li-Se batteries.

3 | SE-BASED CATHODES

Due to the limited chemical strategies to synthesize Se, most Se-based cathodes are usually prepared by a melting-diffusion strategy. Specifically, commercial Se powders are firstly ground with the host materials (e.g., porous carbon), then the mixed powders are subjected to heat treatment at a typical temperature of 260°C for 12 h in Ar atmosphere, during which molten Se will diffuse into the pores of host materials via capillary force. After cooling to room temperature, Se-based cathodes can be obtained, in which Se will be uniformly distributed in the host materials. Therefore, great enthuisiasms are devoted to developing new strategies to enhance Li-Se batteries. Several key strategies, such as the conductive skeletons for Se, physical confinement of Se, chemisorption of Se, and catalytic conversion of PSes, are intensively explored to address the challenges of Se cathodes, for example, poor conductivity of Se, shuttle effect of PSes, and sluggish kinetics of the reaction between PSes and Li. To clearly distinguish these strategies, the state-of-the-art Se-based cathodes are classified below, and further summarized with important structural and electrochemical parameters in Table 1.

3.1 | Conductive skeletons for Se

Pure Se cathodes suffer from low utilization of Se because of the low conductivity of Se, resulting in the low capacity of Li-Se batteries. An effective strategy is to composite Se with conductive carbon nanomaterials, for example, one-dimensional (1D) carbon nanotubes (CNTs), and two-dimensional (2D) graphene, which can serve as conductive skeletons to fast transport electrons across hybrid cathodes. Furthermore, free-standing electrodes effectively eliminate the usage of auxiliary polymer binders and heavy metal current collectors, with the help of these carbon nanomaterials, high mass loading electrodes with high energy densities can be constructed. As a typical example, Se nanowires with a diameter of <150 nm and micrometer length (1–2 μm) were prepared after the addition of ascorbic acid into the mixed solution of SeO₂ and β-cyclodextrin in the presence of CNTs. Then, the filtration and drying processes were conducted to synthesize free-standing Se/CNT composite paper with a diameter of 7 cm, in which Se nanowires were well interwoven with CNTs. Impressively, the hybrid electrodes with a thickness of 23 μm and Se content of 60 wt% showed a remarkable capacity of 537 mAh/g at 1 C. To construct high mass loading electrodes, three-dimensional (3D) printing is a feasible strategy. For instance, the Ketjenblack (KB)/SeS₂ hybrid was firstly synthesized via a melting-diffusion strategy at 160°C for 12 h, which was further mixed with CNTs and poly(vinylidene fluoride) in N-methyl-2-pyrrolidone, giving birth to homogeneous KB/SeS₂@CNT ink with high concentration of 333.3 mg/mL. Finally, 3D free-standing electrodes were obtained via direct ink writing on quartz substrates, phase inversion, and freeze-drying process (Figure 4A). Elemental mapping visually demonstrated the uniform dispersion of Se and C in the printed electrode (Figure 4B), and scanning electron microscope (SEM) image further confirmed the uniform mixture of KB/SeS₂ and CNTs (Figure 4C). Most importantly, 3D printed cathodes achieved high areal SeS₂ loading up to 7.9 mg/cm², and impressive areal capacity of 9.5 mAh/cm². However, limited cycling life with only 80 cycles was recorded due to serious shuttle effect of PSes in such high mass loading electrodes. It is suggested that the presence of carbon materials mainly improve the conductivity of thick cathodes, and thus, additional strategies are highly needed to further enhance the cycling stability.

Moreover, a mixed suspension of multiwalled CNTs (MWCNTs) and graphene was firstly syringe-filtrated into a barrier layer, and then active layer was fabricated on the top of the barrier layer via syringe filtration of suspension containing carbon nanofiber/Se (CNF/Se) composites, MWCNTs, and graphene. After repeating the above processes, the free-standing layered Se-based cathodes were constructed, in which active layers and barrier layers were alternately aligned (Figure 4D), and Se areal loadings from 2.25 to 13.5 mg/cm² could be adjusted by changing layer numbers. Notably, the recorded Se loading of 13.5 mg/cm² obviously exceeded the previously reported values (Figure 4E). Importantly, the layered cathode with 6.75 mg/cm² of Se showed exceptionally high capacity and cycling stability over 300 times (Figure 4F).

To achieve high volumetric capacity Li-Se batteries, low-cost and sustainable nanocelluloses were assembled into free-standing films with high mass density of 2.37 g/cm³, when Se was infiltrated into the film via a melting-diffusion strategy, and the resulting free-standing hybrid cathode performed a remarkable volumetric capacity of 1028 mAh/cm³ and energy density of 1727 Wh/L. And the largest volumetric energy density could be up to 2467 Wh/L, which was comparable to the state-of-the-art LiNi₀.₅Co₀.₁₅Al₀.₃Fe₀.₅O₂ (NCA) electrodes, and higher than those of common cathodes such as LiCoO₂ and LiFePO₄. However, the cycling performance of such electrodes is
| Classification                        | Cathode materials                                                                 | Se Content (wt%) | Areal loading (mg/cm²) | Capacity (mAh/g) | Refs. |
|--------------------------------------|-----------------------------------------------------------------------------------|------------------|------------------------|------------------|-------|
| Conductive skeletons for Se          | graphene-Se@CNT composite                                                       | 30               | —                      | 315(0.1 C)       | 19    |
|                                      | Se/graphene/CNT hybrid                                                           | 36.3             | —                      | 504(0.2 C)       | 20    |
|                                      | Se/CNT hybrid                                                                    | 60               | —                      | 401(1 C)         | 21    |
|                                      | KB/SeS₂ hybrid                                                                   | —                | 7.9                    | 9.5 mA/cm²(1.8 mA/cm²) | 22    |
|                                      | layered Se based cathode                                                          | —                | 2.25                   | 580(50 mA/g)     | 23    |
| Physical confinement of Se           | Se/microporous carbon                                                            | 50               | 1.2                    | 508.8(0.1 C)     | 24    |
|                                      | Se/mesoporous graphitic carbon microspheres                                      | 70               | 1.2                    | 584(0.5 C)       | 25    |
|                                      | Se/nano-cellulose derived mesoporous carbons                                     | 70               | 6.64                   | 508(0.2 C)       | 26    |
|                                      | Se/paper cup derived porous carbon                                               | 57               | 1.1                    | 431.9(0.2 C)     | 27    |
|                                      | Se/porous carbon nanoplate                                                       | 55               | 1.06                   | 589(0.2 C)       | 28    |
|                                      | Se/hierarchically porous activated carbon                                        | 33~41            | 1.0-1.2                | 655(0.1 C)       | 29    |
|                                      | Se/hierarchical porous tubular carbon                                            | 53               | 0.6                    | 515(0.2 C)       | 30    |
|                                      | Se/pomegranate-like porous carbon                                                | 70               | —                      | 600(0.1 C)       | 31    |
|                                      | Se/hollow carbon spheres                                                          | —                | 0.72                   | 400(0.5 C)       | 32    |
|                                      | Se/MOF-derived carbon nanosheets                                                 | —                | 1.0                    | 311.8(2 C)       | 33    |
|                                      | Se/MOF-derived porous carbon microcubes                                          | 49.7             | —                      | 425.2(0.2 C)     | 34    |
|                                      | alkaline lignin derived porous carbon                                            | 51               | 2.4                    | 453(0.5 C)       | 35    |
|                                      | Se/MOF-derived porous carbon nanofibers                                          | 55               | 0.4                    | 588(0.5 C)       | 36    |
|                                      | graphene encapsulated selenium/carboxylated CNTs                                 | 48.7             | 1.0                    | 592              | 37    |
|                                      | Se/graphite platelet nanofiber                                                    | 75               | —                      | 384.7(0.1 C)     | 38    |
|                                      | graphene/PANI-coated selenium/carbon composites                                  | 51.9             | 2.0-3.0                | 588.7(0.2 C)     | 39    |
|                                      | Se/PANI                                                                          | —                | 1.0-1.5                | 298.7(0.5 C)     | 40    |
| Chemisorption of polyselenides       | Se/N-containing hierarchical porous carbon                                       | 56.2             | 0.7-1.0                | 305(2 C)         | 41    |
|                                      | Se/N-doped carbon                                                                | 80               | —                      | 462(0.5 C)       | 42    |
|                                      | Se/N-containing mesoporous carbon spheres                                        | 60               | 1.0-1.5                | 526.5(0.2 C)     | 43    |
|                                      | Se/N-doped carbon polyhedrons/crumpled graphene balls                            | 60               | 1.8                    | 462(0.5 C)       | 44    |
|                                      | MOF derived hierarchical C-Co-N/Se                                               | 76.5             | 2.0                    | 574.2            | 45    |
|                                      | Se@CN₉ nanobelts                                                                 | 62.5             | 1.9                    | 608.8            | 46    |
|                                      | Se/MOF-derived N-doped core–shell hierarchical porous carbon                     | 54               | 1.5                    | 555(0.2 C)       | 47    |
|                                      | Se/N, O dual-doped hierarchical porous carbon                                    | 48               | 1.5-3.0                | 545(0.5 C)       | 48    |
|                                      | MOF@Se@MnO₂                                                                      | 38               | 1.0                    | 306(1 C)         | 49    |
|                                      | TiO₂-Se composite                                                                | 70.8             | —                      | 158(0.1 C)       | 50    |
|                                      | Se/malic acid-Mn-derived porous carbon                                           | 72               | —                      | 580(1 C)         | 51    |

(Continues)
Table 1 (Continued)

| Classification                  | Cathode materials                        | Se Content (wt%) | Areal loading (mg/cm²) | Capacity (mAh/g) | Refs. |
|--------------------------------|------------------------------------------|-----------------|------------------------|-----------------|-------|
| Catalytic conversion of polyselenides | Se/CoSe₂-porous carbon composite        | 43              | 1.0-1.2                | 408 (1 C)       | 52    |
|                                | CoP/N-doped carbon arrays/Se hybrid     | -               | 2.6                    | 1026 (0.2 A/g)  | 53    |
|                                | Co, N-doped hollow porous carbon/Se hybrid | 57             | 0.8                    | 563 (0.1 C)     | 54    |

Figure 4 Conductive skeletons for Se. (A) The schematic of synthesis procedure of KB/SeS₂ hybrid cathodes, involving 3D printing and subsequent phase inversion and freeze drying processes. (B) Elemental mapping analysis and (C) SEM image of KB/SeS₂ hybrid. Reproduced with permission from Ref. [22]. Copyright 2020, Elsevier. (D) Cross-section SEM image of layered Se-based cathodes with alternative active layers and barrier layers. (E) A comparison of layered Se-based cathodes with reported electrodes in terms of areal capacity and Se loading. (F) Cycling performance of layered Se-based cathodes with different Se loading at 50 mA/g. Reproduced with permission from Ref. [23]. Copyright 2019, Elsevier

not satisfied, therefore, the conventional introduction of Se into conductive skeletons is not enough to guarantee ideal Li-Se battery performance, and other effective strategies are highly required, which will be discussed as followed.

3.2 Physical confinement of Se

3.2.1 Porous carbon hosts

Generally, porous materials possess higher surface energies than bulk counterparts, and thus, they are employed to physically confine PSes in the porous nanospaces to improve Li-Se battery performance. In consideration of the insufficient conductivity of Se-based cathodes, porous carbon hosts are the ideal candidates for Se. Therefore, compared with nonporous carbon/Se hybrid electrode, porous carbon/Se cathodes usually exhibit excellent cycling stability in Li-Se batteries. In this regard, the key is to reasonably design and engineer such carbons with specific pore structures.

So far, various strategies have been developed to rationally synthesize porous carbons. For example, polystyrene (PS) spheres were employed as soft templates for hydrothermal carbonization of glucose at 180°C for 24 h. After heat treatment at 900°C for 3 h in Ar, hollow carbon spheres (HCSs) with a shell thickness of approximately 50 nm were fabricated, and when HCSs served as the host, the corresponding Li-Se batteries exhibited remarkable capacity of approximately 400 mAh/g at 0.5 C even after 400 cycles. Moreover, metal-organic frameworks (MOFs) with metal ion nodes and organic molecule linkers are the multifunctional precursors for porous carbon hosts for Se. For instance, nickel-based MOFs (Ni-MOFs) were hydrothermally synthesized in dimethylformamide at 150°C for 12 h with nickel nitrate
and benzene-1,3,5-tricarboxylic acid precursors. Then, HCSs (MHPCS) with typical sizes of 300−400 nm were obtained after annealing Ni-MOFs at 800 °C in Ar, followed by subsequent acid etching of Ni species. Finally, Se was infiltrated into the pores of MHPCS through a melting-diffusion process at 260 °C for 20 h in Ar, giving birth to MHPCS/Se hybrid (Figure 5A). With this designed host, a low capacity fading of 0.08% per cycle at 0.5 C was observed over 500 cycles.58

Further, hollow mesoporous carbon spheres (HMCS) were prepared via coating SiO2/resorcinol formaldehyde (SiO2/RF) shell on SiO2 nanospheres, carbonization, and SiO2 etching processes (Figure 5B). The diameter and shell thickness of HMCS were approximately 300 and 10 nm, respectively. When Se was infiltrated into the mesoporous (∼3.9 nm) shells of HMCS, the resulting Se@HMCS hybrid well inherited the hollow sphere structure of HMCS (Figure 5C). Importantly, Se@HMCS cathodes delivered high capacity of 710 mAh/g even after 800 cycles at 500 mA/g.59 In addition, commercial ordered mesoporous carbons (CMK-3) with high specific surface area (SSA) of 1113 m2/g and concentrated mesopores (3.76 nm) have been used as the Se hosts to construct stable solid-state Li-Se batteries (Figure 5D).60

It should be noted that microporous carbon (MiC) may exhibit better electrochemical performance than those of mesoporous and macroporous counterparts due to the small pore diameter for strong confinement effects of Se species. For instance, NaY zeolite and furfuryl alcohol (FA) were selected as hard template and carbon precursor, respectively. Then, the carbonization of FA and subsequent chemical vapor deposition of acetonitrile were conducted.
at 800°C. Lastly, NaY templates were etched by HF acid, generating microporous carbon with high SSA of 1757 m²/g and concentrated pore size distribution of 1.02 nm (Figure 5E). Importantly, the resulting MiC/Se hybrid with Se content of 44.2 wt% showed one discharge/charge plateau in carbonate-based electrolyte, indicating the phase conversion between Se and Li₂Se without involving the PSes. Thereby, high rate capacity of 363 mAh/g at 5 C and long service life of 500 times at 0.5 C were achieved.12 Although excellent cycling performance is observed in Se/microporous carbon hybrid cathodes,11,12,62,63 microporous carbons usually possess low pore volume for Se accommodation, thus, the energy densities of such cathodes may be not sufficient. In this case, rational design of hierarchical porous carbon hosts may be a good choice to develop high-performance Li-Se batteries,64,65 in which the micropores and mesopores can physically confine Se or PSes in nanopores and promote high Se utilization to endow long-term cyclability and high capacity, and macropores can significantly facilitate electrolyte diffusion for high rate capability.

3.2.2 Coating layers

With the consideration of open feature of porous structure, only confinement of Se species in porous hosts is not possible to totally prohibit the diffusion of PSes into electrolytes. To address this issue, constructing outer coating layers on the surface of Se-based cathodes is another key strategy to physically confine Se or PSes.67

To achieve this purpose, polymer monomers can be precisely assembled on the heterogeneous interface of Se-based materials via adjusting polymerization time and other parameters, resulting in uniform polymer coating shells on Se-based cathode materials.68 As a typical example, CMK-3/SeS₂ hybrid was firstly synthesized with CMK-3 and SeS₂ precursors via a melting-diffusion strategy (Figure 6A), and then dopamine was added into the CMK-3/SeS₂ suspension containing tris-buffer solution. After overnight, polydopamine (PDA) were stably polymerized on the surface of CMK-3/SeS₂ (Figure 6B), resulting in CMK-3/SeS₂@PDA hybrid. The presence of uniform PDA layer on CMK-3/SeS could be visually observed, and the
thickness of PDA was 10–15 nm (Figure 6C). The key role of PDA layer was confirmed by the immersing experiment, in which CMK-3/SeS₂@PDA and CMK-3/SeS₂ cathodes with different discharge states were immersed in DOL for 2 h (Figure 6D and E). In a sharp contrast, the color of DOL with CMK-3/SeS₂@PDA was much lighter than that with CMK-3/SeS₂ (Figure 6E), indicative of the unique role of PDA in preventing diffusion of PSes from CMK-3 host. Further, CMK-3/SeS₂@PDA cathode demonstrated a capacity of 783 mAh/g at 0.2 A/g after 150 cycles, higher than that of CMK-3/SeS₂ cathode (419 mAh/g after 100 cycles).¹⁴

To overcome the limited conductivity of common polymer, conductive polymer coating layers on Se-based materials are usually employed to facilitate fast electron transfer across the electrodes for Li-Se batteries. As a low-cost conductive polymer, polyaniline (PANI) has been frequently employed to modify functional materials. For instance, SeS₂ was infiltrated into the nanopores of two spherical surfaces in double-layered hollow micro-/mesoporous carbon spheres (DSMCs), resulting in DSMC-SeS₂ hybrid (Figure 6F). Then, HCl solution containing aniline monomer was mixed with DSMC-SeS₂ suspension under the protection of N₂. Subsequently, peroxydisulfate dissolved in HCl solution was poured into the above mixture. After polymerization reaction of aniline at 0°C for 10 h, PANI was successfully coated on DSMC-SeS₂, giving birth to PANI-DSMC-SeS₂ composite.⁶⁶ Notably, PANI-DSMC-SeS₂ cathode exhibited higher capacity of 731 mAh/g at 0.2 A/g after 200 cycles than that of DSMC-SeS₂ (535 mAh/g), indicating the physical confinement of PANI shells for enhanced cycling stability.

Moreover, graphene nanosheets with atomic thickness, high conductivity, unique 2D structure, and excellent mechanical properties are promising coating layers for Se-based materials. Typically, the Se/C hybrid was firstly coated by PANI layers, resulting in PANI@Se/C hybrid. Then, graphene nanosheets were coated on PANI@Se/C via electrostatic assembly of graphene oxide (GO) and PANI@Se/C and subsequent reduction of GO (Figure 6G). As a result, the dual coating layers of PANI and graphene on Se/C (PANI@Se/C-G) guaranteed excellent cycling stability over 500 times at 2 and 5 C,³⁹ suggesting the feasibility of dual coating of PANI and graphene on Se based nanostructures.⁶⁹

### 3.3 | Chemisorption of polyselenides

It is well accepted that the intermediates of PSes and final discharged product of Li₂Se possess high polar surface, which are hardly bonded or captured by the nonpolar carbon hosts. Consequently, it is hard to realize totally physical confinement of PSes species into nonpolar carbon hosts due to poor interactions. Therefore, the construction of nonpolar and polar sites in Se hosts plays key role in stabilizing both Se and various PSes for enhancing battery performance. In general, the interactions between the polar sites and PSes can be considered as chemisorption of PSes. In the following section, the key methodologies to synthesize such high-performance hosts with chemisorption mechanism will be elaborated in detail.

#### 3.3.1 | Heteroatom doped carbon adsorbers

The electronegativities of element F, O, N, S, C, P, and B, are 3.98, 3.44, 3.04, 2.58, 2.55, 2.19, and 2.04, respectively. And, these heteroatoms are readily doped into carbon substrates, which will change the distribution of local electron density around carbon atoms. Consequently, heteroatom doped carbons can exhibit enhanced conductivities and polarities for chemisorption of PSes.⁴²

Typically, N-doped carbons are frequently reported to serve as Se hosts. And MOFs with diverse atoms provide the possibilities to synthesize heteroatom doped carbon.⁴⁴,⁷¹ For instance, N-doped carbon (N-CSHPC) with microporous core and mesoporous shell was fabricated by pyrolysis of zeolitic imidazolate framework (ZIF)-based core-shell (ZIF-8@ZIF-67) precursors and HCl etching process, and the N-CSHPC cathodes displayed stable cyclability over 200 cycles at 1 C.⁵⁷ To further reveal the underlying chemical effects between N species and Li₂Se, density functional theory (DFT) was carried out, in which the pyridinic (N₁), pyrrolic (N₂), and graphitic (N₃) nitrogen exhibited strong binding energies of 4.49, 3.78, and 1.84 eV with Li₂Se (Figure 7A), obviously higher than that of pure graphene (1.66 eV). In addition, with MOFs and PAN precursors, N-doped CNFs were fabricated for efficient Se/PSes hosts via electrospinning, carbonization, and KOH activation.³⁶ Moreover, N-doped mesoporous carbon was synthesized by bottom-up strategy to achieve physical and chemical confinement of PSes for stable Li-Se batteries.⁷²

Dual-element heteroatom codoped carbon hosts may exhibit better chemisorption of PSes than single element heteroatom doped counterparts, indicative of possible synergistic effect for enhanced Li-Se performance. As a typical example, conductive poly (3,4-ethylenedioxythiophene) polymer was employed as the precursor to synthesize S and O dual-doped hierarchical porous carbon (SO-HPC) via carbonization and KOH activation (Figure 7B),⁷⁰ which possessed high conductivity (4.0 S/m) and hierarchical porous structure with high SSA of 1487.7 m²/g. When the Se was loaded into SO-HPC, the as-fabricated Se₅₀/SOHPC₃ cathodes with Se content of 50 wt% exhibited...
ultralong service life over 1700 cycles, and negligible PSES were found in corresponding separator. In a sharp contrast, a great deal of orange PSES was visually observed in the separator corresponding to Se cathode (Figure 7C).

First-principle calculations were further employed to better understand the underlying mechanisms, in which the binding energies between Li₂Se and O, S doped carbon ranged from -2.21 to -2.44 eV (Figure 7D), much higher than that of S doped carbon (-1.46 to -1.16 eV) or O doped carbon (-0.96 to -1.01 eV), demonstrative of the enhanced chemisorption of PSES and Li₂Se on the surface of SO-HPC. Similarly, it was further confirmed by lignin-derived S, O coproporous carbon with experimental results and theoretical simulations. In addition, N, O coproporous carbon also endowed Se with a low capacity decay rate of 0.0074% per cycle over 1500 cycles at 0.5 C in carbonate electrolyte. Notably, high areal loading cathode is of great importance for practical applications of high energy density Li-Se batteries. Recently, the PAN-derived N-doped porous CNFs were developed to achieve ultrahigh areal Se loading up to 37.31 mg/cm², indicative of the promises of heteroatom doped carbon for advanced Li-Se batteries. Despite the great progress in doped carbon hosts for Li-Se batteries, the heteroatom doping levels are still very low (mainly <10 at%). Therefore, high-content heteroatom-doped carbons with novel synthesis strategies are highly needed for boosting high-performance Li-Se batteries.

### 3.3.2 Inorganic material-based adsorbers

Inorganic materials (e.g., metal, metal oxides, metal carbides, and metal sulfides) with polar surfaces could be employed to chemically anchor PSES, avoiding the shuttle effects. For instance, the Co nanoparticles with the size of 5-10 nm were embedded into N-doped porous carbon matrix by carbonization of ZIF-67 polyhedrons (C-Co-N) (Figure 8A and B). On one hand, C-Co-N hosts with abundant micropores and mesopores guaranteed fast electron transfer and rapid ion diffusion during charge/discharge cycles. On the other hand, the presence of Co nanoparticles and N species effectively chemisorbed PSES to avoid the occurrence of shuttle effect (Figure 8C). As a result, the C-Co-N/Se cathode with a Se loading of 76.5 wt% delivered a high capacity of 196.9 mAh/g at 10 C (Figure 8D). Besides the metals, metal oxide hosts were also reported as chemical adsorbers for PSES. For instance, TiO₂ with the merits of outstanding chemical stability, excellent electronic properties, and environmental friendliness was used as Se immobilizer for Li-Se batteries. Notably, a discharge capacity of 481 mAh/g was realized at 0.1 C, obviously higher than that of Se (343 mAh/g). In another example, Kang and coworkers successfully developed graphitic carbon (GC) microspheres embedded with TiO nanocrystals (GC-TiO) via annealing of activated carbon (A-C) microspheres in the presence of Fe(NO₃)₃ and titanium.
isopropoxide (TTIP) under H₂ atmosphere, and subsequent low-temperature oxidization and HCl etching of Fe species (Figure 8E). Due to the abundant TiO nanocrystals and mesopores (4-50 nm) (Figure 8F), GC-TiO microsphere hosts ensured a high Se loading of 70 wt%, most importantly, the as-prepared GC-TiO/Se exhibited a capacity of 584 mAh/g at 0.5 C after 850 cycles (Figure 8G).²⁵ Further, MnO₂ nanoparticles (~5 nm) were uniformly dispersed on the surface of ZIF-67@Se, resulting in ZIF-67@Se@MnO₂ hybrid with a sandwiched structure. With the physical confinement and chemical adsorption of PSe by MnO₂ layers, ZIF-67@Se@MnO₂ cathodes displayed superior capacity and cycling life to ZIF-67@Se electrode.⁴⁹ In addition, it is theoretically predicted that transition metal disulfides and 2D transition metal carbide (MXene) were the promising anchoring materials for various PSe, and revealed their strong anchoring energies with PSe.⁷⁵,⁷⁶

### 3.4 Catalytic conversion of polyselenides

The reaction between Li and Se undergoes complex chemical composition and phase changes, and the chemical kinetics between liquid intermediates (e.g., Li₂Se₄) and solid Li₂Se₂/Li₂Se are quite sluggish during charge/discharge process, leading to unsatisfactory rate capability and limited service life of Li-Se batteries. To accelerate the phase transition with fast chemical kinetics, catalysts (e.g., metals, metal sulfides, metal selenides, and metal phosphides) are chemically anchored in Se host materials.²²,²³ For example, CoSe₂ nanoparticles/porous carbon hybrids (Se@CoSe₂-PC) were prepared as efficient Se hosts for high-rate Li-Se batteries.²² Notably, the polarization curves of Se@CoSe₂-PC based symmetrical cells with Li₂Se₄-based electrolyte manifested significant peak in the range of 0.8-1.5 V. In a sharp contrast, negligible
peak was observed in the case of Se@PC-based counterpart without CoSe$_2$ particles. It was indicated that fast redox kinetics from PSes to solid products catalyzed by CoSe$_2$ nanoparticles was realized, resulting in enhanced rate capability and cycling performance in Se@CoSe$_2$-PC cathode.\textsuperscript{52}

To expose more active surface area, hollow CoP nanoparticles (10-15 nm) were decorated on 2D N-doped carbon arrays on carbon cloth (CC) via growth of 2D Co-based MOFs, carbonization, and phosphorization processes (Figure 9A). And the resulting hybrid of CoP-N/C@CC with Li$_2$S$_8$ catholyte exhibited an accumulated capacity of 45.2 mAh/g during Li$_2$S precipitation tests, higher than that of Co-N/C@CC (36.7 mAh/g) (Figure 9B and C). With the consideration of the similar electrochemical behaviors of Li$_2$Se and Li$_2$S, fast kinetics during Li$_2$Se nucleation and deposition cycles were revealed, indicating the catalytic effect of CoP on Li-Se batteries. Further, theoretical calculation results also demonstrated the higher binding energies between CoP and various PSes than the values of Co and corresponding PSes (Figure 9D). Namely, the soluble PSs and PSes chemically absorbed by CoP nanoparticles would be catalytically converted to solid discharged products of Li$_2$S and Li$_2$Se (Figure 9E). Consequently, CoP-N/C@CC endowed Se$_2$ with good cycling stability without obvious capacity decay for 100 cycles at 0.5 A/g.\textsuperscript{53}

Furthermore, single atom catalysts (SACs) with unique coordinated environment and high atomic utilization have also drawn much attention for Li-Se batteries. As a typical example, cobalt single atoms/nitrogen-doped hollow porous carbon (Co$_{SA}$-HC) was rationally synthesized via zinc- and cobalt-based ZIF growth on PS spheres and carbonization (Figure 9F), in which Co single atoms in Co$_{SA}$-HC particles were demonstrated to be positively charged, and the corresponding coordination environment of Co was revealed to be Co-N tetrahedral coordination (Co-N$_4$).\textsuperscript{54} Compared with both hollow carbon (HC) and Co nanoparticles modified HC, Co$_{SA}$-HC enabled Se as a smaller voltage hysteresis, indicating the electrocatalytic effect of single atom Co for lowering polarization. Further, it is disclosed from DFT calculations that the conversion from Li$_2$Se$_2$ into Li$_2$Se was the rate-determining process during the whole discharge process. And the Gibbs free energy...
of single atom Co on N-doped carbon (Co-NC) was calculated to be 0.85 eV (Figure 9G), lower than the value of NC (0.96 eV), clearly suggesting the catalytic conversion from Li$_2$Se$_2$ to Li$_2$Se with fast electrochemical kinetics in Se@Co$_{SA}$-HC electrodes. Because of the great promises of SACs with unique structures and coordinated environments, other metal based SACs are highly needed to accelerate their catalytic conversion of PSes for Li-Se batteries.

4 | INTERLAYERS

The presence of the interlayers between cathodes and separators can physically block the diffusion of PSes from cathodes to Li anode sides, alleviating the occurrence of shuttle effects of PSes, and some chemical effects are also expected to synergistically improve PSes shuttle when the functional materials are incorporated into the interlayers. So far, the interlayers include the free-standing films and the films on traditional PP separators, therefore, rational design of suitable interlayers is deemed as an efficient strategy to construct high-performance Li-Se batteries.

4.1 | Free-standing interlayers

Carbon materials are easily processed into the free-standing films or aerogels, which could be directly employed as the interlayers between Se-based cathodes and Li anodes. For example, free-standing carbon films were prepared by carbonization of cellulose-based filter papers, and applied as the interlayers to enhance the performance of Se/TiO$_2$ hybrid cathode. When the polar sites are introduced in the free-standing interlayers, chemisorption of PSes can be achieved to improve service life of Li-Se batteries. Typically, hydrothermal reaction of GO and thiocarbohydrazide was conducted at 90 °C to produce N, S codoped graphene (N,S-G) nanosheets, which were further vacuum-filtered into free-standing flexible films with a thickness of 32 μm. Importantly, the Li-Se batteries with such N,S-G interlayers exhibited high rate capacity of 301.4 mAh/g at 4 C and long service life over 500 times, outperforming the batteries without N,S-G interlayers.

Further, the free-standing hybrid films (GST) consisting of graphene and conductive TiN nanowires (32.8 wt% content) were synthesized by filtration of graphene and hydrogen titanate nanowires and subsequent ammonization process at 800 °C. When the GST film was inserted between SeS$_2$/MWCNTs cathode and Li anode (Figure 10A), TiN nanowires not only chemically absorbed PSs/PSes, but also effectively accelerated the kinetics of the multiphase redox reactions between Li and SeS$_2$. Moreover, the abundant pores in the GST layer and high conductivity of both TiN and graphene provided fast electron/ion transport pathways (Figure 10B), significantly reducing the voltage polarization of SeS$_2$/MWCNTs cathode. Consequently, the as-fabricated Li-SeS$_2$ cells with the GST interlayers performed high capacities of 877 and 739 mAh/g at the 1st and 150th cycles at 0.5 A/g (Figure 10C), respectively, higher than the corresponding values of the batteries with graphene interlayers. Moreover, PAN nanofiber films were fabricated by electrospinning and carbonization, and employed as free-standing interlayers to avoid the shuttle effect of PSes. In addition, a free-standing nickel foam foil was also developed as the interlayer to enhance the performance of TiO$_2$ nanofibers/Se hybrid cathode. However, the presence of nickel with high mass density would reduce the energy density of Li-Se batteries. In this aspect, light-weight and free-standing carbon nanomaterials are more suitable for developing advanced Li-Se batteries.

4.2 | Interlayers on separators

Traditional Celgard or PP separators possess abundant macropores with large pore sizes, which are too large to effectively block the diffusion of small PSes from Se-based cathode to Li anode. To this end, the coating of functional materials on PP flexible separators as the interlayer would be a good choice to physically and/or chemically prohibit the shuttle effect of PSes. For example, graphene nanosheets were coated on traditional polymer separators, and the graphene coating layer with a thickness of 5 μm and an areal loading of 0.3 m/cm$^2$ could ensure pure Se electrodes with high Se content of 70 wt% and long cycling life over 1000 times with a small capacity fading rate of 0.048%, highlighting the promises of graphene for advanced Li-Se batteries. When doped graphene nanosheets were used as the interlayer materials on separators, the chemisorption and even catalytic conversion of PSes could be expected to achieve better Li-Se performance.

To further optimize the electrochemical performance of Li-Se cells by chemical effects, metal oxides or carbides were coated on the separators. Typically, 2D MXene nanosheets with atomic ultrathin thickness were reported to assemble into MXene-based film interlayer for Li-Se batteries. Specifically, 2D structures can physically block the diffusion of PSes to Li anode side, the polar functional groups on the MXene surfaces can chemically anchor PSes, and conductive MXene nanosheets can greatly reduce the voltage polarization of corresponding Li-Se batteries. As a typical example, 1D cetrimonium bromide modified CNTs (CCNT) and 2D MXene
Figure 10  (A) The schematic of configuration of Li-SeS$_2$/MWCNTs batteries with GST interlayers and (B) corresponding energy storage mechanism. (C) Cycling performance of SeS$_2$/MWCNTs cathodes with GST interlayer. Reproduced with permission from Ref. [79]. Copyright 2020, Wiley-VCH. (D) The schematic of synthesis of CCNT/MXene/PP hybrid separator. (E) Cycling stability of Li-Se batteries with PP, MXene/PP, CCNT/PP and CCNT/MXene/PP separators. Reproduced with permission from Ref. [82]. Copyright 2020, Wiley-VCH. (F) The schematic of interaction between TPB-DMTP-COF and LiTFSI. (G) The schematic illustration of TPB-DMTP-COF coated separators for addressing the shuttle of PSES. (H) Cycling performance of Li-Se batteries with TPB-DMTP-COF coated separator. Reproduced with permission from Ref. [83]. Copyright 2019, Royal Society of Chemistry.

Nanosheets were electrostatically assembled and filtrated into an ultrathin hybrid film (~270 nm) on PP separator (Figure 10D), and the resulting CCNT/MXene/PP hybrid separator displayed a smaller contact angle of 10.12° with electrolyte than that of PP (38.49°). Therefore, the Li-Se cells with CCNT/MXene/PP separators showed reduced resistance recorded in electrochemical impedance spectroscopy. And CCNT/MXene/PP separators enabled a carbon black/Se hybrid cathode a remarkable capacity of 554 mAh/g at 0.1 C at the 100th cycle (Figure 10E), obviously higher than the batteries with PP and MXene nanosheets modified PP separator (MXene/PP), suggestive of synergistic effect of MXene and CCNT on suppressing the shuttle of PSES.

Moreover, covalent organic frameworks (COFs) bonded with light-weight nonmetal elements display the advantageous features of lightweight, high porosity with precise nanochannels, large SSA, and easy functionalization. When COFs with unique pore structures and functional groups are coated on the separators as the interlayer materials, the lithium ion and PSES pathways are expected to display different mechanisms. For instance, 1, 3, 5-tri(4-aminophenyl) benzene (TPB), 2, 5-dimethoxyterephthalaldehyde (DMTP) based COFs (TPB-DMTP-COF) were solvothermally synthesized in Ar atmosphere, and then TPB-DMTP-COF were coated on traditional Celgard separator to effectively boost the performance of Li-SeS$_2$ batteries. Specifically, TPB-DMTP-COF with high SSA of 2800 m$^2$/g possessed abundant mesopores (3.03 nm), and thus, the diffusion of the intermediate PSES species could be effectively blocked (Figure 10F and G). Further, LiTFSI in electrolytes was revealed to strongly interact with methoxy groups or benzene rings of TPB-DMTP-COF via hydrogen bonds (Figure 10G), greatly improving the Li ion conductivity of hybrid separator. Benefited from the above advantages,
CONCLUSIONS AND PROSPECTS

In summary, we summarized the recent advances of the cathodes and interlayers in high-performance Li-Se batteries. First, this review introduced the main Se-based chemistries in Li-Se batteries, and then the key progresses of Se based cathodes and interlayers in high-performance Li-Se batteries were elaborated with typical examples, highlighting the importance of synthesis methodologies for constructing advanced cathodes and interlayers. Specifically, the main strategies in cathodes for addressing shuttle effects of PSees were generalized including physical confinement of Se, chemisorption, and catalytic conversion of PSees. Further, advanced interlayers were classified with free-standing interlayers and interlayers on separators. Despite great progress of Li-Se batteries, several prominent challenges remain unsolved for practical application of Li-Se batteries as follows.

First, rational selection of specific Se species is key for thick electrodes (>10 mg/cm²) with high energy densities (Figure 11A). High mass electrodes require sufficient electron and ion conductivity to guarantee high utilization of active materials for high areal capacity. Generally, the poor electron conductivity of Se needs the use of conductive carbon to provide electron pathways, however, these inactive carbons inevitably lower the energy density of the corresponding electrodes. Therefore, rational selection of specific Se species is of great importance to solve the above dilemma. In this regard, selenium sulfides (SeSₓ) may be the right choice, owing to its superior electron conductivity and theoretical energy density to pure Se.88

The second issue is the design and synthesis of advanced Se hosts with multifunctions (Figure 11B). As mentioned above, the advanced Se hosts are expected to combine the synergistic effect of physical confinement, chemical
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