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Advances and challenges of nanostructured electrodes for Li-Se batteries

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As an alternative to the energy storage system of lithium-sulfur (Li-S) batteries, the lithium-selenium (Li-Se) battery system has attracted much attention due to its high-energy (power) density, high theoretical capacity, good cycle performance, excellent rate performance, moderate output voltage, low cost and environmental benignity. However, the application of Li-Se batteries is hindered by various challenges including low loading and utilization of active materials, low coulombic efficiency, capacity fading, poor electrical conductivity and shuttling of polyselenide intermediates. In order to overcome these shortcomings and enhance the electrochemical performance, many efforts have been made in recent years including employing micro/nanostructured carbon materials/Se, transition metal oxide/Se, Se compounds, Se alloys or fully lithiated Li_2Se as electrodes and functional interlayer adsorbents and electrolyte additives. Herein, the recent advances of nanostructured electrodes for Li-Se batteries and their characterizations and mechanisms are reviewed and discussed.

1. Introduction

Rechargeable lithium ion batteries (LIBs) have been regarded as the most promising candidates for portable electronic devices and emerging electric vehicle.¹⁻³ However, the relatively low energy density of typical LIBs has largely limited their large-scale applications.⁴ As a next-generation metallic battery, the lithium-sulfur (Li-S) battery has gained enormous attention due to its non-toxicity, low cost, and high theoretical capacity and energy density.⁵⁻¹¹ Despite these considerable advantages, the Li-S battery still suffers from the insulating nature of S and the solubility of intermediate lithium polysulfide species during cycling, which causes the redox shuttling effect and deposition of Li_2S on the Li anode, leading to low coulombic efficiency and poor cyclability.¹²⁻²⁰ It is of extreme importance to develop novel cathode materials with high electrical conductivity, cyclic stability, and high energy density. Selenium, another element in group XVI like S, has been considered as a prospective candidate, possessing similar chemical properties as S but higher electrical conductivity.

Since the pioneering work by Amine's group,²¹ lithium-selenium (Li-Se) batteries, using Se as the cathode material, have been widely investigated with a redox reaction of $\text{Se} + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Li}_2\text{Se}$ as shown in **Figure 1**. Se, a *d*-electron

containing element from the same group, has been utilized as a cathode material for rechargeable Li or Na-ion batteries. Li-Se batteries have better rate and cycle performance owing to the higher electrical conductivity of Se ($1 \times 10^{-3} \text{ S m}^{-1}$), compared with S ($5 \times 10^{-28} \text{ S m}^{-1}$).²¹ Then, Li-Se batteries deliver a higher output voltage (approximately 0.5 V higher than that of Li-S batteries) and thus a higher energy density. Moreover, Se has a high theoretical volumetric capacity (3253 mAh cm^{-3}) and a theoretical gravimetric capacity (675 mAh g^{-1}).²¹⁻²³ These advantages make Se a prospective cathode material for lithium storage.

Figure 1. The lithiation-delithiation process of C/Se electrode. (a) Phase transformation of Se and Li_2Se for C/Se electrode, (b) discharge-charge curve and corresponding pair distribution functions $G(r)$ at various discharged (yellow) or charged (green) states.²¹ Copyright 2012, American Chemical Society.

In general, Se exists in several allotropic forms: gray trigonal Se (containing Se_n helical chain polymers); rhombohedral Se (containing Se_8 molecules); three deep-red monoclinic forms:

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α -, β -, γ -Se (containing Se_8 molecules); amorphous red Se and black vitreous Se.²⁴ Among various forms, the amorphous Se is more active than crystalline Se because the former one possesses “dangling bonds” and a higher specific surface area. In order to investigate the different chemical (de)lithiation mechanisms between amorphous Se and crystalline Se cathodes in the Li-Se battery, Zhou *et al.* prepared amorphous Se (a-Se) nanowires (NWs), crystalline Se (c-Se) NWs and crystalline/amorphous Se (c/a-Se) NWs through a facile high-energy ball-milling method.²⁴ During the lithiation process, the Se helical chains in a-Se NWs were first reduced to Li_2Se_n ($n \geq 3$) and then to Li_2Se_2 and Li_2Se , as shown in **Figure 2**. For c-Se NWs, the Se helical chains were reduced fast to Li_2Se because of its active state and weakened covalence band in Se_n helical chains coming from the sufficient electronic and van der Waals forces between the Se_n helical chain.

Figure 2. (a) TEM image of Se NWs, initial discharge-charge curves of (b) a-Se, (c) c/a-Se and (d) c-Se NWs at 0.1 C in Li-Se cell.²⁴ Copyright 2015, American Chemical Society.

Unfortunately, similar to the issues in Li-S batteries, the dissolution and shuttling of lithium polyselenides together with significant volume change are present in Li-Se batteries during electrochemical cycling.²⁵⁻²⁸ Such dissolution and shuttling result in fast capacity fading, poor cycle performance, and low coulombic efficiency.²⁹ Then, bulk Se cannot completely deliver the theoretical capacity upon cycling with a low utilization of ca. 45%.²² Moreover, the Li^+ diffusion and electrical conductivity in the Li-Se system are not fast enough, although the electrical conductivity of Se is much higher than that of S. In order to address these problems of Li-Se, several approaches have been utilized, such as confinement of Se in porous carbon,^{29, 30} adsorption of polyselenides by metal oxide,³¹ adsorption of polyselenides by inserted carbon interlayer,³² and design of Se nanostructures.^{33, 34}

Based on the previous researches in recent years,³⁵⁻³⁷ the Li^+ diffusion time (T_{eq}) in the electrode materials primarily depends on the diffusion path length (L) and diffusion efficiency (D) according to the relation: $T_{\text{eq}} = L^2/D$, where L is the size or dimension of electrode materials while D represents

the ease of Li^+ movement. The lower the T_{eq} is, the better the electrochemical performance will be. This means that it is essential to enhance D and reduce L by exploiting nanostructured materials to reduce T_{eq} . Thus far, various nanostructured materials, including nanoparticles,^{38, 39} nanowires,^{40, 41} nanotubes,^{42, 43} and nanosheets,^{44, 45} have been designed to enhance the Li^+/e^- transport kinetics as well as buffer the volume expansion/contraction during the cycling process. Nevertheless, these low-dimensional nanostructures tend to aggregate during the cycling process, resulting in poor cycle lifetime and low capacities at a high rate.^{46, 47} Thus, engineering rationally designed electrodes with hierarchy on structural, morphological, porous component levels through introducing conductive component, porous and micro/nanostructures is key to their practical applicability in LIBs.⁴⁸⁻⁵⁸ The design and engineering of hierarchically micro/nanostructured electrodes (including Se hosts and Se) for Li-Se batteries can significantly enhance the conductivity and stability of the Se electrodes, and greatly facilitate the electrochemical performance of Li-Se batteries.^{23, 28, 59-67}

This review mainly focuses on the recent research progress in design and synthesis of micro/nanostructured electrodes for Li-Se batteries, including carbon-based host/Se electrodes, transition metal compounds electrodes and Se alloys electrodes. Discuss some emerging requirements for advanced Se electrodes, which will shed some light on the future development of nanostructured Se electrodes for Li-Se batteries.

2. Carbon-based host/Se electrodes

The Se cathodes undergo the dissolution of high-order polyselenides, resulting in fast capacity fading and low coulombic efficiency. In order to facilitate the electrochemical performance of Se cathodes, many strategies have been explored as mentioned above. Pure nano-sized Se were synthesized and directly used as a battery cathode, but only few related researches were reported in the literature (*e.g.*, nanofibrous Se³³ and nanoporous Se³⁴). Liu *et al.* synthesized nanoporous Se as the cathode with a reversible capacity of 206 mAh g^{-1} after 20 cycles at 100 mA g^{-1} .³⁴ To further improve the electrochemical performance, an optimal strategy is to confine Se into carbon materials, such as micro/nanostructured carbon^{22, 23, 68-70} and free-standing carbon matrix^{71, 72}, resulting in the enhancement of electrical conductivity of the Se electrode and the restraining of solubility of lithium polyselenides. In 2012, Amine *et al.* reported the use of bulk C/Se as a cathode through pre-milling and subsequent melt-diffusion at 260 °C under argon atmosphere flow.²¹ The Li-Se system displayed a better active material utilization than a typical Li-S system, leading to a much better activity and a weaker shuttling effect than the S cathode. Wang *et al.* synthesized a carbon-selenium bonded composites (C/Se) by *in-situ* carbonization of perylene-3,4,9,10-tetracarboxylic dianhydride and Se mixture in a sealed vacuum glass tube.⁷³ The formed chemical bonding between Se and carbon could

mitigate the shuttle reaction of polyselenides. This C/Se maintained a high reversible capacity of 430 mAh g^{-1} after 250 cycles at 100 mA g^{-1} . Adopting a similar strategy, Wu *et al.* prepared a C/Se composite through a ball milling process and low-temperature treatment.⁷⁴ The obtained C/Se composite could deliver a reversible capacity of 270 mAh g^{-1} after 20 cycles at 100 mA g^{-1} . Unfortunately, this capacity of 270 mAh g^{-1} was much lower than the theoretical capacity of 675 mAh g^{-1} . Besides, the weak interaction between bulk Se and the carbon substrate led to polyselenide dissolution and poor cycling stability.

2.1. Micro/nanostructured carbon-based hosts

In order to facilitate the overall electrochemical performance (including reversible capacity, coulombic efficiency, rate capability and cycle performance), the most common strategy is to fabricate C/Se composite with various architectures, morphologies, shapes, porosities and components (Table 1).^{75–77} The micro/nanostructured carbon materials with high specific surface areas and good conductivities are the preferred choices for Se confinement. The micro/nanostructured carbon materials with diverse morphologies and architectures can provide enough space for Se loading and porous channels to facilitate electrolyte infiltration into the hybrid cathode materials, improve electrical conductivity and reduce Li^+ diffusion length.

2.1.1. Porous carbon hosts

To address the issues of low conductivity and shuttling effect and further facilitate the electrochemical performance of Se cathodes, porous carbon host materials with higher surface areas, higher electrical conductivities and larger pore volumes have been utilized to encapsulate the Se molecules.²² Using porous (mesoporous and microporous) carbon as a conductive matrix can significantly improve the conductivity of Se and retard polyselenide dissolution and shuttling.^{78, 79}

(1) Mesoporous carbon hosts

The mesoporous carbon materials associated with high specific surface areas, suitable pore size distributions (2–50 nm) and particular architectures possess many advantages such as outstanding confinement capabilities, large contact areas with Se, and shortened diffusion lengths for Li^+ .²² Based on this strategy, Guo and co-workers used a typical ordered mesoporous carbon CMK-3 matrix with a large surface area of $1386 \text{ m}^2 \text{ g}^{-1}$ to encapsulate Se molecules as shown in Figure 3a–c and e. The CMK-3/Se composite (with 49 wt% Se) exhibited excellent cycling stability with a capacity of 600 mAh g^{-1} after 50 cycles.²² Recently, another CMK-3/Se composite (Figure 3d) was *in-situ* fabricated via a carbon thermal reduction route of SeO_2 using CMK-3 as a nanoreactor and reduction agent.⁸⁰ The obtained CMK-3/C with 54 wt% Se maintained a stable capacity of 619 mAh g^{-1} after 1000 cycles at 2 C.

Figure 3. (a) TEM image of pristine CMK-3, (b) SEM image of CMK-3/Se, and (c) EDX spectrum, annular dark-field TEM image and corresponding C and Se elemental mapping of CMK-3/Se.²² Copyright 2013, Wiley-VCH. (d) TEM of *in-situ* synthesized CMK-3/Se.⁸⁰ Copyright 2016, Royal Society of Chemistry. (e) Proposed charge-discharge process of CMK-3/Se.²² Copyright 2013, Wiley-VCH.

Mesoporous carbon spheres with high surface areas and suitable pore sizes have been used as promising Se matrices. Huang and co-workers developed a novel Se composite confined within porous carbon nanospheres (PCNs/Se) as the cathode.⁸¹ The obtained PCNs with a mean particle size of $\sim 98 \text{ nm}$ and a large surface area of $853 \text{ m}^2 \text{ g}^{-1}$ could realize a high Se loading of 70.5 wt%. The PCNs/Se cathode demonstrated a high capacity (650 mAh g^{-1}), long cycling stability (1200 cycles with a capacity decay of $\sim 0.03\%$ per cycle) and excellent rate capability (386 mAh g^{-1} at 20 C), which could be ascribed to the high loading of active material Se, effective protective film formed on the Se surface and strong adsorbing ability of $\text{Se/Li}_2\text{Se}_x$ provided by the pore carbon structure (Figure 4). Meanwhile, Wang *et al.* broke Se_{12} into Se_8 at 600°C and impregnated Se_8 in mesoporous carbon spheres to alleviate the dissolution of polyselenides.²⁹ This mesoporous C/Se₈ composite showed excellent rate capability.

Figure 4. (a) SEM images of PCNs/Se, (b) cycle performance, and (c) proposed (de)lithiation processes of PCNs/Se.⁸¹ Copyright 2014, Elsevier.

The carbonization of organic compounds or organic salts can be used to prepare the porous carbon matrices. Qian's group reported a baked-in-salt approach to enable Se to better infiltrate into metal-complex-derived porous carbon (MnMC/Se).⁸² The obtained MnMC/Se cathode demonstrated a capacity of 580 mAh g^{-1} after 1000 cycles at 1 C and an excellent rate capability of 510 mAh g^{-1} at 20 C. In this Se/C system, Se could be functionalized through the interaction between the Se–O bond and C–O bond to form a concomitant homogeneous adsorption within the porous MnMC, thus

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addressing the issues of capacity fading, poor cycling stability, and low coulombic efficiency. Zhao *et al.* synthesized a porous carbon with a unique 3D structure by carbonization of potassium tartrate and then encapsulated amorphous Se into the porous carbon structure to form a C/Se composite.⁸³ This porous C/Se cathode showed a high capacity of 485 mAh g⁻¹ after 80 cycles at 0.24 C and delivered a stable capacity of 452 mAh g⁻¹ at 1.2 C. Recently, a rich mesoporous carbon material/Se (PCM/Se) composite was fabricated through the carbonization of silk cocoons.⁶⁵ This PCM/Se cathode delivered a reversible capacity of 230 mAh g⁻¹ after 510 cycles at 2 C.

It should be stated that the metal-organic frameworks (MOFs) with high surface areas and large pore volumes can also be used as a sacrificial template to synthesize porous carbon hosts for Li-Se electrodes.⁸⁴ Lai *et al.* confined Se in a mesoporous carbon matrix (meso-C@Se) derived from a special MOF structure⁸⁵ and this meso-C@Se displayed a reversible capacity of 280 mAh g⁻¹ after 100 cycles at 2 C. Later, Xu's group prepared a mesoporous carbon matrix-derived from a MOF structure *via* a hydrothermal method and used it to encapsulate Se.²⁵ The fabricated C@Se composite exhibited an initial capacity of 600 mAh g⁻¹ and retained a high capacity of 417 mAh g⁻¹ after 100 cycles at 3 C.

(2) Microporous carbon hosts

Microporous carbon materials with various architectures have also been regarded as suitable Se hosts owing to their high specific surface areas, large adsorption volumes and fine porosity structures for Se impregnation. Especially, the microporous carbon materials with smaller pore sizes (<2 nm) can effectively restrict the dissolution of polyselenides due to volume constraints.⁸⁶ Guo's group loaded single-chain Se molecules into microporous slits of high surface density in a microporous pyrolytic carbon (MPC) coating supported on a carbon nanotube (CNT) as shown in **Figure 5** and investigated the fundamental electrochemistry of this CNT@MPC/Se cathode.⁸⁷ In detail, only helical Se_x chains among the four major allotropes (cyclo-Se₈ in monoclinic crystals, helical Se_x chains in hexagonal crystals, a deformed chain allotrope in amorphous Se and polymeric Se rings containing >1000 atoms in vitreous Se) had the suitable dimensions to fit into the C slit pore in MPC. Based on the experimental and theoretical calculation results, it was found that the Se atoms were well matched in size to the slit width of the micropores in MPC, leading to a stronger confinement and excellent cyclability (352 mAh g⁻¹ after 1000 cycles at 1 C). Similarly, Dai *et al.* fabricated a novel Se-carbon composite through embedding Se in a microporous carbon polyhedron (Se@MICP).⁸⁸ The MICP with a large surface area (890 m² g⁻¹) and a small pore size (1.1 nm) could effectively confine Se and suppress polyselenide dissolution in the electrolyte. Thus, the Se@MICP delivered a high capacity of 341 mAh g⁻¹ after 3000 cycles at 1 C and a good rate performance of 241 mAh g⁻¹ at 5 C.

Figure 5. (a) Schematic preparation diagram of CNT@MPC/Se, (b) TEM, (c) HRTEM image, (d) annular dark-field TEM image and elemental mappings of (e) Se and (f) C of CNT@MPC/Se composite, (g) cycle performance of CNT@MPC/Se at 1 C.⁸⁷ Copyright 2016, American Chemical Society.

(3) Hierarchically porous carbon hosts

As mentioned above, the mesoporous and microporous carbon materials with various architectures have been designed for efficient entrapping of Se-involved molecules. The mesoporous hosts are typically used for Se encapsulation, but the cycling stability is relatively poor. The electrolyte solvents and polyselenide can still shuttle in the structure. Microporous hosts with smaller pore sizes (<2 nm) can significantly minimize the shuttling effect, but the Se loading may be limited. Therefore, it can be assumed that the hierarchically porous carbon materials, combining of different pore sized carbon, are promising Se hosts. Zhang *et al.* also prepared novel bimodal porous carbon (BPC) with a high surface area by a hydrothermal route and KOH activation process and then synthesized a BPC/Se composite through a melt-diffusion process.⁸⁹ The BPC/Se electrode showed a reversible capacity of 264 mAh g⁻¹ after 80 cycles at 1 C. Guo's group reported a hierarchically meso-microporous carbon sphere/Se (MPCS/Se) nanocomposite.⁹⁰ With the unusual chain-like Se_n molecules hosted in an MPCS substrate, the hierarchical MPCS/Se nanocomposite exhibited a high capacity of 660 mAh g⁻¹, a long lifespan of 1000 cycles, and a favorable rate capability (430 mAh g⁻¹ at 5 C). To more effectively encapsulate Se into the carbon host, Yushin and co-workers prepared a Se-infiltrated ordered meso-microporous silicon carbide derived carbon (OM-SiC-CDC) composite with a high Se content of 60 wt%.²³ The hierarchical CDC/Se cathode exhibited a high reversible capacity of ca. 500 mAh g⁻¹ after 150 cycles at 0.2 C in 5 M LiTFSI electrolyte. Shen *et al.* prepared a hierarchically

macro-microporous biochar-based (MMPBc) framework by carbonization of pomelo pericarp and KOH mixture and then used it as a porous matrix for Se loading to form an MMPBc/Se composite.⁶³ The MMPBc/Se cathode delivered a high reversible capacity of 467 mAh g⁻¹ after 300 cycles at 0.2 C. The hierarchically porous structure and bimodal pores of the MMPBc predominantly determined the excellent electrochemical performance.

2.1.2. Carbon nanofibers/CNTs-based hosts

Carbon nanofibers (CNFs) and carbon nanotubes (CNTs) with outstanding physical and chemical properties can satisfy the requirements as Se hosts.^{68, 69, 91} Liu *et al.* fabricated a microporous carbon nanofiber/Se (MCNF/Se) composite through binding Se in microporous CNFs under vacuum and heat treatment.⁹² The MCNF/Se cathode exhibited excellent cyclability (400 mAh g⁻¹ after 2000 cycles at 1 C) and high rate performance (420 mAh g⁻¹ at 5 C). The conductive carbon nanofibers and the formed chemical bonding between Se_n molecules and inner surfaces of microporous CNFs could not only promote the robust and intimate contact between Se and CNF matrix but also alleviate the active material dissolution during the cycling process. Besides, the CNFs could construct an interconnected porous network with high porosity for promoting electrolyte infiltration and buffering volume change during the electrochemical reaction. For instance, Zhang *et al.* prepared interconnected porous nanofiber webs (PCNFWs) cross-linked fibers through carbonization of PPy nanofibers and used PCNFWs as a carbon matrix to encapsulate Se.⁶⁸ The PCNFWs/Se cathode delivered a high reversible capacity of 324 mAh g⁻¹ after 300 cycles at 1 C, showing that the combination of the favorable aspects of interconnected porous nanostructures, abundant channels and high specific surface area could effectively improve the electrochemical performance.

Multi-walled CNTs (MWCNTs) based on sp² hybridized carbon can enhance the electrical conductivity and optimize the electrochemical performance of the Se electrode. However, the utilization of Se is relatively low and the capacity still decays fast when Se is intimately mixed with CNTs.⁹¹ This is due to the poor contact between C and Se in the electrode. Surface functionalization of CNTs can effectively anchor polyselenides through the chemical bonds between functional groups and Se molecules. Zhang's group prepared MWCNTs/Se composites *via* solution-based (employing ethylenediamine as the solvent) and a melt-infusion processes, respectively.⁶⁹ The MWCNTs/Se-S showed a very smaller charge transfer resistance (~28 Ω) than the MWCNTs/Se-M (~58 Ω), demonstrating that MWCNTs/Se-S possessed a better electrical conductivity than MWCNTs/Se-M. The MWCNTs/Se-S composite delivered a high initial capacity of 646 mAh g⁻¹ and a reversible capacity of 356 mAh g⁻¹ after 100 cycles. As mentioned above, the porous carbon materials could benefit the Se encapsulation and suppress the dissolution of polyselenides into the electrolyte. It is possible to design hybrid carbon materials that combine highly conductive CNTs

with porous carbon to obtain high-performance C/Se electrodes. Balakumar *et al.* utilized a novel mesoporous carbon encapsulated MWCNT to accommodate Se to form a tube-in-tube carbon/Se (TTC/Se) composite.⁹¹ The MWCNT backbone based on sp² hybridized carbon could provide high electrical conductivity, while the surrounding mesoporous carbon based on sp³ hybridized carbon could inhibit the loss of active material and the dissolution of polyselenides. This TTC/Se composite demonstrated a decreased charge transfer resistance (~32 Ω) and a high utilization of Se (50 wt% Se), and an insignificant capacity decay of 0.01% per cycle for 4000 cycles.

2.1.3. Carbon nanoshell-structured hosts

Among various cathode materials, the carbon nanoshell-structured electrode materials show unique advantages for Li-Se batteries.^{64, 93} The carbon nanoshell-structured hosts can load more Se, compared with nanoparticles, nanofibers, and nanosheets. They can provide enough space to buffer volume change during the charge-discharge process.⁶⁴ In addition, they can also restrain the polyselenide dissolution and improve the cycle performance. Qian *et al.* fabricated interconnected porous hollow carbon bubbles/Se (PHCBs/Se, shown in Figure 6a-c) composites by dispersing Se in PHCBs *via* a melt-diffusion method.⁷⁰ This PHCBs/Se displayed a reversible capacity of 606 mAh g⁻¹ (Figure 6d) after 120 cycles. Zhang *et al.* prepared a hollow carbonized polyaniline spheres/Se (HCPS/Se, in Figure 6e-h) composite through a combination method of self-assembly, pyrolysis and vapor phase infusion processes.⁹⁴ The HCPS/Se electrode exhibited a high reversible capacity of 299 mAh g⁻¹ after 100 cycles at 0.5 C (Figure 6i), benefiting from the high conductivity and hollow structure of the carbonized polyaniline spheres. Then, Peng *et al.* utilized the reduced graphene oxide to uniformly encapsulate Se nanoparticles (Se@rGO) through a simple self-assembly process.⁹⁵ The large Se content (80% wt), highly dispersed Se nanoparticles and high electrical conductivity of the Se@rGO composite could synergistically facilitate the Li⁺ storage.

Figure 6. (a) SEM image, (b) TEM image, and (c) EDS elemental mapping images of the Se_{50}/C composite: Se (red) and carbon (green), (d) cycle performance of $\text{Se}_{40}/\text{PHCBs}$, $\text{Se}_{50}/\text{PHCBs}$ and $\text{Se}_{60}/\text{PHCBs}$. Copyright 2014, Royal Society of Chemistry. (e) TEM image of HCPS/Se, elemental mapping of (f) Se, (g) N, (h) C, and (i) cycle performances of pristine Se and HCPS/Se composite at 0.5 C. ³⁴ Copyright 2014, Elsevier.

These micro/nanostructured carbon materials represent one direction for the development of Se cathodes. However, the polyselenide shuttling is still apparent in many C/Se cathodes. The modification of carbon surface with functional groups (*e.g.*, carbonyl and carboxyl groups) and heteroatoms (*e.g.*, nitrogen) can be used to further improve the electrochemical performance of Li-Se batteries.

2.1.4. Conducting polymer-assisted carbon hosts

Conducting polymers (such as polyaniline, polypyrrole and polyacrylonitrile) have been used to assist in the encapsulation of Se and the mitigation of polyselenides in C/Se electrodes because they have functional groups (*e.g.*, carbonyl and carboxyl groups), unique chain structures and good electrochemical activities. ^{33, 96, 97} The conducting polymer with soft and flexible structures can be used to address many problems (*e.g.*, volume expansion and electrode collapse) during the charge-discharge process and enhance the cycle performance. Qian's group designed and synthesized a nanocomposite of graphene-encapsulated Se/polyaniline core-shell nanowires (G@Se/PANI) under the condition of low temperature without heating as shown in **Figure 7a-d**. ⁹⁶ The G@Se/PANI nanocomposite exhibited a high capacity of 567 mAh g^{-1} after 200 cycles (Figure 7e). Later, Kundu *et al.* fabricated Se nanofibers (20–50 nm) with PPy/graphene coating (Figure 7f-g) through a surfactant-free solution method. ³³ This hybrid composite demonstrated a high capacity of 678 mAh g^{-1} and good rate performance.

Figure 7. (a-c) Schematic preparation illustration of G@Se/PANI , (d) elemental mapping images of G@Se/PANI , and (e) cycle performance of G@Se/PANI at 0.2 C. ⁹⁶ Copyright 2015, Elsevier. TEM images of (f) PPy coated Se fibers and (g) graphene wrapped Se fibers. ³³ Copyright 2013, Elsevier.

In addition to directly confine the Se species, the conducting polymers can also be used as precursors to fabricate porous C/Se composites. ⁹⁸ Guo *et al.* synthesized a novel type of organic selenide fibers composed of carbonized polyacrylonitrile/Se (CPAN/Se) by heating PAN/Se fibers. ⁹⁸ The CPAN/Se electrode delivered a high capacity of 600 mAh g^{-1} for

500 cycles. Recently, a microporous N-doped carbon confined Se composite was fabricated through carbonization of polypyrrole (PPy) and KOH mixture. ⁹⁹ The unique microporous structure and the N-doping of carbonized PPy could improve the electrical conductivity and promote the performance, especially the high rate performance (303 mAh g^{-1} at 20 C).

2.1.5. Heteroatom-doped carbon hosts

Heteroatom doping (*e.g.*, nitrogen doping) can assist in the formation of carbon functional group-selenium bonds that mitigate the polyselenide shuttling. ⁹⁹ It can improve the electrical conductivity of carbon hosts, increase the reaction active sites, and improve the wettability, accessibility and absorption of the electrolyte. ¹⁰⁰ As a result, the heteroatom-doped carbon materials with high specific surface areas can further facilitate the electrochemical performance of Li-Se batteries. Yin *et al.* fabricated N-doped carbon sponges (NCS) composed of hierarchically microporous carbon layers through carbonization of MOFs under Ar and NH_3 flow and then impregnated Se into 0.4–0.55 nm micropores of NCS to form a NCS/Se composite as shown in **Figure 8a-d**. ⁶¹ The NCS/Se electrode showed much smaller charge transfer resistance of ($\sim 30 \Omega$) than the CS/Se one ($\sim 50 \Omega$), indicating that the N-doping could improve the electrical conductivity of the C/Se electrode. This NCS/Se demonstrated a high capacity of 443 mAh g^{-1} after 200 cycles (Figure 8e).

Figure 8. (a) TEM, (b) HRTEM, and (c-d) Se elemental mapping images of NCS/Se composite; (e) cycle performances of NCS/Se and CS/Se composites at 0.5 C. ⁶¹ Copyright 2015, Royal Society of Chemistry. (f) SEM, (g) TEM, (h) HRTEM, (i) HADDF-STEM, and (j) energy filter TEM images of N-MPCS/Se; the corresponding EFTM maps of (k) C, (l) N and (m) Se. ⁶⁶ Copyright 2015, Royal Society of Chemistry.

To combine the advantages of the microporous carbon matrix and N-doping, Xiong's group reported novel confined Se in N-doped microporous carbon spheres (N-MPCS, in Figure 8f-m) accompanied by a small proportion of mesopores between graphitized carbon thin layers. ⁶⁶ The abundant micropores in a

carbon matrix and the strong adsorptive power could effectively hold Se molecules, while the nitrogen-doping and carbon matrix could synergistically facilitate the electrical conductivity of the composite electrode. The N-MPCS/Se composite demonstrated a high capacity of 440 mAh g^{-1} at 4.7 C. Zhang *et al.* prepared novel N-containing hierarchical porous carbon (NCHPC) by a template process.⁶² The NCHPC could facilitate Se infiltration in the interconnected macro-meso-micropores, improve the electrical conductivity and reduce the Li^+ diffusion length. The hierarchical NCHPC/Se composite delivered a capacity of 305 mAh g^{-1} after 60 cycles at 2 C.

2.2. Free-standing carbon hosts

For many reported Se-based electrodes, auxiliary additives (e.g., conductive carbon agent and binders) have been commonly introduced to improve their mechanical integrity and electrical conductivity, but decrease the relative proportion of Se, leading to a lower energy density. Therefore, it is necessary to design a flexible, free-standing and binder-free Se-host electrode, in which all the electrode components can participate in lithium storage.^{32, 101} Furthermore, the cell packing process can be significantly simplified by using such a configuration. Many free-standing electrodes have been constructed using nanofibers, nanotubes or nanobelts as skeletons through various processes including electrospinning, templating, freeze-drying and vacuum filtration.^{59, 71, 72, 102, 103} Yu's group prepared a flexible and free-standing porous carbon nanofibers/Se (PCNFs@Se, shown in Figure 9a-g) composite by infiltrating Se into electrospun PCNFs.⁷² The porous carbon with optimized mesopores could accommodate Se and effectively suppress the active material dissolution and provide mechanical stability. The obtained PCNFs@Se electrode delivered a high stable capacity of 516 mAh g^{-1} after 900 cycles at 0.5 A g^{-1} , and displayed an excellent rate performance (306 mAh g^{-1} at 4 A g^{-1}). Zeng *et al.* synthesized a C/Se composite by co-heating the Se powder and polyacrylonitrile (PAN)-CNT nanofibers at 600°C in a sealed vessel.⁷¹ The additive CNTs, the 3D interconnected carbon nanofibers and the good confinement of Se in the carbon matrix could synergistically improve the electrical conductivity and electrolyte infiltration. Such a freestanding electrode exhibited improved cyclability (517 mAh g^{-1} after 500 cycles at 0.5 A g^{-1}) and rate capability (485 mAh g^{-1} at 1 A g^{-1}). Most recently, Cai *et al.* reported a freestanding cathode composed of hollow double-shell N-doped carbon@Se ($\text{CN}_x\text{@Se}$) nanobelts through a hydrothermal method combined with a vacuum filtration process.¹⁰³ This hollow $\text{CN}_x\text{@Se}$ freestanding electrode (Figure 9h-i) could buffer the volume change during cycling, improve the Li^+ diffusion, electrical conductivity and absorb the polyselenides, leading to a highly stable capacity (609 mAh g^{-1} at 675 mA g^{-1} after 400 cycles) and an excellent rate capability (474 mAh g^{-1} at 1600 mA g^{-1}).

3D graphene architecture has been widely used in supercapacitors, lithium ion batteries and Li-S batteries, since it possesses a high specific surface area, large adsorption volume and effective conductive framework as well as flexible

mechanical network.^{6, 104, 105} It is reasonable that such architecture can be used to fabricate the free-standing cathode. He *et al.* synthesized a 3D graphene-CNT@Se (3DG-CNT@Se) aerogel with CNT/Se sandwiched between graphene nanosheets through a solvothermal method combined with a freeze-drying process (in Figure 10).⁵⁹ The free-standing 3DG-CNT@Se cathode demonstrated a high reversible capacity of 558 mAh g^{-1} at 1 C. The unique 3D mesoporous, conductive network could provide highly efficient channels for charge transport, prevent fast dissolution of polyselenides and suppress volume expansion of Se upon cycling.

Figure 9. (a, b) Schematic preparation illustrations of PCNFs@Se electrode; (c) FESEM image and (d) photograph of a free-standing PCNFs@Se electrode; (e) STEM image and corresponding element mapping; (f) Se and (g) C. Copyright 2014, Wiley-VCH. (h) Optical image and (i) cross-sectional SEM image of the hierarchically hollow $\text{CN}_x\text{@Se}$ freestanding electrode. Copyright 2017, Elsevier.

Figure 10. (a) Schematic preparation illustration of the 3DG-CNT@Se composite; SEM images of (b) CNT-Se and (c, d) 3DG-CNT@Se composites.⁵⁹ Copyright 2016, American Chemical Society.

As highlighted in this section, numerous micro/nanostructured C/Se electrodes demonstrate remarkable electrochemical performance. Among these C/Se composite electrodes, the electrode with the suitable pore characteristic, high specific surface area and particular size dimensionality can always encapsulate a large amount of Se, suppress the dissolution of polyselenides and generate high energy density. The modification of carbon surface with functional groups (*e.g.*, carbonyl and carboxyl groups) and heteroatoms (*e.g.*, nitrogen) can also be used to further improve the electrochemical performance of Li-Se batteries.

3. Transition metal compound electrodes

Previous researches have shown that S host materials with polar surface could efficiently solve the problems of polysulfide dissolution owing to their strong interactions with the polar lithium polysulfides compared to the common nonpolar carbon hosts in Li-S batteries.¹⁰⁶ Similar to those in Li-S batteries, many inorganic polar materials can also be utilized as efficient Se hosts in Li-Se batteries, including Fe_2O_3 ,¹⁰⁷ NiO ,¹⁰⁸ SnO_2 ,¹⁰⁹ ZnO ,⁶⁷ TiO_2 ,³¹ NiCoO_2 ,¹¹⁰ ZnSe ,¹¹¹ Bi_2Se_3 ¹¹² and MoSe_2 .¹¹³ For instance, Fu *et al.* fabricated a $\text{Fe}_2\text{O}_3/\text{Se}$ nanocomposite thin film through a pulsed laser deposition (PLD) method and the $\text{Fe}_2\text{O}_3/\text{Se}$ electrode displayed a high capacity of 650 mAh g^{-1} .¹⁰⁷ During the first discharge process, Fe, Li_2O and Li_2Se were found in the electrode, while FeSe and Fe_2O_3 were formed in the first charge process. The reversible oxidation/reduction of Fe_2O_3 and selenidation/reduction of FeSe were then performed in following cycles. Fu *et al.* also fabricated a ZnO/Se film through a PLD method and the ZnO/Se displayed a high capacity of 505 mAh g^{-1} .⁶⁷ ZnLi , Li_2O and Li_2Se were formed in the first discharge process, while ZnO and ZnSe could be found in the electrode after the charging process. The subsequent cycles involved the reversible oxidation/reduction of ZnO and selenidation/reduction of ZnSe . A SnO_2/Se film was also fabricated through the PLD method and the SnO_2/Se electrode exhibited a high reversible capacity and good cycle performance.¹⁰⁹

TiO_2 has been widely used as the host of S to efficiently encapsulate it in Li-S batteries to improve the cycle life and capacity retention.¹¹⁴⁻¹¹⁶ The TiO_2 used in the coating layers or shell structures could promote the interaction between TiO_2 and S, which could form an electrostatic attraction (S-Ti-O) and enhance the surface adsorption of polysulfide on the TiO_2 .¹¹⁷ Similarly, porous TiO_2 can be regarded as a great potential Se host for Li-Se batteries. Zhang *et al.* synthesized a TiO_2/Se composite by a melt-diffusion method.³¹ The polyselenide intermediates could be adsorbed in the porous TiO_2 during the cycling process. The mesoporous TiO_2/Se composite showed a good cycle performance. Unfortunately, the reversible capacity of this TiO_2/Se electrode is not very high, and more efforts (*e.g.*, constructing hollow architecture, doping and hybrid) are

needed to further facilitate the overall electrochemical performance in the future.

Metal selenide (MSe_x) materials have been investigated as promising electrodes with high theoretical capacity.^{111, 118-122} Among various metal selenide materials, ZnSe showed a high theoretical capacity of *ca.* 557 mAh g^{-1} .¹²⁰ Xue *et al.* fabricated a ZnSe film through a PLD method and the obtained crystalline ZnSe demonstrated an initial discharge capacity of 543 mAh g^{-1} .¹²⁰ Nevertheless, it exhibited a large capacity loss and a poor capacity retention upon cycling. Many efforts have been made to further facilitate the lithiation kinetics. For instance, Zhang *et al.* fabricated a spherical-like ZnSe with $0.5\text{--}1 \mu\text{m}$ diameter via a hydrothermal method using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and Na_2SeO_3 as Zn and Se sources, respectively.¹²¹ The spherical ZnSe displayed a reversible capacity of 433 mAh g^{-1} after 50 cycles at 100 mA g^{-1} .

The conductive agents (*e.g.*, carbon and graphene) can be utilized to enhance the electrical conductivity of ZnSe electrodes and improve the electrochemical performance. For example, Park *et al.* fabricated a C/ZnSe nanocomposite by a simple solid-state route.¹¹¹ Many ZnSe nanocrystallites with the size of $5\text{--}10 \text{ nm}$ were uniformly distributed in a conductive carbon matrix. This C/ZnSe composite displayed a high capacity of 705 mAh g^{-1} after 300 cycles. Surprisingly, these ZnSe materials exhibited rising reversible capacities upon the cycling process. Afterward, in order to explore the origin of additional capacities in the C/ZnSe composite, Xu *et al.* fabricated a $\text{C}@\text{ZnSe}$ composite (Figure 11) through a hydrothermal method and then employed *ex-situ* X-ray photoelectron spectroscopy (XPS) along with cyclic voltammetry to investigate the (de)lithiation process.¹²³ The $\text{C}@\text{ZnSe}$ composite exhibited an initial capacity of *ca.* 600 mAh g^{-1} and a rising reversible capacity of 960 mAh g^{-1} after 400 cycles when charged at 0.2 A g^{-1} (Figure 11d). The additive rising capacity of $\text{C}@\text{ZnSe}$ electrode could be attributed to the activation of Se and the oxidation of Li_2Se to Se during the cycling process.

Figure 11. (a) TEM and (b) HRTEM images of $\text{C}@\text{ZnSe}$ composite; (c) discharge-charge voltage profiles and (d) cycle performance of $\text{C}@\text{ZnSe}$ at 0.2 A g^{-1} after 100 cycles.¹²³ Copyright 2016, Elsevier.

Bi_2Se_3 crystal possesses a layered structure, in which between layers is van der Waals interaction while within layers is predominantly covalent bonding.¹²⁴ The Li^+ ions can insert into the layered structure (van der Waals gaps).¹²⁵ Ali *et al.* synthesized Bi_2Se_3 rectangular nanosheets with a thickness of 200–500 nm through a thermochemical method and it possessed an initial discharge capacity of 726 mAh g^{-1} .¹²⁶ Unfortunately, this Bi_2Se_3 suffered from a capacity loss during the cycling process. Constructing hierarchical nanostructures is an effective way to improve the lithium storage properties of Bi_2Se_3 .¹²⁷ Xu *et al.* fabricated hierarchical Bi_2Se_3 stacking nanosheets composed of thin nanosheets through a green method.¹²⁷ The obtained hierarchical Bi_2Se_3 showed a higher capacity of 715 mAh g^{-1} than single Bi_2Se_3 nanosheets, but its cycling stability needs further investigation for improvement.

Doping (e.g., S and In-doping) can efficiently enhance the electrochemical performance of Bi_2Se_3 .^{112, 128, 129} For example, Jin *et al.* synthesized a hierarchically flower-like $\text{Bi}_2\text{Se}_{3-x}\text{S}_x$ microarchitecture consisted of polycrystalline nanosheets through a solvothermal route.¹²⁸ With the ultrathin nanosheet, porous structure, high specific surface area and good conductivity, this hierarchical $\text{Bi}_2\text{Se}_{3-x}\text{S}_x$ demonstrated a higher initial capacity of 920 mAh g^{-1} than the hierarchical Bi_2Se_3 nanosheets. Mao *et al.* fabricated hierarchical S-doped Bi_2Se_3 microspheres assembled by stacked nanosheets through a one-step solvothermal process.¹²⁹ The obtained S-doped Bi_2Se_3 microspheres exhibited a higher capacity of 771 mAh g^{-1} , a better cycling stability, and a higher rate performance than pure Bi_2Se_3 . Han *et al.* synthesized hierarchical In-doped Bi_2Se_3 nanostructures through an *in-situ* cation exchange route from the In_3Se_4 nanostructure template.¹¹² The In-doped Bi_2Se_3 displayed a high discharge capacity of 998 mAh g^{-1} and a reversible charge capacity of 523 mAh g^{-1} , which were much higher than those of pure Bi_2Se_3 nanostructures.

Molybdenum diselenide (MoSe_2), belonging to the family of transition metal dichalcogenides (TMDs), presents a lamellar structure consisting of Se-Mo-Se sandwich layers and stacked together by weak van der Waals interaction.¹³⁰ The weak interlayers allow Li^+ ions to intercalate/deintercalate between the layers.^{131–133} Wang *et al.* fabricated MoSe_2 nanocrystals via a thermal-decomposition process and then investigated the phase transition mechanism and electrochemical properties of nanocrystalline MoSe_2 .¹³² The MoSe_2 nanocrystals delivered a high initial capacity of 782 mAh g^{-1} and retained a capacity of 405 mAh g^{-1} after 50 cycles. Through the first-principles simulation results (Figure 12a–c), a phase transition from 2H- MoSe_2 to O- MoSe_2 in the initial discharge process at 0.9 V and Mo cluster occurred as more Li atoms intercalated into the MoSe_2 lattice, resulting in the formation of Mo and Li_2Se . Based on a quasi-2D energy favorable trajectory, Li^+ diffused from octahedron to tetrahedron in MoSe_2 lattice. Lee *et al.* fabricated mesoporous MoSe_2 with 2D layered crystalline frameworks and 3D porous structures through a melting-infiltration-assisted nano-replication method using a KIT-6 template (Figure 12d).¹³⁴ The obtained MoSe_2 possessed high electrical conductivity and short pathways for lithium insertion

and thus showed a high reversible capacity of 728 mAh g^{-1} , highly stable capacity retention, and good rate performance.

Although MoSe_2 demonstrates high capacity, it still suffers from inferior cycling stability and unsatisfactory rate capability caused by the inherently low electrical conductivity. The combination with conductive agents (e.g., carbon, CNTs and rGO) has been regarded as an efficient strategy to improve the conductivity and electrochemical performance of MoSe_2 electrodes. Liu *et al.* synthesized a sheet-like C/ MoSe_2 composite through a hydrothermal method and a subsequent annealing treatment.¹¹³ The obtained C/ MoSe_2 composite demonstrated a higher capacity of 577 mAh g^{-1} after 50 cycles than pure MoSe_2 (Figure 12e). It was found that carbon in the C/ MoSe_2 composite could not only improve the electrical conductivity but also maintain the structural stability and hinder the aggregation of MoSe_2 . Later, Sánchez *et al.* manufactured MoSe_2 nanoplatelets and single-walled CNTs/ MoSe_2 nanoplatelets using a spray-deposition method.¹³⁵ The SWCNTs/ MoSe_2 electrode demonstrated a higher capacity of 798 mAh g^{-1} than pure nanoplatelets.

Figure 12. (a–b) Li^+ diffusion path in the lattice of MoSe_2 , and (c) energy curve along the plotted Li^+ diffusion path.¹³² Copyright 2015, American Chemical Society. (d) TEM image of mesoporous MoSe_2 .¹³⁴ Copyright 2016, Royal Society of Chemistry. (e) TEM image of C/ MoSe_2 composite.¹¹³ Copyright 2015, Royal Society of Chemistry. (f) TEM image of rGO/ MoSe_2 hybrids, (g) cycle performance of rGO/ MoSe_2 at 1000 mAh g^{-1} .¹³⁶ Copyright 2016, Royal Society of Chemistry. (h) TEM image of rGO/ MoSe_2 composite.¹³⁷ Copyright 2015, Elsevier.

Similar to SWCNTs, rGO can also be used to enhance the conductivity and structural stability of MoSe_2 electrode. Luo *et al.* synthesized novel 2D hybrid nanosheets constructed by few layered MoSe_2 grown on rGO via a facile solvothermal reaction.¹³⁶ The rGO/ MoSe_2 hybrid maintained an excellent capacity of 637 mAh g^{-1} after 1000 cycles at 1 A g^{-1} (Figure 12g). Later, Yao and co-workers utilized the 3D graphene foam to accommodate the MoSe_2 and prepared a self-assembled rGO/ MoSe_2 foam through a hydrothermal process.¹³⁷ The

rGO/MoSe₂ (Figure 12h) delivered a high capacity of 470 mAh g⁻¹ after 600 cycles at 210 mA g⁻¹.

Constructing heterostructures between MoSe₂ nanosheets and different ultra-small transition metal oxides has also been considered as an efficient way to facilitate the electrochemical performance.^{138, 139} Zhao *et al.* synthesized a nanocomposite consisting of MoO₃ nanoparticles embedded between MoSe₂ nanosheets (MoO₃@MoSe₂, in Figure 13a) and it demonstrated a long cycling stability with a high capacity of 520 mAh g⁻¹ at 2 A g⁻¹ after 400 cycles.¹³⁸ In the MoO₃@MoSe₂ nanocomposite, MoSe₂ nanosheets provided a flexible substrate for MoO₃ nanoparticles, while MoO₃ nanoparticles could hinder the aggregation of nanosheets and retain the desired active surface to the electrolyte. The heterojunctions at the interface between MoSe₂ and MoO₃ could promote the Li⁺ insertion/extraction process through introducing a self-built electric field. Meanwhile, Wu *et al.* fabricated a heterostructure of MoSe₂ nanosheets decorated on C/TiO₂ nanobelts through a hydrothermal process.¹³⁹ In the MoSe₂@C/TiO₂ heterostructure (Figure 13b-e), ultrathin MoSe₂ nanosheets embedded on TiO₂ nanobelts were coupled with carbon as strong skeletons. It could provide more reaction active sites, high conductivity and sufficient void spaces. As a result, the MoSe₂@C/TiO₂ heterostructure demonstrated a high capacity of 987 mAh g⁻¹ after 100 cycles at 500 mA g⁻¹ (Figure 13f).

Figure 13. (a) SEM image of MoO₃@MoSe₂ heterostructure,¹³⁸ Copyright 2016, Royal Society of Chemistry. (b) SEM image of pure MoSe₂ nanoflowers, (c) TEM image of MoSe₂@C/TiO₂ heterostructures, (d) SEAD patterns with illustration in (e), and (f) cycle performance of MoSe₂@C/TiO₂, MoSe₂/TiO₂, pure MoSe₂ nanosheets and bare TiO₂ nanobelts at 500 mA g⁻¹.¹³⁹ Copyright 2016, Royal Society of Chemistry.

Additionally, some other metal selenides have also been investigated as electrodes for LIBs, including SnSe,^{140, 141} WSe₂,¹³⁴ Sb₂Se₃,¹⁴²⁻¹⁴⁵ In_xSe_y,¹⁴⁶⁻¹⁴⁸ and CuSe.^{149, 150}

4. Selenium alloy electrodes

Although Se has been widely investigated as a cathode, it suffers from relatively lower mass capacity (675 mAh g⁻¹), compared with the S electrode (1675 mAh g⁻¹). Generally, Se possesses a stable cycling capability but a low reversible capacity; while S shows a high reversible capacity but a poor cycling capability. As a result, the heteroatomization of Se and S molecules in carbon or other hosts, which utilizes the advantages of both Se and S, is a promising strategy to enhance the electrochemical performance of Se electrodes for LIBs.^{26, 151-156}

For example, Guo *et al.* fabricated a 3D network N-doped carbonized polyacrylonitrile/SeS_{0.1} (NCPAN/SeS_{0.1}) composite through a one-step *in-situ* solid-state method.¹⁵³ The formed NCPAN/SeS_{0.1} composite displayed a higher initial capacity of 1387 mAh g⁻¹ than NCPAN/Se. It was found that the alloying of Se and S could facilitate the electrochemical performance of Se. Zhang *et al.* prepared a C/Se₂ composite with Se₂ encapsulated into 3D interconnected mesoporous carbon aerogels (MCAs).¹⁵² The 3D interconnected MCAs could effectively decrease the interface resistance of electrodes and trap polysulfide and polyselenide intermediates during the cycling process. The SeS₂@MCAs (with 49.3 wt% SeS₂) showed a high initial capacity of 1150 mAh g⁻¹ and a capacity of 601 mAh g⁻¹ after 10 cycles at 500 mAh g⁻¹. Recently, Yu's group synthesized a double-layered hollow carbon sphere/SeS₂ (DLHC/SeS₂) composite and SeS₂ was predominantly encapsulated in the interlayer space of DLHCs with a high loading amount of 75 wt% SeS₂ (Figure 14).¹⁵⁷ As shown in Figure 14e, the DLHC/SeS₂ composite demonstrated a higher capacity (930 mAh g⁻¹ at 0.2 A g⁻¹) and a better rate capability (400 mAh g⁻¹ at 6 A g⁻¹) than SLHC/SeS₂, DLHC/Se, and DLHC/S. The DLHC/SeS₂ composite displayed an ultra-long cycle life with 89% capacity retention over 900 cycles at 1 A g⁻¹ (Figure 14f). This hierarchical DLHC structure with hollow cavity and interlayer void could not only provide improved electrical conductivity and buffer the volume expansion during cycling process, but also minimize the loss of active materials and shuttling effect. Both the SeS₂ and the double-layered hollow structure were responsible for the excellent electrochemical performance. Amorphous Se₂S₅ was confined in a meso-microporous carbon matrix (MPC/Se₂S₅) through a modified vaporization-condensation method.¹⁵⁸ The Se₂S₅/MPC composite delivered a reversible capacity of 430 mAh g⁻¹ after 100 cycles at 0.5 C. The *in-situ* X-ray absorption near edge spectroscopy (XANES) results showed that the lithiation/delithiation reversibility of Se component gradually decreased in ether-based electrolytes, leading to an aggravated formation of long-chain polyselenide upon continuous cycling. The theoretical calculations also revealed that the binding energies of polyselenides (Li₂Se_n) with the carbon host ranked in the order of Li₂Se₆>Li₂Se₄>Li₂Se.

Figure 14. (a) Schematic preparation illustration of DLHC/Se₂S₆; (b) SEM image, (c) TEM image, and (d) line scanning EDX spectra of DLHC/Se₂S₆; (e) cycle performances of pure Se₂S₆, SLHC/Se₂S₆, DLHC/Se₂S₆ at 0.2 A g⁻¹; and (f) long-term cycle performance of DLHC/Se₂S₆ at 1 A g⁻¹. Copyright 2016, Springer.

Figure 15. (a) Schematic model of the NMC/Se₂S₆ structure, (b) SEM image of NMC/Se₂S₆, and (c) cycle performance and (d) coulombic efficiency of NMC/Se₂S₆ (n=1-3) at 250 mA g⁻¹. Copyright 2016, American Chemistry Society.

To design heteroatomic Se-S molecules as reversible electrode materials in an ether-base electrolyte for high-performance batteries, Shi's group fabricated N-doped mesoporous carbons (NMCs) to homogeneously confine the heteroatomic Se_nS_{8-n} molecules through a facile melt-impregnation route (Figure 15a-b).¹⁵⁹ The optimal NMC/Se₂S₆ composite demonstrated a high capacity of 883 mAh g⁻¹ after

100 cycles at 250 mA g⁻¹ (Figure 15c-d). From the density-functional-theory calculation results, the heteroatomic Se₂S₆ molecules with higher polarizability could bind more strongly with NMCs than homoatomic S molecules, further suppressing the shuttling effect of polysulfide and polyselenide. Qian's group immobilized S in porous carbon with a small amount of Se to prepare amorphous S-rich C/S_{1-x}Se_x (x≤0.1) composites.¹⁶⁰ The confinement of S_{1-x}Se_x in porous carbon and strong S-Se bonds could effectively restrict the dissolution of polysulfur and polyselenide intermediates and enhance the cycle performance of the S_{1-x}Se_x composites. The optimal C/S_{0.94}Se_{0.06} composite demonstrated a high capacity of 910 mAh g⁻¹ at 1 A g⁻¹ over 500 cycles, and a good rate capability of 617 mAh g⁻¹ at 20 A g⁻¹.

Germanium selenide (GeSe) has also been utilized as the electrode in LIBs because of its structural robustness with isotropic lithiation kinetics and high rate capability.^{161, 162} However, the GeSe electrode suffers from poor structural stability and cycle performance. Designing rational hierarchical GeSe micro/nanostructure can efficiently buffer volume change, and ensure fast lithiation/delithiation kinetics and thus excellent electrochemical performance with high capacity, long cycle life, and good rate capability. For example, Im *et al.* synthesized GeSe_x nanocrystals through gas-phase laser photolysis reaction.¹⁶¹ The obtained GeSe and GeSe₂ demonstrated high capacities of 771 and 574 mAh g⁻¹ respectively when charged at 0.1 C for 70 cycles. The experimental and theoretical results revealed the cubic-tetragonal phase conversion of Ge upon lithiation/delithiation processes to support the distinctive capacity. Klavetter *et al.* prepared slurry cast electrodes with micro-sized Ge_{0.9}Se_{0.1} and Ge particles and evaluate their electrochemical performance.¹⁶³ The Ge_{0.9}Se_{0.1} particles possessed a highly Li-permeable amorphous Li-Se-Ge inactive phase that could effectively buffer the large volume change during the Li (de)alloying process in the particles, leading to a stable structure with long-cycle performance. This Ge_{0.9}Se_{0.1} demonstrated a reversible capacity of 800 mAh g⁻¹ after 900 cycles at 1 C. Afterwards, Kim *et al.* synthesized a unique hierarchical GeSe nanostructure consisted of nanocombs on a backbone through a facile vapor-solid process.¹⁶⁴ The void space between the nanocomb teeth could effectively buffer the large volume change. The anisotropic structure could provide a short charge diffusion pathway, enhance the lithiation/delithiation kinetics and improve the Li⁺ storage properties. Hence, this hierarchical GeSe nanocombs maintained a high reversible capacity of 726 mAh g⁻¹ after 1000 cycles at 1.01 A g⁻¹.

According to the researches on Li-S batteries,¹⁶⁵⁻¹⁶⁹ the replacement of S with Li₂S is an effective way to avoid safety issues (such as large volume change, capacity fading and lithium dendrite formation) when the metallic lithium anode is used. The Li₂S is compatible with metallic lithium anode and carbonaceous materials. Like Li₂S electrodes for Li-S batteries,¹⁶⁶ the fully lithiated Li₂Se rather than Li-free Se could serve as promising electrodes for the Li-Se batteries. Li₂Se can

offer theoretical gravimetric and volumetric capacities of 578 mAh g⁻¹ and 1659 mAh cm⁻³, respectively.¹⁷⁰ Furthermore, Li₂Se displays low volume change during the cycling process. Wu *et al.* fabricated uniform nanostructured carbon-Li₂Se composites with additional carbon shells through a versatile solution-based method.¹⁷⁰ The 10-20 nm Li₂Se nanoparticles

embedded in the conductive carbon matrix could enhance the mechanical stability and suppress the polyselenides dissolution in the C-Li₂Se@C electrode. The produced C-Li₂Se@C showed a stable capacity of 300 mAh g⁻¹ after 100 cycles at a 0.5 C rate without capacity loss.

Table 1. Summary of representative Li-Se batteries.

Cathode material	Synthesis method	Initial capacity (mAhg ⁻¹)	Capacity retention (mAhg ⁻¹)	Cycle No.	Rate	Se amount	Electrolyte	Ref.
Se NWs	BM	500	360	100	0.1C	100%	1M LiPF ₆ /EC-DMC-DEC	24
C/Se	MD260	600	417	100	3C	48%	1M LiTFSI/DOL-DME+LiNO ₃	25
C-rGO/Se	BM+MD260	432	385	1300	1C	62%	1M LiTFSI/DOL-DME	28
C/Se	MD600	~500	480	1000	0.25C	70%	1M LiTFSI/DME	29
CMK3/Se	MD260	>900	~300	500	1C	49%	1M LiPF ₆ /EC-DMC	22
CMK3/Se	TD	1379	619	1000	2C	54%	1M LiPF ₆ /EC-DEC-DMC	80
3DG-CNT/Se	Hydrothermal	633	504	150	0.2C	36.3%	1M LiTFSI/DOL-DME	59
HMC/Se	MD260	600	309	100	0.5C	56%	1M LiTFSI/DOL-DME+LiNO ₃	60
N-C/Se	MD260	980	443	200	0.5C	50%	1M LiPF ₆ /EC-DEC	61
N-C/Se	MD260	435	305	60	2C	56.2%	1M LiTFSI/DOL-DME	62
N-C/Se	MD260	1000	460	1600	2C	50%	1M LiPF ₆ /EC-DMC-DEC	66
G@Se/PANI	Sol-reaction	~680	567	200	0.2C	66.2%	1M LiPF ₆ /EC-DEC	96
C/Se	BM+BSA260	864	580	1000	1C	72%	1M LiPF ₆ /EC-DEC	82
C/Se	MD350	~750	~550	1200	1C	70.5%	1M LiPF ₆ /EC-DMC	81
MPC/Se	MD260	341	249	3000	1C	51%	1M LiPF ₆ /EC-DEC	88
N-C/Se	MD350	664	506	150	1C	60%	1M LiTFSI/DOL-DME+LiNO ₃	99
CNF/Se	MD260	581	400	2000	1C	50%	1M LiPF ₆ /EC-DEC	92
MWCNT/Se	MD260	646	356	100	0.5C	56.2%	1M LiTFSI/DOL-DME	69
HC/Se	MD350	603(2th)	525	1000	0.5Ag ⁻¹	59.5%	1M LiPF ₆ /EC-DEC	93
HCPS/Se	MD260	572	299	100	0.5C	41.2%	1M LiTFSI/DOL-DME	94
rGO@Se	Sol-reaction	533	265	200	0.2C	80%	1M LiTFSI/DOL-DME+LiNO ₃	95
CNT-C/Se	MD600	781	517	500	0.5Ag ⁻¹	35%	1M LiPF ₆ /EC-DMC	71
PCNFs/Se	MD260	1159	516	900	0.5Ag ⁻¹	52.3%	1M LiPF ₆ /EC-DMC	72
CN _x @Se	Hydrothermal	905	609	100	1 C	62.5%	1M LiPF ₆ /EC-DEC	103
CPAN/Se	MD600	560	~600	500	0.41Ag ⁻¹	36%	1M LiPF ₆ /EC-DEC	98
TiO ₂ /Se	MD260	481	158	50	0.1C	70.8%	1M LiTFSI/DOL-DME	31
C/SeS ₂	BM+MD260	~670	512	30	50mAg ⁻¹	50%	1.2M LiPF ₆ /EC-DMC	21
CPAN/SeS	MD600	~800	780	1200	0.6Ag ⁻¹	33%	1M LiPF ₆ /EC-DEC	151
C/SeS ₂	MD160	1150	601	10	0.5Ag ⁻¹	49.3%	1M LiTFSI/DOL-DME+LiNO ₃	152
C/Se ₄ S ₅	MD500	~1180	796	100	0.5C	50%	1M LiTFSI/DOL-DME	155

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N-C/Se _n /S _{8-x}	MD500	1200	883	100	0.25Ag ⁻¹	60	1M LiTFSI/DOL-DME	159
C/S _{0.94} Se _{0.06}	MD260	~1550	910	500	1Ag ⁻¹	50%	1M LiPF ₆ /EC-DMC	160

BM: ball milling; MD: melt diffusion; TD: two-step melt diffusion; HCPS: hollow carbonized polyaniline spheres; HC: hollow carbon; HMC: hierarchically meso-microporous carbon; CPAN: carbonized polyacrylonitrile.

5. Conclusions and outlook

Generally, Se has been regarded as an alternative promising high-energy electrode material with good rate performance, due to its relatively high conductivity, a comparably high theoretical volumetric capacity, and a moderate output voltage. This review highlights the most recent developments of hierarchically micro/nanostructured electrode materials for state-of-the-art Li-Se batteries. The Se electrode in the Li-Se battery suffers from various issues including the Se loading amount, low utilization of Se, dissolution of polyselenide intermediates, large volume expansion, low electrical conductivity, low coulombic efficiency and poor cycle performance.

Many efforts have been made to solve these problems, including utilizing micro/nanostructured carbon materials (*e.g.*, porous carbon, CNTs and CNFs), free-standing conductive matrices, transition metal compounds (*e.g.*, ZnO, TiO₂, ZnSe and MoSe₂), and Se alloys (*e.g.*, SeS_x and SeGe). The micro/nanostructured carbon with suitable porous structures, high specific surface areas, particular size dimensionality and surface functionalization can benefit the conductivity and loading of active Se in the electrode, absorb the polyselenide intermediates, buffer the volume change, and thus facilitate the overall electrochemical performance. The Se host materials can be further expanded to the polarization, heteroatom-doped and hybrid multi-functional materials.

In addition, more attention needs to be paid to the stability of electrodes and the suppression of shuttling effect during the charge-discharge process, which hinders the practical applications of Li-Se batteries. Constructing a stable, efficient solid electrolyte interphase (SEI) layer could effectively inhibit the polyselenide dissolution and facilitate the cycle performance. For instance, Lee *et al.* utilized fluoroethylene carbonates (FEC) as an electrolyte additive and *in-situ* formed an SEI coating on the Se cathode during the first cycle.¹⁷¹ The formed ionically conductive SEI layer is largely impermeable to Li ions and can distinctly hinder the dissolution of polyselenides, thus dramatically enhancing the cycle stability. Several other approaches can also be used to settle the polyselenide dissolution, such as liquid electrolyte modification and polymer or solid electrolyte utilization. Typically, LiNO₃ has been widely used as an effective electrolyte additive (as shown in Table 1) to form a passivation layer which suppresses redox shuttle of lithium polyselenides.^{23, 60, 95} Moreover, non-Li materials (*e.g.*, C and Si) can be used to replace Li metal as an alternative anode material and facilitate the cycle performance. Another way is to focus on the construction of a functional polyselenide

absorbent interlayer between the cathode and separator. Such an interlayer can effectively prevent the migration of polyselenides to the anode region by absorbing and trapping them in the separator.¹⁷²⁻¹⁷⁵

Among the various challenges, based on the utilizations of advanced characterization techniques, a fundamental understanding of the Li-Se redox reaction mechanism in the battery is very meaningful and inspiring for future researches and applications. The *ex-situ* characterizations such as Raman, XRD, SEM and TEM are relatively facile to be implemented in sample preparation and testing, but the *ex-situ* results may be different from the real redox reaction that occurs in the Li-Se battery. Fortunately, the *in-situ* techniques can help to investigate the real redox reaction occurring in the battery. For example, Li *et al.* recently used an *in-situ* TEM technique to investigate lithiation and sodiation reactions with crystalline Se nanotubes, and found that the lithiation process of Se exhibited a one-step reaction mechanism with phase transformation from single-crystalline Se to Li₂Se, while the sodiation process had a three-step reaction mechanism.¹⁷⁶ Although the *in-situ* characterizations can investigate the real redox reaction in the battery, it is challenging to analyze the operating battery because they require stringent conditions such as the air-tightness of batteries, the complexity of redox reactivity intermediates and products, the stability of polyselenides, and the quality of testing signals. It is of significant importance for mechanism understandings and practical applications to develop the database of Raman, FTIR, XPS, SEM, TEM and XANES combined with theoretical models for the Li-Se redox reaction.

In summary, although challenges remain in the investigation and commercialization of Li-Se batteries, their inherent advantages will further promote their developments and applications in energy storage, with the advances of nanostructured Se-based cathodes and Li or non-Li (*e.g.*, C and Si) anodes, functional surface-coated separators and modified electrolytes combined with customized cell configurations.

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Figure 1. The lithiation-delithiation process of C/Se electrode. (a) Phase transformation of Se and Li_2Se for C/Se electrode, (b) discharge-charge curve and corresponding pair distribution functions $G(r)$ at various discharged (yellow) or charged (green) states.²¹ Copyright 2012, American Chemical Society.

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Figure 2. (a) TEM image of Se NWs, initial discharge-charge curves of (b) a-Se, (c) c/a-Se and (d) c-Se NWs at 0.1 C in Li-Se cell.²⁴ Copyright 2015, American Chemical Society.

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Figure 3. (a) TEM image of pristine CMK-3, (b) SEM image of CMK-3/Se, and (c) EDX spectrum, annular dark-field TEM image and corresponding C and Se elemental mapping of CMK-3/Se.²² Copyright 2013, Wiley-VCH. (d) TEM of in-situ synthesized CMK-3/Se,⁸⁰ Copyright 2016, Royal Society of Chemistry. (e) Proposed charge-discharge process of CMK-3/Se.²² Copyright 2013, Wiley-VCH.

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Figure 4. (a) SEM images of PCNs/Se, (b) cycle performance, and (c) proposed (de)lithiation processes of PCNs/Se.⁸¹ Copyright 2014, Elsevier.

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Figure 5. (a) Schematic preparation diagram of CNT@MPC/Se, (b) TEM, (c) HRTEM image, (d) annular dark-field TEM image and elemental mappings of (e) Se and (f) C of CNT@MPC/Se composite, (g) cycle performance of CNT@MPC/Se at 1 C.⁸⁷ Copyright 2016, American Chemical Society.

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Figure 6. (a) SEM image, (b) TEM image, and (c) EDS elemental mapping images of the Se₅₀/C composite: Se (red) and carbon (green), (d) cycle performance of Se₄₀/PHCBs, Se₅₀/PHCBs and Se₆₀/PHCBs.⁷⁰ Copyright 2014, Royal Society of Chemistry. (e) TEM image of HCPS/Se, elemental mapping of (f) Se, (g) N, (h) C, and (i) cycle performances of pristine Se and HCPS/Se composite at 0.5 C.⁹⁴ Copyright 2014, Elsevier.

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Figure 7. (a-c) Schematic preparation illustration of G@Se/PANI, (d) elemental mapping images of G@Se/PANI, and (e) cycle performance of G@Se/PANI at 0.2 C.⁹⁶ Copyright 2015, Elsevier. TEM images of (f) PPy coated Se fibers and (g) graphene wrapped Se fibers.³³ Copyright 2013, Elsevier.

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Figure 8. (a) TEM, (b) HRTEM, and (c-d) Se elemental mapping images of NCS/Se composite; (e) cycle performances of NCS/Se and CS/Se composites at 0.5 C.⁶¹ Copyright 2015, Royal Society of Chemistry. (f) SEM, (g) TEM, (h) HRTEM, (i) HADDF-STEM, and (j) energy filter TEM images of N-MPCS/Se; the corresponding EFTEM maps of (k) C, (l) N and (m) Se.⁶⁶ Copyright 2015, Royal Society of Chemistry.

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Figure 9. (a, b) Schematic preparation illustrations of PCNFs@Se electrode; (c) FESEM image and (d) photograph of a free-standing PCNFs@Se electrode; (e) STEM image and corresponding element mapping: (f) Se and (g) C.⁷² Copyright 2014, Wiley-VCH. (h) Optical image and (i) cross-sectional SEM image of the hierarchically hollow CN_x@Se freestanding electrode.¹⁰³ Copyright 2017, Elsevier.

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Figure 10. (a) Schematic preparation illustration of the 3DG-CNT@Se composite; SEM images of (b) CNT-Se and (c, d) 3DG-CNT@Se composites.⁵⁹ Copyright 2016, American Chemical Society.

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Figure 11. (a) TEM and (b) HRTEM images of C@ZnSe composite; (c) discharge-charge voltage profiles and (d) cycle performance of C@ZnSe at 0.2 A g⁻¹ after 100 cycles.¹²³ Copyright 2016, Elsevier.

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Figure 12. (a-b) Li⁺ diffusion path in the lattice of MoSe₂, and (c) energy curve along the plotted Li⁺ diffusion path.¹³² Copyright 2015, American Chemical Society. (d) TEM image of mesoporous MoSe₂.¹³⁴ Copyright 2016, Royal Society of Chemistry. (e) TEM image of C/MoSe₂ composite.¹¹³ Copyright 2015, Royal Society of Chemistry. (f) TEM image of rGO/MoSe₂ hybrids, (g) cycle performance of rGO/MoSe₂ at 1000 mA g⁻¹.¹³⁶ Copyright 2016, Royal Society of Chemistry. (h) TEM image of rGO/MoSe₂ composite.¹³⁷ Copyright 2015, Elsevier.

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Figure 13. (a) SEM image of MoO₂@MoSe₂ heterostructure,¹³⁸ Copyright 2016, Royal Society of Chemistry. (b) SEM image of pure MoSe₂ nanoflowers, (c) TEM image of MoSe₂@C/TiO₂ heterostructures, (d) SEAD patterns with illustration in (e), and (f) cycle performance of MoSe₂@C/TiO₂, MoSe₂/TiO₂, pure MoSe₂ nanosheets and bare TiO₂ nanobelts at 500 mA g⁻¹.¹³⁹ Copyright 2016, Royal Society of Chemistry.

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Figure 14. (a) Schematic preparation illustration of DLHC/SeS₂; (b) SEM image, (c) TEM image, and (d) line scanning EDX spectra of DLHC/SeS₂; (e) cycle performances of pure SeS₂, SLHC/SeS₂, DLHC/SeS₂ at 0.2 A g⁻¹ and (f) long-term cycle performance of GLHC/SeS₂ at 1 A g⁻¹.¹⁵⁷ Copyright 2016, Springer.

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Figure 15. (a) Schematic model of the NMC/ Se_2S_6 structure, (b) SEM image of NMC/ Se_2S_6 , and (c) cycle performance and (d) coulombic efficiency of NMC/ $\text{Se}_n\text{S}_{8-n}$ ($n=1-3$) at 250 mA g^{-1} .¹⁵⁹ Copyright 2016, American Chemistry Society.

71x64mm (300 x 300 DPI)

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In this review, the recent advances of nanostructured electrodes for lithium-selenium batteries and their characterizations and mechanisms are reviewed and discussed.

ToC Figure