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## Carbon-based materials for more reliable solid-state Li batteries

Ying Shi,<sup>a</sup> Lei Wen,<sup>a</sup> Huicong Yang,<sup>a</sup> Zhenhua Sun  <sup>ab</sup> and Feng Li  <sup>ab</sup>

Solid-state Li batteries (SSLBs) exhibiting high energy density and high safety have been considered the most promising energy storage devices for future applications. However, issues including inadequate interfacial compatibility, insufficient properties of solid electrolytes, and dendrite growth on Li anodes hinder their practical applications. The multi-functional features of carbon-based materials, particularly their inherent attributes of high electronic conductivity and lightweight characteristics combined with tunable structural configurations and surface chemistries, have shown significant potential and attracted growing attention for addressing critical challenges in the application of SSLBs. In this review, we comprehensively summarize the state-of-the-art applications of carbon-based materials in SSLBs, focusing on their special effects on more stable cathodes, more effective solid-state electrolytes and dendrite-free Li anodes. The primary mechanisms underlying their functions of resolving interfacial issues, constructing high-performance solid-state electrolytes, and developing dendrite-free Li anodes to address the current challenges in SSLBs are further discussed and systematically elucidated. Finally, the persistent challenges in fully utilizing carbon-based materials to enhance solid-state batteries are presented, along with perspectives and suggestions for future development of carbon-based materials toward more reliable SSLBs.

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### 1. Introduction

As ensuring a secure and sustainable energy supply is a pivotal social and scientific challenge, the fields of energy storage and conversion have garnered continuous worldwide attention. Due to its high efficiency and environmental benignity, electrochemical energy storage plays a significant role in the rational utilization of

<sup>a</sup>Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China. E-mail: fli@imr.ac.cn

<sup>b</sup>School of Materials Science and Engineering, University of Science and Technology of China, Shenyang 110016, China



Ying Shi

Ying Shi is a senior engineer at Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Science (IMR, CAS). She graduated from Dalian University of Technology with an MS degree in 2009. Since then, she has worked at IMR, CAS, and was mainly engaged in the application of carbon-based materials for electrochemical energy storage. In 2023, she received her PhD in Energy and

Environmental Protection from the University of Science and Technology of China. Her current research interests mainly focus on the development of carbon-based materials for new electrochemical energy storage and flexible electronics devices.



Lei Wen

Lei Wen is an associate professor in the Advanced Carbon Research Division at Shenyang National Laboratory for Materials Science, the Institute of Metal Research, Chinese Academy of Sciences (IMR, CAS). He received his PhD in Materials Science from North Eastern University, China, in 2004. His research interests focus mainly on lithium ion batteries and energy storage devices.



renewable energy.<sup>1</sup> Among the electrochemical energy storage technologies, Li-ion batteries (LIBs) have been most widely applied due to their high power and energy density, long life span and low self-discharge. Since their commercialization by the Sony company in 1991, LIBs have been used in fields ranging from information, communication, transportation to healthcare and aerospace, entering our daily lives and revolutionizing the human society.<sup>2,3</sup> However, based on their intercalation chemistry, current LIBs have nearly approached their theoretical energy-density limit.<sup>4-6</sup> Although Li metal has shown its great potential for the desired high energy-density battery due to its ultra-high theoretical specific capacity (3860 mAh g<sup>-1</sup>) and the most negative electrochemical potential (-3.04 V *versus* standard hydrogen electrode),<sup>7,8</sup> challenges such as safety concerns still exist and need to be overcome for practical application. Li tends to deposit in a dendritic form, and these dendrites are a primary cause of internal short circuits, which can lead to thermal runaway or even explosion during charge and discharge processes. In addition, when using



Huicong Yang

advanced battery systems.

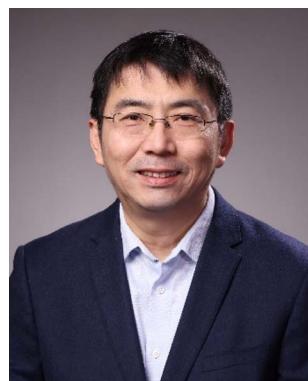


Zhenhua Sun

Zhenhua Sun is currently a Full Professor at the Institute of Metal Research, Chinese Academy of Sciences. He received his BS degree in 2001 and PhD in 2006, both in inorganic chemistry from Jilin University. From 2007 to 2009, he conducted postdoctoral research at The Chinese University of Hong Kong. His research interests focus on advanced electrochemical energy storage systems, particularly non-metallic materials and next-generation battery technologies such as lithium-sulfur batteries and solid-state batteries. He has authored over 130 publications in peer-reviewed journals, including *Nature Communications* and *Advanced Materials*, accumulating more than 14 000 citations with an H-index of 59.

conventional liquid electrolytes, the flammability and easy leakage of the organic electrolyte would accelerate this thermal runaway. Therefore, the development of novel battery systems with higher energy density and safety is of great importance. From this point of view, solid-state Li batteries (SSLBs) would be undoubtedly a suitable candidate for next-generation energy storage systems because the high capacity of Li metal anodes will greatly increase energy density, while the solid-state electrolytes (SSEs) would well address the safety concern caused by flammable liquid electrolytes.<sup>9,10</sup>

Although SSLBs have demonstrated significant promise for next-generation energy storage systems, several fundamental obstacles remain to be overcome before their application. The main challenges include the following three aspects: (1) inadequate interfacial compatibility. In contrast to the conventional LIBs with liquid electrolytes, the interfacial contact between the electrodes and the electrolytes of SSLBs is usually poor.<sup>11</sup> As the liquid electrolyte and separator of LIBs have been replaced by a solid-state electrolyte of SSLBs, the interfaces between the cathode and the electrolyte and the one between the electrolyte and the Li anode both have changed from liquid-solid to solid-solid accordingly, leading to an increased interfacial impedance inevitably. Meanwhile, the unstable interfacial chemistry may also trigger violent reactions, ultimately leading to the degradation of battery performance. (2) Insufficient properties of solid electrolytes. SSEs usually include inorganic electrolytes and polymer electrolytes.<sup>12</sup> The ionic conductivity of polymer electrolytes still needs to be further improved for practical applications, especially at room temperature.<sup>13</sup> Though some of the inorganic electrolytes have shown comparable ionic conductivity with that of the liquid electrolytes,<sup>14,15</sup> the transport of electrons and ions in the SSLB is still impeded by the poor solid-solid interfaces.<sup>16,17</sup> Moreover, the stability of SSEs at high potential and high temperature is another essential issue to be addressed.<sup>18,19</sup> (3) Dendrite growth of the Li anode. Even for inorganic electrolytes with high mechanical strength, Li metal can still grow along their grain boundaries,



Feng Li

Feng Li has been a Professor at the Institute of Metal Research, Chinese Academy of Science (IMR, CAS), since 2013. He received his PhD in materials science at IMR, CAS, in 2001 supervised by Prof. Hui-Ming Cheng. He mainly works on energy materials. He has published more than 390 papers in peer-reviewed journals, such as *Nature Energy*, *Energy Storage Materials*, and *Adv. Mater.* with over 70 000 citations and H-index about 115. He obtained the awards of National Science Fund for Distinguished Young Scholars by the National Natural Science Foundation of China and Highly Cited Researcher by Clarivate Analytics from 2016 to 2024.



defects or cracks.<sup>20</sup> The formed dendrites could penetrate the electrolyte and lead to short-circuiting or even thermal runaway of batteries. Therefore, the breakthroughs of these multiscale challenges in SSLBs necessitate the establishment of innovative material systems that comprehensively cover the entire electrode-electrolyte-interface issues.

Carbon materials, characterized by their lightweight, high thermal and chemical stability, superior conductivity, and diverse structures, have been widely used to enhance the charge transfer kinetics, mechanical integrity, as well as the electrochemical performance of LIBs in the past three decades. Carbon materials can function in multiple ways, including as electrode materials, conductive additives, supporting or buffering materials and current collector components, playing a crucial role in the design and construction of both materials and devices.<sup>21-26</sup> With these advantages, carbon materials have also shown great potential in the application of SSLBs. Beyond their conventional roles as in the LIBs, carbon materials can play their unique roles in advanced solid-state battery systems. For example, their structural variety and chemical stability can demonstrate exceptional capabilities in optimizing electrode-electrolyte interfaces, their large surface area can provide sufficient Li-ion adsorption sites for effectively enhancing ion-diffusion kinetics in solid-state electrolytes, and their superior conductivity can help to form even Li deposition, suppressing lithium dendrite growth. In addition, due to their ultra-light properties, carbon materials can work with a negligible weight, which is crucial for maintaining the high energy density in the SSLBs. These attributes enable carbon materials to emerge as critical materials which address the main challenges in SSLBs through innovative functional designs. Furthermore, carbon materials can be easily functionalized by heteroatom doping or oxidation to form modified carbon materials with specific functions, which are referred to as carbon-based materials together with carbon materials. Therefore, a further understanding of the effects of carbon-based materials on the electrode-electrolyte-interface in the solid-state battery system will bring new opportunities for the development of SSLBs.

Though the existing papers have extensively reviewed research progress and improvement strategies for solid-state electrolytes

and solid-state batteries in detail,<sup>10,12,16,17,27,28</sup> there remains a lack of systematic summarization focusing on the application of carbon-based materials in SSLBs. Aiming to bridge this knowledge gap and address the current challenges in SSLBs, this review systematically summarizes the critical roles and recent progress of carbon-based materials in the cathodes, SSEs and Li anodes for resolving interfacial issues, constructing high-performance solid electrolytes, and developing dendrite-free lithium anodes, as shown in Fig. 1. Finally, the forward-looking perspectives and suggestions on the future directions of carbon-based materials for more reliable SSLBs are proposed.

## 2. Carbon-based materials for more stable cathodes

A typical SSLB usually comprises a cathode, a solid-state electrolyte, a lithium anode, and current collectors. Since there is no liquid present in the solid electrolyte, it is impossible to achieve sufficient contact with the electrodes through electrolyte infiltration. This absence of wetting effect leads to a serious decrease in the ion diffusion ability at interfaces, resulting in a series of interface issues, such as the uneven current distribution, increased interfacial impedance, and side reactions at the interface. To reduce the interface resistance between the cathode and the SSE, an appropriate amount of SSEs is necessary to incorporate in the cathode in addition to the conductive additives and binders during the fabrication. However, the presence of SSEs can decrease the ratio of conductive additives in the cathode, thereby affecting the transfer of electrons in the cathode. The imbalance between the electronic and ionic conductivity is one of the most driving factors for inhomogeneous reactions in the cathode, which would lead to local overcharging and rapid degradation of electrochemical performance. Therefore, the balance of ion transport and electron transfer in the cathode is important for achieving the stable performance of SSLBs.<sup>29-32</sup>

Due to the poor conductivity of most cathode materials for SSLBs, such as inorganic oxide and sulfur, the performance of cathode highly relies on the choice and amount of carbon

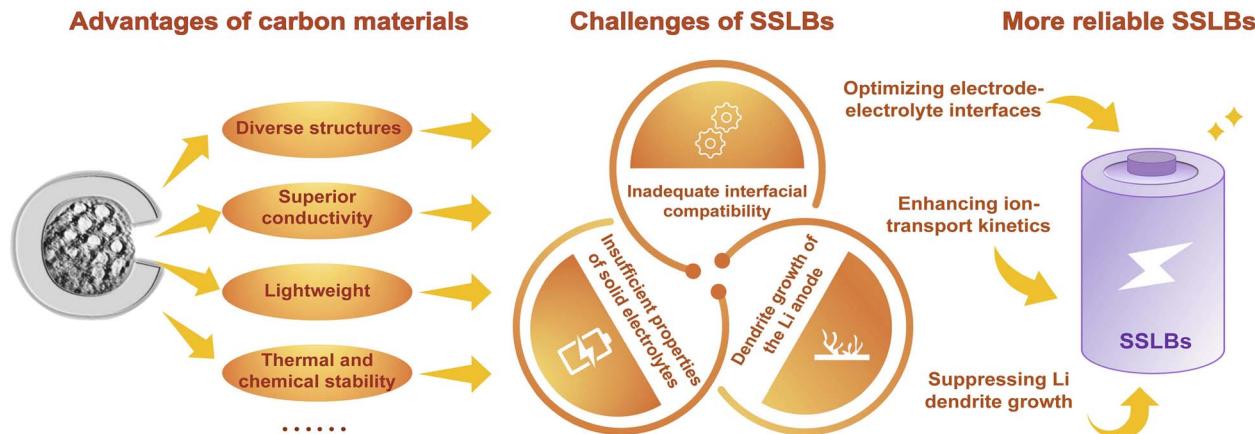


Fig. 1 Critical roles of carbon materials in advanced SSLBs.



materials. With superior electronic conductivity and diversified structures, carbon-based materials such as acetylene black (CB), carbon nanotubes (CNTs), graphene and vapor-grown carbon nanofibers (VGCFs)<sup>31–38</sup> have been widely used as conductive additives to generate a well-developed electron-percolating network for most cathodes of SSLBs. Among these carbon-based materials, additives with a fibrous morphology such as CNTs and VGCFs have emerged as a preferred choice, because their unique one-dimensional nanostructure provides exceptionally high axial electronic conductivity, which can establish interconnected conductive networks, bridge electroactive particles and minimize electron transport resistance. Therefore, they have been used to partially replace the CB<sup>31</sup> or form hybrids with other carbon materials<sup>39,40</sup> to efficiently enhance electron transfer processes and create preferential pathways for Li motion in the cathode composite. For instance, 1D graphitized carbon materials consisting of CNTs and carbon nanofibers used as hybrid conductive additives can simultaneously provide both short- and long-range conductivity pathways, form well-

interconnected electric networks, and balance the electronic and ionic conductivity, consequently achieving a stable performance of SSLBs.<sup>40</sup> With the combination of ultrahigh aspect ratio (length-to-diameter ratio) and exceptional mechanical strength, single-walled carbon nanotubes (SWCNTs) have displayed great potential in the cathodes of SSLBs. They can form more efficient conductive networks with less amounts while functioning as binders to fasten the active materials to maintain the structural stability of the cathode as well. Serving as both conductive additives and binders simultaneously, SWCNTs can assist to form a flexible free-standing electrode, which is particularly effective in boosting the structural and electrochemical stability of cathodes,<sup>38</sup> as shown in Fig. 2a. Moreover, reducing the use of insulating binders in the cathode can further enhance the kinetics of both electronic and ionic conduction. Optimizing the ratio of the electronic and ionic conductors in the composite cathode is also important for the balance of ion-electron transfer. By adjusting the ratio of carbon additives and SSEs in the cathode, an optimal balance between

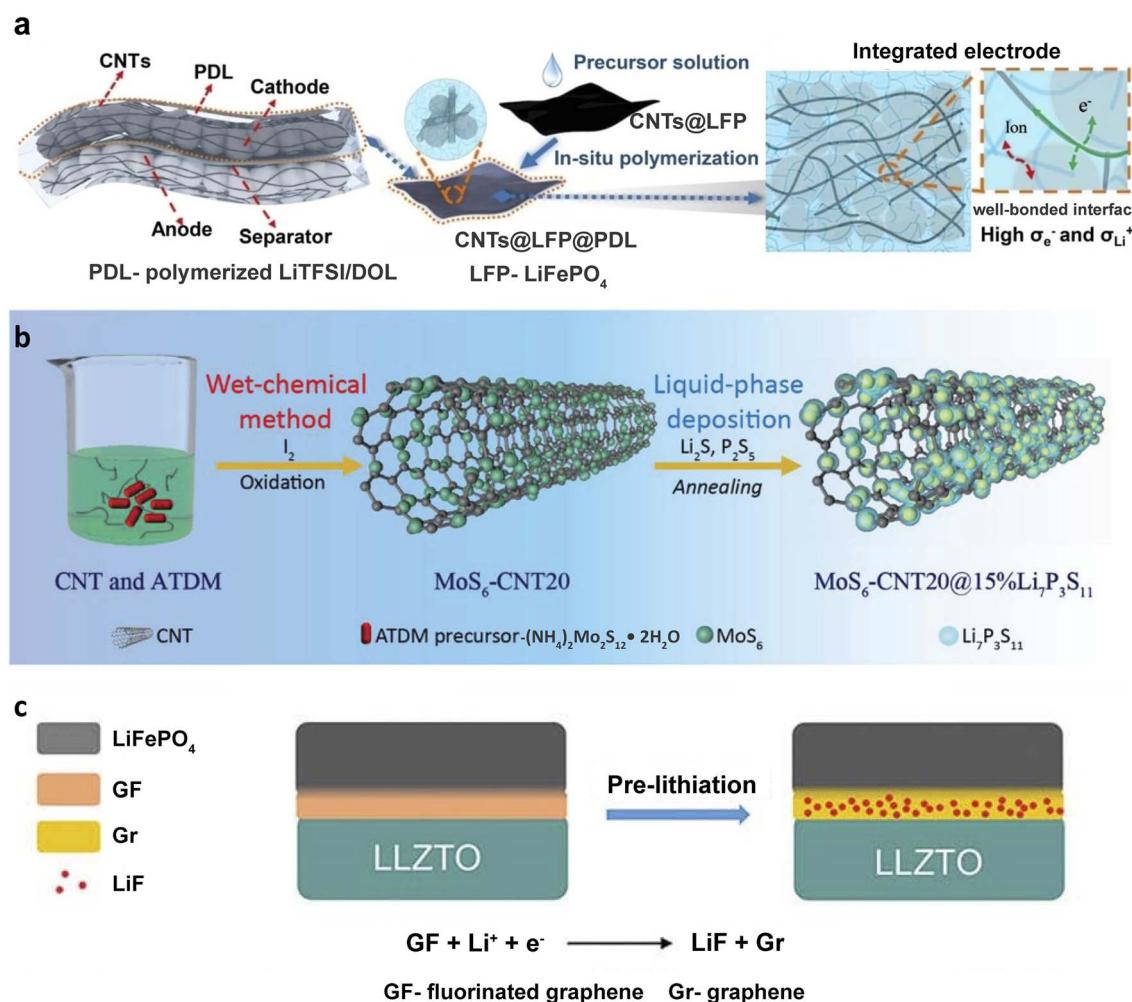


Fig. 2 Main effects of carbon-based materials on the cathodes of SSLBs. (a) A flexible integrated free-standing electrode with CNT-fastened active materials (LFP) and its highly efficient electron/ion transport. Reproduced from ref. 38 with permission from Wiley-VCH, copyright 2023. (b) CNT used as a conductive support for MoS<sub>6</sub>-CNT<sub>20</sub>@15%Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> in the cathode. Reproduced from ref. 41 with permission from Wiley-VCH, copyright 2023. (c) Fluorinated graphene used as an inorganic composite interlayer between a cathode and a garnet SSE (Li<sub>6.4</sub>La<sub>3</sub>Zr<sub>1.4</sub>Ta<sub>0.6</sub>O<sub>12</sub>, LLZTO) to enhance interfacial compatibility. Reproduced from ref. 42 with permission from the Royal Society of Chemistry, copyright 2020.



ion and electron transport can be finally achieved, enabling good stability and high electrochemical performance for the all-solid-state Li-sulfur batteries.<sup>29</sup> This strategy also provides an important basis for the design of composite cathodes with balanced ion-electron conduction in SSLBs.

Apart from the role of constructing highly efficient electron-percolating networks, carbon-based materials can be used as conductive supports for cathode materials and alleviate the volume changes during the charge-discharge process as well.<sup>41,43-45</sup> Owing to their superior conductivity, light weight and large surface area, carbon-based materials such as graphene and CNTs can be used as ideal conductive supports for the cathode materials, facilitating a good charge transfer among the active particles. Combined with the incorporation of solid-state ion conductors, such as coating with Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> electrolytes, they can further assist in constructing a balanced and efficient electron-ion conduction network in the cathode,<sup>41,44,45</sup> as shown in Fig. 2b. Furthermore, their good flexibility demonstrates an excellent confinement effect for some active materials with large volume changes during the charge-discharge process, such as sulfur.<sup>43,46</sup> This confinement effect can alleviate the volume changes, ensuring intimate contact between active materials, carbon-based additives and SSEs and maintaining structural stability of the cathode.

Owing to the adjustable structural and chemical properties, carbon-based materials can also be used to improve the interfacial stability of the cathode in SSLBs. On the one hand, the intrinsic chemical inertness of carbon materials enables them to act as an ideal protective layer against side reactions. For instance, as sulfide electrolytes are very sensitive to oxygen, the cathode materials containing oxygen can react with some sulfide electrolytes and form increased interfacial resistance. To

eliminate the influence of oxygen on the cathode, the chemical inertness of carbon materials, such as diamond-like carbon, can be adopted as a protective coating layer on the surface of cathode materials to reduce the interface reactions and improve the electrochemical properties of the SSLBs.<sup>47</sup> Meanwhile, graphitic carbon-based materials can also be used as the coating layer of the sulfide electrolytes to offer a continuous three-dimensionally connected electron pathway within the cathode and reduce inhomogeneous interfacial side reactions.<sup>30</sup> On the other hand, carbon materials can also be modified with heteroatoms, which endow them with specific functions such as enhancing the interfacial compatibility. For instance, fluorinated graphene can be used as an inorganic interlayer between a cathode and garnet SSE, as shown in Fig. 2c. By a simple pre-lithiation process, this inorganic interlayer can be converted into graphene and the *in situ* generated LiF, which is uniformly distributed among the graphene. As LiF with high stability and low surface diffusion barrier can accelerate lithium-ion transport and flexible graphene can maximize the interfacial contact, this combination largely reduces the cathode/SSE interfacial resistance, ensuring a good interfacial compatibility.<sup>42</sup>

The main functions of the carbon-based materials for a more stable cathode in SSLBs can be summarized into the following four aspects: (1) constructing effective electron-percolating pathways to balance ion transport and electron transfer, (2) serving as a conductive structural support for cathode materials, (3) mitigating mechanical stress and volume expansion during charge-discharge, and (4) enhancing interfacial compatibility between the cathode materials and the SSEs, as illustrated in Fig. 3.

Nevertheless, it is worth noting that the presence of some carbon-based materials in the cathode can also induce

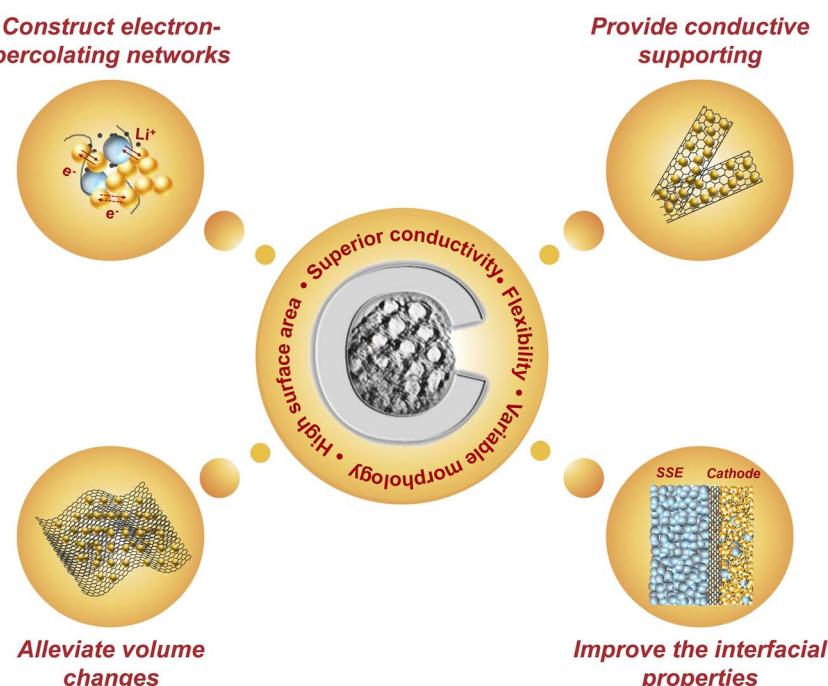


Fig. 3 Functions of carbon-based materials for more stable cathodes in SSLBs.



undesirable side reactions, leading to the electrochemical decomposition of certain SSEs, especially the sulfide solid electrolytes.<sup>18,40,48–51</sup> Although the incorporation of carbon facilitates uniform current distribution within cathodes and ensures high utilization of the active materials, it is also found to promote the electrochemical decomposition of some sulfide solid electrolytes during cycling by providing sufficient electronic percolation paths toward the current collector.<sup>52</sup> Furthermore, the presence of oxygen-containing groups on the surface of some carbon-based materials can lead to specific decomposition reactions at the interface between carbon-based additives and sulfide electrolytes.<sup>48</sup> Moreover, it is found that nanosized carbon materials with a higher surface area such as carbon black could promote the decomposition of sulfide electrolytes compared to those with a lower surface area.<sup>50</sup> The insulative decomposition products would result in large interfacial impedance and accelerated capacity degradation. Therefore, it is significant to choose appropriate carbon-based materials and optimize their application strategies in the cathode for SSLBs.

Many efforts have been devoted to addressing this problem by reducing and/or preventing the side reactions between the carbon materials and SSEs. One effective strategy is to establish a physical separation to prevent direct contact between carbon

materials and solid electrolytes. For instance, a ZnO nanoparticle coating on the surface of VGCF additives can efficiently prevent carbon–SSE interactions, which significantly enhances the cycling stability of the SSLBs<sup>53</sup> (Fig. 4a). Besides coating with the inactive materials, active materials such as the organic cathode material ( $\text{Li}_4\text{C}_8\text{H}_2\text{O}_6$ ) can be coated on the surface of CNTs by an *in situ* coating method, which effectively alleviated the electrochemical decomposition of the electrolytes and enabled high capacity retention<sup>54</sup> (Fig. 4b). Moreover, the atomic layer deposition on the whole electrode containing carbon additives rather than only on the active materials can further help to reduce the electrochemical oxidation of poly(ethylene glycol) (PEO)-based solid polymer electrolytes and enhance the cycling performance of the batteries.<sup>55</sup> An unconventional cathode–carbon structure design with a reduced graphene oxide (rGO) framework embedded beneath the cathode particles is also available, in which electronic conduction among cathode particles can be achieved through the rGO framework, while the detrimental interface between the carbon material and the SSE can be avoided or minimized.<sup>56</sup>

A rational selection of carbon-based additives is another strategy to avoid the side reaction and decomposition of SSEs. As it is verified that the functional group on carbon is an origin for causing the decomposition of sulfide solid electrolytes in the

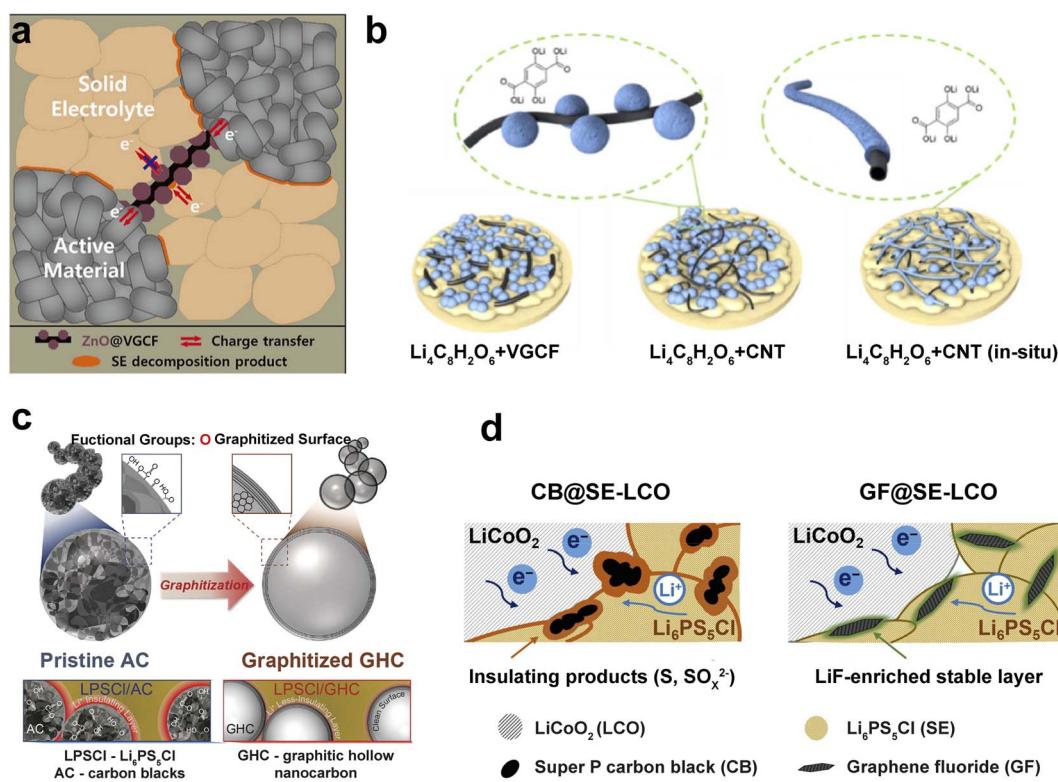


Fig. 4 Strategies to reduce and/or prevent side reactions between the carbon additives and SSEs. (a and b) Spatial isolation to prevent direct contact between carbon and the SSE. (a) ZnO nanoparticle coating on the vapor-grown carbon nanofiber (VGCF) additives by atomic layer deposition to prevent carbon–SSE interactions. Reproduced from ref. 53 with permission from the American Chemical Society, copyright 2023. (b) *In situ* coating the organic cathode material ( $\text{Li}_4\text{C}_8\text{H}_2\text{O}_6$ ) on the surface of CNTs. Reproduced from ref. 54 with permission from Elsevier, copyright 2023. (c and d) Rational selection of carbon-based additives. (c) Selection of a graphitic hollow nanocarbon consisting of a few graphene layers with nearly eliminated functional groups to avoid side reactions. Reproduced from ref. 57 with permission from Wiley-VCH, copyright 2019. (d) Introduction of graphene fluoride to form an LiF protective layer *in situ* to suppress undesirable decomposition reactions and facilitate the ion transport. Reproduced from ref. 58 with permission from Elsevier, copyright 2022.



composite cathode, using a more stable carbon material without functional groups, such as the graphitic hollow nanocarbon with hardly any functional groups and low defect density, is considered to be useful to prevent the side reactions at the interfaces<sup>57</sup> (Fig. 4c). In addition, using carbon-based materials with special functions is also an effective way. For instance, graphene fluoride containing a C–F bond in the graphene skeleton can induce the *in situ* formation of LiF protective layer, which can act as a stable SSE/carbon interface to suppress the undesirable decomposition reactions and simultaneously facilitate the ion transport, thereby improving the overall electrochemical stability<sup>58</sup> (Fig. 4d).

In summary, by constructing highly efficient electron-percolating networks to balance the ion-electron transfer, providing conductive supporting for active materials, alleviating volume changes during the charge–discharge process, and improving the interfacial properties, carbon-based materials can assist SSLBs to achieve more stable cathodes from many aspects. It should be noted that though some carbon materials can also induce detrimental interfacial decomposition of certain SSEs, the interfacial side reactions can be systematically suppressed by reasonable selection and design of the applied carbon-based materials, while preserving the beneficial effects of carbon-based materials. In the future, carbon-based materials with higher efficiency and multi-functions that can minimize the amount used in the cathode as much as possible without compromising electrochemical performance and serve as both conductive additives and binders, such as the SWCNTs, would be used more widely in the SSLBs.

### 3. Carbon-based materials for more effective solid-state electrolytes

SSE is the most crucial component for SSLBs, as there is a comprehensive agreement that the transition from liquid electrolytes to solid electrolytes would significantly increase the safety of batteries, especially for the batteries with Li as the anode.<sup>59,60</sup> An ideal SSE should have high ionic conductivity, good interfacial compatibility, mechanical strength and thermal, chemical and electrochemical stability as well.<sup>28</sup> However, the properties of the existing SSEs still cannot meet the needs for practical application. For polymer electrolytes, insufficient ionic conductivity at room temperature and mechanical strength are the major challenges, while for the inorganic electrolyte, the main issue is the poor interfacial compatibility. To achieve more effective SSE, both fundamental and technical research work still needs to be further implemented.

In addition to the improvement of the electron conduction in electrodes due to their exceptional electronic conductivity, carbon-based materials have also exhibited versatile capabilities in interfacial engineering and mechanical reinforcement.<sup>61</sup> In recent years, their emerging capabilities in modifying SSEs have attracted growing attention as well.<sup>62–64</sup> This section comprehensively reviews the advanced progress of carbon-based materials in the SSEs and elucidates their main functions and related mechanisms. Generally, carbon-based materials can help to form more effective SSEs from the following three aspects, including acceleration of Li-ion transport, reinforcement of mechanical strength, and surface modification at the interface, as shown in Fig. 5.

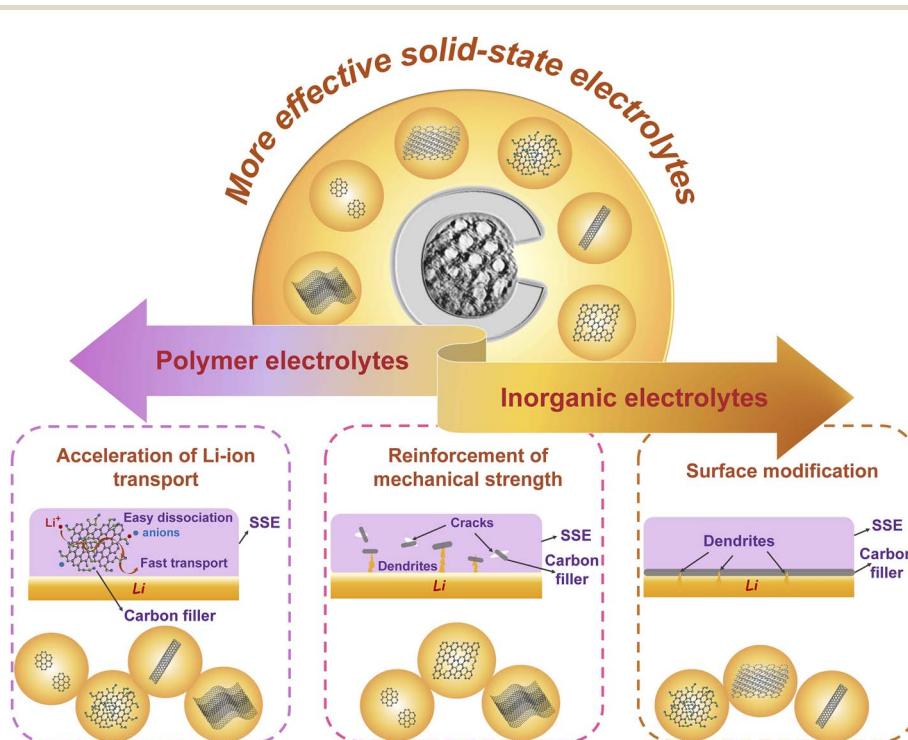


Fig. 5 Multi-functions of carbon-based materials for more effective solid-state electrolytes.



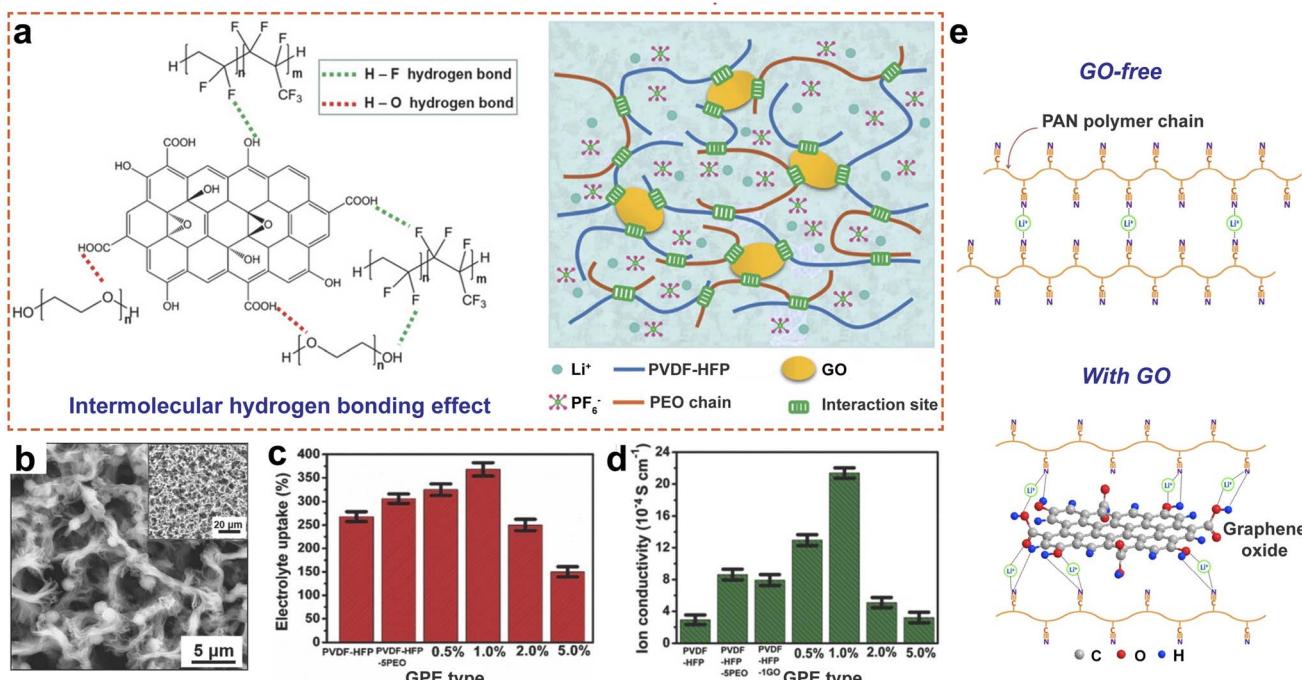
### 3.1 Acceleration of Li-ion transport in the polymer electrolytes

Ionic conductivity at room temperature is a crucial property of SSEs. However, for most polymer electrolytes, ionic conductivity is still several orders of magnitude lower than that of liquid electrolytes. Therefore, the acceleration of ion transport becomes a main target for the development of polymer electrolytes.<sup>60</sup> Adding inert nanofillers into the polymer electrolytes has been considered as one of the most efficient strategies for the enhancement of ionic conduction at room temperature. Thus far, commonly used nanofillers include the inorganic ceramic nanofillers such as  $\text{TiO}_2$ ,<sup>65</sup>  $\text{SiO}_2$ ,<sup>66,67</sup> and  $\text{Al}_2\text{O}_3$ ,<sup>68</sup> ferroelectric materials such as  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ , and  $\text{LiNbO}_3$ ,<sup>69</sup> and carbon-based materials such as graphene oxide (GO), CNTs, and carbon quantum dot (CQDs).<sup>59,62,63,70</sup> Compared with those ceramic and ferroelectric materials, the ultralight weight, thermal stability and good mechanical property make carbon-based materials more suitable for the improvement of polymer electrolytes as nanofillers. In the following text, promoting effects on the ion transport and related mechanisms of carbon-based materials as nanofillers are discussed in detail.

Before discussing, understanding the ion transport mechanism of polymer electrolytes will help us to gain a deeper clarity of the promoting roles of carbon-based materials. Generally, polymer electrolytes for Li-based batteries contain gel polymer electrolytes (GPEs) and solid polymer electrolytes (SPEs).<sup>71</sup> For the GPEs, the transport of Li-ions is mainly through the liquid plasticizers containing dissolved Li salts, while the polymer matrices act as the supporting material to ensure mechanical

strength. As Li-ion conduction in liquid is much faster than that in the polymer, the more liquid electrolyte uptake usually means higher ionic conductivity.<sup>60</sup> While for the SPEs, the mobility of Li-ions in the polymer is crucial for the ionic conductivity, as the main transport mechanism is the Li-ion hopping in polymer chain or between polymer segments, which is affected by the dissociation degree of Li salts, the crystallinity of polymer matrices, and the interaction between Li-ions and polymer chains.

As a typical two-dimensional layered material with single-atom thickness, GO has an ultra-large surface area, good mechanical strength and flexibility.<sup>26,72</sup> There are various oxygen functional groups on the surface of GO, such as C-OH, C=O, C-O-C and O=C-OH, which disrupt the  $\text{sp}^2$  hybridization of carbon and long-range  $\pi$ -stacking and make GO less electronically conductive.<sup>59,73</sup> As these oxygen functional groups can both function as the anchoring sites for Li-ions and interact with the polymer matrix, GO has been widely used in the polymer electrolytes and played an important role with special functions.<sup>74,75</sup> First, it can form the intermolecular hydrogen bonding effect with the polymer matrix, such as PVDF-HFP and PEO, making polymer chains more disordered in the copolymer and facilitating the formation of a three-dimensional (3D) porous polymer network, as shown in Fig. 6a. The porous structure can help increase the electrolyte uptake in GPE, therefore enabling a high ionic conductivity of  $2.1 \text{ mS cm}^{-1}$  (Fig. 6b-d).<sup>76</sup> By adjusting the GO content, the electrolyte uptake of the polymer host PVDF-HFP could reach as high as 398%, enabling the highest ionic conductivity of  $2.221 \text{ mS cm}^{-1}$ .<sup>77</sup>



**Fig. 6** Main functions of GO nanosheets in polymer electrolytes. (a) Intermolecular hydrogen binding effect between GO, PVDF-HFP, and PEO in the polymer and the schematic of the interaction mechanisms, (b) SEM image of the 3D porous polymer network, (c) electrolyte uptake and (d) ion conductivity of the GPE. Reproduced from ref. 76 with permission from Wiley-VCH, copyright 2018. (e) Schematic of the Li-ion conduction mechanism with GO in a  $\text{LiClO}_4$ -PAN-based SPE. Reproduced from ref. 75 with permission from Elsevier, copyright 2017.



With a higher dielectric polymer matrix such as poly(vinylidene fluoride-tri-fluoroethylenechlorofluoroethylene) (PTC), only 0.95 wt% GO addition can assist to increase the liquid electrolyte uptake in the pores and endow the GPE with an ionic conductivity of  $2.28 \text{ mS cm}^{-1}$  and an  $\text{Li}^+$  transference number of 0.599.<sup>78</sup>

Furthermore, the addition of GO nanosheets can disrupt the ordered semi-crystalline PEO chains and reduce polymer crystallinity, facilitating Li salt dissociation and increasing ion conductivity in SPE.<sup>79-82</sup> The GO nanosheets in the polymer matrix can also increase the chain mobility.<sup>74</sup> For instance, in a “polymer-in-salt” system based on polyacrylonitrile (PAN), the strong Lewis acid and base interaction between oxygen-containing groups of GO and Li-ions could greatly weaken the interaction between Li-ions and N atoms of PAN, facilitating the free mobility of Li-ions.<sup>83</sup> In addition, Li-ion transport along the channels constructed by GO nanosheets is faster than the segmental movement of the host polymer, boosting the ionic conductivity of SPEs. Another similar work considered that the functional groups in GO could alleviate the polarity of “ $-\text{C}\equiv\text{N}:^-$ ” by interaction with the lone pair electrons so as to make the polymer “soft” and provide electrons to dissociate Li-ions in the  $\text{LiClO}_4$ , as shown in Fig. 6e, resulting in a higher Li-ion transfer rate.<sup>75</sup> Moreover, the chemical stability of GO can broaden the electrochemical window of the SPEs to as high as 5.0 V.<sup>83,84</sup>

Although GO has played an important role in modifying the polymer electrolytes with its special functions, some intrinsic inadequacies still need to be overcome, such as its inhomogeneous dispersion within the polymer matrix and the size effect on the tortuosity of the ion-transport path. To address the inherent issues of GO, graphene-derived carbon-based materials, such as chemically modified and structurally regulated

graphene or graphene oxide, have been used for the improvement of polymer electrolytes.

As a typical strategy of chemical modification, grafting or functionalization of GO has been adopted to improve the dispersion of the nanofiller in the polymer matrix and further increase the ionic conductivity.<sup>59,85</sup> Fluorinated graphene has been reported to have the ability to induce the grain refinement effect in a PVDF-HFP-based SPE.<sup>86</sup> Significant reduction of the grain size in polymer can enhance interfacial Li-ion transport and homogenize Li-ion flux, thereby improving Li-ion conductivity and promoting uniform Li plating/stripping. Sulfonated graphene oxide can be applied in a PVDF-based polymer electrolyte to improve both physical and electrochemical properties.<sup>87</sup> It can also be used to participate in a chemical lithiation with the Nafion membrane by an ion-exchange reaction in a  $\text{LiOH}$  solution, as shown in Fig. 7a.<sup>88</sup> Li-ions can form coordination bonds with sulfonic groups of Nafion and/or sulfonated graphene oxide and the carboxylic oxygen of the carbonate ester molecules, forming molecular complexes and physical cross-linking, which enable the Li-ions to move from one site to another through a conformational transformation assisted by the segmental motion of the polymer chains and the solvent molecules, as illustrated in Fig. 7b.

Structural regulation of carbon-based materials is another effective strategy for the enhancement of the polymer electrolytes. By annealing a mixture of GO with Mn species, followed by a diluted HCl purification process, a 3D holey graphene with abundant oxygen vacancies can be obtained and applied in the SPE by forming a cross-linked structure with PEO matrix.<sup>89</sup> The holey structure and the edges are more favorable for the formation of tightly cross-linked PEO chains perpendicular to the (002) plane of graphene, facilitating Li-ion diffusion in one

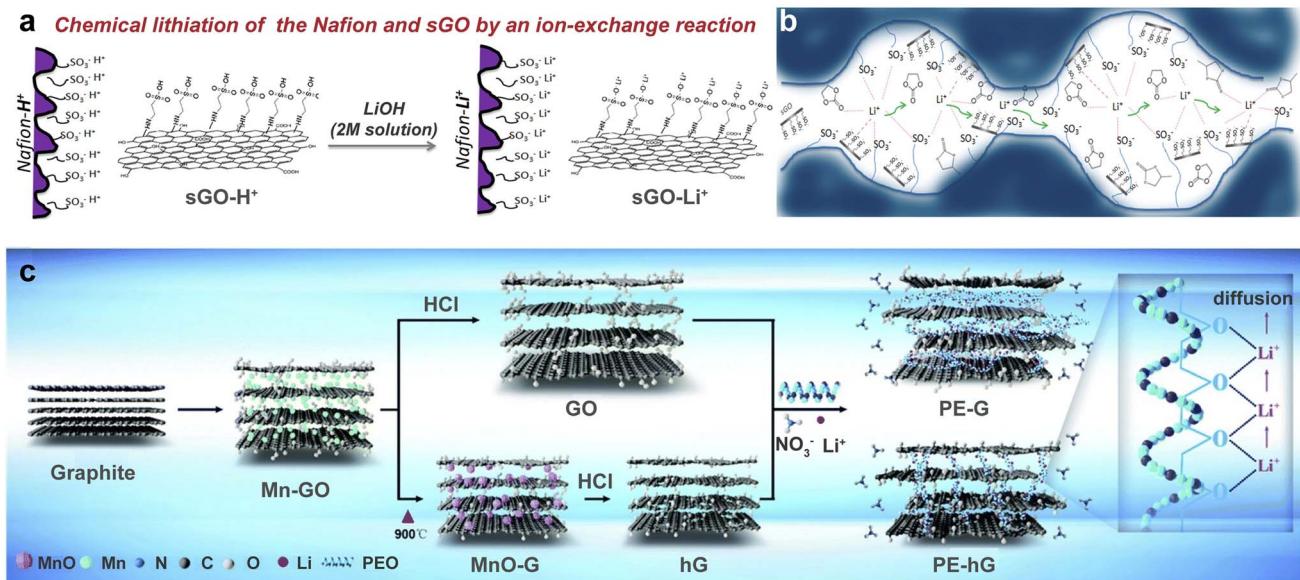


Fig. 7 Graphene-derived materials used in the polymer electrolytes. (a) Chemical lithiation of the Nafion membrane and sulfonated GO by an ion-exchange reaction. (b) Li-ion transport mechanism in the lithiated Nafion-sulfonated graphene oxide (sGO) films. Reproduced from ref. 88 with permission from the American Chemical Society, copyright 2019. (c) 3D holey graphene (hG) used in forming cross-linked PEO chains for faster Li-ions transport. Reproduced from ref. 89 with permission from the Royal Society of Chemistry, copyright 2022.



direction (Fig. 7c). Therefore, the obtained SPE displayed an improved ionic conductivity of  $2.1 \times 10^{-4} \text{ S cm}^{-1}$  at  $80^\circ\text{C}$ , and better electrochemical stability with a wider electrochemical window ( $>4.65 \text{ V}$ ) as well.

The size effect of carbon-based materials is another key factor for their uniform dispersion in the polymer. In addition, the mechanical strength and electrochemical performance of electrolytes increase with the decrease in the size of fillers.<sup>90</sup> Therefore, CQDs with smaller size and better dispersibility have been considered as promising nanofillers for the polymer electrolytes. Besides the good dispersibility, CQDs can improve the transport kinetics of the polymer electrolytes with their specific functionalities, such as impeding the anion migration and promoting the Li-ion transport.

Immobilizing the existing anions or impeding the anion migration in the polymer matrix is one of the main strategies to obtain more free Li-ions, enabling faster Li-ion transport. With a small size of 3–11 nm, the graphene oxide quantum dots can be well dispersed in a polymer framework comprising poly(acrylonitrile-*co*-vinylacetate) (PAV) and poly(methyl methacrylate) (PMMA).<sup>90</sup> As shown in Fig. 8a, the existence of ion–solvent clusters in the liquid electrolyte can impede ion transport both in the electrolyte bulk and at the electrode–electrolyte interface, while the graphene oxide quantum dot-decorated polymer chains are highly attractive to  $\text{PF}_6^-$ . Therefore, they can suppress the formation of ion–solvent clusters by immobilizing the anions, enabling a GPE with higher ionic conductivity and Li-ion transference number. Besides, increasing the volume of individual anions in the polymer matrix is effective. For instance, the large size of the CQD-based anions and hydrogen

bonding interaction with the PEO matrix can hinder the anion migration, granting the SPEs a higher Li-ion transference number of 0.94.<sup>91</sup>

The functionalization of the CQDs can further promote Li-ion transport by reducing the crystallinity of the polymer matrix. CQDs with abundant oxygen-containing functional groups dispersed in a PEO-based polymer electrolyte can effectively increase the dissociation of lithium and sodium salts, the adsorption of anions, and the reduction of the PEO's crystallinity, boosting the segmental motion and enabling faster  $\text{Li}^+/\text{Na}^+$  transport (Fig. 8b).<sup>92</sup> Molecular dynamics simulations have also proved the promoting effect of functional groups, such as hydroxy and carboxy from graphene quantum dots, on the ionic conductivity of PEO-based polymer electrolytes.<sup>93</sup> Furthermore, it has been found that the diverse elements on the carbon dots have different effects for the SPE. N and S exhibit capabilities in engaging in Li-ion transport and interface regulation, while F primarily contributes to the regulation of interface components.<sup>94</sup> The highly fluorinated carbon dots (HF-CDs) display good dispersibility with an adjustable diameter and their addition in PEO can significantly decrease migration energy barrier of the interaction between Li-ions and the functional groups, ensuring a continuous pathway for ion transport in the polymer electrolyte,<sup>95</sup> as shown in Fig. 8c.

In addition to the GO, graphene-derived materials and CQDs mentioned above, CNTs can act as effective fillers in the polymer electrolyte as well. For instance, in a PEO-based nanofiber electrolyte, the incorporation of CNTs even by a low ratio (0.35 wt%) can increase the ionic conductivity by 5 times.<sup>70</sup> However, the high intrinsic electronic conductivity of CNTs also

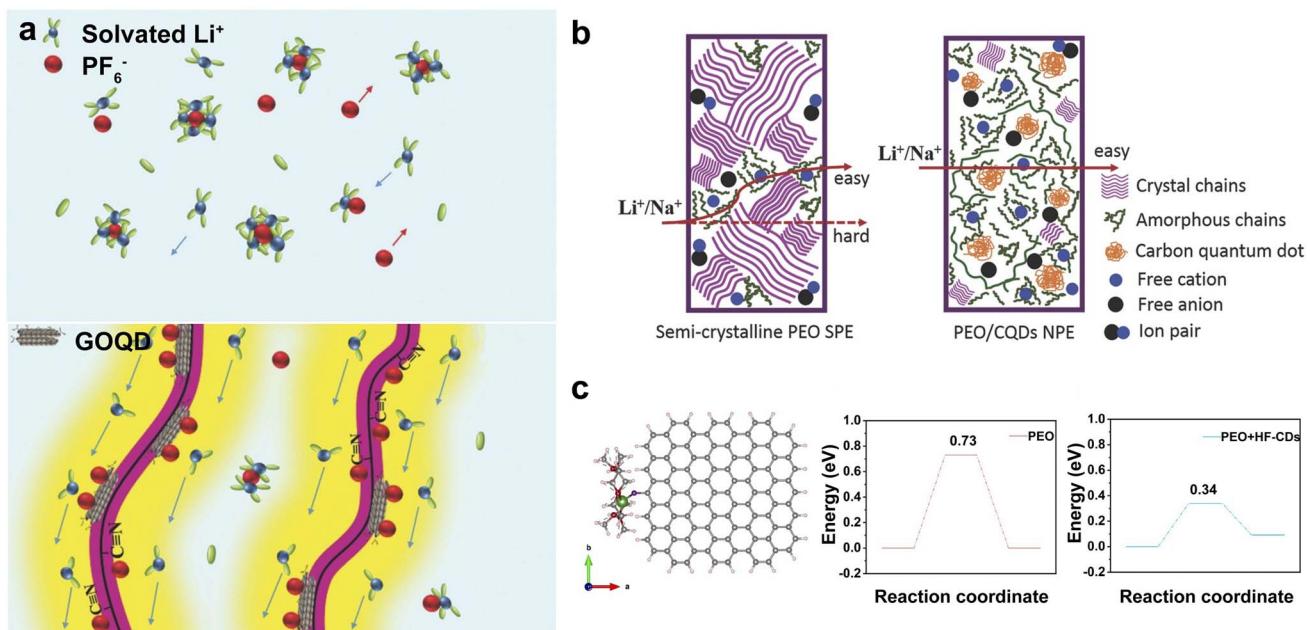


Fig. 8 Roles of carbon quantum dots in the improvement of polymer electrolytes. (a) Immobilizing effect of  $\text{PF}_6^-$  by the graphene oxide quantum dot (GOQD)-decorated polymer. Reproduced from ref. 90 with permission from Wiley-VCH, copyright 2018. (b) Schematic illustration showing the ion transport mechanism in a PEO-based SPE without and with CQDs. Reproduced from ref. 92 with permission from Wiley-VCH, copyright 2018. (c) Transition state of Li-ion migration barrier in PEO and PEO with the HF-CD electrolyte. Reproduced from ref. 95 with permission from the American Chemical Society, copyright 2023.



Table 1 Overview of the ionic conductivity and mechanical strength with various carbon-based materials as nanofillers in polymer electrolytes

Carbon-based materials	Polymer matrices	Nanofillers	Ionic conductivity (mS cm <sup>-1</sup> )	<i>t</i> <sub>Li<sup>+</sup></sub>	Testing temperature	Tensile strength (MPa)	Ref.
GO	PEO	1 wt% GO	0.02		RT	1.27	74
	PEO	1 wt% GO	0.0154	0.42	RT	1.31	84
	PAN	0.9 wt% GO	0.11	0.4	30 °C		83
	PAN	1 wt% GO	0.26	0.42	RT		75
	PEO <sup>a</sup>	0.21 wt% GO	0.057	0.47	RT	0.3 ± 0.06	70
	PVDF-HFP <sup>a</sup>	0.375 wt% GO	2.221		RT		77
	PVDF-HFP-PEO <sup>a</sup>	1 wt% GO	2.1		RT		76
	PTC/PEO <sup>a</sup>	0.95 wt% GO	2.28	0.599	RT		78
	PEGMA	0.2 wt% PEG-grafted GO	0.21		30 °C		85
	PVDF	0.004 wt% sGO	6.2	0.93	RT	1.4	87
Graphene-derived materials	Lithiated Nafion <sup>a</sup>	sGO	0.5	≈1	RT		88
	PVDF-HFP	5 wt% fluorinated graphene	0.132	0.47	30 °C	5.1	86
	PEO	1 wt% 3D holy graphene	0.21	0.87	80 °C		89
	PAV/PMMA <sup>a</sup>	0.2 wt% GOQDs	1.5	0.77	30 °C		90
	PEO	CQDs	0.14	0.48	RT	1.19	92
Carbon/graphene quantum dots	PEO	0.286 wt% PLLSCQDs	0.202	0.94	RT	5.1	91
	PEO	3 wt% GQDs	0.016	0.32	RT		93
	PEO	3 wt% NSFCDs	0.064	0.58	30 °C		94
	PEO	5 wt% FCDs	0.075	0.48	RT	3.53	95
	CNTs	PEO	0.35 wt% CNTs	0.048	0.51	RT	0.43 ± 0.10

<sup>a</sup> GPE containing liquid plasticizers or SPE with a little liquid electrolyte during cell assembling. PEGMA: poly(ethylene glycol)methyl ether methacrylate; PEG: poly(ethylene glycol); PLLSCQDs: lithium 4-styrene sulfonate-based carbon quantum dots; GQDs: graphene quantum dots, NSFCDs: carbon dots with N, S and F elements; FCDs: fluorinated carbon dots.

presents a significant challenge in SSEs, as excessive incorporation may induce internal short-circuiting through the continuous conductive pathways. This inherent safety concern associated with CNT-based electrolytes has consequently limited its application in SSEs. Therefore, the use of CNTs in SSEs should be carefully designed, such as being packaged within insulating materials,<sup>79</sup> or keeping the adding amount below the percolation threshold, to prevent short-circuiting while retaining their improved performance.

To address the major challenges of insufficient ionic conductivity at room temperature for the polymer electrolytes, carbon-based materials with various structures and functional groups have played important roles. The improvement of the ionic conductivity and tensile strength in polymer electrolytes by various carbon-based materials is summarized in Table 1. By rationally controlling the type and number of the functional groups or doped elements, customized carbon-based nanofillers with superior dispersibility and functionalities would be achieved according to the demand.

### 3.2 Reinforcement of mechanical strength

SSEs with sufficient mechanical strength can ensure the SSLBs with good electrochemical performance and high safety. However, it remains a challenge to develop mechanically robust SSEs, as the polymer electrolytes are usually soft and not mechanically strong enough to suppress lithium dendrites, while the inorganic electrolytes are usually very brittle, particularly when their thickness is reduced aiming for high energy density.<sup>90</sup> With high mechanical strength, adjustable structures and lightweight, carbon-based materials have demonstrated

their unique advantages as fillers in SSEs. In addition to accelerating the Li-ion transport, they can simultaneously function as a nanoscale reinforcer to increase the mechanical strength of both polymer and inorganic electrolytes.

Mechanical reinforcement of polymer electrolytes is essential for their practical application. Aiming for this, strategies generally contain copolymerization and functionalization of polymer matrices, and incorporation of inorganic nanoparticles as fillers. As mentioned in Section 3.1, carbon-based materials, such as GO, graphene-derived materials and CQDs have abundant functional groups, which can complex with Li salts, while forming a tight cross-linking with polymer matrices. The strong interaction between the carbon-based materials and the polymer as well as the Li-ions and anions can endow the polymer electrolyte with a significantly enhanced mechanical property.<sup>74,75,89</sup> For instance, with only 1.0 wt% GO incorporating in the PAN-based SPE, the tensile modulus can be increased from 37 MPa of the bare SPE to 80 MPa.<sup>75</sup> A 260% increase in the tensile strength can be obtained with 1.0 wt% GO in the PEO-based SPE.<sup>74</sup> Moreover, 1 wt% 3D holy graphene could form a cross-linking structure with PEO, endowing the electrolyte film with a superior Young's modulus up to 12.9 MPa, which is more than 7 times that of cross-linked PEO (~1.8 MPa).<sup>89</sup> A unique grain refinement effect of fluorinated graphene has been observed in a PVDF-HFP-based SPE,<sup>86</sup> as shown in Fig. 9a-d. The reduction in particle size can induce the fine grain strengthening effect, greatly improving the mechanical properties of the electrolyte without excessively increasing the thickness of the polymer electrolyte.

The improvement of fracture toughness in inorganic electrolytes is critical for preventing lithium dendrite penetration.



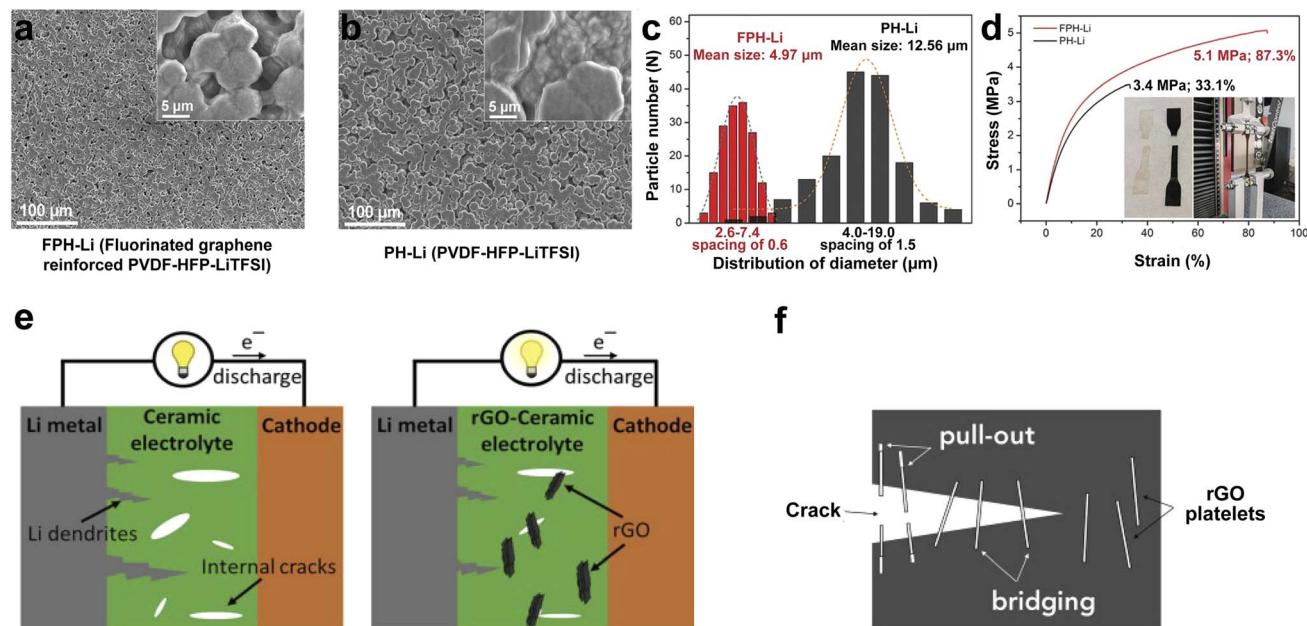


Fig. 9 Mechanical reinforcement effect of carbon-based materials on the SSEs. (a–d) Grain refinement effect of fluorinated graphene in polymer electrolytes. (a and b) Particle size with and without fluorinated graphene in the SPE. (c) Size distribution and (d) stress–strain curves of the two SPEs. Reproduced from ref. 86 with permission from Wiley–VCH, copyright 2022. (e) Schematics of SSLBs using ceramic electrolytes without and with rGO. Reproduced from ref. 98 with permission from Elsevier, copyright 2020. (f) Schematic of the reinforcement effect of fracture toughness by rGO. Reproduced from ref. 97 with permission from Elsevier, copyright 2020.

However, the reinforcement of fracture toughness is often with the compromises of ionic conductivity, as the fracture toughness increases with the decrease in relative density, while the ionic conductivity decreases. To balance the ionic conductivity and fracture toughness, rGO with good mechanical strength can be used as an additive incorporating in the  $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  (LATP) ceramic electrolyte, leading to 120% improvements in fracture toughness without compromising the ionic conductivity of electrolytes.<sup>97,98</sup> The increased fracture toughness in the composites is believed to be primarily caused by crack deflection, followed by bridging and pull-out of the rGO platelets, as shown in Fig. 9e and f. Moreover, by adding a small amount of rGO, such as 1 vol%, the electronic conductivity was still lower than the ionic conductivity, while increasing the rGO to 5 vol% would lead to an undesirable electronic percolation. Therefore, when incorporating carbon-based materials as reinforcers in SSEs, the precise regulation of their adding content emerges as a critical consideration, necessitating optimization below percolation thresholds to balance the mechanical properties with ionic transport characteristics.

### 3.3 Surface modification in the inorganic electrolytes

Although some inorganic electrolytes process a comparable ionic conductivity to liquid electrolytes, they usually suffer from intrinsic brittleness, limited contact area, and incompatibility against Li anode, leading to a large interfacial resistance and poor cycling performance. Therefore, surface modification of the inorganic electrolytes for improving the interfacial contact and decreasing the interfacial impedance is necessary. In order to increase the compatibility between inorganic electrolytes and

Li metal, many inorganic materials such as  $\text{Al}_2\text{O}_3$ ,<sup>99</sup>  $\text{ZnO}$ <sup>100</sup> and amorphous  $\text{Si}$ <sup>101</sup> have been used as coating layers by atomic layer deposition or plasma-enhanced chemical vapor deposition. However, these materials are all rigid with poor ductility and compressibility, and these methods are somewhat complicated and costly. Moreover, it is found that soft substrates could release the compressive stress during lithium deposition and impede the lithium dendrite growth.<sup>102</sup> Therefore, carbon-based materials with good flexibility, low cost, as well as structural and chemical adjustability are more suitable to act as soft coating layers of inorganic electrolytes to improve their interfacial compatibility with Li anode.

With good ductility and compressibility, graphite can be used as a soft interfacial layer to provide a close connection at the interface. By drawing the surface of garnet-type ceramic electrolyte with a pencil, a graphite-based soft interlayer between the garnet solid electrolyte and Li metal has been achieved to enhance the interfacial wettability and interfacial contact, decreasing interfacial impedance,<sup>103</sup> as shown in Fig. 10a. Besides, the graphite-based interface layer could be lithiated to form  $\text{LiC}_6$ , forming a lithiated graphite layer spontaneously at room temperature. This lithiated graphite layer enables the diffusion of both Li-ions and electrons, ensuring the uniform distribution of Li-ions in the interfacial layer. Moreover, the soft interfacial layer due to the good ductility and flexibility of graphite endowed the garnet electrolyte with excellent interfacial stability, enabling a good electrochemical cycling performance of SSLB. Besides graphite, hard carbon is a promising candidate for serving as the functional interfacial layer. For instance, a porous hard carbon interfacial layer has



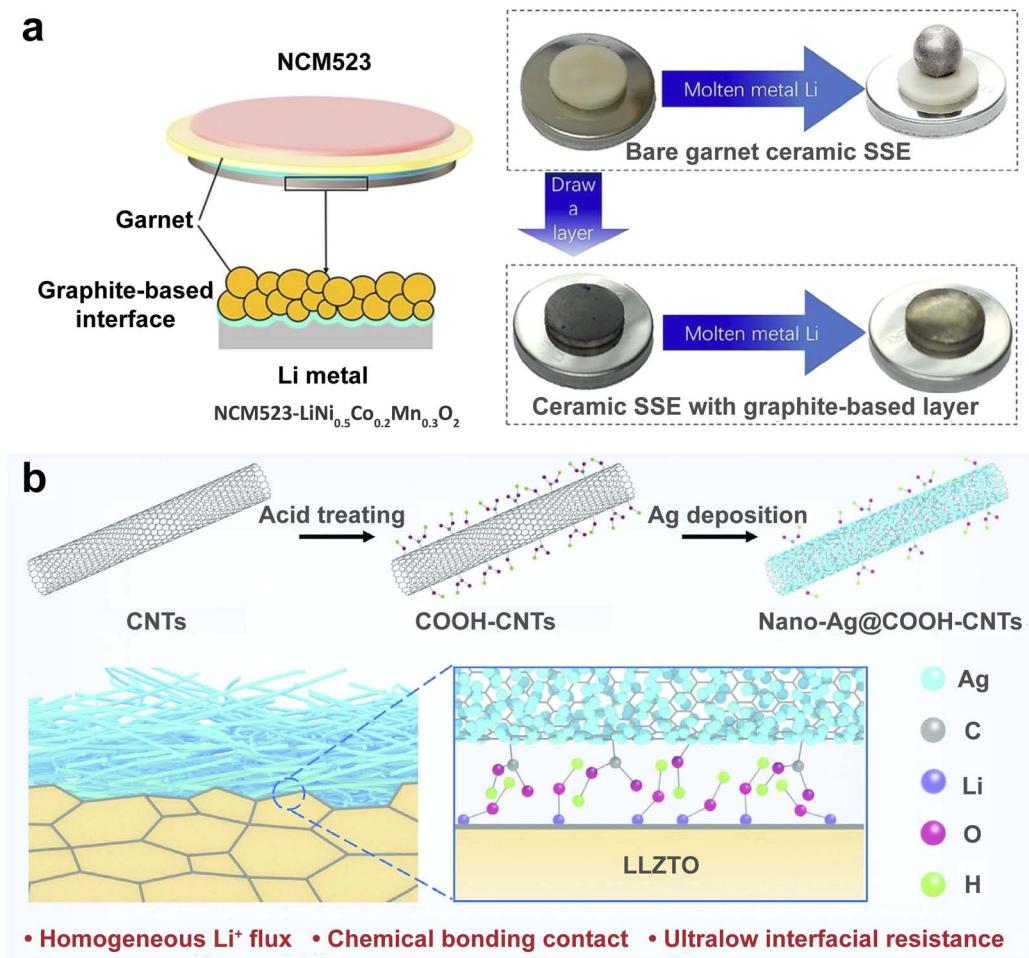


Fig. 10 Surface modification of inorganic electrolytes by carbon-based materials. (a) Schematic of the improved interfacial wettability of garnet electrolytes by physical contact with a graphite-based soft interface. Reproduced from ref. 103 with permission from the American Chemical Society, copyright 2018. (b) Schematic of the enhanced interfacial compatibility of LLZTO by chemical bonding contact with the Ag nanoparticle-decorated acid-oxidized CNTs. Reproduced from ref. 106 with permission from Wiley-VCH, copyright 2024.

been introduced on the garnet-type  $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$  (LLZTO) surface.<sup>104</sup> With the hierarchical pore structure, the hard carbon interlayer can provide capillary force and large specific surface area, assisting to promote the molten Li infiltration with garnet electrolyte, increase the contact area and decrease the local current density. Meanwhile, hard carbon is also conducive to the transport and diffusion of Li-ions, which can improve the rate performance at a large current density. In addition to improving the wettability and reducing the interface resistance of Li/LLZTO, low graphitized carbon with amorphous structure as the interfacial layer has also promoted air stability of LLZTO.<sup>105</sup>

Besides the above-mentioned good physical contact, carbon-based materials with chemical adjustability can form a chemical bonding contact with SSEs. For instance, ultrafine Ag nanoparticles grown on acid-oxidized CNTs have been used as a silver/carbon interlayer.<sup>106</sup> The Ag-decorated COOH-CNTs can bond with LLZTO *via* reactions with the alkaline surface of LLZTO, converting the initially loose physical solid-solid contact into an intimate chemical bonding contact, as shown in

Fig. 10b. This chemical bonding contact can enhance Li-ion transport at the LLZTO/Li interface while inhibiting the formation of Li dendrites.

Apart from improving interfacial contact, carbon-based materials can be used to form a protective layer for the inorganic electrolyte against the side reaction with the Li anode at the interface. For instance, GO can act as a coating layer on the surface of  $\text{Li}_7\text{P}_3\text{S}_{11}$  (LPS) particles to partially isolate the LPS from Li metal, mitigating the interfacial reaction between them and effectively enhancing the interfacial stability.<sup>107</sup> However, as the GO can be reduced to rGO by Li, the GO content in the solid electrolyte should be limited to a low range, such as no more than 1 wt%, to prevent the formation of conductive percolation pathways throughout the electrolyte. In fact, to prevent interfacial side reactions between solid electrolytes and the Li anode, carbon-based materials act more from the Li anode side than the SSE side. The applications of carbon-based materials for the regulation of Li anode can be discussed in detail in the next chapter.



In summary, due to their diverse structures, abundant functional groups and superior mechanical properties, carbon-based materials have exhibited multi-functional characteristics in SSEs, including the acceleration of Li-ion transport in polymer electrolytes, surface modification of inorganic electrolytes, and reinforcement of mechanical strength for both polymer and inorganic electrolytes. These characteristics endow the carbon-based materials with tremendous potential for the more effective solid-state electrolytes.

## 4. Carbon-based materials for dendrite-free Li anodes

Dendrite growth on Li metal during the charge-discharge process is one of the greatest challenges for the batteries with Li metal anodes, which can lead to poor cycling stability and safety hazards.<sup>8</sup> Even for the SSLBs, it is still a long-standing problem that dendrite can penetrate the SSE and cause short-circuiting.<sup>11</sup> To address this issue, many efforts have been made to mitigate or block the nucleation and growth of Li dendrites, including enhancing the mechanical strength of the SSEs, constructing a stable interlayer or interphase between the Li anode and SSEs, and inducing uniform Li deposition by functionalized surface or the particular 3D structure of the Li host. As most carbon-based materials possess high chemical and thermal stability and sufficient mechanical strength, they can be used to produce state-of-the-art structures with variable physical and chemical properties. This chapter reviews the main functions of carbon-based materials on the improvement of Li anode, focusing on their roles as (1) interfacial layer for suppressing dendrite growth, (2) host for Li metal, and (3) artificial interlayers for anode-free Li deposition, as illustrated in Fig. 11.

### 4.1 Interfacial layer

Different from liquid electrolytes, SSEs usually have insufficient solid-solid interfacial contact with the Li anode, which causes

large resistance and hinders Li-ion diffusion, leading to the uneven surface of the Li anode after the continued stripping, the dendrite growth and subsequent cell failure. Therefore, stabilizing the interface between Li metal and the solid electrolyte is crucial for improving both the cycling performance and safety of SSLBs. The ideal interfacial layer for the Li metal anode should be chemically stable even at a high potential and/or temperature, mechanically robust against the penetration of Li dendrites and sufficiently flexible to accommodate the volumetric expansion of Li deposition. As many carbon-based materials, such as graphene and CNTs, almost have all the prerequisites needed for constructing a good interfacial layer, they have shown great promise for achieving a dendrite-free Li anode of SSLBs.

As the amorphous carbon is chemically stable with Li metal and has a high enough Young's modulus to suppress the Li dendrite growth, a monolayer of flexible, interconnected and amorphous hollow carbon nanosphere coating was designed to help isolate the Li metal deposition and facilitate the formation of a stable solid electrolyte interphase,<sup>108</sup> as shown in Fig. 12a. Meanwhile, the hollow carbon nanospheres can act as an adjustable interfacial layer to provide a good connection between Li and SSE during cycling, thereby ensuring the efficient ion-transport. These unique characteristics endowed the battery with a highly stable cycling coulombic efficiency of ~99% for more than 150 cycles without nucleation of lithium dendrites.

Graphene with flexibility, light weight and excellent conductivity is another promising material for constructing the interfacial layer of the Li anode. Utilizing the reactivity of GO with Li metal, a spontaneously reduced graphene coating on the surface of Li metal can be formed by dipping or spray-painting with a homogeneous GO solution, as illustrated in Fig. 12b.<sup>109</sup> The existence of spontaneously reduced graphene coating functioned as a protection layer to suppress dendrite growth and offered a stable solid electrolyte interface (SEI) layer to

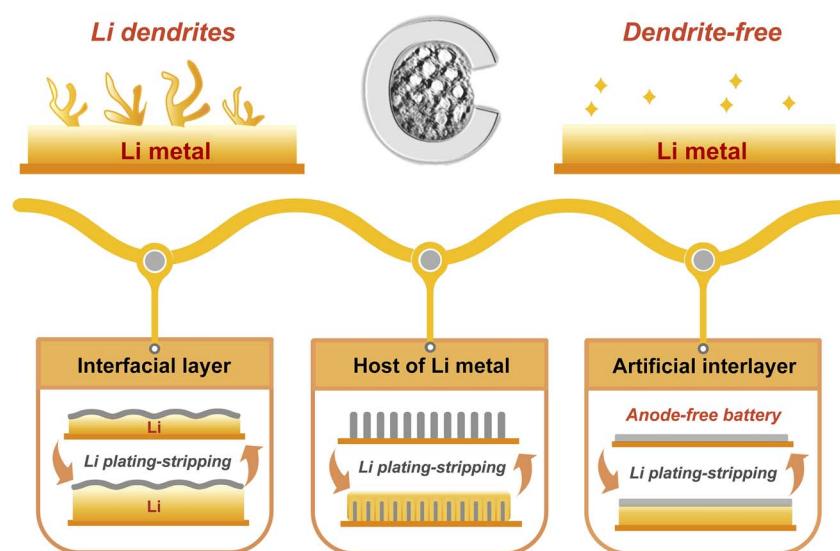


Fig. 11 Carbon-based materials for the dendrite-free Li anode of SSLBs.



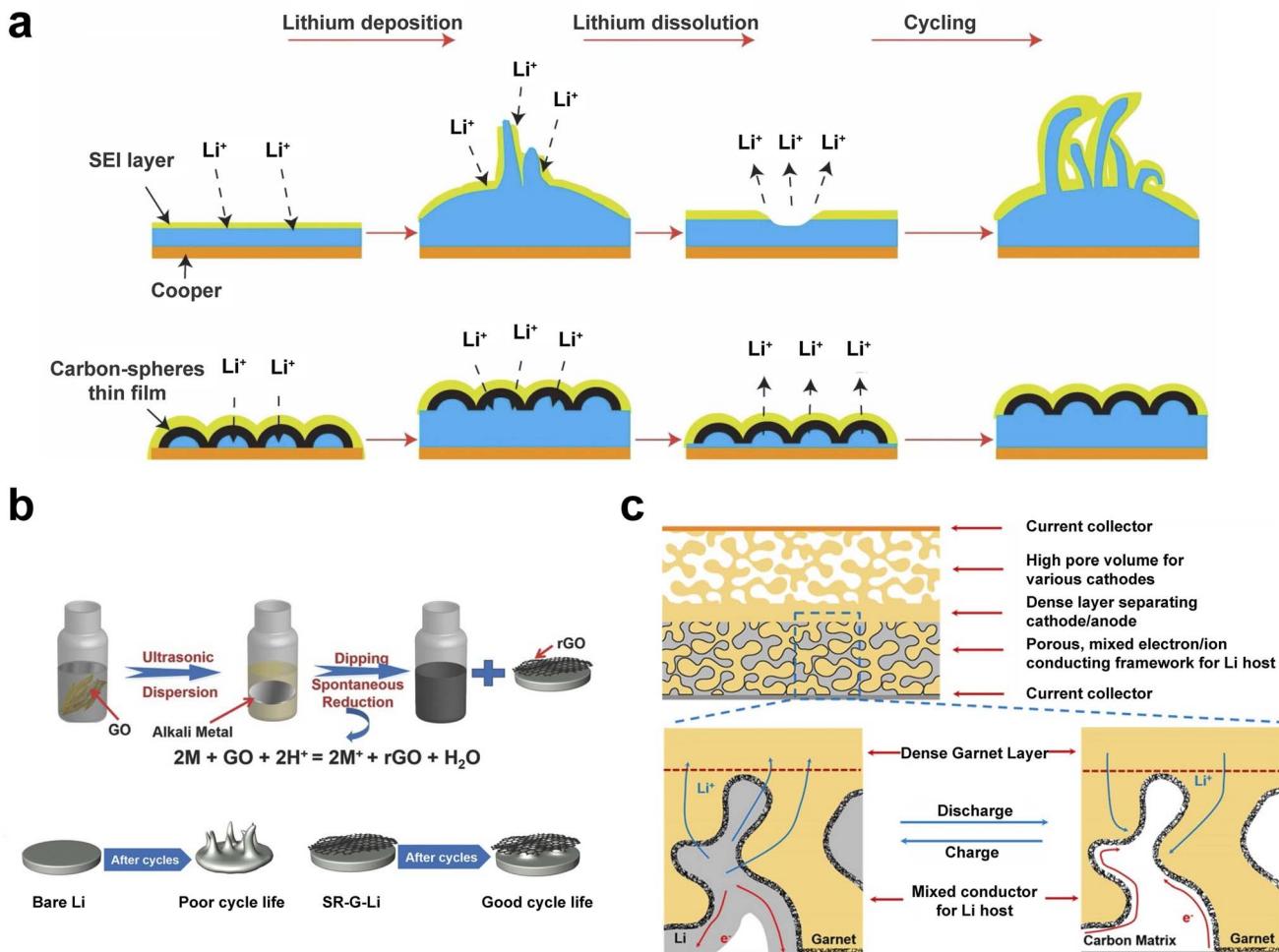


Fig. 12 Carbon-based materials acted as the interfacial layer of the Li anode. (a) Schematics of the Li anode structure without and with the carbon-sphere thin film. Reproduced from ref. 108 with permission from Springer Nature, copyright 2014. (b) Schematics of the fabrication of the spontaneously reduced graphene coating on the surface of the Li metal (SR-G-Li) anode and the Li plating behavior of the bare Li and SR-G-Li anodes. Reproduced from ref. 109 with permission from Wiley-VCH, copyright 2018. (c) Schematic of the working principle of the 3D Li metal anode based on a 3D mixed electron/ion conducting framework. Reproduced from ref. 111 with permission from the American Chemical Society, copyright 2018.

avoid the increase in internal resistance, therefore achieving an ultralong cycle life of 1000 cycles at a practical current density of  $5 \text{ mA cm}^{-2}$  without short-circuiting. Though the tests in this work were taken with a liquid electrolyte, the method with rGO coating layer for dendrite-free Li anode can also be extended to the batteries with SSEs.<sup>110</sup>

With similar characteristics of graphene, CNTs can be also used to form a good interfacial layer between the Li metal and solid electrolyte. Through conformally coating on a porous garnet electrolyte, the CNTs can assist in creating a composite with mixed electron/ion conductivity as a 3D host for the Li metal.<sup>111</sup> In this 3D mixed electron/ion conducting framework, the continuous CNT coating and its seamless contact with the garnet could enable highly uniform Li deposition in the porous garnet structure, as shown in Fig. 12c. Besides working as an independent interlayer, CNTs can be used to construct a composite interlayer to tune the Li deposition. For instance, by combining with a solid electrolyte  $\text{Li}_7\text{N}_2\text{I}$  to form a porous

lithiophobic interlayer, CNTs can help to achieve a balanced ionic and electronic conductivity and induce Li depositing at the specific location for Li dendrite suppression in SSLBs.<sup>112</sup> The as-formed  $\text{LiC}_6$  interfacial layers due to the intercalation reaction between carbon and Li is beneficial to the wettability of Li,<sup>113</sup> as well as the ion diffusion, making the carbon-based materials much more suitable as the multi-functional interfacial layer of the Li anode.

#### 4.2 Host of Li metal

With various structures from 0D to 3D, variable surface chemical properties, high active surface area and more Li metal nucleation sites, carbon-based materials have played significant roles in the improvement of electrochemical performance for the batteries with the Li anode. A variety of carbon-based materials can be used as the host of Li metal to reduce or inhibit dendrite growth in the batteries with a liquid



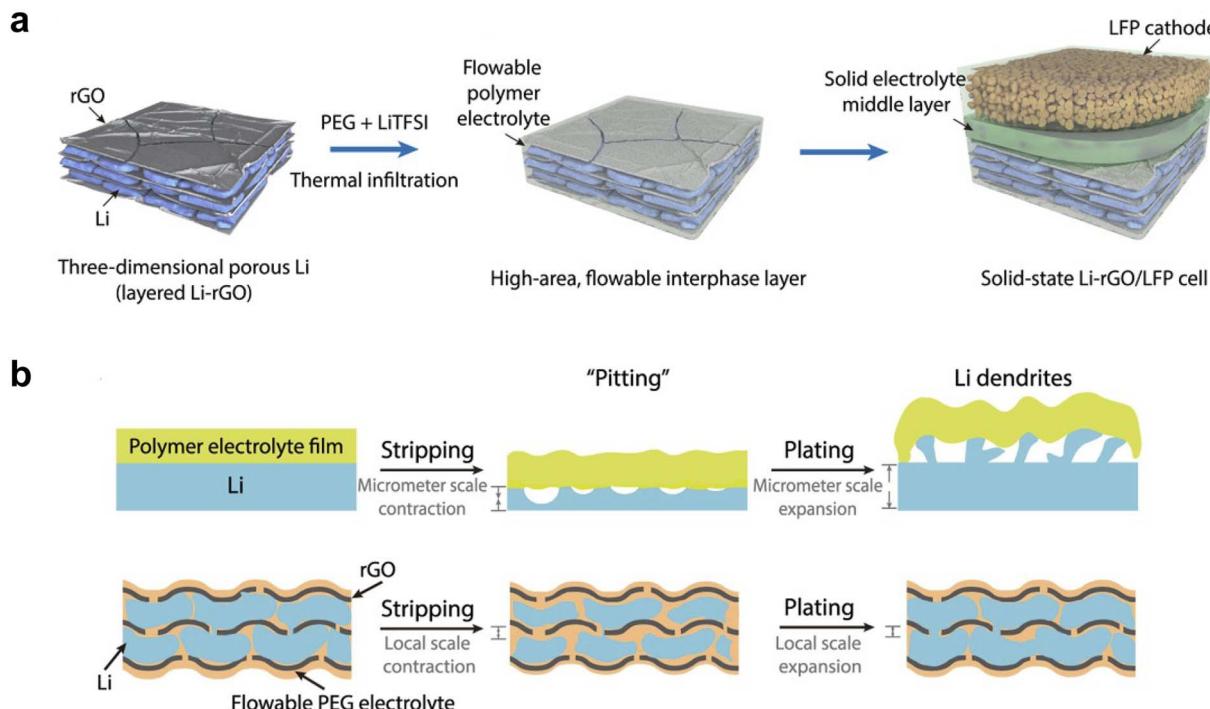


Fig. 13 Lithiophilic rGO as a stable scaffold for the Li anode in SSLBs. (a) Schematics of the fabrication process of the 3D Li anode with flowable interphase and (b) the stripping/plating process of Li foil and the 3D Li-rGO anode in SSLBs. Reproduced from ref. 128 with permission from the American Association for the Advancement of Science, copyright 2017.

electrolyte.<sup>114</sup> These carbon-based materials include CNTs,<sup>115–118</sup> graphene,<sup>119–121</sup> carbon fibers,<sup>113,122</sup> nanodiamond,<sup>123</sup> graphitized carbon,<sup>124</sup> and atom-doped carbon materials,<sup>125</sup> which would play a more important role in SSLBs. In fact, carbon-based materials characterized by good flexibility and high surface area are more suitable for the Li anode in SSLBs to address the elevated interface resistance caused by the poor solid–solid interfacial contact. This section reviews the distinctive design strategies of carbon-based materials as the host of Li anode, particularly focusing on the specific applications in SSLBs.

Though limited in ionic conductivity, most carbon materials readily intercalate Li-ion. The resulting product  $\text{LiC}_6$  is thermodynamically stable against Li metal and exhibits both electronic and ionic conductivity. Crucially, this lithiophilic compound also facilitates uniform Li deposition. For instance, within a 3D composite framework of graphite and  $\text{Li}_3\text{PS}_4$  solid-state electrolyte, lithiated graphite channels Li plating into the porous host matrix – away from the electrolyte/anode interface, which suppresses the Li dendrite formation while enhancing the cycle life.<sup>126</sup> Therefore, the lithiophilicity of carbon-based materials proves critical for the effective 3D Li host design. With the unique high lithiophilicity and large surface area, rGO can act as a supporting film in forming a layered Li-rGO electrode with molten Li infusion into its uniform nanogaps.<sup>127</sup> This layered rGO can offer a stable scaffold for Li stripping/plating, which significantly mitigates the volume change at the electrode level during cycling, while the top rGO cap layer provides an electrochemically and mechanically stable artificial

interface. Moreover, by a thermal infiltration, poly(ethylene glycol) plasticized by LiTFSI can be impregnated into this Li-rGO to construct a flowable interphase for SSLBs,<sup>128</sup> as shown in Fig. 13a. The incorporation of the flowable polymer electrolyte interphase can accommodate the interfacial fluctuation during cycling to maintain a more intimate contact, ensuring a significantly reduced overpotential and greatly improved cycling stability (Fig. 13b). Furthermore, the rGO scaffold can support additional lithiophilic sites embedded in it to further enhance the electrochemical performance of SSLB. For instance, it is found that by incorporating AlN nanoparticles into the rGO scaffold, the generated  $\text{Li}_3\text{N}$  and Li-Al alloy after the reaction between AlN and Li can effectively mitigate the dendrite growth and immensely improve the cycling stability.<sup>129</sup> Similarly, with good lithiophilicity, Ag nanoparticles uniformly dispersed in the rGO can induce Li to fill the carbon host, enabling reversible Li cycling at low stack pressure.<sup>130</sup>

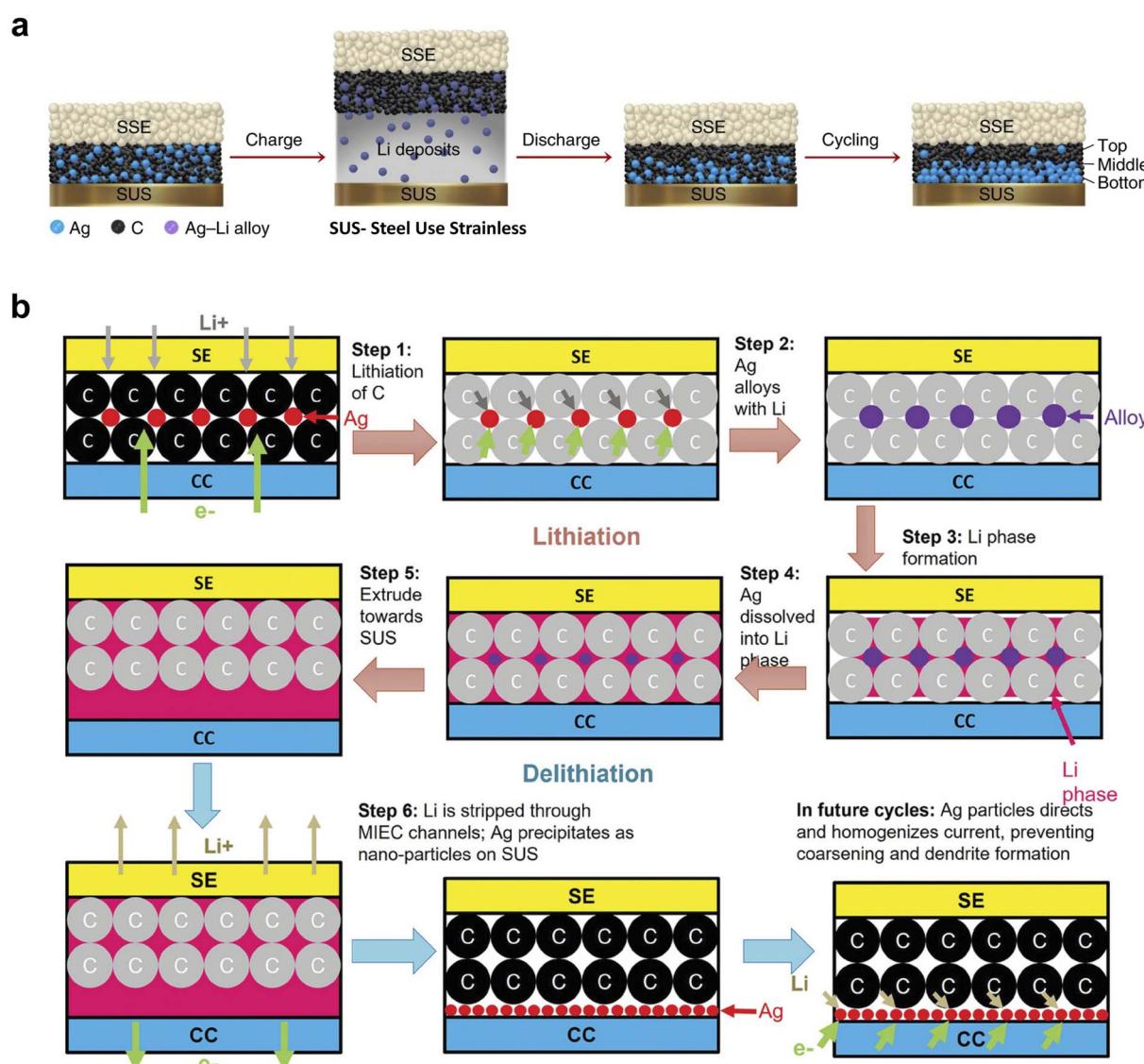
The structural defects within the graphene lattice could decrease the energy barrier of Li nucleation according to the density functional theory calculations. Therefore, a vertical graphene with abundant oxygen defects on a 3D commercial copper mesh was constructed by a chemical vapor deposition process.<sup>121</sup> As the stable nucleation sites, oxygen defects are lithiophilic and can guide uniform Li growth at the initial plating stage. Owing to the modification of early Li plating behavior by a 3D lithiophilic graphene matrix, the vertical graphene on copper mesh as a novel 3D hybrid anode presented a lower polarization and enhanced cycling stability in the batteries with both liquid electrolytes and SSEs.



For carbon-based materials, lithiophilicity and/or structural defects can be easily obtained through functionalization, etching or heteroatom doping to induce uniform Li nucleation. As discussed in Section 4.1, most carbon-based materials become compatible with Li after lithiation due to their ability for Li intercalation. For instance, though without lithiophilicity, CNTs can still function as hosts for Li, because they can accommodate intercalated Li. When lithiated, they can act as mixed electron/ion conductors and form a stable interface with Li. The CNT framework can also help to maintain effective contact with SSEs during stripping and increase the Li-ion diffusion coefficient in the SSLBs.<sup>131</sup>

### 4.3 Artificial interlayer for anode-free Li batteries

Owing to the superior energy density, anode-free SSLBs are considered as one of the most promising technologies for Li-based batteries. However, the absence of initial Li metal usually leads to inefficiency of Li plating and stripping and rapid capacity degradation.<sup>132</sup> As the anode-free Li batteries largely rely on high coulombic efficiency during cycling, a continuous and stable interface between solid electrolyte and the current collector substrate is crucial for uniform and highly reversible deposition of Li metal. An ideal interface of the anode-free Li battery can reduce the local current density, enhance the adhesion of Li plating layer to the current collector substrate, produce a smooth SEI with uniform Li-ion flux, and inhibit the side reaction between Li and the electrolyte.<sup>133</sup>



**Fig. 14** Ag–C composite interlayer to effectively regulate Li deposition in a Li metal-free anode. (a) Schematic of Li plating–stripping on the current collector with an Ag–C layer. Reproduced from ref. 136 with permission from Springer Nature, copyright 2020. (b) Microscopic lithiation–delithiation mechanism of the Ag–C interlayer during the first few cycles. Reproduced from ref. 137 with permission from Wiley–VCH, copyright 2024.



Similar to the interfacial layer of Li anode mentioned in Section 4.1, carbon-based materials can be used to form artificial interlayers on the current collector substrate to modulate the Li plating behavior as well. Carbon-based materials, such as graphene and amorphous carbon, have been considered as excellent choice to modify the metal substrate. For instance, an ultrathin multilayer graphene can be coated on Cu by chemical vapor deposition as an artificial layer between the deposited Li and Cu substrate.<sup>134</sup> Such lightweight multilayer graphene coating can enhance the contact between Li and Cu, reinforce the SEI film formed upon Li deposition, and prevent the Li dendrite penetration, resulting in a stable electrode interface and uniform Li-ion flux. Nucleation and early growth of Li metal is critical to the performance of anode-free Li batteries. An amorphous carbon film deposited by direct current magnetron sputtering can be prepared as an interlayer between the Cu and the LiPON solid electrolyte. The amorphous carbon films could promote homogeneous Li plating without dendrite formation at the current collector/solid electrolyte interface by acting as an initial nucleation seed layer.<sup>135</sup>

Carbon-based materials can also form an artificial interlayer with other materials to synergistically enhance the reversibility of Li plating and stripping. A thin Ag–C interlayer has been designed to effectively regulate Li deposition in a Li metal-free anode, leading to a long cycling performance.<sup>136</sup> In this structure, as shown in Fig. 14a, as the lithiophilic Ag can reduce the Li nucleation energy, it assists the uniform deposition of Li on the current collector, while the lithiophobic carbon black mainly acts as a separator to keep the SSE layer away from Li metal. During the lithiation process, Ag–Li alloy first forms in the Ag–C layer, and then part of the Ag moves to the current collector and forms a solid solution with Li metal, thus facilitating a uniform Li plating. In the subsequent delithiation process, the Li metal layer completely disappears, the Ag dissolved in the Li layer does not return to the Ag–C interlayer but remains between the current collector and the Ag–C interlayer. The microscopic mechanism of the Ag–C interlayer has been further explained by using first-principles atomistic and continuum modeling,<sup>137</sup> as shown in Fig. 14b. It is reported that the amorphous carbon within the Ag–C interlayer was lithiated before Ag and rapidly saturated with Li to form LiC<sub>6</sub> at the beginning of lithiation, subsequently functioning as a mixed ionic–electronic conductor. After the processes of alloying with Li, dissolving, and flowing toward the current collector, the Ag nanoparticles finally formed uniformly distributed precipitation on the current collector, helping guide Li-ion away from surface tips and suppressing dendrite growth in subsequent cycles.

In summary, carbon-based materials with various characteristics have shown great potential in the application of SSLBs with dendrite-free Li anode. First, with intrinsic Li-insertion ability and superior electronic conductivity, they can easily form a mixed ionic–electronic conductive interfacial layer, enhancing the ion-diffusion in the interface between the SSE and the Li anode, as well as reducing the interfacial resistance. Besides, their good flexibility and mechanical properties endow the interfacial layer strong enough to protect against dendrite

penetration and relieve volume changes. Second, with controllable structures and adjustable surface chemistry, they can serve as the host of Li metal for a much efficient deposition, enabling a reduced overpotential and greatly improved cycling stability. Third, some carbon-based materials with good chemical stability, lightweight and special lithiophobic properties can also act as artificial interlayers to assist in regulating the Li-ion deposition pathway, as well as keeping the SSE layer away from Li metal to prevent side reactions.

## 5. Summary and perspectives

### 5.1 Summary

Carbon-based materials with superior electronic conductivity, light weight, diverse structures, and adjustable surface chemistry have already been widely used for many kinds of energy storage systems over the past decades. Their critical roles are also increasingly concerned and show significant potential in the development of SSLBs. In this review, we summarize the state-of-the-art applications of carbon-based materials in SSLBs, covering their special applications for more stable cathodes, more effective SSEs and dendrite-free Li anodes. The primary mechanisms for their functions of resolving interfacial issues, constructing high-performance SSEs, and developing dendrite-free Li anodes to address the current challenges in SSLBs are further discussed and systematically elucidated as follows.

(1) Improving the interfacial properties. With good flexibility and mechanical strength, carbon-based materials can properly mitigate the mechanical stress and volume expansion derived from the charging and discharging process, reducing the resulting interfacial resistance of both the cathode/SSE and SSE/Li. Meanwhile, the intrinsic Li intercalation ability and the excellent electronic conductivity enable them to serve as a special ion/electron mix conductor, effectively facilitating the interfacial ionic and electronic transport. In addition, due to their stable chemical properties, carbon-based materials can also act as a protective layer to prevent interfacial side reactions.

(2) Promoting the ion transport kinetics of SSE. With large surface area, carbon-based materials can be functionalized with different heteroatoms or functional groups, which endow them with various surface chemistry, benefiting for the cross-linking with polymer electrolytes to reduce crystallinity, enhance segment motion and promote the dissolution of Li salts. Moreover, the functionalized carbon-based materials can also enhance the interfacial ion transport of both inorganic and polymer electrolytes with the cathode by an intimate chemical bonding contact.

(3) Inhibiting dendrite growth of the Li anode. With controllable structures and surface chemistry, carbon-based materials can serve as host and/or initial nucleation seed layer of Li metal and assist to regulate the Li-ion deposition pathway for a more uniform Li deposition, enabling a reduced dendrite growth and greatly improved cycling stability. Besides, they can act as a protective interlayer between the SSE and Li metal to prevent undesirable interfacial reactions and assist to protect against the penetration of Li dendrites with their good



mechanical strength, providing a strong safeguard to the Li anode.

## 5.2 Perspectives

As carbon-based materials have already been extensively utilized as conductive additives or composite matrices in conventional lithium-ion battery cathodes, the well-established technologies could be progressively transitioned to the cathodes of solid-state battery to enhance both electronic conductivity and interfacial contact. This requires no subversion to existing manufacturing processes, ensuring technological continuity with only formulation optimization. Therefore, carbon-based materials possess the highest near-term commercialization viability for the cathodes in SSLBs. However, to fully unlock the capabilities of carbon-based materials, the following issues still need further consideration to achieve their maximum utilities in the application of SSLBs.

**5.2.1 Reasonable modification of carbon-based materials for special functionality.** In order to achieve special functionality, modification of carbon-based materials is essential for their application in SSLBs. With different modification, carbon-based materials can be precisely regulated to apply to various specific situations. Therefore, carbon-based materials should be reasonably modified according to the specific requirement. For instance, doping with N or S atoms can increase the electronic conductivity of carbon materials, which is beneficial for constructing highly efficient electron-percolating networks for the cathodes, while the fluoridization of carbon materials is more suitable for constructing a more stable interface with Li anode. For the polymer electrolytes, functional groups can form the intermolecular hydrogen bonding effect with the polymer matrix, which promotes the Li-ion conduction and assists in the dispersion of carbon-based materials. However, they may induce some undesirable side reactions upon contact with inorganic solid electrolytes. In addition, lithiophilicity can be affected by the modification of carbon-based materials, which should be carefully considered and designed to achieve a particular Li deposition.

**5.2.2 Optimizing the additive amount of carbon-based materials for a balanced electronic and ionic transport.** Superior electronic conductivity is one of the most important characteristics of carbon-based materials, however, it is not always suitable for all the situations when used in SSEs, as some carbon-based materials with excellent electronic conductivity would make the electron-percolating pathways throughout the electrolyte, leading to a short circuit of battery, while some additives with large sheets would also obstacle the ion-transport. Therefore, when incorporating carbon-based materials as additives in SSEs, the content should be limited to a relatively low range to balance the electronic and ionic transport. Moreover, reasonable additive amount can also affect the mechanical properties of SSEs that should be carefully optimized.

**5.2.3 Developing carbon-based materials with a novel structure.** In addition to expanding the application of the existing carbon-based materials to achieve their maximum

utilities, developing carbon-based materials with new structures is also of great importance to pave new routes toward technological breakthroughs in SSLBs. For instance, as a new structural carbon material, graphdiyne composed of  $sp$  and  $sp^2$  hybridized carbon atoms features uniform pore structures and excellent electronic/ionic transport performance, which can be used as a nanofiller in SPE to enhance the ion-transport and can be chemically modified to inhibit the growth of Li dendrites.<sup>138,139</sup> Through structural innovation and material design, carbon-based materials will play a more significant role in advancing the commercialization in SSLBs.

In addition to the above fundamental issues, perspectives and development trends of carbon-based materials for more reliable SSLBs also include the following aspects.

**(1) Synergistic regulation of Li deposition by lithiophilic-lithiophobic hybrid carbon materials:** As reviewed in Section 4, both lithiophilic and lithiophobic carbon materials have displayed the capabilities in regulating the nucleation and deposition behavior of Li. Nevertheless, they function with different mechanisms. Lithiophilic carbon materials, such as GO and N-doped graphene, can guide the nucleation of metallic Li through chemical interactions, promoting the Li metal to distribute uniformly on the anode surface,<sup>125</sup> while the lithiophobic carbon materials can induce Li to deposit along a particular path through physical repulsion or structural confine. Recently, some works have combined lithiophilic metals or metal oxides with lithiophobic carbon materials to construct a lithiophilic-lithiophobic composite interlayer to induce the directional deposition of Li and suppress dendrite growth.<sup>112,117,136</sup> The adjustable surface properties of carbon-based materials enable their changing between lithiophilic and lithiophobic states through atomic doping and functionalization. This unique characteristic provides a technical pathway for designing gradient hybrid carbon architecture with spatially modulated lithiophilicity-lithiophobicity characteristics. Such gradient architecture allows synergistic regulation of Li deposition behavior while minimizing the requirement for metallic heteroatom dopants, thereby enhancing the practical energy density of SSLBs through optimized component integration.

**(2) Theoretical simulation and machine learning for material screening:** Functionalization has emerged as a critical strategy for optimizing the surface chemistry of carbon-based materials to enhance their performance in solid-state batteries. However, the optimum types of introduced functional groups/dopants and their underlying reaction mechanisms still need further research. Due to the inherent physicochemical properties and diverse structures of carbon materials, their interactions with functional groups, heterogeneous elements, and solid electrolytes are very complex, especially under the electric field. Therefore, experimental research for functional carbon-based materials will face enormous challenges. Theoretical simulation methods such as density functional theory and molecular dynamics have enabled valuable predictions regarding structure–property relationships in carbon-based materials with tailored surface chemistry, providing essential guidance for experimental synthesis.<sup>140,141</sup> In



addition, the emergence of machine learning techniques presents new opportunities to complement current methodologies. By leveraging artificial neural networks and advanced data analytics, machine learning demonstrates unique advantages in modeling complex systems such as catalyst synthesis and nanocarbon growth, which can maintain the accuracy of density functional theory-level while significantly improving computational efficiency and transferability across different material systems.<sup>142,143</sup> Therefore, the combination of theoretical simulation and machine learning will greatly promote the application of functionalized carbon-based materials in SSLBs in the near future.

## Conflicts of interest

There are no conflicts of interest to declare.

## Data availability

No primary research results, software or code has been included and no new data were generated or analysed as part of this review.

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