

## REVIEW

# Carbon materials for stable Li metal anodes: Challenges, solutions, and outlook

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## Abstract

Lithium (Li) metal is regarded as the ultimate anode for next-generation Li-ion batteries due to its highest specific capacity and lowest electrochemical potential. However, the Li metal anode has limitations, including virtually infinite volume change, nonuniform Li deposition, and an unstable electrode–electrolyte interface, which lead to rapid capacity degradation and poor cycling stability, significantly hindering its practical application. To address these issues, intensive efforts have been devoted toward accommodating and guiding Li deposition as well as stabilizing the interface using various carbon materials, which have demonstrated excellent effectiveness, benefiting from their vast variety and excellent tunability of the structure–property relationship. This review is intended as a guide through the fundamental challenges of Li metal anodes to the corresponding solutions utilizing carbon materials. The specific functionalities and mechanisms of carbon materials for stabilizing Li metal anodes in these solutions are discussed in detail. Apart from the stabilization of the Li metal anode in liquid electrolytes, attention has also been paid to the review of anode-free Li metal batteries and solid-state batteries enabled by strategies based on carbon materials. Furthermore, we have reviewed the unresolved challenges and presented our outlook on the implementation of carbon materials for stabilizing Li metal anodes in practical applications.

## KEYWORDS

carbon materials, interface engineering, Li deposition regulation, Li metal anode, structure stabilization

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## 1 | INTRODUCTION

High-energy rechargeable batteries play a significant role in powering portable electronics and electric vehicles (EVs).<sup>1</sup> Currently, the most prevalent technology is lithium (Li)-ion batteries (LIBs), which theoretically can provide a specific energy density of up to 350 Wh kg<sup>-1</sup>.<sup>2,3</sup> However, LIBs still cannot meet the rapidly increasing requirement of high-energy-density batteries for future use, for example, long-range EVs and grid-scale electricity storage, even after they are pushed to their uppermost limit in energy density. Various kinds of post-LIBs technologies have been developed to overcome this bottleneck.<sup>4-6</sup> In particular, Li metal batteries (LMBs) are considered as one of the promising candidates because the Li metal anode possesses a theoretical specific capacity of ~3861 mAh g<sup>-1</sup>, more than 10-fold that of the graphite anode (372 mAh g<sup>-1</sup>) used in commercial LIBs, and the lowest electrochemical potential (-3.04 V vs. the standard hydrogen electrode), resulting in high output voltage during operation.<sup>7-10</sup> When the Li metal is paired with layered transition-metal compounds (e.g., LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>1-x-y</sub>O<sub>2</sub>, etc.), which are commonly used cathode materials in LIBs, the resulting LMB can provide an ~40% increase in specific energy density compared with LIBs.<sup>4,11</sup> Moreover, since the Li metal anode can act as a Li reservoir, many Li-free cathode materials can potentially be used, such as elemental sulfur, oxygen, and carbon dioxide, making it possible to achieve even higher energy density (>500 Wh kg<sup>-1</sup>).<sup>12</sup>

Despite the merits, the practical application of LMBs has been impeded by their poor cycle life and safety hazards, rooted in the fundamental challenges of the Li metal anode,<sup>13-15</sup> including the following: (1) tremendous volume change of Li metal anodes during stripping/plating processes, (2) nonuniform charge distribution, which is triggered by the rough surface of Li, resulting in the preferential nucleation and deposition of Li on the protuberant tips due to the "tip effect," resulting in dendritic growth, and (3) unstable Li-electrolyte interface, where the Li plating/stripping is accompanied by continuous growth and dynamic evolution of a commonly termed solid-electrolyte interphase (SEI). Various kinds of functional materials, including carbon,<sup>16-18</sup> polymers,<sup>19,20</sup> metals,<sup>21,22</sup> fluorides,<sup>23</sup> oxides,<sup>24,25</sup> nitrides,<sup>26,27</sup> and so forth, have been used to address these challenges. Among these materials, carbon materials have drawn particularly intensive research interest, owing to their following advantages:

- (1) Carbon materials are resource-abundant and low cost. Further, most carbon materials can be synthesized on a large scale, showing economic viability.
- (2) Carbon materials are lightweight, which can retain the high-energy-density feature of LMBs.
- (3) Carbon materials have various forms, such as graphite, graphene, reduced graphene oxide (rGO), and carbon nanotubes (CNTs), with different physicochemical properties, providing numerous possibilities for stabilizing Li metal anodes.
- (4) Tunable porosity, adjustable surface area, and easy functionalization of carbon materials provide the possibility of designing carbon materials with specific functions for Li metal anode stabilization.

These fascinating features of carbon materials result in their functional versatility, rendering carbon as one of the most widely used materials to stabilize Li metal anodes.<sup>28-32</sup> For instance, highly electrically conductive and porous carbon materials can act as hosts to effectively stabilize the electrode structures by accommodating the volume changes upon Li plating/stripping and to induce homogeneous Li deposition by delocalizing the charge distribution.<sup>33</sup> Carbon materials with defects/vacancies, heteroatom doping, or lithiophilic coating can guide uniform Li deposition by regulating the distribution of Li ions and reducing the energy barrier for Li nucleation and growth.<sup>17</sup> Carbon materials with high mechanical strength and Li<sup>+</sup> conductivity can serve as a stable and protective interphase layer/artificial SEI to avoid contact between the deposited Li and electrolyte, thus suppressing continuous undesirable reactions in between.<sup>18</sup>

This review is intended as a guide through the fundamental challenges of Li metal anodes to recent progress, the remaining challenges, and the outlook of carbon materials for stabilizing Li metal anodes. We will first introduce the three fundamental issues of Li metal anodes for practical application, followed by the respective solutions using carbon materials. The solutions are categorized based on the specific functionalities and configurations of carbon materials in LMBs, such as acting as Li hosts to stabilize the electrode structure, serving as Li-ion distribution regulators to guide Li deposition, and acting as an interfacial layer to enhance the stability of the SEI. In addition to the stabilization of the Li metal anode in liquid electrolytes, solid-state LMBs and anode-free LMBs are also reviewed. The current progress as well as the relationship between these strategies are discussed as well.

Moreover, we provide a critical review of the limitations and the remaining challenges of these approaches and present an outlook into the future development of carbon materials in stabilizing Li metal anodes. Note that there are a couple of review articles on carbon materials for Li metal anodes,<sup>34,35</sup> but none of them has reviewed the research progress based on the specific functionalities

of carbon materials to solve the fundamental challenges of Li metal anodes, and none has provided a comprehensive and insightful outlook into the future development of carbon materials toward the practical realization of Li metal anodes.

## 2 | MAJOR CHALLENGES OF STABLE LI METAL ANODES

Though the Li metal anode can provide very high energy density, its practical implementation is impeded by major challenges. Among them, there are three most critical ones limiting the performance of Li metal anodes, which are detailed below.

### 2.1 | Major challenges

#### (1) Drastic structural change

The Li metal anode undergoes a drastic volume change in the process of plating and stripping during the operation of LMBs. In the stripping process, as a large amount of Li metal is oxidized into Li ions and dissolves in the electrolyte, the volume of the Li metal anode decreases drastically. In the following plating process, Li ions are reduced and Li metal deposits on the electrode, increasing the electrode volume. In addition, Li metal tends to deposit in tree- or lump-like morphologies. These structures are highly porous (typically  $\sim 30\ \mu\text{m}$  in thickness, compared with  $4.85\ \mu\text{m}$  in thickness if nonporous, for plating  $1\ \text{mAh cm}^{-2}$  of Li metal), which exacerbates the volume change of Li metal anodes.<sup>36</sup> Such a drastic volume variation results in poor mechanical stability and thus poor electrochemical stability of the electrode. During operation, the volume change severely threatens the cycle life of LMBs.<sup>37</sup>

The volume change of Li metal poses even more serious problems in anode-less and solid-state LMBs. (i) In the anode-less cell configuration, Li is stored on the cathode side as Li ions, and the anode consists of only a current collector, that is, Li-free. When the current collector is a planar foil, the volume change of the Li metal anode induced by Li plating and stripping would be virtually infinite. (ii) In solid-state batteries, especially those using inorganic solid electrolytes, the electrolytes are too rigid to deform and thus cannot contact seamlessly with the structurally varying Li metal during stripping/plating, which worsens the ion transport and thus increases the cell polarization.<sup>38</sup>

#### (2) Nonuniform Li deposition

The surface of the Li metal anode contains many pits and grooves, leading to significant local variations in the current densities. Besides, the already-deposited Li and its SEI may further alter the electric field near the surface of the Li metal anode, resulting in a nonuniform charge distribution across the surface area of the current collector. This causes preferential deposition of Li metal at the localized regions with a stronger electrical field, thus inducing nonuniform Li plating behavior, and is proposed to be the underlying reason for dendrite growth.<sup>39</sup>

It should be mentioned that apart from the non-uniform charge distribution theory, alternate theories have been proposed to explain the driving force for Li dendrite growth, including the space charge theory,<sup>40</sup> the stress-induced theory,<sup>41</sup> the spherical diffusion theory,<sup>42</sup> the fragile SEI-induced theory,<sup>39</sup> and so forth. Among them, the space charge theory has been verified in some experiments.<sup>43</sup> The space charge theory predicts that, for LMBs using a polymer electrolyte, when the following condition is satisfied:

$$\frac{dC}{dx} > 2C_0/L, \quad (1)$$

where  $C_0$  represents the initial concentration of Li ions in the electrolyte and  $L$  is the distance between the cathode and the anode, Li dendrite would evolve at time  $\tau$ , termed as “Sand’s time,”

$$\tau = \pi D \left( \frac{C_0 e}{2J t_a} \right)^2, \quad (2)$$

$$t_a = 1 - t_{\text{Li}^+} = \frac{\mu_a}{\mu_a + \mu_{\text{Li}^+}}, \quad (3)$$

where  $D$  is the diffusion coefficient,  $e$  is the electron charge,  $J$  is the effective current density for the electrode, and  $t_a/t_{\text{Li}^+}$  and  $\mu_a/\mu_{\text{Li}^+}$  are the transference numbers and the mobility of anions and Li ions, respectively.

Therefore, decreasing the effective current density by increasing the electrode surface area and/or by improving the mobility of Li ions is essential for prolonging Sand’s time, and thus delaying Li dendrite formation.

#### (3) Unstable SEI

Since the chemical potential of Li metal is above the lowest unoccupied molecular orbital (LUMO) of most organic electrolytes, Li reacts with the electrolytes, forming an SEI composed of both inorganic components (e.g., LiF, Li<sub>2</sub>O, etc.) and organic components

(e.g.,  $\text{ROCO}_2\text{Li}$ ,  $\text{ROLi}$ , etc.).<sup>44</sup> As a result, the SEI on the Li metal anode is unstable and evolves in terms of both structure and chemical composition with cycling. Specifically, the SEI is not mechanically strong and flexible enough to withstand the tremendous stress induced by Li dendrites and the drastic volume change of the Li metal anode. Therefore, it would break during the Li plating/stripping process, and consequently, fresh and unprotected metallic Li is exposed at the broken regions of the SEI, where it reacts with the electrolyte to form a new SEI. Since the reaction consumes Li and is irreversible, the capacity of LMBs decreases gradually. Besides, Li ions preferentially deposit at the broken SEI regions due to more favorable thermodynamics and faster kinetics, exacerbating nonuniform Li plating behavior.<sup>39</sup>

In solid-state batteries, the high reactivity of metallic Li also results in the reduction of solid electrolytes, which, together with the similar behaviors of dendritic Li growth and electrode volume change as in liquid organic electrolytes, also destabilizes the Li–electrolyte interface. This exacerbates the poor interfacial contact between Li metal and solid electrolytes, making the Li-ion transport across the interfaces significantly more problematic than that in liquid electrolytes and leading to deterioration in the electrochemical performance.<sup>45</sup>

## 2.2 | Interplay of the challenges

The three aforementioned challenges occur simultaneously in LMBs and are strongly correlated as well as aggravate each other, as shown in Figure 1. For instance, the large volume change and dendritic Li growth exert tremendous mechanical stress, cracking the SEI layer. In turn, unstable SEI leads to preferential Li deposition where SEI cracks, intensifying the nonuniform Li-ion deposition and volume variation. The nonuniform charge distribution leads to localized Li deposition, resulting in dendritic Li growth and drastic volume change at specific areas.

## 3 | STRATEGIES USING CARBON MATERIALS FOR STABILIZING LI METAL ANODES

Carbon materials of various forms and tunable structures have been widely utilized in LMBs, serving as Li hosts,<sup>17,46,47</sup> separator modifiers,<sup>48</sup> interlayer and artificial SEI,<sup>49</sup> and so on, and have been demonstrated to be rather effective in addressing the aforementioned challenges. For



**FIGURE 1** Correlation between the three major challenges of Li metal anodes

example, Three-dimensional (3D) carbon materials and modified current collectors with porous structures as Li hosts can accommodate the volume changes of the Li metal anode.<sup>50</sup> Besides, their high surface areas can reduce the local current density, delocalizing the charge distribution and delaying the dendrite formation.<sup>51</sup> Li-thiophilically engineered carbon materials can improve their wettability toward molten Li and regulate the Li-ion distribution.<sup>17</sup> Interlayers based on carbon materials act as Li hosts or smoothen the Li surface by blocking reactive species from the cathode side.<sup>48</sup> An artificial SEI or interphase layer based on carbon with high mechanical and (electro-)chemical stability considerably enhances the stability of the SEI.<sup>49</sup>

In this section, we comprehensively review the state-of-the-art strategies for stabilizing Li metal anodes, in which carbon materials play a key role. Strategies involving carbon materials, which, however, do not contribute to a major function in these strategies, are beyond the scope of the current review. It is noteworthy that many of the carbon-based approaches for stabilizing Li metal anodes are multifunctional and capable of solving more than one of the aforementioned challenges. In this review, we categorize the functionalities of carbon materials on the basis of the major function(s) identified by the authors in the referenced works.

### 3.1 | Structural stabilization of the Li metal electrode

To address the volume change of “hostless” Li metal anodes, hosts with a porous structure are essential to provide space for accommodating the volume expansion.<sup>52,53</sup> Carbon materials are promising as hosts to accommodate the volume change of the Li metal



anode due to their designable architecture, tunable porous structure, and easy functionalization.<sup>34,54–56</sup> In particular, 3D conductive hosts with high surface areas can reduce the effective current density, which will delay the dendrite formation according to the “Sand’s time” model and prolong the battery cycle life.<sup>57,58</sup> Hosts with lithophilic sites can not only improve the wettability toward molten Li, facilitating the large-scale fabrication of the Li composite using the facile molten Li infusion method, but can also support uniform Li nucleation suppressing Li dendrite growth.<sup>59</sup>

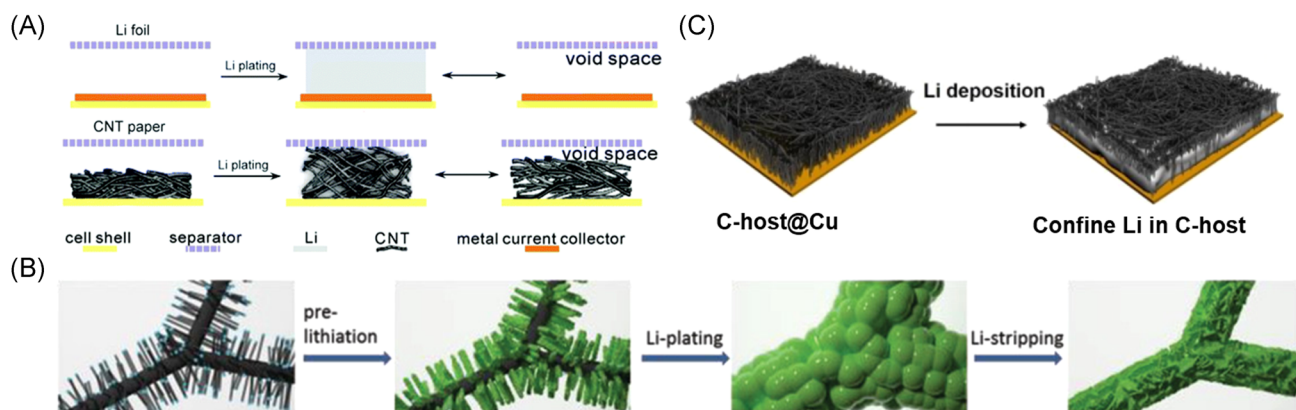
### 3.1.1 | Carbon host for anode-free LMBs

An anode-free cell configuration with zero-excess Li would improve the energy density as well as the manufacturing processability of LMBs.<sup>60</sup> The most attractive characteristic of anode-less Li electrodes is the high energy density of their LMBs. Despite the high theoretical capacity of the Li metal anode, LMBs with a thick (500  $\mu\text{m}$ ) Li foil have a low specific energy density of  $<150 \text{ Wh kg}^{-1}$ , which is even lower than that of advanced LIBs ( $\sim 250 \text{ Wh kg}^{-1}$ ).<sup>61</sup> In comparison, the energy density of LMBs could be significantly improved to  $>350 \text{ Wh kg}^{-1}$  when using a thin (e.g., 30  $\mu\text{m}$ ) Li foil combined with a lean electrolyte.<sup>62</sup>

A Li host such as a 3D carbon scaffold is essential for stabilizing the structure of an anode-less Li electrode. To achieve a high energy density for anode-less LMBs, lightweight carbon hosts are particularly advantageous over metallic ones. When used as a host for an anode-less Li metal anode, a carbon-based (i) freestanding film and (ii) a modification layer on the current collector have attracted intensive research attention.

3D freestanding carbon materials are promising Li metal hosts due to their interconnected conductive network and mechanical robustness, which enable the accommodation of volume expansion, release of mechanical stress, and reduction of local current density during Li deposition.<sup>63</sup> 3D freestanding films based on conductive nanocarbon materials (such as CNTs, graphene, and electrospun nanofiber) are promising materials as Li metal hosts because of their high specific surface area.<sup>64–67</sup> For example, Sun et al.<sup>67</sup> prepared CNT paper via chemical vapor deposition (CVD) as a freestanding framework, and Li could be compactly deposited inside. The Li/CNT electrode showed a small change in thickness (27.6  $\mu\text{m}$ ) when stripping 10 mAh  $\text{cm}^{-2}$  Li thanks to the robust and expandable structure of CNT paper, while the Li metal foil underwent a change in thickness of 48.5  $\mu\text{m}$  (Figure 2A).

However, despite the merits of nanocarbon materials, their ultrahigh surface area exacerbates the side reaction between the deposited Li and electrolyte, increasing the formation of SEI and making the system more sensitive to related issues. To address this aspect, 3D freestanding carbon based on microcarbon materials (such as commercial carbon cloth and carbon cloth derived from cotton/wood) appears to be attractive as a host for Li deposition due to its moderate surface area and favorable mechanical strength.<sup>70–72</sup> For instance, Liu et al.<sup>72</sup> reported a freestanding hollow carbon fiber framework derived from renewable cotton serving as a container for a Li metal anode. The volume change of the Li metal anode was suppressed by accommodating Li within the void space in between and inside the hollow fibers. Another approach is the hybridization of nano- and microcarbon materials to integrate their advantages and to overcome their disadvantages.<sup>68,73–76</sup> For example, Xie



**FIGURE 2** (A) Schematic of volume expansion of carbon nanotube (CNT) paper as a Li host during Li stripping/plating. Reproduced with permission: Copyright 2018, Wiley.<sup>67</sup> (B) Schematic showing the morphological changes of carbon nanotube-decorated carbon sponges (CNTs-MC) during Li plating/stripping. Reproduced with permission: Copyright 2018, Wiley.<sup>68</sup> (C) Schematic illustration of Li deposition on carbon nanotubes grown on a Cu foil (C-host@Cu). Reproduced with permission: Copyright 2018, Elsevier<sup>69</sup>

et al.<sup>68</sup> designed flexible CNTs grown on a stiff carbon sponge (CNTs-MC) as a Li metal host by annealing nickel-decorated melamine sponges (Figure 2B). The volume change was diminished due to the porous structure, and the strain induced during the Li plating/stripping process was effectively relieved owing to the synergistic benefits of the stiff carbon scaffold and flexible CNTs.

Apart from a self-supported carbon film, metal foils (such as Cu foils) are widely used as current collectors of Li metal anodes due to their high electronic conductivity, favorable electrochemical stability, and excellent mechanical strength. However, metal foils cannot accommodate the volume change of the Li metal anode during plating/stripping due to their planar geometry. To address this issue, 3D carbon materials have also been utilized to modify metal foils.<sup>69,77–82</sup> Shen et al.<sup>69</sup> reported a CNT sponge grown on a Cu foil via the CVD method as a Li host, which alleviated the volume change upon Li deposition (Figure 2C). Besides, Yan et al.<sup>82</sup> reported nanocapsules of hollow carbon spheres with Au nanoparticle seeds inside coated on a Cu foil as Li host, which enabled predominant Li deposition inside the hollow carbon, effectively suppressing the volume change of the electrode.

Furthermore, 3D metal foils (such as nickel foam) have also been used as hosts for Li metal due to their porous structure, but they still show a limited specific surface area.<sup>83–85</sup> To improve the surface area, nanostructured carbon materials with high specific surface areas have been adopted to modify metal scaffolds.<sup>86–88</sup> For instance, Xie et al.<sup>88</sup> explored a 3D graphene@Ni foam by CVD growth of graphene on a Ni foam as a Li host. Due to an improvement of the surface area from the graphene layer, the 3D graphene@Ni foam showed extremely low effective current density, suppressing the growth of Li dendrites and stabilizing the electrode structure.

### 3.1.2 | Carbon host for Li–C electrodes

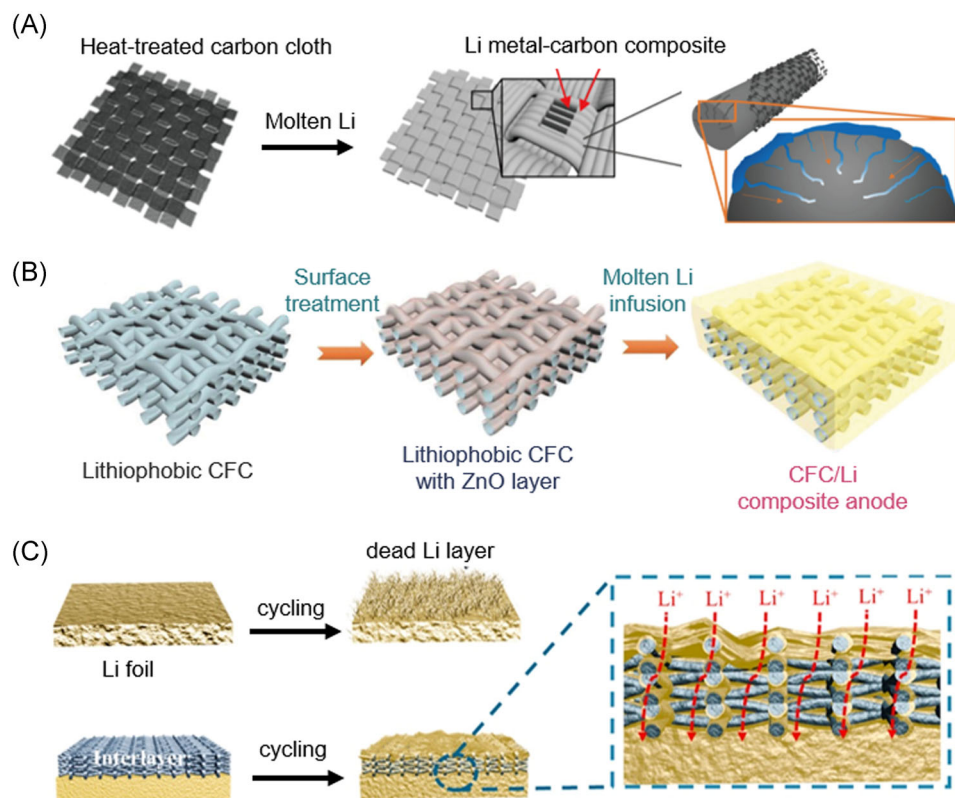
Li–C electrodes are classified into two categories: (i) Li/C composite electrodes with carbon as the host for Li and (ii) a carbon-based interlayer on top of a planar Li electrode.

Molten Li infusion into a 3D carbon host is a facile and scalable method to fabricate a Li/C composite electrode, but it requires the carbon host to have high lithiophilicity (i.e., wettability of molten Li).<sup>89</sup> Carbon hosts doped with heteroatom(s) (e.g., graphene oxide [GO], doped graphene, and carbon-derived biomass) show high molten Li wettability, ascribed to their richness in lithiophilic functional groups, which promote the

fabrication of Li/C composites.<sup>17,61,90–94</sup> Lin et al.<sup>17</sup> reported the fabrication of a layered rGO/Li composite film via Li-assisted reduction of a vacuum-filtered GO film. A “spark” reaction occurred on placing a GO film into molten Li; GO was reduced to rGO by molten Li, while Li was infused into the formed nanogaps of rGO. The rGO with a large surface area, nanogaps, and excellent lithiophilicity mitigated the volume change and guaranteed uniform Li deposition. Furthermore, Go et al.<sup>90</sup> developed carbon fibers rich in oxygen-containing functional groups and nano-crevasses by heating commercial carbon cloths (Figure 3A). The oxygen-containing functional groups and nano-crevasses of carbon fibers facilitate the penetration of molten Li into the carbon scaffold via chemical interaction and capillary forces.

Moreover, to improve the wettability of molten Li toward carbon hosts and to facilitate the facile fabrication of Li/C composite electrodes, coating of functional materials, such as Si,<sup>97</sup> Al<sub>2</sub>O<sub>3</sub>,<sup>98</sup> SnO<sub>2</sub>,<sup>99</sup> ZnO,<sup>95,100–102</sup> and porphyrin,<sup>103</sup> on the carbon host has been widely used. Zhang et al.<sup>102</sup> fabricated ZnO-coated carbonized wood as a Li host. The spontaneous reaction between ZnO and molten Li yielded more lithiophilic species (Li<sub>x</sub>Zn/Li<sub>2</sub>O), which reduced the contact angle of molten Li on the surface of carbon materials and enabled the infusion of molten Li into the channeled structure of carbonized wood. The 3D channeled structure of the carbonized wood helped to accommodate the volume change and enhanced the cycling performance. Following this study, several other channeled carbon hosts with lithiophilic coating have also been explored.<sup>101,104</sup> Furthermore, Liu et al.<sup>95</sup> developed ZnO-decorated carbon fibers (ZnO/CFC) as “straw” skeletons to accommodate molten Li “clay” (Figure 3B). ZnO enabled the infusion of molten Li into ZnO/CFC, which led to accommodation of the volume change and reduction of the current density due to the porous CFC structure.

Another approach is the utilization of a carbon material-based interlayer on the Li metal, which acts as a Li host upon plating on the anode side and/or protects Li by blocking reactive species from the cathode side.<sup>96,105–108</sup> For example, Zhao et al.<sup>96</sup> reported commercial carbon paper as an interlayer on the anode side to obtain a dendrite-free Li metal anode (Figure 3C). The porous interlayer not only provides buffer space for Li plating/stripping, thus accommodating the volume change, but also yields a smaller effective current density owing to its large surface area. In addition, Kong et al.<sup>107</sup> reported porous carbon derived from corn stalks as a bifunctional interlayer. Using this porous carbon, the shuttle of polysulfides was confined and a smooth surface of the Li metal anode was achieved in Li–S batteries.



**FIGURE 3** (A) Schematic of the synthesis of a Li/carbon composite electrode. Reproduced with permission: Copyright 2019, American Chemical Society.<sup>90</sup> (B) Schematic illustration of a carbon fiber/Li (CFC/Li) anode by the ZnO-induced molten method. Reproduced with permission: Copyright 2018, Elsevier.<sup>95</sup> (C) Schematic illustration of Li stripping/plating behavior with and without a carbon paper interlayer. Reproduced with permission: Copyright 2018, Elsevier<sup>96</sup>

## 3.2 | Regulating Li ions for uniform deposition

To achieve uniform and dendrite-free Li deposition, various carbon materials have been explored to homogenize the Li-ion distribution and to facilitate widespread Li nucleation, avoiding the presence of “hot spots” where Li growth is uncontrollable.<sup>109</sup> In this regard, carbon materials with a large specific surface area have been used to delocalize the Li distribution, while lithiophilicity-engineered carbon materials have been utilized to reduce the energy barrier for Li nucleation, and nanosized carbon particles have acted as Li-ion carriers and redistributors in electrolytes to facilitate smooth Li deposition.

### 3.2.1 | Delocalizing the Li distribution with 3D carbon frameworks

Among the strategies for regulating Li-ion distribution, the most commonly used one is to replace the planar metallic substrate with 3D conductive networks, which has been discussed in Section 3.1 and will not be detailed

here. In general, along with their functionality of accommodating the volume change upon Li plating/stripping and stabilizing the electrode structure, these 3D carbon matrices show large specific surface areas, delocalizing the Li distribution and reducing the local current density, thus delaying the dendrite formation according to Sand's time.<sup>43</sup> Meanwhile, these 3D conductive matrices are rich in active sites for the initial Li nucleation, delocalizing the Li-ion distribution and suppressing Li dendrite growth.

### 3.2.2 | Regulating Li nucleation through lithiophilic engineering for an anode-free configuration

Though 3D conductive carbon can delocalize the Li distribution, electrochemical Li deposition suffers from limitations in spreading and infiltrating into the graphitic carbon hosts due to the lithiophobic property.<sup>110</sup> Li nucleation on a substrate is controlled by both thermodynamic and kinetic factors. A higher binding energy of the lithiophilic substrate with Li can lead to a lower



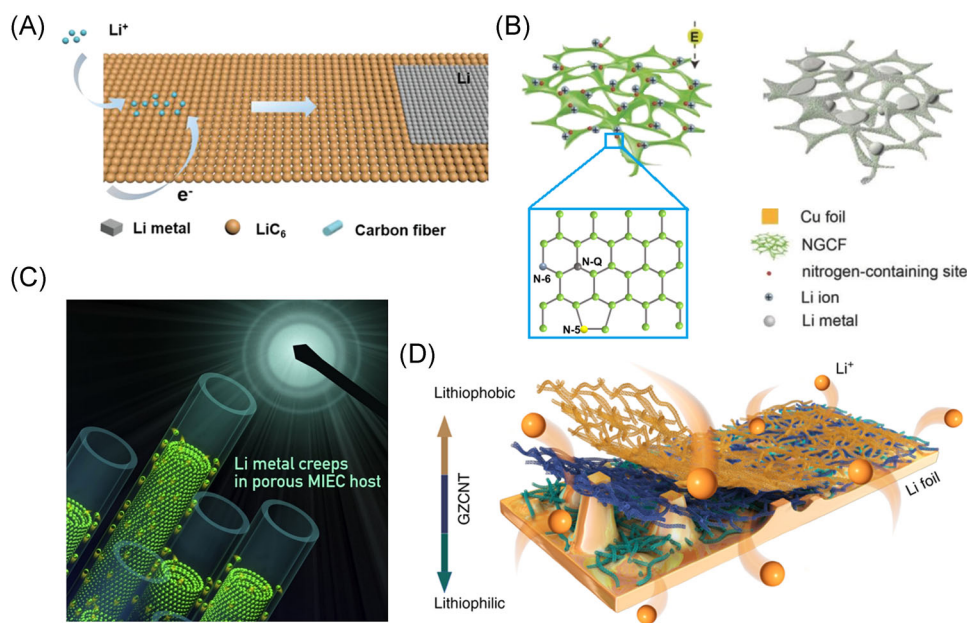
energy barrier and reduce overpotential for Li nucleation, facilitating uniform Li nucleation and deposition.<sup>111</sup> To homogenize the Li distribution and to support nucleation in the porous substrates, approaches for improving the affinity between Li and the substrates, that is, lithiophilicity, and facilitating Li deposition within the substrates have attracted intensive research attention.

Carbon turns lithiophilic when it contains enough lattice defects<sup>112</sup> or sufficient number of functional groups on the surface, for example, in the case of rGO.<sup>81,113</sup> Liu et al.<sup>81</sup> reported crumpled graphene balls with a large number of surface oxygen functional groups as lithiophilic scaffolds. It leads to a lower energy barrier and overpotential for Li nucleation due to the high binding energy between oxygen from functional groups and Li, which facilitates uniform Li nucleation and deposition. Meanwhile, the carbon substrate also turns lithiophilic upon lithiation of its surface layer.<sup>114–117</sup> Shi et al.<sup>114</sup> reported a Li–carbon fiber (Li–CF) composite electrode prepared by rolling-pressing metallic Li with CFs, where a lithiophilic LiC<sub>6</sub> layer was formed in situ, transforming the intrinsically lithiophobic CFs into a lithiophilic CF–LiC<sub>6</sub> framework. This design resulted in a low Li nucleation overpotential and superior electrochemical cycling stability (Figure 4A).

Moreover, by chemically engineering the carbon substrate, for example, doping with elements and coating with materials that bind Li more strongly, the carbon substrate is transformed from lithiophobic to

lithiophilic, facilitating Li nucleation on the carbon substrates. Doping with one or more types of atoms (e.g., N,<sup>118,120–126</sup> O,<sup>127,128</sup> and B<sup>127</sup>) on carbon has been proven to be effective in improving its lithiophilicity. Among these dopants, N-doping has attracted the most research attention. For example, Liu et al.<sup>118</sup> reported lightweight N-doped graphitic carbon foams (NGCFs) (Figure 4B), which have evenly distributed sites for Li nucleation, guiding uniform Li nucleation and subsequent growth during Li plating. In addition, Gan et al.<sup>121</sup> used tent-like N-doped porous carbon microcavities decorated on carbon cloth (NPCM@CC) as substrates for Li deposition. The NPCM@CC could simultaneously delocalize the Li distribution and reduce the Li nucleation overpotential, regulating the Li nucleation and growth behavior toward controllable and dendrite-free Li plating/stripping. Besides, Chen et al. reported that O-doped graphite shows a Li nucleation overpotential of 15.0 mV at 0.50 mA cm<sup>−2</sup>, lower than that of N-doped graphite (19.4 mV), and the O/B-co-doped carbon achieves even superior lithiophilicity due to a large local dipole.

The lithiophilicity of carbon-based hosts can also be enhanced by coating with lithiophilic materials, such as Li-alloying materials (e.g., Ag,<sup>129–131</sup> Au,<sup>82,132</sup> Zn,<sup>133–135</sup> etc.), metal oxides (e.g., ZnO,<sup>136–142</sup> Al<sub>2</sub>O<sub>3</sub>,<sup>143</sup> Co<sub>3</sub>O<sub>4</sub>,<sup>144</sup> etc.), metal nitrides (e.g., Mo<sub>2</sub>N,<sup>145</sup> Co<sub>4</sub>N,<sup>146</sup> Mg<sub>3</sub>N<sub>2</sub>,<sup>147</sup> TiN,<sup>148</sup> etc.), and non-active materials (e.g., Cu,<sup>149</sup> Co,<sup>125</sup> Cu/Fe/Ni,<sup>150</sup>



**FIGURE 4** (A) Lithiophilic carbon fiber–LiC<sub>6</sub> framework for Li deposition. Reproduced with permission: Copyright 2019, Wiley.<sup>114</sup> (B) Uniform Li nucleation/growth induced by N-doped graphitic carbon foams (NGCFs). Reproduced with permission: Copyright 2018, Wiley.<sup>118</sup> (C) Li metal creeps into a porous 3D host made of an electrochemically stable mixed Li ion and electronic conductor (MIEC). Reproduced with permission: Copyright 2020, Elsevier.<sup>119</sup> (D) Guiding the Li deposition using a lithiophilic–lithiophobic gradient carbon nanotube (CNT) interlayer. Reproduced with permission: Copyright 2018, Elsevier.<sup>80</sup>



functional organic groups,<sup>61</sup> etc.). The lithiophilic coating of materials usually appears as uniformly decorated nanoparticles or thin films on the substrates, serving as seeds for Li nucleation, facilitating Li nucleation, delocalizing the Li distribution on the carbon substrates, and eventually resulting in uniform Li deposition. It is pertinent to mention that the lithiophilic materials in these cases are not carbon and therefore beyond the scope of this review and are not discussed in detail.

Moreover, advanced designs taking advantage of the synergistic merits of lithiophilicity and other features (e.g., geometric patterns and lithiophilicity/lithiophobicity) have been reported.<sup>113,119,132,138,139,151</sup> For example, Chen et al.<sup>119,139</sup> reported that reversible Li plating/stripping could occur inside lithiated carbon tubules (~100 nm), which represented a mixed ionic–electronic conductor (MIEC), via diffusional Coble creep along the boundary between Li and MIEC (Figure 4C). In addition, Zhang et al.<sup>80</sup> designed a lithiophilic–lithiophobic gradient CNT interfacial layer composed of lithiophilic ZnO-coated CNT on the bottom and lithiophobic CNT on top, which effectively induced Li deposition within the interlayer with stable cycling (Figure 4D). Besides, Wang et al.<sup>152</sup> showed that stable Li metal anodes could be achieved via horizontal centripetal plating and stripping in the voids of the patterned rGO/Li composite electrode. Specifically, the electric field as well as the Li-ion flux in the voids were shifted to the edges of the patterned anodes. Eventually, Li nucleated preferentially at the void edges, with the Li deposits separated by the rGO sheets, resulting in horizontal centripetal Li deposition.

### 3.2.3 | Smoothing the Li deposition with co-deposition agents

Another effective approach to regulate the Li-ion distribution toward uniform deposition is to modify the

Li-ion carrier (i.e., the electrolytes) with new electrolyte formulations (such as salt, solvents, and additives<sup>153</sup>). In this regard, nanosized carbon materials have been used as additives in the electrolyte. To date, a few reports on carbon-based electrolyte additives have been published, in which nanosized carbon particles serve as carriers for Li ions in the electrolyte. The co-deposition of carbon nanoparticles next to Li ions on substrates induced smooth Li deposition. For instance, Cheng et al.<sup>154</sup> utilized a nanodiamond-based electrolyte additive as a heterogeneous nucleation seed for Li adsorption, lowering the Li-ion nucleation energy barrier and leading to uniform rather than dendritic Li deposition (Figure 5A). Besides, Jiang et al.<sup>155</sup> introduced nitrofullerene (nitro-C<sub>60</sub>) as an electrolyte additive, which anchors on the non-smooth Li metal surface, facilitating a homogeneous Li distribution. At the same time, it can be reduced to NO<sub>2</sub><sup>−</sup> groups, which react with Li to form a stable SEI layer.

### 3.2.4 | Separator engineering

In addition to the strategies discussed above, coating of carbon material on separators can also guide Li deposition toward controlled behavior.<sup>48,157</sup> Yang et al.<sup>48</sup> reported a vapor-grown carbon fiber (VGCF) coated on a glass fiber separator to induce Li deposition into the voids of the VGCF host, avoiding uncontrollable and dendritic Li growth. Besides, functional carbon material coating on a separator can also suppress parasitic reactions on the Li metal anode, for example, polysulfide crossover in Li-S batteries,<sup>158,159</sup> resulting in a smooth Li metal surface. In addition, a functional nanocarbon (FNC)-coated separator was demonstrated to be able to control the dendrite growth direction.<sup>160</sup> Li dendrites grew from both the FNC layer and the Li metal and subsequently made contact with each other. Consequently, a dendrite-free and dense Li layer was formed between the coated separator and the electrode.

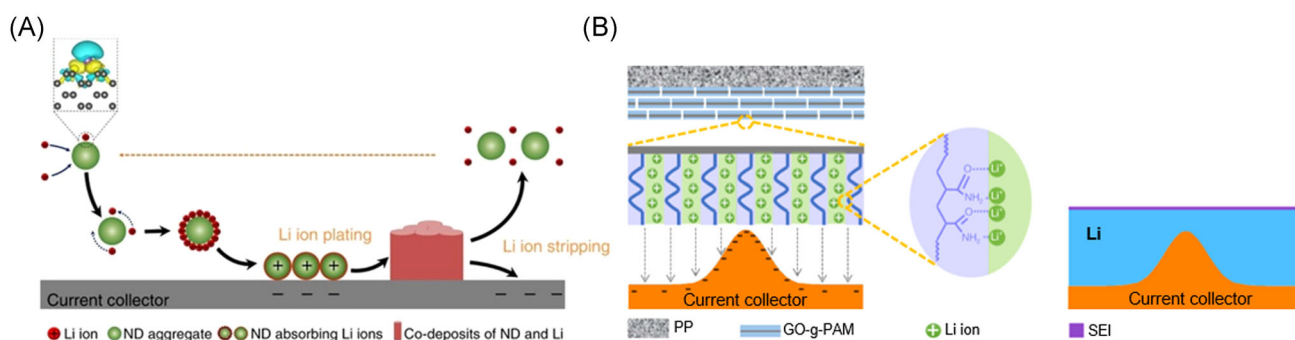


FIGURE 5 (A) Uniform Li deposition induced by the co-deposition of nanodiamond (ND) electrolyte additives. Reproduced with permission: Copyright 2017, Springer Nature.<sup>154</sup> (B) Schematics showing Li deposition behavior with a polyacrylamide-grafted graphene oxide-coated separator (PAM-g-GO@PP). Reproduced with permission: Copyright 2019, Springer Nature<sup>156</sup>

Furthermore, carbon-based hybrid materials also showed high efficiency in enabling uniform Li deposition to obtain a smooth Li metal surface.<sup>156,161</sup> Li et al.<sup>156</sup> reported that a polyacrylamide-grafted GO-coated separator (PAM-g-GO@PP) could enable molecular-level homogeneous and fast Li ionic flux on the surface of Li electrodes due to the lithiophilic feature of PAM chains and fast electrolyte diffusion pathways with the excellent mechanical strength of GO nanosheets (Figure 5B). As a result, dendrite-free uniform Li deposition with ultra-stable Li plating/stripping at a high current density was achieved.

### 3.3 | Stabilizing SEI

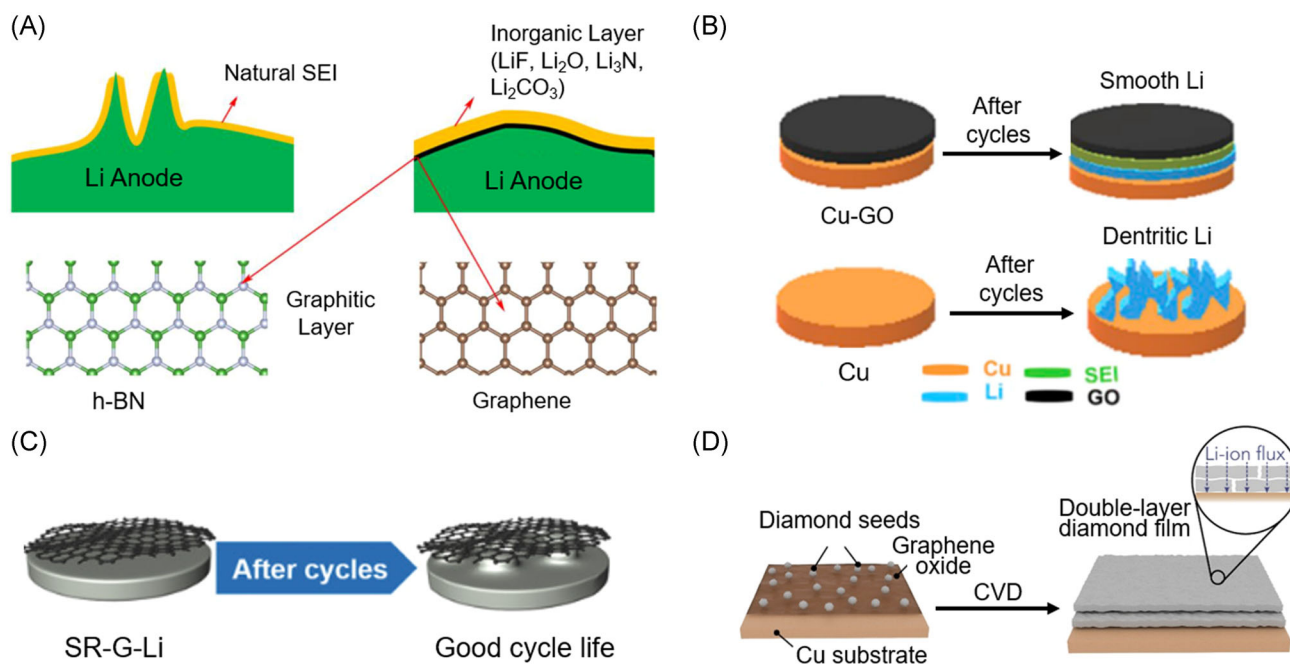
The SEI formed on the Li metal plays a key role in the Li plating/stripping processes. An ideal SEI should be uniform and Li-ion-conductive to obtain homogeneous and high Li-ion flux, while being electrically insulating to facilitate Li deposition underneath the SEI layer. Moreover, it should be chemically stable, acting as a blocking layer to prevent undesired reactions between the Li metal and the electrolyte, as well as mechanically flexible to constrain structural changes of the Li electrode.

A stable SEI results in a stable Li metal anode, and vice versa. However, the SEI obtained in practice is

unstable and rigid, which undergoes cracking upon uneven/dendritic Li deposition, exacerbating dendritic Li growth and parasitic reactions between Li and the electrolyte.<sup>162</sup> Different types of materials have been used to stabilize the SEI on Li metal.<sup>163–166</sup> Among these materials, carbon has been proven to be promising as an artificial SEI and interphase layer to stabilize the Li metal anode. Note that an artificial SEI has the same nature as that of a real SEI, being Li-ion-conductive and electrically insulating, while an interphase layer is an MIEC.

#### 3.3.1 | Artificial interface

Construction of an artificial SEI with high ionic conductivity and mechanical strength offers an alternative route to protect Li anodes by regulating Li-ion flux, suppressing dendrite formation, and physically isolating the reactive Li from electrolytes. Carbon materials possess a high mechanical strength and are chemically and electrochemically stable in battery systems, which make them an ideal candidate for artificial SEI.<sup>167,168</sup> For example, Zhu et al.<sup>167</sup> designed a bilayer artificial SEI (BL-SEI) consisting of covalent graphitic materials (graphene and h-BN) and inorganic components (LiF, Li<sub>2</sub>O, Li<sub>3</sub>N, and Li<sub>2</sub>CO<sub>3</sub>) to stabilize the Li metal anode (Figure 6A). BL-SEI is rationally designed through first-principle



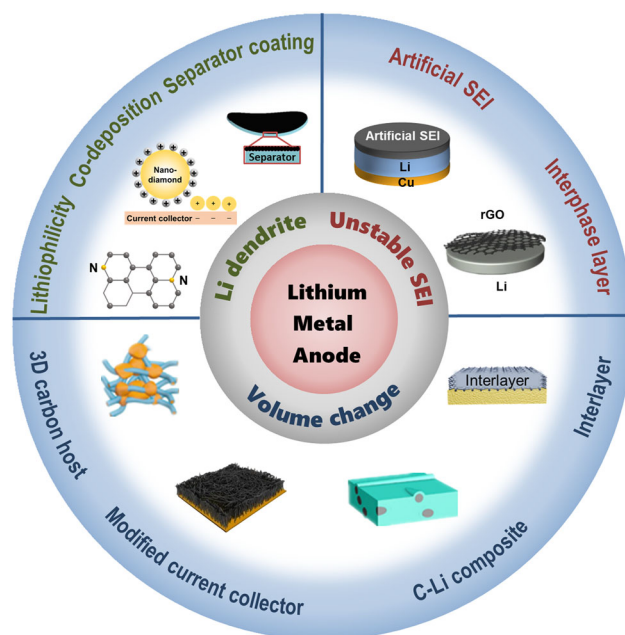
**FIGURE 6** (A) Schematic of a natural solid-electrolyte interphase (SEI) and an artificial SEI composed of covalent graphitic materials and inorganic components. Reproduced with permission: Copyright 2019, Elsevier.<sup>167</sup> (B) Schematic of Li behavior on bare Cu and Cu@GO electrodes. Reproduced with permission: Copyright 2020, Elsevier.<sup>168</sup> (C) Schematic illustration of Li deposition behavior of a spontaneously reduced graphene coating layer on the Li surface (SR-G-Li). Reproduced with permission: Copyright 2018, Wiley.<sup>49</sup> (D) Schematic of the nanodiamond interface. Reproduced with permission: Copyright 2018, Elsevier<sup>18</sup>

calculations; the graphene/LiF combination shows the best interfacial stability and electrochemical performance because graphene with high mechanical strength and stiffness can effectively release the stress induced by the deposition of Li, while the LiF layer can prevent the corrosion of graphitic layers by the electrolyte and stably cover the Li metal surface. Besides, Wondimkun et al.<sup>168</sup> developed a binder-free ultrathin spin-coated GO to regulate the deposition of Li metal (Figure 6B). The GO-coated artificial SEI in synergy with LiF derived from a fluoroethylene carbonate (FEC) additive leads to uniform Li deposition due to the capability to stabilize the electrode/electrolyte interface.

### 3.3.2 | Interphase layer

The interphase layer is also introduced to stabilize SEI and to yield a dendrite-free Li metal anode. To differentiate it from the interlayer in Section 3.1.2, which is a relatively thick and porous matrix working as a Li host during Li plating, the interphase layer discussed in this section is a thin film with no apparent thickness for stabilizing SEI. Moreover, different from the artificial SEI in Section 3.3.1, which should be Li-ion-conductive and electrically insulating, an interphase layer reviewed in this section can be electrically conductive as well.

A desired interphase layer should be electro/chemically stable to stabilize the SEI formation, with strong mechanical strength and high flexibility to accommodate the volume expansion of Li as well as to constrain the Li dendrite growth, and also should have high ionic conductivity to control the flow of Li ions for uniform Li deposition. Carbon materials have been shown to be promising materials for an ideal interphase layer toward the achievement of stable Li metal anodes.<sup>16,18,49,169,170</sup> For example, Bai et al.<sup>49</sup> designed a spontaneously reduced graphene coating layer on the Li surface (SR-G-Li) as a protective layer. This interlayer is useful in stabilizing SEI and preventing the Li dendrite formation (Figure 6C). Liu et al.<sup>18</sup> fabricated a double-layer nanodiamond thin film as an interfacial layer, which protected the Li metal anode while ensuring uniform Li-ion flux, and reinforced the native SEI layer (Figure 6D). Zheng et al.<sup>16</sup> developed a hollow carbon nanosphere-based interphase layer. It has been found that Li metal deposition is isolated underneath the carbon nanosphere layer, which facilitates the formation of a stable SEI. In addition, Salvatierra et al.<sup>169</sup> reported lithiated multiwall carbon nanotubes (Li-MWCNTs) as a controlled Li diffusion interlayer to suppress the formation of Li dendrite and to stabilize SEI. A smooth morphology of Li metal was obtained as a consequence of the regulated Li-ion flux and stable SEI.



**FIGURE 7** Overview of the challenges of the Li metal anode and the respective solutions based on carbon materials. Reproduced with permission: Copyright 2017, Elsevier<sup>72</sup>; Reproduced with permission: Copyright 2018, Elsevier<sup>69</sup>; Reproduced with permission: Copyright 2018, Elsevier<sup>130</sup>; Reproduced with permission: Copyright 2018, Elsevier<sup>96</sup>; Reproduced with permission: Copyright 2018, Wiley<sup>49</sup>

In a solid-state LMBs system, the anodic interface suffers from a major problem of poor interfacial contact and stability, for which one solution is to introduce an interphase layer.<sup>171–173</sup> Shao et al.<sup>171</sup> developed a graphite-based soft interphase layer on top of a solid-state electrolyte. It has been found that a lithiated interface with good Li-ion and electronic conductivity was formed due to the reaction between the graphite-based layer and Li metal, which improved the interfacial contact and stability. Besides, Feng et al.<sup>172</sup> fabricated a carbon layer on  $\text{Li}_{6.75}\text{-La}_{3.75}\text{Ta}_{0.25}\text{O}_{12}$  (LLZTO) by thermal-decomposition vapor deposition. Due to protection of the carbon layer, a contaminant-free surface and stability of LLZTO in air as well as high current density endurance of the Li/LLZTO were achieved.

## 4 | SUMMARY AND OUTLOOK

The three major fundamental challenges with the use of Li metal anodes and the respective solutions using carbon materials reported to date are summarized in Section 3 and shown in Figure 7. Note that some Li-metal-stabilizing approaches based on carbon materials are similar, but the major functions of these carbon materials are different. For instance, (1) the lithiophilic

engineering-related strategies reviewed in Sections 3.1.2 and 3.2.2 are categorized as different ones. Lithiophilic coating on carbon hosts is reviewed in Section 3.1.2, with the aim of improving the molten Li wettability against carbon for facile preparation of Li/C composite electrodes. In comparison, in Section 3.2.2, lithiophilic engineered carbon materials are used on a Li-free anode, to guide electrochemical Li deposition during a battery operation. (2) The interlayer discussed in Section 3.1.2 and the interphase layer reviewed in Section 3.3.2 work in different ways to regulate Li deposition and to stabilize the Li electrode. The former is thick and serves mainly as a host for Li deposition to avoid the electrode volume/structure change, while the latter appears to be a thin film working mainly as a protective layer for Li metal to suppress the dendrite growth and to stabilize the SEI.

Moreover, among the strategies that utilize carbon materials with the major functions of minimizing the structural change of the Li electrode (Section 3.1), regulating Li deposition (Section 3.2), and stabilizing the SEI on Li metal (Section 3.3), many are bi- or multifunctional due to the versatility of carbon materials and the interplay between the challenges of the Li metal anode. For instance, a 3D carbon-based host can not only accommodate Li deposits but also delocalize the Li-ion distribution. A lithiophilic carbon host can simultaneously prevent the volume change and facilitate homogeneous Li nucleation and growth. Moreover, strategies that can lead to uniform Li deposition are beneficial for the formation of a stable SEI. However, despite their versatility, none of the reported strategies could perfectly resolve all three of these major challenges, especially for anode-free LMBs. For instance, carbon-based Li hosts have limited capability to stabilize the SEI layer, and a stabilized Li-electrolyte interface is insufficient to eliminate the volume change of the Li metal anode.

Although carbon materials show promising results in stabilizing Li metal anodes, several challenges remain, and significant advances are required for the future development of carbon-stabilized Li metal anodes.

- (1) The introduction of carbon materials, which are either electrochemically inactive or active but with a low capacity, will reduce the gravimetric energy density of Li metal anodes. Besides, the 3D carbon hosts have rather large volumes due to their porous structure and low packing density, leading to the decrease of the volumetric energy density of Li metal anodes. To maximize the specific energy density, the volume/mass ratio of carbon should be controlled. For a quantitative estimation, assuming that the carbon materials in Li electrodes have no capacity for Li-ion storage, the capacity of a

Li-C electrode (equivalent to  $\text{LiC}_x$ ) amounts to  $(3861 \times 6.94)/(6.94 + 12.01x) [\text{mAh g}^{-1}]$ . Thus, to ensure a capacity of  $>1000 \text{ mAh g}^{-1}$  for the Li-C electrode, the Li/C ratio should not be less than 1:1.65. In addition, high mechanical strength should be ensured when using low density or less amount of carbon.

- (2) Though the porous structure and large surface area of nanostructured carbon hosts can effectively reduce the local current density, parasitic reactions (e.g., SEI formation) will be exacerbated due to the large specific surface area, leading to a low Coulombic efficiency. To address this issue, it is worthwhile to further investigate carbon hosts with a moderate surface area. Nanosized carbon materials usually have a high specific surface area of  $>100 \text{ m}^2 \text{ g}^{-1}$  (e.g., 118,<sup>67</sup> 177.7,<sup>65</sup> and  $1666 \text{ m}^2 \text{ g}^{-1}$ ).<sup>151</sup> In comparison, micro-sized carbon materials usually have a limited specific surface area of  $<20 \text{ m}^2 \text{ g}^{-1}$  (e.g., 12<sup>136</sup> and  $15.6 \text{ m}^2 \text{ g}^{-1}$ ).<sup>197</sup> Therefore, the authors suggest a moderate specific surface area in the range of  $20\text{--}100 \text{ m}^2 \text{ g}^{-1}$  (median:  $60 \text{ m}^2 \text{ g}^{-1}$ ) for carbon material-based Li hosts.
- (3) Effective approaches for stabilizing Li metal anodes in past reports frequently involve the sophisticated design and synthesis of functional carbon materials, which are complex and time-consuming, posing challenges for their scalability and applications in Li metal pouch cells. Functionalized carbon materials synthesized using scalable methods for stable Li metal anodes must be developed.
- (4) To facilitate the ongoing energy transition toward carbon neutrality, future research should also be focused on developing carbon materials from sustainable sources and green chemistry, wherever applicable. The recycling ability and efficiency of the carbon materials and Li metal anodes based on these should be explored as well, which is critical for long-term sustainability of the whole process and a cyclic economy.
- (5) The electro/chemical stability of carbon materials during battery operation, especially under different operation windows, should be monitored. At low operation voltage ranges (e.g.,  $<1.5 \text{ V vs. Li}^+/\text{Li}$ ), carbon materials could be lithiated vigorously, involving both chemical and electrochemical lithiation. At high operation windows, carbon suffers from poor electrochemical stability. Under both conditions, carbon materials undergo compositional and structural changes, and their functionality for stabilizing Li metal anodes may deteriorate. For instance, lithiation of carbon materials improves their lithiophilicity. However, this process



consumes Li via irreversible or poorly reversible reactions, and it is unclear whether lithiation will affect the mechanical property and electro/chemical stability of the carbon materials.

- (6) There is a lack of fundamental understanding of the electrochemical behavior of the carbon materials during Li plating/stripping, which plays a key role in stabilizing Li metal anodes. Therefore, advanced and operando/in situ characterization monitoring of the carbon materials along with battery operation should be carried out. Besides, theoretical computation could provide a comprehensive and in-depth understanding of the underlying working mechanisms. For instance, density functional theory can be used to calculate the binding energies between Li and different functional groups of carbon materials, which could be correlated to the lithiophilicity of carbon materials and their effects on stabilizing the Li metal anode. Meanwhile, in recent years, machine learning has been incorporated into the research fields of energy materials, which would also be a very effective way to predict the properties and to accelerate the development of carbon materials for future LMBs.
- (7) The long-lasting durability of the effectiveness of these carbon-based approaches in maintaining their functionalities, especially lithiophilicity, along with battery operation remains limited. For example, a lithiophilic coating layer (e.g., Si) on the carbon host has a significant specific capacity of storing Li ions, which would lead to cracking and pulverization of the coating layer together with additional SEI formation, and eventually adversely affect the lithiophilic functionality. Defect migration, loss of functional groups, diffusion of dopants, and so forth may also lead to a loss of lithiophilicity over extended cycling. In this regard, degradation and long-lasting effects of the carbon-based Li-hosts, lithiophilic treatment, and SEI stabilization should be studied.
- (8) Carbon materials have limited efficiency in stabilizing the SEI due to their limited Li-ion conductivity and mechanical flexibility. Hybridization of carbon with Li-ion conductive and mechanically superior polymeric and/or non-carbon inorganic materials could be a good solution to reinforce the stability of SEI but remains largely underdeveloped.
- (9) In past research, a thick Li metal foil ( $>100\ \mu\text{m}$ ) is often used in excess to compensate for the irreversible capacity loss and to maintain the cycling performance, which, however, undergoes large volume change during battery operation and compromises the gravimetric energy density of the whole cell. To resolve these issues, a thin (e.g.,  $<25\ \mu\text{m}$ ) and

mechanically strong carbon host is required for fabricating stable Li-free or Li/C composite electrodes with reduced amount of excessive Li.

- (10) Anode-less Li electrodes (with zero-excess Li), especially those with a lean electrolyte, can significantly increase the energy density of LMBs from 150 to  $350\ \text{Wh kg}^{-1}$ ,<sup>62</sup> but pose tremendous challenges due to the virtually infinite volume expansion upon Li deposition, and continuous and electrolyte-consuming SEI growth. For the realization of this design, a carbon-based host with predefined porosity and volume is required to accommodate Li deposition, and synergistic strategies for guiding uniform Li deposition and stabilizing the Li-electrolyte interface are also required.
- (11) Past research on the utilization of carbon materials to stabilize the Li-electrolyte interface has focused on liquid electrolyte-based LMBs, with carbon-based strategies for stabilizing interface between the Li metal and the solid electrolyte in solid-state LMBs largely underdeveloped.
- (12) Practical pouch cells with thin Li face major challenges of large structural changes due to the lack of stack pressure in pouch cells. To achieve high-energy-density and stable pouch cells, lightweight, thin, and mechanically robust carbon materials are required to work as Li hosts. Moreover, scalable production of multifunctionalized carbon materials (see (3)) and processing of thin Li electrodes are essential to boosting their commercial viability.

In an ideal scenario, the authors believe that a Li metal anode for future LMBs should have minimal Li excess to simultaneously maximize the energy density from a cell perspective and extend its cycle life. A carbon-based host should be developed for the Li metal anode to synergistically guide homogeneous Li deposition within the host structure and stabilize the Li-electrolyte interface. To this end, an ideal carbon host should have the following features: high electro/chemical stability during battery operation; considerable but not excessive volume and porosity to accommodate Li deposition; excellent electronic conductivity; sufficient surface area to delocalize the Li-ion distribution (but not a very large surface area to suppress parasitic reactions); high and durable lithiophilicity to facilitate homogeneous Li nucleation and growth; high mechanical strength to maintain the electrode structure/volume (especially in an anode-free configuration); excellent flexibility to maintain enable seamless contact with rigid solid electrolytes in solid-state batteries. In addition, the carbon host should be produced from sustainable sources with green and scalable methods and can be recycled with high efficiency.

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## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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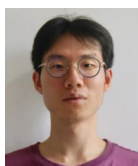
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