Review

Recent advances in lithiophilic materials: material design and prospects for lithium metal anode application

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Abstract

The rapid development of electronic technology and energy industry promotes the increasing desire for energy storage systems with high energy density, thus calling for the exploration of lithium metal anode. However, the enormous challenges, such as uncontrollable lithium deposition, side reaction, infinite volume change and dendrite generation, hinders its application. To address these problems, the deposition behavior of lithium must be exactly controlled and the anode/electrolyte interface must be stabilized. The deposition of lithium is a multi-step process influenced by multi-physical fields, where nucleation is the key to final morphology. Hence, increasing investigations have focused on the employment of lithiophilic materials that can regulate lithium nucleation in recent years. The lithiophilic materials introduced into the deposition hosts or solid electrolyte interphases can regulate the nucleation overpotential and facilitate uniform deposition. However, the concept of lithiophilicity is still undefined and the mechanism is still unrevealed. In this review, the recent advances in the regulation mechanisms of lithiophilicity are discussed, and the applications of lithiophilic materials in hosts and protective interphases are summarized. The in-depth exploration of lithiophilic materials can enhance our understanding of the deposition behavior of lithium and pave the way for practical lithium metal batteries.

INTRODUCTION

The rapidly increasing demand for lightweight electronic devices and electric vehicles, as well as the promotion of renewable energy sources based on sunlight, wind, tides, and so on, have led to the development of efficient and safe energy storage systems. Commercial lithium-ion batteries (LIBs) are one of the most widespread energy storage devices for the desirable energy density and reversibility. However, after continuous research, the energy density of LIBs has almost reached the theoretical limit (~300 Wh kg^{-1}) for the capacity limitation of common graphite anode (~372 mAh g^{-1})[1]. Therefore, the development of next-generation anodes is imperative to meet the explosively increasing demand for electronic applications and renewable energy storage.

Li metal anode is considered a promising alternative to traditional graphite anode for its low electrochemical redox potential (-3.04 V *vs.* standard hydrogen electrode) and ultrahigh theoretical capacity (3,860 mAh g^{-1})[2]. Nevertheless, the uncontrollable deposition behavior and the dramatic reactive activity of lithium metal anode result in poor reversibility and security concerns which hinders its application[3]. Different from the intercalation/deintercalation process of common graphite anode, the plating/stripping process of lithium metal anode is a conversion pattern without a host structure. Therefore, the infinite volume change will result in the destruction of the solid electrolyte interphase (SEI) and persistent electrolyte consumption[4]. In addition, the disordered deposition of lithium metal easily leads to the generation of lithium dendrites which can lose electric connection with the bulk lithium and form "dead" lithium, causing rapid capacity loss. The microstructure of lithium dendrites can also trigger partial short circuits, inducing thermal runaway and even severe safety concerns. Hence, promoting the uniform deposition of lithium and preventing the generation of dendrites is crucial to the application of next-generation lithium metal batteries (LMBs) with high energy density and acceptable cycle life.

The deposition of lithium is a complicated process influenced by multi-physical fields including electric field, concentration field, temperature field, and so on[5]. An in-depth understanding of the deposition mechanism of lithium and the factors influencing the deposition process is the foundation of further control over the process. Generally, the deposition of lithium undergoes two processes: nucleation and growth[6]. The nucleation process precedes the growth process and the morphology of lithium develops based on the nucleation structure. Hence, the nucleation and early growth processes play a key role in the final morphology of deposited lithium and the intensive exploration of the nucleation process is conducive to dendrite inhibition strategies and promoting safe LMBs with high energy density.

To preferably describe the nucleation and growth process of lithium, many insightful models have been proposed, such as the heterogeneous model[7], surface diffusion model[8,9], space charge model[10], and the SEI-induced model[11-13]. Among them, the heterogeneous model presented by Ely *et al.* through thermodynamic and kinetic simulations can commendably depict the heterogeneous nucleation process of lithium deposited on current collectors[7]. The nucleation and growth of lithium is identified into five regimes: the nucleation suppression regime, long incubation time regime, short incubation time regime, early growth regime, and late growth regime. In the nucleation suppression regime, the embryos first exhibit thermodynamic instability and have the propensity to dissolve back into electrolytes. Then, the embryos that are thermodynamically favored continue to grow over the course of the long incubation time regime after a few variations of the multi-physics fields. When the critical overpotential is exceeded, lithium with a critical kinetic radius quickly nucleates with an increase in overpotential during the short incubation time

regime, which is advantageous to the narrow size distribution of embryos. Finally, during the early and then later growth regimes, the nuclei with thermodynamic and kinetic stability expand to the same size at a constant rate. Based on the five regimes of the heterogeneous model, the specific processes during nucleation can be explored and regulated. To gain further insight into factors influencing nucleation process, many studies have been conducted. Pei *et al.* explored the relationship between current density and nuclei areal density, size and shape and proposed overpotential as a key parameter related to the nucleation distribution[14]. The size of lithium nuclei is inversely proportional to the overpotential and the number density is proportional to the cubic power of overpotential. Two characteristic overpotentials are observed during lithium deposition: the nucleation overpotential (η_n) and the plateau overpotential (η_p). η_n is the voltage spike at the onset of lithium deposition, which is below the equilibrium potential of Li/Li$^+$ to drive the nucleation of lithium embryos. After the nuclei are stabilized, the overpotential increases to η_p during the subsequent growth of lithium because the barrier of lithium growth on existing nuclei is lower. The relationship between the size of electrodeposited lithium nuclei and overpotential as well as the current density can be explained by the classical nucleation equation[15-17]. The critical radius of nuclei can be expressed as follows:

$$r_{crit} = \frac{2\gamma V_m}{F|\eta_n|}$$

where γ is the surface energy of the interface between Li and the electrolyte, V_m is the molar volume of Li and F is Faraday's constant.

Hence, the relationship between the lithium nuclei distribution and overpotential can be reflected. In addition, many researchers have studied the nucleation behavior depending on the temperature[18,19], concentration distribution[10,20], current collector[21,22], and so on. The growth of lithium and the final deposition morphology are highly dependent on the distribution of lithium nuclei. These models and explorations are conducive to our understanding of the nucleation behavior of lithium and the formulation of modification strategies.

Nucleation is the foundation of the subsequent growth of lithium and thus determines final morphology. Hence, serious effort has been made to regulate nucleation. Recently, the concept of lithiophilic materials has been proposed and has attracted much attention for regulating the nucleation behavior of lithium. Various lithiophilic strategies have been employed on lithium hosts and protective interphases to achieve desirable affinity to lithium. However, the concept and mechanism behind these traits of lithiophilic materials are still underexplored. The lithiophilic modification of materials is generally thought to improve the affinity to lithium, effectively reduce the nucleation overpotential on onset of deposition and facilitate selective nucleation by providing nucleation sites. Many strategies have been employed in the lithiophilic modification of hosts and interphases, including accommodating lithium deposition by alloying process, adjusting the adsorption of lithium atoms by optimizing the adsorption and diffusion energy via atom-doping, and regulating the preferred lattice orientation of lithium by crystallography modification [Figure 1]. These strategies express distinct mechanisms for regulating the nucleation behavior of lithium but are all thought to be lithiophilic modifications. Hence, an overview of the advances in lithiophilic materials is essential to define and understand the essence of lithiophilicity.

In this review, the exploration and application of lithiophilic materials on host structures and interphases are summarized and the remaining challenges and perspectives are proposed. This is conducive to understanding lithiophilic characteristics and the lithium nucleation mechanism from different perspectives and facilitates the effective implementation of lithiophilic materials.
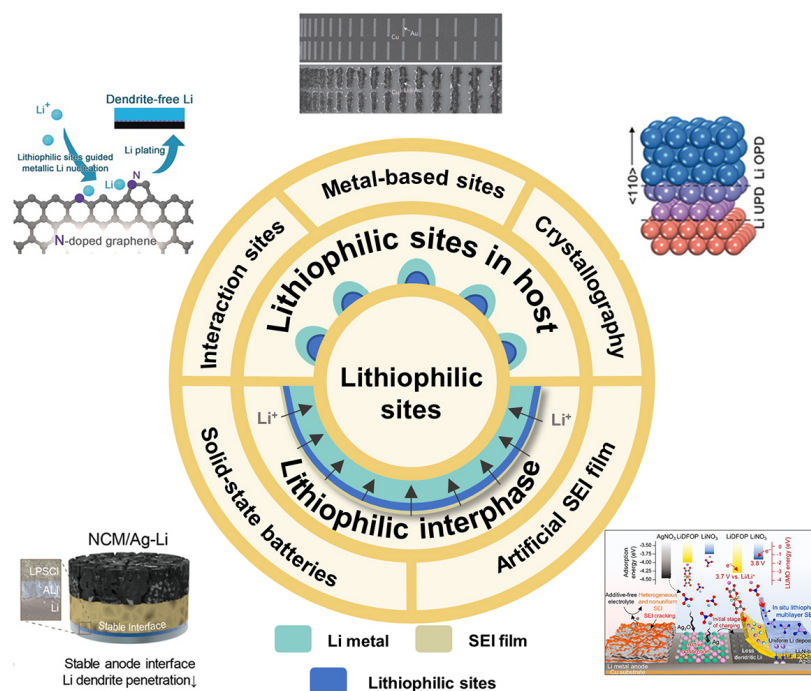
Figure 1. A schematic summary of the application of lithiophilic sites in the lithium host and interphase.

APPLICATION OF LITHIOPHILIC MATERIALS IN HOST

Due to the infinite volume change during the plating/stripping of lithium, the interphase between the electrode and electrolyte withstands sustained destruction and repair, which causes irreversible consumption of electrolyte and deterioration of deposition morphology. Hence, it is sensible to employ structured substrates as stable hosts to accommodate the deposition of lithium. The rational design of hosts can effectively alleviate the volume expansion and stress variation and stabilize the interface between the lithium anode and electrolyte. Therein, 3D hosts with defined structures, such as layered[23,24], arrayed[21,25], spherical[26,27] and porous[28,29] structures, have attracted extensive attention due to the ample inner space to accommodate the deposition of lithium. However, most materials exhibit poor affinity to lithium, resulting in large deposition barriers and high nucleation overpotential. In addition, the uncontrollable deposition of lithium in 3D substrates would cause the accumulation of lithium on top of the host, preventing the entire 3D structure from being utilized. Hence, the lithiophilic modification of substrates is proposed. Many studies have focused on the introduction of lithiophilic sites in substrates to enhance the affinity to lithium, thus uniformizing the deposition of lithium and optimizing the utilization of the 3D structure of hosts. Many kinds of lithiophilic sites, such as metal-based sites, atom-doping sites and crystallography modified sites, have been extensively explored and introduced to construct desirable substrates for lithium deposition. The following discussion of different kinds of lithiophilic sites is helpful in understanding the mechanism and application of lithiophilic materials.

Metal-based lithiophilic sites

Metal-based materials that possess definite solubility in lithium are the most widely employed lithiophilic sites because they can effectively reduce nucleation overpotential and induce selective nucleation of lithium. By forming alloy phases with metal-based sites, the heterogeneous nucleation of lithium can be converted to a selective alloying process, and the nucleation barrier is greatly reduced. Many researchers have explored the lithiophilicity of various metals and introduced them into substrates to induce the uniform deposition of

lithium. Yan *et al.* explored the substrate-dependent deposition of lithium on different metal substrates[26]. They found that the deposition of lithium exhibits no nucleation barriers and negligible overpotential for metals with a definite solubility in lithium such as Au, Ag, Zn, Mg, Al and Pt [Figure 2A], whereas apparent overpotential is observed for metals with little solubility such as Cu, Ni, C, Sn and Si [Figure 2B]. The selective deposition of lithium was also explored. The materials without overpotential (Au strips) were decorated on the substrate with appreciable overpotential (Cu substrate) to observe the selective deposition of lithium. It was found that lithium only deposited on the Au strips rather than the Cu surface, indicating the preferential nucleation of lithium at the lithiophilic metal [Figure 2C]. Based on the selective deposition behavior, they further designed a desirable host by encapsulating lithiophilic seeds (Au nanoparticles) inside hollow carbon spheres and demonstrated commendable cycle performance for lithium metal anode. The low nucleation overpotential and highly selective nucleation of lithium at specific "seeds" is commonly defined as lithiophilicity, which is a promising method to control the deposition of lithium and prevent the generation of dendrites.

Nevertheless, what is the mechanism behind the lithiophilic deposition behavior of lithium? Can lithiophilic metals work at any spatial position on the substrate or continuously work during a prolonged cycle? It is still not well understood how lithiophilic materials work and how they fail. To further explore the essence of lithiophilicity, Pande *et al.* presented a new method to survey potential metal substrates by the free energy of lithium adsorption and lithium surface diffusion barrier on different substrates via density functional theory (DFT) calculations[30]. They proposed that the nucleation overpotential of lithium is determined by the adsorption free energy of lithium on substrates and that further diffusion of adsorbed lithium is determined by the surface diffusion barrier [Figure 2D]. These two processes motivate the deposition behavior of lithium and are conducive to understanding the mechanism behind the selective nucleation of lithium on the lithiophilic sites. Compared with transition metals, lithium alloys exhibit much better lithium nucleation and lithium surface diffusion, thus exerting little nucleation overpotential and desirable lithiophilicity. The authors suggested that the best substrates should possess a lithium adsorption energy close to zero and great surface diffusion, thus, lithium alloys are promising candidates. This provides an in-depth perspective to understand lithiophilicity and guide the screening of lithiophilic metal substrates. However, except for the early regulation of lithium nucleation, the optimization of follow-up lithium growth and repeated plating/ stripping of lithium is also very important. These lithiophilic metals, which can form alloys with lithium, also exhibit different lithiophilic mechanisms during prolonged cycles. Zhang *et al.* found that there is a wide variety of plating/stripping behaviors on different lithiophilic substrates, which is highly dependent on the alloy phase diagram[31]. Although most lithiophilic metals exert definite solubility in lithium, which is the key to their affinity to lithium, the alloying process of these metals can still be divided into two models [Figure 2E]. The substrates (such as Ag and Mg) that only form solid solutions with lithium [Figure 2F] exhibit slight structural variation during the repeated alloying/dealloying process, thus ensuring structural stability and sustaining lithiophilic properties. In contrast, the substrates (such as Au, Al, Zn, Si, and Sn) that form intermetallic compounds with lithium [Figure 2G] can become lithium-saturated, resulting in the invalidation of modulation to the deposition of lithium. Hence, the regulation effect of these lithiophilic metals can only take effect at the early stage of lithium deposition and the late stage of lithium dissolution. In addition, the considerable structural variation and potential overdissolution of lithium could lead to structural collapse during prolonged cycling, leading to undesirable stability and cycling performance. It needs to be emphasized that the materials forming intermetallic compounds with lithium can still be employed as lithiophilic sites combined with host matrixes to regulate the early nucleation of lithium. Based on the reversible solid solution alloy mechanism, Jin *et al.* proposed an innovative Li-Ag alloy anode that shows inward-growth plating of lithium atoms into the metal foil and extraction of lithium atoms inside the metal foil during cycling[Figure 2H], expressing a high reversible capacity of 1,660 mAh g^{-1}[32]. The Li$_{20}$Ag anode displayed an average Coulombic efficiency (CE) of approximately 99.5% for 400 cycles, which is
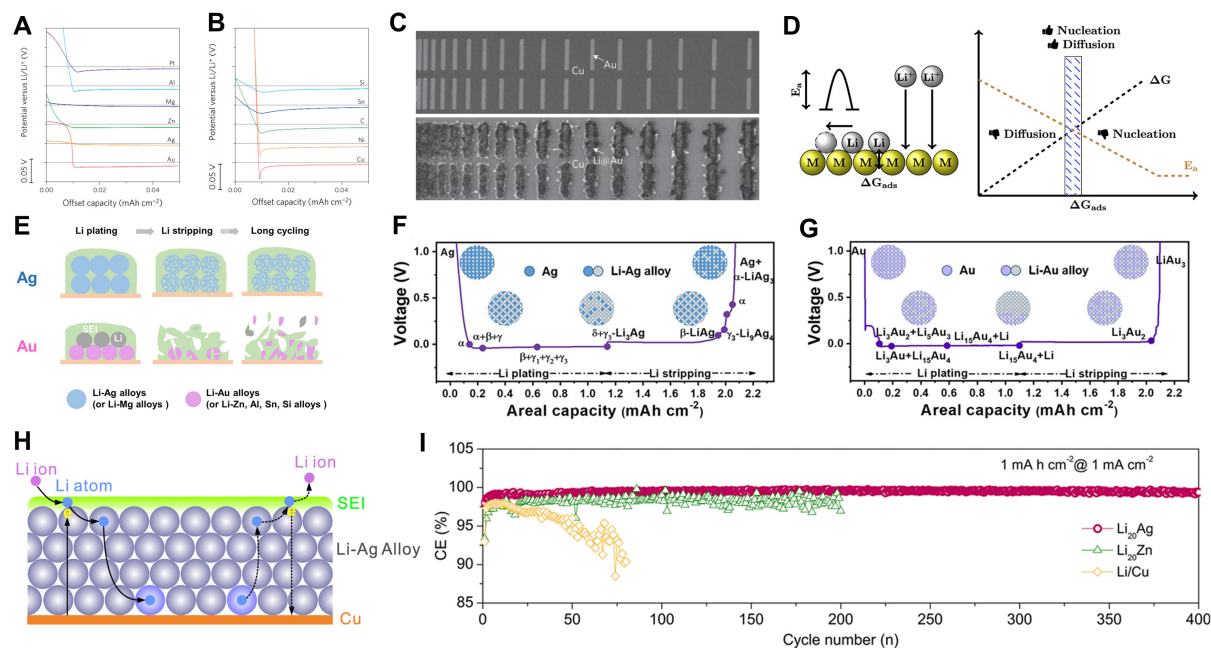
Figure 2. Voltage profiles of substrates with certain solubility in Li (A) and substrates with negligible solubility in Li (B) when Li deposited at a current density of 10 μA cm^{-2}. (C) SEM images of Cu substrate with gold strip arrays before (top) and after (bottom) Li deposition. Reproduced with permission from Ref.[26]. Copyright 2016 Macmillan. (D) The relationship between thermodynamic nucleation overpotential and Li surface diffusion activation energies. Reproduced with permission from Ref.[30]. Copyright 2019 American Chemical Society. (E) The repeated alloying and dealloying behavior of materials that only form solid solutions with lithium (top) and materials that form lithium intermetallic compounds (bottom). The schematic diagram and the corresponding potential profiles of the alloying and dealloying process of Ag@Cu (F) and Au@Cu (G) substrates during the initial lithium plating and stripping at a current density of 0.5 mA cm^{-2}. Reproduced with permission from Ref.[31]. Copyright 2021 American Chemical Society. (H) The schematic diagram of the inward-growth plating of Li atoms into the Li-Ag alloy foil. (I) CE versus cycle number plot of Li$_{20}$Ag, Li$_{20}$Zn, and Cu anode. Reproduced with permission from Ref.[32]. Copyright 2020 American Chemical Society.

much higher than that of its counterparts [Figure 2I]. This provides us with a novel pattern for energy storage for next-generation LMBs. The selective nucleation of lithium on lithiophilic metal sites and the reduction of nucleation overpotential provide us with an effective strategy to optimize the spatial distribution of lithium deposition and facilitate the uniform growth of lithium without dendrites. Combined with various 3D substrates with abundant inner space, the lithiophilic metal sites can induce the deposition of lithium inside the cavity of the substrate, thus maximizing the utilization of inner structure of 3D substrate to accommodate the volume change of lithium during cycling and stabilize the interface.

The intrinsic properties of lithiophilic materials are the foundation of the regulation of lithium nucleation. However, simply using lithiophilic substrates is not sufficient in most cases. The combination of lithiophilic sites and other structured 3D matrixes can maximize the utilization of the commendable regulation function. Hence, the distribution of lithiophilic sites is vital to the architecture of 3D hosts for lithium metal anode. Liu *et al.* manifested that nonuniform lithiophilic sites will result in high local current density, leading to rigorous tip deposition of lithium[33]. Wu *et al.* proposed that the increase in lithiophilic sites density will continuously decrease the nucleation overpotential, while the lithium-ion mobility will weaken in the subsequent lithium plating stage when the lithiophilic sites density further increases[34]. The undesirable distribution of lithiophilic sites in the 3D hosts will also accelerate the failure of lithiophilic sites. Zhan *et al.* revealed the failure mechanism of lithiophilic sites under practical conditions. The failure can mainly be ascribed to the accumulation of "dead" lithium, which covers the lithiophilic sites and blocks the lithium-ion diffusion channels[35]. Nevertheless, the lithiophilic sites can recover once the "dead" lithium is

removed and the sites are exposed again. Hence, the rational design of 3D hosts with uniform distribution and more exposure of lithium sites is vital to the application of lithium metal anode. These findings provide a guideline for the design of lithiophilic 3D substrates.

Carbon materials are the most common 3D host materials for lithium metal anode due to their excellent electronic conductivity, chemical and electrochemical stability, high specific surface area and low density[36]. However, most carbon materials exhibit disappointing affinity to lithium, and it is difficult to deposit lithium inside the inner space of carbon hosts[37], resulting in the disordered accumulation of lithium upon the host. Hence, introducing lithiophilic metal sites in carbon hosts is an effective measure. Many researchers have proposed various strategies to decorate the inside of carbon hosts with lithiophilic sites to enhance their affinity to lithium and induce the inner deposition of lithium inside the carbon matrixes, thus optimizing utilization of the inner space to inhibit the formation of lithium dendrites. Yang *et al.* induced ultrafine Ag nanoparticles as lithiophilic seeds on carbon nanofibers (CNFs) by a facile Joule heating method to direct the deposition of lithium within the 3D matrix[38]. The Ag nanoparticles observably reduced the nucleation overpotential and guided the uniform deposition of lithium in the host, free from dendrites [Figure 3A], while undecorated CNFs as a host resulted in local accumulation of lithium [Figure 3B]. Graphene is widely employed as a carbon matrix for its unique sheet structure, which is convenient to assemble into a specific structure. Many researchers have induced uniform lithiophilic metal particles in designed graphene matrixes as desirable lithium metal anode substrates. Pu *et al.* proposed a sandwich composite anode composed of stacked reduced graphene with uniformly distributed Au nanoparticles (Au NPs)[39]. Because the Au NPS can induce the preferential nucleation of lithium, the uncontrollable lithium deposition upon the layered graphene matrix can be converted to nucleation-guided deposition between the interlayers [Figure 3C and D]. The interlayer lithium plating mode avoids the in-plane distortion of the structure and instead accommodate the plating/stripping of lithium by the through-plane expansion and shrinking. This mechanism can minimize the morphological changes of the interface, thus preventing the destruction of the SEI film during cycling. Due to these advantages, the Au-rGO electrode delivered excellent stability and reversibility with a high CE of up to 98% for at least 200 cycles with a capacity of 2 mAh cm^{-2} for 1,600 h. Liu *et al.* also demonstrated a facile gamma-ray irradiation method to prepare a graphene composite anchored with Ag nanoparticles as a desirable lithium metal anode host which is appropriate for mass production[24].

In addition to carbon materials, lithiophilic sites have also been widely applied to various 3D substrates. Ke *et al.* modified 3D Ni foam skeletons by lithiophilic $AuLi_3$ particles via the lithiation of electrodeposited Au nanoparticles[40]. The $AuLi_3$ particles significantly lowered the nucleation overpotential, induced the uniform deposition of lithium in the void space of foam and suppressed the dendrites [Figure 3E]. Luan *et al.* demonstrated that Sn is also a superior lithiophilic metal that can form a Li-Sn alloy by prelithiation and optimized the plating/stripping behavior of lithium [Figure 3F][41]. The coating of Sn on 3D Cu mesh significantly reduces the nucleation overpotential to 2.8 mV, close to that of Au and Ag. Wang *et al.* further sowed Ag nanowires (Ag NWs) inside the bulk of lithium foil by a calendaring method[42]. The stainless-steel mesh loaded with Ag NWs (Ag@SSM) was rolled and attached to bare lithium foil by polytetrafluoroethylene rods [Figure 3G]. After removing the SSM, the Ag NWs can be sowed into the interconnected ditches inside the lithium foil and form the ditch-patterned and Ag-modified composite lithium anode (D-Ag@Li). The ditches can provide space to accommodate the volume change of lithium during cycling and the Ag NWs can provide lithiophilic sites inside the ditches to induce the uniform nucleation of lithium from the bottom of the patterned ditches [Figure 3H]. The employment of lithiophilic metals can maximize the utilization of the inner space of 3D substrates and maintain the stability of interface, thus facilitating the uniform deposition of lithium.
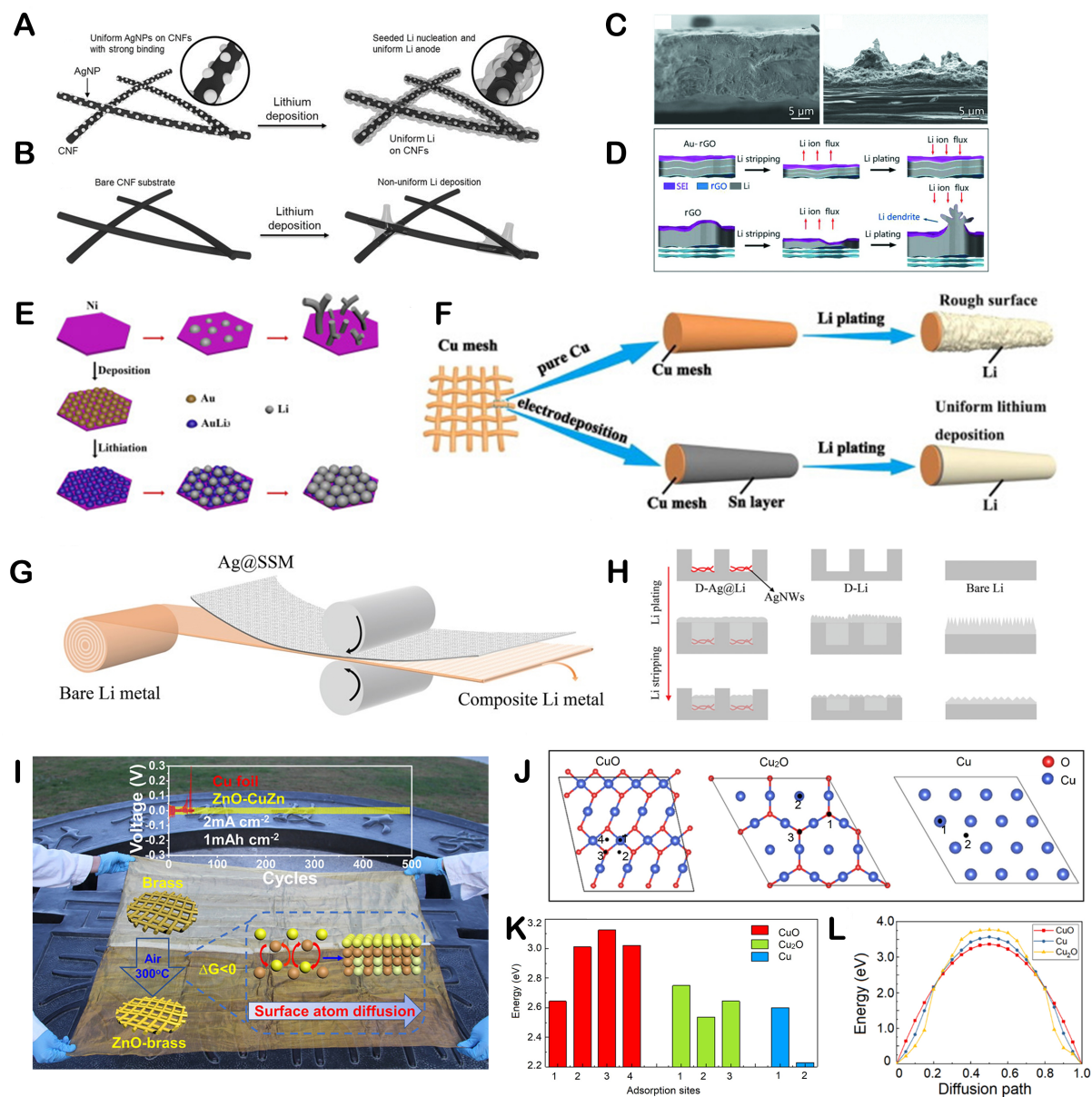
Figure 3. Schematic illustration of the uniform deposition of lithium on CNFs with AgNPs (A) and on bare CNFs without AgNPs (B). Reproduced with permission from Ref.[38]. Copyright 2017 WILEY. (C) SEM images of Au-rGO (left) and rGO (right) after cycling. (D) Schematic diagrams of lithium stripping/plating behaviors of Au-rGO (top) and rGO (bottom). Reproduced with permission from Ref.[39]. Copyright 2018 WILEY. (E) Schematic diagram of the deposition of lithium on the bare Ni foam (top) and AuLi$_3$@Ni foam (bottom). Reproduced with permission from Ref.[40]. Copyright 2019 Elsevier. (F) Schematic illustration of the deposition of lithium on the bare Cu mesh and Sn layer coated Cu mesh. Reproduced with permission from Ref.[41]. Copyright 2020 Elsevier. (G) Schematic illustration of the fabrication process of the D-Ag@Li composite. (H) Schematic illustration of the plating/striping behaviors of D-Ag@Li, D-Li and bare Li. Reproduced with permission from Ref.[42]. Copyright 2021 WILEY. (I) Schematic diagram of ZnO decorated commercial brass mesh and corresponding cycle performance. Reproduced with permission from Ref.[44]. Copyright 2019 American Chemical Society. Schematic diagram of adsorption sites (J) and adsorption energy of single lithium atom at different adsorption sites (K) for CuO, Cu$_2$O and Cu. (L) The migration barrier of Li ions on the surface of Cu (1 1 1), Cu$_2$O (1 1 1) and CuO (1 1 1). Reproduced with permission from Ref.[46]. Copyright 2022 Elsevier.

Due to their structural diversity and convenient processing property, metal-based compounds are increasingly being applied as lithiophilic composites. Many researchers have proposed that many metal inorganics, such as ZnO[43,44], Cu$_x$O[45,46], Co$_3$O$_4$[47,48], Mo$_2$N[49], and AlN[50], exhibit desirable lithiophilicity,

which can also reduce the nucleation barrier and induce uniform deposition. Huang *et al.* construct a uniform lithiophilic ZnO nanoparticles coating on 1 m² commercial brass mesh, which can achieve long-term cycling stability of 500 cycles at 2.0 mA cm⁻² [Figure 3I][44]. Nie *et al.* proposed a facile and scalable method to prepare a Cu_xO (0 < x < 2) based 3D matrix whose composition can be adjusted by controlling the sintering process[46]. They calculated by DFT and nudged elastic band (NEB) that CuO and Cu_2O exhibit higher Li adsorption energy [Figure 3J and K] and lower migration barrier of Li atom [Figure 3L] than Cu, resulting in preferential adsorption, low nucleation overpotential and uniform plating of lithium. Xiong *et al.* proposed a lithiophilic AlN layer by simple blade casting method which can guide the uniform deposition of lithium by the *in situ* formed ionically super conductive Li_3N and lithiophilic Li-Al alloy[50]. Recently, metal-organic frameworks (MOFs)[51] and covalent organic frameworks (COFs)[52] have been applied as alternative lithiophilic materials via functionalization and structuration.

In summary, the nucleation of lithium can be effectively regulated and lithium growth can be further optimized by anchoring metal-based lithiophilic sites in 3D substrates. However, the precise design and choice of lithiophilic materials and their spatial distribution are vital to exert their functions and maintain their stability. Sustained effort is still indispensable to construct ideal substrates with rational lithiophilic sites for practical lithium metal anode.

Local interaction modified lithiophilic sites
Carbon matrixes are the most widely employed host materials for lithium metal anode. However, due to the poor lithiophilicity of common carbon materials, modification is essential to improve their affinity to lithium. Except for adding lithiophilic materials in carbon matrixes, optimizing the local interaction of matrixes to regulate their lithiophilicity nature is also an effective path. Recently, researchers proposed another perspective to clarify the lithiophilicity of carbon materials from optimizing the local interaction of lithium atoms on lithiophilic sites. Lithium will preferentially nucleate at the lithiophilic sites due to the strong adsorption energy, thus regulating lithium nucleation behavior and inhibiting lithium dendrite growth. Hence, atom-doping, which can adjust the interaction with lithium, is considered as a promising lithiophilic site to improve the lithiophilicity of carbon matrixes and regulate lithium nucleation[53,54]. However, the exact mechanism of interaction between lithium and lithiophilic sites is still unrevealed.

Compared with the addition of lithiophilic particles in the carbon matrixes, atom doping can exactly amend the intrinsic property of a stable carbon host, thus providing an ideal model to reveal the mechanism behind lithiophilicity. By exactly adjusting the atomic and electronic structure of non-lithiophilic carbon materials to optimize the interaction between lithium and matrixes, the mechanism and core factors of lithiophilicity can be uncovered. Chen *et al.* investigated the interaction between lithium and carbon matrixes to unveil lithiophilicity chemistry via first-principles calculations and experiments[55]. The Li⁺ driven to the lithiophilic sites could form chemical bonds and be reduced to lithium metal due to charge transfer [Figure 4A]. The binding energy between lithium and substrate was used as the quantitative descriptor of lithiophilicity, and a series of heteroatom-doped graphene nanoribbons (GNRs) were constructed to observe the interaction [Figure 4B and C]. The authors proposed that the lithiophilicity of heteroatom dopes originates from the adjustment to three key factors: electronegativity, local dipole, and charge transfer. Several rules are proposed to create the strong anchoring effect of lithiophilic sites to lithium: (1) The doped atoms should form electronegative sites to interact with Li⁺, and more negative charge state sites could induce stronger interaction with Li⁺; (2) The doped atoms should form strong local dipoles to render strong ionic dipole force and deliver induced dipole around the absorbed Li⁺ to increase the binding energy; (3) Electron-deficient sites or doping atoms with large electronegativity are more recommended to achieve strong interaction because charge transfer above 0.9 e⁻ is imperative. Hence, the O-doping and O/B-co-doping exhibit the best lithiophilicity among single-doped and co-doped carbon, respectively, reflected in the
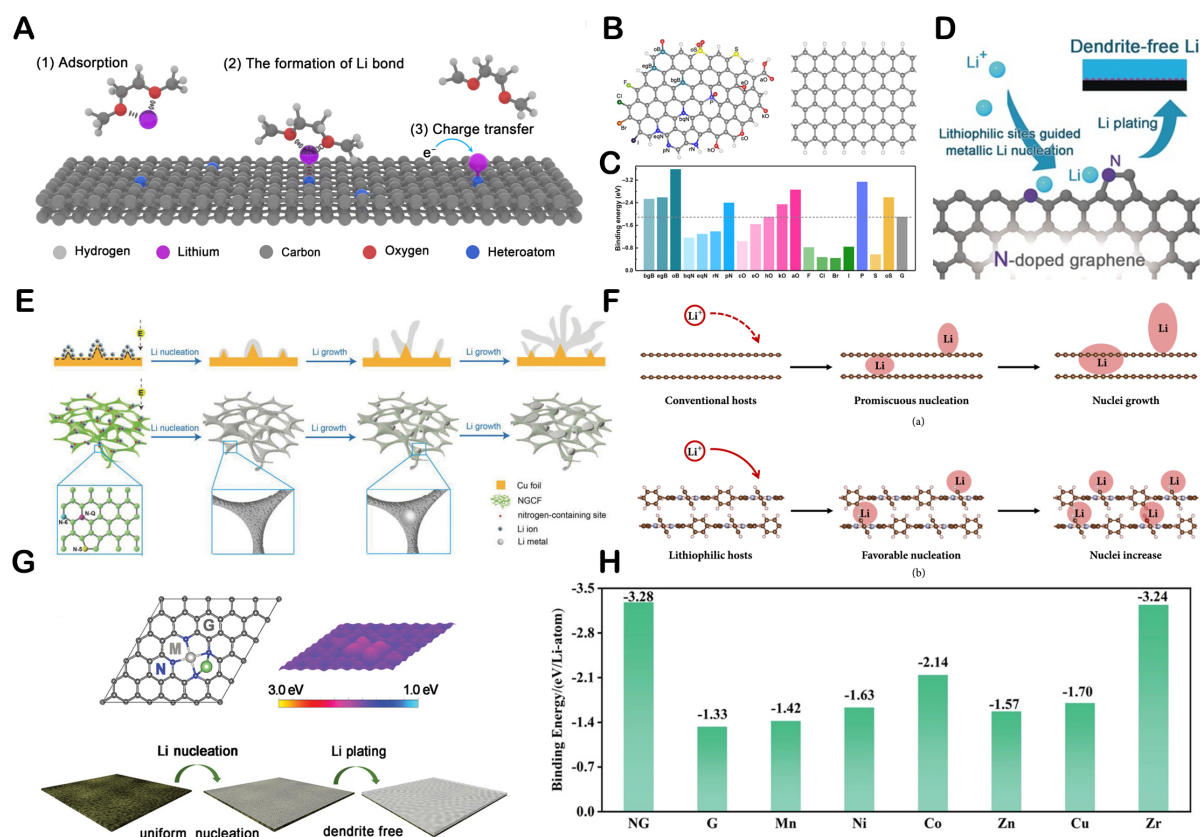
Figure 4. (A) Schematic diagram of the Li nucleation on conductive frameworks. (B) Modeling of heteroatom-doped carbons and pristine GNR model. (C) Summary of calculated binding energy between heteroatom-doped carbon and a Li atom. Reproduced with permission from Ref.[55].Copyright 2019 American Association for the Advancement of Science. (D) Schematic diagram of the Li nucleation and plating process on N-doped graphene substrate. Reproduced with permission from Ref.[57].Copyright 2017 WILEY. (E) Schematic diagrams of the nucleation and growth process of lithium on the Cu foil (top) and NGCF (bottom). Reproduced with permission from Ref.[58].Copyright 2017 WILEY. (F) Schematic of the nucleation of lithium on conventional hosts (top) and lithiophilic hosts. Reproduced with permission from Ref.[60].Copyright 2018 Science & Technology Review. (G) Schematics illustrations of the distribution mappings of Li adsorption energy(top) and corresponding Li nucleation and plating process on SA metal-NG electrode(bottom). Reproduced with permission from Ref.[61].Copyright 2019 Wiley. (H) Binding energy of Li atoms on different substrates including graphene, NG, SAMn@NG, SANi@NG, SACo@NG, SAZn@NG, SACo@NG, and SAZr@NG. Reproduced with permission from Ref.[63].Copyright 2022 WILEY.

reduction of nucleation overpotential and more uniform nucleation distribution. This explanation of the chemical essence of lithiophilic sites enhanced our understanding of lithiophilicity and rendered the potential to promote the lithium affinity of substrates by heteroatom doping strategies. Xie *et al.* designed an O/B-co-doped honeycomb carbon skeleton (OBHcCs) with abundant lithiophilic O- and B-containing functional groups, which can enhance the absorption of carbon skeleton to Li ions due to the high binding energy (-2.23 eV) towards Li atoms[56]. Therefore, the substrate exhibited stable plating/stripping behavior of lithium and improved cycle stability. Zhang *et al.* generated an N-doped graphene matrix with uniform lithiophilic sites to render desirable lithium nucleation [Figure 4D][57]. Herein, nitrogen and pyrrolic nitrogen were dominant nitrogen-containing functional groups that displayed larger binding energies with Li atoms (-4.26 and -4.46 eV, respectively) than Cu (-2.57 eV) and graphene (-3.64 eV). Hence, the N-doping sites can interact strongly with Li atoms, and the stronger Li binding energies always lead to better Li ion adsorption, thus advancing the lithiophilicity of the graphene host. This verified the outstanding lithiophilicity of pyrrole nitrogen and pyridine nitrogen, thus promoting the extended design of chemical structure. Liu *et al.* fabricated *in situ* N-doped 3D graphitic carbon foams (NGCFs) as a lightweight

substrate from environmentally friendly melamine foam[58]. The well distributed N-containing functional groups can induce the uniform nucleation of lithium with a small nucleation overpotential [Figure 4E]. Wen *et al.* further proposed an N-doped carbonized cellulose fiber host fabricated by a bridge reaction of polyacene[59]. In addition to inducing uniform lithium nucleation, the bridging reaction of nitrogen contributes to the desirable mechanical strength and flexibility. Li *et al.* further proposed the precise design of lithiophilic sites with respect to the chemical structure and geometrical position at the atomic level[60]. A framework porphyrin (POF) with precise lithiophilic sites was fabricated as a lithiophilic host, and four electron-rich pyrrolic nitrogen atoms conjugated with the porphyrin units served as precise lithiophilic sites [Figure 4F].

However, the irreversible side reaction between heteroatoms and lithium is inevitable, which will poison the heteroatom-doped lithiophilic sites during long cycles. For instance, due to the strong binding energy between nitrogen and lithium atoms, the carbon-nitrogen bond length undergoes sharp change, and N-doped graphene may react with lithium to form LiN, leading to the loss of active sites[61]. A promising solution is introducing single metal atoms in the matrixes to form $M-N_x-C$ sites and moderate the binding energy, thus enhancing the stability of the atomic structure. In addition, the single metal atoms can also act as lithiophilic sites without side reactions with lithium, which can maximize the atomic efficiency of metal atoms compared to metal nanoparticles or oxides[62]. Zhai *et al.* reported the introduction of single metal atoms (Ni, Pt, Cu) into N-doped graphene matrixes as lithium deposition hosts[61]. The high-density and isolated metal atoms can coordinate with nitrogen atoms and increase the local adsorption energy of lithium atoms around metallic atoms with a moderate adsorption energy gradient, thus alleviating the damage to atomic structure and inducing the uniform deposition of lithium during long cycles [Figure 4G]. Thereafter, they developed a universal and controllable method to prepare six kinds of metal atom-anchored N-doped graphene (SAM@NG, M = Mn, Ni, Co, Zn, Cu, or Zr) to explore the mechanism of different single metal atoms to regulate the nucleation of lithium via experiments and DFT calculations [Figure 4H][63]. The weak binding interaction between graphene and lithium atoms will lead to uncontrollable dendrite deposition of lithium, while moderate binding strength between SAM@NG and lithium can induce the uniform nucleation of lithium. However, higher binding energy does not always indicate better performance. The NG and SAZr@NG, which show the highest binding energy (-3.28 eV and -3.24 eV, respectively), represented dissatisfactory performance because the excessive binding interaction can result in destruction of the structure. This provides a reference to regulate the lithiophilicity of carbon hosts by atom doping. Huang *et al.* proposed an ordered mesoporous N-doped carbon with lithiophilic single atoms as a lithium anode host and expressed desirable cycle performance for the abundant lithiophilic single-atom sites[64].

In summary, atom-doping strategies provide a microscopic perspective of lithiophilicity from the atomic interaction between lithiophilic sites and lithium. This can directly improve the intrinsic lithiophilicity of carbon matrixes without introducing extra particles, which is beneficial for the construction of lightweight carbon matrixes and avoiding the nonuniform distribution of lithiophilic sites. The key is to rationally adjust the binding energy of lithiophilic sites to absorb the lithium ion for uniform nucleation while simultaneously avoiding the destruction of structure.

Crystallography modified lithiophilic sites
The nucleation and growth of lithium is intrinsically an electrocrystallization process, and the crystal orientation will dramatically affect the final morphology[65]. Recently, many researchers have attempted to depict lithiophilic issues from a crystallography viewpoint and regulate the crystallization process of lithium by optimizing the crystallographic parameters of substrates, such as lattice structure and defection. By customizing the crystal orientation of substrates to promote the degree of lattice matching between lithium

and substrates, lithium ions can accumulate with ordered lattice structures during nucleation[66]. In addition, the optimized crystal structure of substrates can reduce the surface energy barrier[67] and promote rapid lithium diffusion[68]. By optimizing the crystallographic structure of substrates, the intrinsic lithiophilicity can be improved to facilitate the oriented nucleation and growth of lithium.

The electrodeposition of metal ions on dissimilar metal substrates is usually preceded by underpotential deposition (UPD)[69]. Under conditions of greater metal-substrate interaction than metal-metal interaction, one to two metal monolayers will form at potentials positive to the equilibrium potential of the metals. The lattice structure of UPD monolayers has a strong correlation with the surface structure of the substrate, and the monolayers will further influence the subsequent crystal orientation of the deposited lithium bulk. For lithium with bbc crystal structure, the < 110 > plane has the densest accumulation of atoms because of the lowest surface energy according to the broken bond model[65,70]. Hence, the UPD monolayers of lithium with (110) lattice plane would guide the subsequent deposition of lithium bulk along the most stable < 110 > direction. Gu *et al.* reported the crystallography design of Cu substrate and explored the lithiophilicity of Cu surfaces with different preferred lattice faces[66]. The cyclic voltammograms (CVs) present the UPD phenomenon of lithium on Cu(111) and Cu(100) planes [Figure 5A], reflecting the strong electronic interaction between Li and Cu [Figure 5B]. Meanwhile, the initial potential of lithium deposition on Cu(100) substantially precedes that on Cu(111) [Figure 5A], indicating its better affinity to lithium. In addition, the Cu(100) surface with fine lattice matching with lithium can induce the deposition of lithium along < 100 > direction via the guidance of Li(110) oriented Li UPD layer [Figure 5C]. Furthermore, an electrochemical method was established to facet the commercial Cu substrate for exposing the lithiophilic (100)-preferred orientations. The modification of surface lithiophilicity can induce the ordered deposition of lithium and facilitate the utilization of 3D cavities without additional lithiophilic materials. Bao *et al.* introduced an orientation-preferred Cu coating on the substrate by magnetron sputtering[71]. Thanks to the excellent interface-crystal plane matching between Cu(100) plane and lithium, the coating layer exhibits commendable surface lithiophilicity and enhanced interface kinetics to facilitate the uniform nucleation and stable growth of lithium [Figure 5D]. Kim *et al.* reported a novel silver-assisted chemical vapor deposition graphene growth method to prepare a wrinkled Cu substrate with a highly preferred (100) plane [Figure 5E][72]. The wrinkled surface can facilitate uniform Li+ flux and the uniform (100) facet provides an equalized Li adsorption energy, thus promoting the uniform deposition of lithium without dendrites. The optimization of the crystallographic structure of carbon materials has also been explored for the construction of lightweight lithium metal anode hosts. The defects introduced into carbon matrixes are always thought to be lithiophilic, which can induce the nucleation of lithium. Mukherjee *et al.* proposed porous graphene networks as hosts with abundant defects that can act as seed points to induce the inner nucleation of lithium [Figure 5F][73]. DFT calculations demonstrated that defects are the most favorable sites for lithium adsorption which can induce the preferential nucleation of lithium [Figure 5G]. Chae *et al.* reported that high-density Ti vacancy defects in the crystal lattice of MXene films can dramatically enhance the lithiophilicity and reduce the nucleation barrier to induce the uniform nucleation of lithium and guide lithium growth [Figure 5H][74]. Nevertheless, the indiscriminate increase in the number of defects in matrixes is not rational. Liu *et al.* determined that highly defective graphene will result in unstable growth of SEI film and accelerate the consumption of fluoroethylene carbonate (FEC) additive in electrolyte, leading to the rapid decay of CE and formation of dendrites[75]. Zhang *et al.* also manifest that the reduction in the density of defects in graphene will also facilitate the desirable electrochemical performance of graphene matrixes as lithium metal anode[76]. The existence of defects is vital to the lithium-ion storage capacity. The regulation of defects in carbon matrixes to balance cycle stability and capacity utilization is the key to construct carbon substrates.
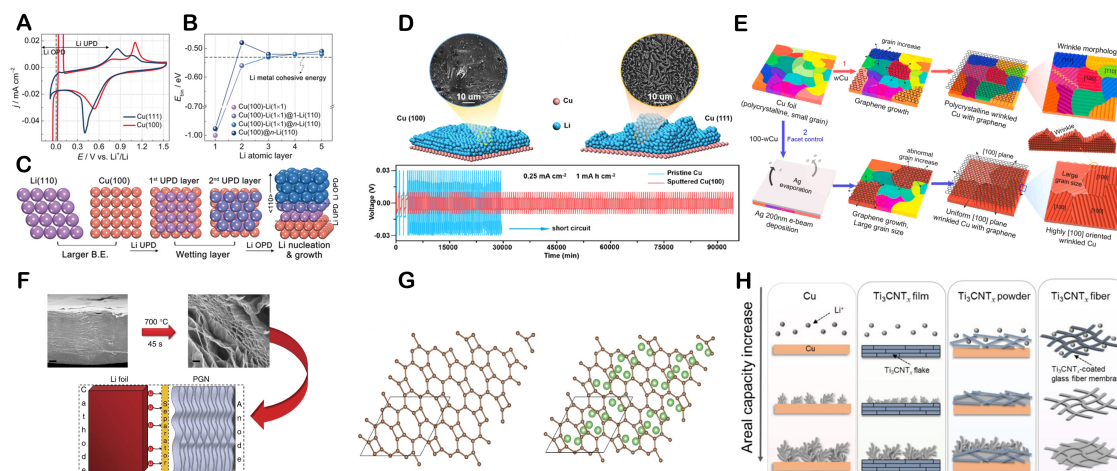
Figure 5. (A) CV diagrams of Cu(111) and Cu(100) electrodes. (B) Binding energy of Li UPD on Cu. (C) Schematic diagrams of the formation of Li UPD layers and the nucleation and deposition of bulk lithium with specific crystallographic orientation. Reproduced with permission from Ref.[66].Copyright 2018 WILEY. (D) Schematic diagrams of the deposition of lithium on substrates sputtered with different orientation-preferred Cu coating (top) and corresponding cycle performance (bottom). Reproduced with permission from Ref.[71].Copyright 2022 American Chemical Society. (E) Schematic illustration of the synthesis of wrinkled Cu. Reproduced with permission from Ref.[72].Copyright 2020 Elsevier. (F) Schematic diagram of the preparation of GO paper by means of thermal shock. (G) Theoretical calculation of the defect-induced nucleation of lithium in graphene. Reproduced with permission from Ref.[73].Copyright 2014 Macmillan. (H) Schematic illustration of deposition process of lithium on Cu, Ti_3CNT_x film, Ti_3CNT_x powder, and Ti_3CNT_x fiber membrane. Reproduced with permission from Ref.[74].Copyright 2022 Elsevier.

The crystallography modification of substrates provides an innovative perspective to regulate the crystallographic process of lithium and is helpful in deepening our understanding of the functional mechanism of lithiophilic sites.

The introduction of lithiophilic sites in a 3D host can effectively convert the chaotic and loose lithium deposition to uniform and compact lithium deposition. The strong regulation function of lithium sites can be ascribed to alloy reaction, strong adsorption to lithium, low diffusion barrier, and lattice matching. Combing with the high specific surface area of 3D host, which can reduce the local current density, the reversible plating/stripping of lithium with high CE can be achieved. The representative lithiophilic sites, combing with the host, and corresponding electrochemical performance are summarized in Table 1.

APPLICATION OF LITHIOPHILIC MATERIALS FOR STABLE INTERPHASE

Lithiophilic interphase is used to pre-construct a stable and strong protective layer on the lithium metal anode or current collector surface. The rapid ion transmission kinetics of the lithiophilic interphase can play a positive role in achieving uniform lithium deposition, and its high oxidation resistance to the electrolyte is beneficial for building a stable electrode-electrolyte interphase[77,78]. Compared with traditional electrode-electrolyte surfaces, lithiophilic interphases have higher ion conductivity and faster Li+ transmission rate, and are helpful in promoting uniform lithium deposition[79,80]. Most lithophilic interphases come from lithiophilic metal metals, lithium-lithiophilic metal alloys, and some carbon-based materials.

Metal-based lithiophilic interphase

For the lithiophilic metal interphase, the lithium deposited early will react with the lithiophilic metal to form an alloy. Later, further lithium deposition on the lithiophilic alloy interphase will be more uniform, thereby inhibiting the growth of lithium dendrites. An even lithium deposition will induce stable SEI film formation on the lithium metal surface and allow a stable electrode-electrolyte interphase to be successfully built. Because lithiophilic metals such as Zn, Mg and Al are relatively active and easily oxidized to form a

Table 1. Electrochemical performance of lithiophilic host in half cells

Host type	Lithiophilic sites	Electrolyte	Current density/capacity	CE/cycle life	Reference
Carbon shell	Au NPs	1.0 M LiPF$_6$ in EC/DEC, with 1 wt% VC and 10 wt% FEC	0.5 mA cm^{-2}/1 mAh cm^{-2}	98%/300 cycles	[26]
Cu foil	Ag NPs	1 M LiTFSI in DOL/DME, with 1 wt% LiNO$_3$	0.5 mA cm^{-2}/1 mAh cm^{-2}	250 cycles	[31]
Li$_{20}$Ag	Ag NPs	1 M LiTFSI in DOL/DME	1 mA cm^{-2}/1 mAh cm^{-2}	99.5%/400 cycles	[32]
Pillared reduced graphene oxide	Au NPs	1 M LiTFSI in DOL/DME, with 1 wt% LiNO$_3$	0.5 mA cm^{-2}/2 mAh cm^{-2}	98%/200 cycles	[39]
Ni foam	AuLi$_3$	1 M LiTFSI in DOL/DME, with 1 wt% LiNO$_3$	0.5 mA cm^{-2}/1 mAh cm^{-2}	100%/98 cycles	[40]
Cu mesh	Sn layer	1 M LiTFSI in DOL/DME, with 1 wt% LiNO$_3$	1 mA cm^{-2}/1 mAh cm^{-2}	96.6%/150 cycles	[41]
Brass mesh	ZnO	0.6 M LiTFSI in DOL/DME, with 0.4 wt% LiNO$_3$	1 mA cm^{-2}/1 mAh cm^{-2}	97.48%/100 cycles	[44]
Cu foam	Cu$_x$O (0 < x < 2)	1 M LiTFSI in DOL/DME, with 2 wt% LiNO$_3$	1 mA cm^{-2}/1 mAh cm^{-2}	97.7%/300 cycles	[46]
Cu foil	AlN	1 M LiTFSI in DOL/DME, with 2 wt% LiNO$_3$	1 mA cm^{-2}/1 mAh cm^{-2}	98.5%/300 cycles	[50]
Honeycomb carbon skeleton	O and B co-dopes	1 M LiTFSI in DOL/DME, with 1 wt% LiNO$_3$	1 mA cm^{-2}/1 mAh cm^{-2}	97.3%/150 cycles	[56]
Graphene matrix	N dopes	1 M LiTFSI in DOL/DME, with 5 wt% LiNO$_3$	1 mA cm^{-2}/1 mAh cm^{-2}	98%/200 cycles	[57]
Graphitic carbon foams	N dopes	1 M LiTFSI in DOL/DME, with 2 wt% LiNO$_3$	2 mA cm^{-2}/2 mAh cm^{-2}	99.6%/300 cycles	[58]
Framework porphyrin	Pyrrolic nitrogen atoms	1 M LiTFSI in DOL/DME, with 5 wt% LiNO$_3$	1 mA cm^{-2}/1 mAh cm^{-2}	98%/300 cycles	[60]
Nitrogen-doped graphene	SANi-N$_x$-C sites	1 M LiTFSI in DOL/DME, with 1 wt% LiNO$_3$	0.5 mA cm^{-2}/1 mAh cm^{-2}	98.45%/250 cycles	[61]
Nitrogen-doped 3D graphene	SAMn-Nx-C sites	1 M LiTFSI in DOL/DME, with 2 wt% LiNO$_3$	1 mA cm^{-2}/1 mAh cm^{-2}	99%/290 cycles	[63]
Cu foam	Cu(100) face	1 M LiTFSI in DOL/DME, with 2 wt% LiNO$_3$	0.5 mA cm^{-2}/1 mAh cm^{-2}	99%/400 cycles	[66]
Cu foil	Cu(100) face	1 M LiPF$_6$ in EC/DEC	0.25 mA cm^{-2}/1 mAh cm^{-2}	98.6%/200 cycles	[71]
Wrinkled copper	Cu(100) face	1 M LiPF$_6$ in EC/DEC, with 1% VC and 10% FEC	0.5 mA cm^{-2}/1 mAh cm^{-2}	99%/250 cycles	[72]
(Ti$_3$CNT$_x$)-MXene-based fiber	Ti and Ti vacancy defects	1 M LiPF$_6$ in EC/DMC	1 mA cm^{-2}/1 mAh cm^{-2}	99%/1,000 cycles	[74]

passivation layer that hinders their alloying reaction with lithium, the primary lithiophilic metals used are Ag[32,81-83] and Au[31,84], which are more chemically stable than others. Guo *et al*. used a simple displacement reaction to cover a lithiophilic Ag layer directly on the lithium surface[82]. The Ag layer not only protects lithium metal but also allows lithium to grow uniformly. Then, pronounced lithium deposition in a spherical or columnar shape rather than a dendrites morphology was observed on the anode [Figure 6A]. Kim *et al*. used AgNO$_3$ as an additive to the ether electrolyte [Figure 6B][81]. As a single molecule, AgNO$_3$ has the lowest LUMO value and adsorption energy in the electrolyte system [Figure 6C]. Thus Ag$^+$ can be preferentially reduced to Ag, which directly acts as the lithiophilic interphase of the lithium metal anode. Qian *et al*. applied the lithiophilic atomic layer of Au on a 3D MXene substrate by ion sputtering to provide sufficient nucleation sites for lithium metal [Figure 6D][84]. The Au layer can reduce the lithium nucleation overpotential and promote uniform lithium deposition. The Li$_x$Au alloy layer, which was formed by the alloying reaction between Au and deposited lithium, can act as a more stable lithiophilic interphase, further promoting uniform deposition and stable circulation of the lithium metal anode. In conclusion, a lithiophilic metal layer can realize uniform deposition by promoting lithium nucleation.
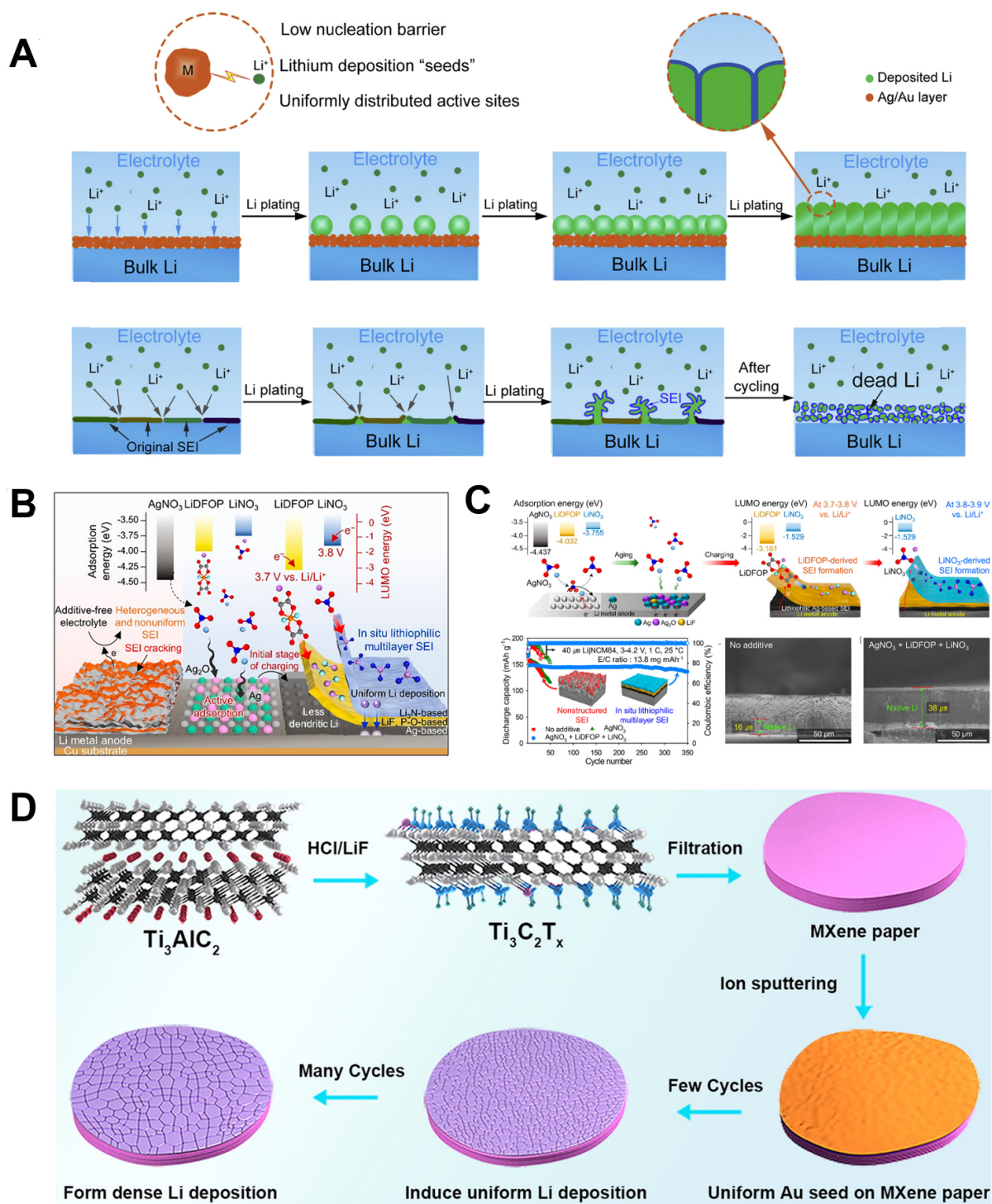
Figure 6. (A) Schematic diagrams of the deposition process of lithium on the Ag (Au)-Li anode and pristine Li anode. Reproduced with permission from Ref.[82].Copyright 2020, Elsevier. (B) Schematic diagrams of the formation of lithiophilic multilayer SEI film on Li metal anode (C) Adsorption energy, LUMO and HUMO, electrochemical cycle performance and cross-sectional SEM images of the Li metal anodes with and without AgNO$_3$@LiDFOP@LiNO$_3$ additive. Reproduced with permission from Ref.[81].Copyright 2022, American Chemical Society. (D) Schematic diagram of the deposition behavior of lithium on Cu foil and MXene@Au paper. Reproduced with permission from Ref.[84].Copyright 2021, Elsevier.

However, the electronic conductivity of metal elements hinders Li$^+$ penetration. This will create the risk of lithium loss caused by the deposition of lithium metal directly on the lithiophilic interphase. The effect of active lithium loss caused by the metal layer forming an alloy with lithium on the CE of previous cycles also cannot be ignored[80]. The large volume change from the alloying reaction is also very unfavorable for building a stable electrode-electrolyte interface[85].These problems are unavoidable for lithiophilic metal interphase layers, and more research will be focused on solving these questions.

The employment of a lithiophilic alloy interphase has been widely explored because it essentially omits the step of an alloying reaction between lithium and lithiophilic metal elements. This means that a corresponding lithium-lithiophilic metal alloy layer on the lithium metal or current collector surface was directly formed to promote even lithium deposition. A lithiophilic alloy interphase can prevent the consumption of active lithium caused by the alloying reaction and effectively improve the CE of LMBs. By introducing an alloy layer directly into the anode, the number of viable material choices would increase, such as lower-cost Zn[86-88], Mg[31], and Al[89,90], which have been used in many situations. Ag and Au, which have excellent lithiophilic properties, are also still widely used[83,91]. The introduction of Sn[92], Sr[93], Bi[94] and In[95] into lithium metal anodes has also been shown. Liu *et al.* formed a Li-Zn alloy layer on the lithium metal surface as an artificial inorganic SEI layer by zinc trifluoromethanesulfonate dissolved in tetrahydrofuran directly reacting with lithium [Figure 7A][86]. Then, a flexible organic SEI layer was further generated on the inorganic Li-Zn alloy by an electrochemical method to protect the lithium metal anode. Tang *et al.* first introduced a B skeleton in the lithium metal as an excellent skeleton to help transport Li$^+$[89]. Then carbon was mixed on the skeleton to improve its mechanical properties. Finally, Al was introduced to provide vast nucleation sites for lithium metal [Figure 7B]. Lithium showed an even deposition morphology on this structural lithiophilic alloy anode. By the substitution reaction of silver trifluoromethanesulfonate with lithium metal, a strong Li-Ag alloy layer was constructed on the Cu foil collector to induce uniform lithium deposition and further form a stable SEI to help establish LMBs with a long cycle lifespan [Figure 7C]. The Li-Ag layer exhibits excellent Li$^+$ transmission performance, resulting in uniform lithium nucleation and growth. Due to FEC as an additive, a uniform and stable LiF layer that can further accelerate the transmission of Li$^+$ was built on the homogeneous lithium surface[91]. Lithiophilic Li-Sn alloys were also used on the lithium metal anode. Du *et al.* deposited a Sn layer on Cu foil current collector, and then, liquid lithium was coated on the Sn layer to obtain a Li-Sn alloy[92]. Lithium showed complete infiltration, and a rapid alloy reaction occurred quickly between the molten lithium and Sn layers [Figure 7D]. The Li-Sn alloy provides a uniform and fast ion transmission channel for Li$^+$, thus, Li$^+$ can quickly penetrate the alloy layer for deposition, which promotes uniform lithium deposition and creates a protective layer of lithium metal [Figure 7E]. Compared with the pure metal layer, the lithium-lithiophilic alloy interphase avoids problems such as unstable interfaces and active lithium loss caused by alloying reactions. Because the electronic conductivity of the alloy layer still exists, it is hard to ensure that Li$^+$ is completely permeable into the interface layer. However, the alloy layer still plays a positive role in reducing the lithium nucleation overpotential and promoting uniform lithium deposition. Meanwhile, the rapid ion transmission rate of the alloy layer helps to inhibit lithium dendrite generation. Future research can focus on reducing the electronic conductivity of the interfacial layer without lowering the transmission rate of Li$^+$ to suppress direct lithium deposition on the interphase.

Carbon-based lithiophilic interphases
Carbon-based materials such as carbon nanospheres[96], carbon nanotubes[97-99] and graphene[100,101] have a large number of lithiophilic sites. Abundant lithiophilic sites can facilitate lithium nucleation and avoid dendrites problems. These materials not only provide sufficient space for lithium metal deposition, but also show strong compatibility with lithium metal. Zheng *et al.* constructed a lithiophilic carbon nanosphere layer on Cu foil to serve as an artificial SEI layer [Figure 8A][96]. Since carbon nanospheres provide a fast
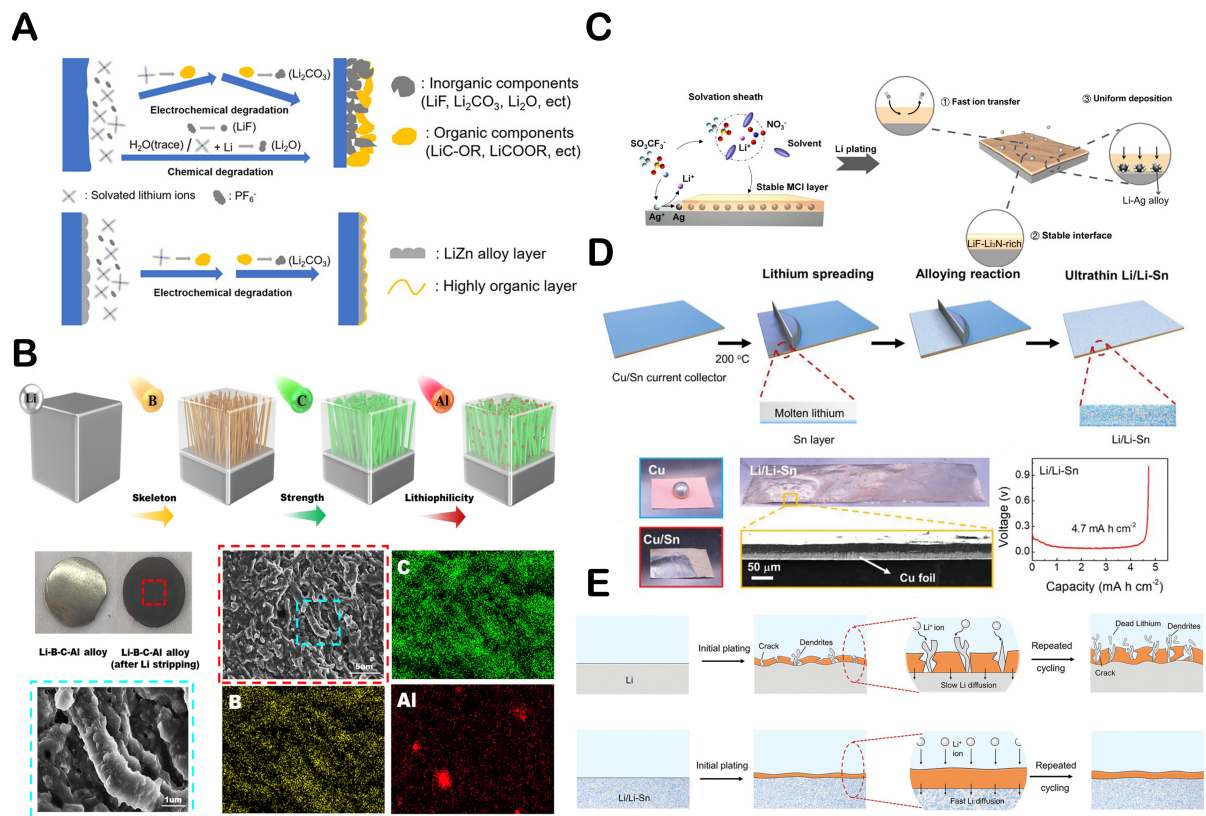
Figure 7. (A) Formation process of common mosaic SEI film and heterojunction-type SEI film. Reproduced with permission from Ref.[86]. Copyright 2022, American Chemical Society. (B) Schematic diagram of the design concept of the 3D Li-B-C-Al alloy and EDS mapping of the Li-B-C-Al alloy. Reproduced with permission from Ref.[89]. Copyright 2022, Wiley. (C) Illustration of the formation and effects of MCI layer on Li metal anode protection. Reproduced with permission from Ref.[91]. Copyright 2022, Elsevier. (D) Schematic of the fabrication of ultrathin Li/Li-Sn electrode and digital photos of molten Li on Cu foil and Sn-coated Cu foil at 200 °C. (E) Schematic illustration of plating/stripping behaviors of bare Li and Li/Li-Sn electrode. Reproduced with permission from Ref.[92]. Copyright 2021, Wiley.

transmission path, Li^+ can be uniformly transported into the interphase. The fast Li^+ transmission promotes uniform lithium deposition at the bottom of nanosphere layer while maintaining the integrity of the SEI [Figure 8B]. The carbon nanosphere substrate exhibited a lower nucleation overpotential than Cu current collector. Meanwhile, it also showed a higher CE and longer cycle lifespan than Cu foil in the electrochemical performance comparison. In another study, a Li-rGO structural anode was obtained by absorbing molten lithium into a lithiophilic rGO. Lithium exhibited excellent wettability in the rGO layer [Figure 8C]. The Li-rGO anode shows excellent flexibility due to lithium metal infiltration. This ductile structural anode can effectively overcome the volume change during the deposition/stripping of lithium and inhibit dendrite generation to obtain long lifespan LMBs[100]. Wang *et al.* used metallurgical techniques to prepare a structural Li-CNTs anode by directly coating carbon nanotubes with molten lithium[102]. The powerful driving force of molten Li into the CNTs network to form a uniform metallic layer comes from favorable thermodynamic and kinetic conditions [Figure 8D]. This work demonstrates a valuable concept in the fabrication of lithium metal anodes toward LMBs, progressing the development of highly functional toward LMBs. In general, when carbon-based materials are directly used as a stable lithophilic interphase, they can effectively promote the penetration of Li^+ and uniform lithium deposition. The huge volume change during lithium plating/stripping is an enormous challenge for carbon-based layers. This requires the lithiophilic layer to exhibit strong flexibility while having excellent Li^+ conductivity. In addition, 3D or layered lithiophilic carbon-based materials can form lithophilic structured anodes after dissolving a certain
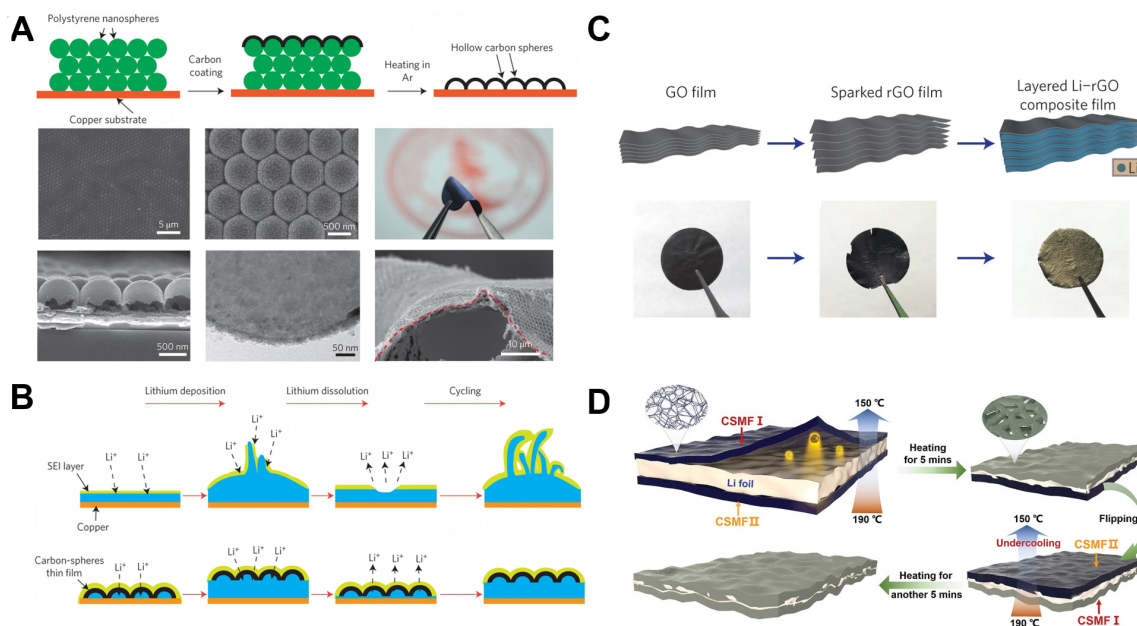
Figure 8. (A) Fabrication process for the hollow carbon nanosphere-modified Cu electrode and SEM images of the carbon-coated polystyrene nanoparticle array. (B) Schematic illustration of the Li deposition process on the pristine Li anode and hollow-carbon-nanosphere coating anode. Reproduced with permission from Ref.[96]. Copyright 2014, Springer nature. (C) Schematic of the synthetic procedures of layered Li-rGO composite film (top) and corresponding digital camera images of the GO film, sparked rGO film and layered Li-rGO composite film (bottom). Reproduced with permission from Ref.[100]. Copyright 2016, Springer nature. (D) Schematic of the preparation of structural Li-CNTs by metallurgical techniques. Reproduced with permission from Ref.[102]. Copyright 2020, Wiley.

amount of lithium, where it is important for lithium to make full use of the substrate space. This means that lithium should be preferentially deposited from the bottom of the substrate material, and then slowly fill the entire substrate space.

Because the lithiophilicity of pristine carbon materials is very poor, the Li deposition behavior in carbon materials is uncontrollable and lithium tends to deposit onto the carbon layer. This will lead to unstable interphase evolution and continuous electrolyte consumption due to the high reactivity of lithium to electrolyte. Hence, the ideal lithium should deposit beneath the carbon layer ideally, and the upper carbon layer can act as a stable interphase to form desirable SEI film. In order to achieve uniform lithium deposition inside carbon materials, in addition to the method described above, introduction of lithiophilic metal particles inside the 3D carbon structure is also a good way to improve their lithophilic. However, more advances are needed to achieve this kind of lithium deposition.

LITHIOPHILIC INTERPHASE IN SOLID-STATE BATTERIES

With the rapid development of several oxide/sulfide-based solid-state electrolytes (SSEs) that exhibit desirable ionic conductivity, the employment of lithium metal anode combined with SSEs is considered a promising energy storage system[103,104]. However, the huge interfacial resistance between solid electrolyte and lithium metal anode makes it difficult to achieve efficient Li$^+$ transmission, resulting in an unstable electrode-electrolyte interface and dendrite generation. Hence, it is necessary to introduce a lithiophilic interphase with high Li$^+$ conductivity to promote uniform lithium deposition and improve the stability between anode and solid electrolyte. A common method is to introduce lithiophilic material into lithium metal anode. The lithiophilic properties are used to control the growth direction of lithium and improve the electrochemical properties of LMBs. Choi *et al.* used roller pressing to bond lithium foil and Ag foil together

to form a Li-Ag alloy, which was treated as an interphase in solid-state batteries [Figure 9A][105]. The Li-Ag alloy layer is beneficial to alleviate the uneven lithium deposition, maintain a stable anode-electrolyte interface and promote the reversible plating/stripping of lithium metal [Figure 9B]. Lu *et al*. constructed an Al_4Li_9 alloy layer on the lithium metal anode[106]. Due to the considerable gradient penetration of Al metal, an Al-rich interface was spontaneously formed between anode and LLZO electrolyte [Figure 9C]. The Li-Al alloy, which has a positive effect on improving the contact between anode and garnet electrolyte, exhibits a stable electrode-electrolyte interface and lower interfacial resistance. A 2D lithiophilic boron nitride nanosheets (BNNS) layer was compounded into lithium metal anode[107]. Li_3N formed by the reaction between BN and lithium can prevent the direct electronic contact between anode and electrolyte, which results in inhibiting lithium dendrite generation and increasing the cycle lifespan of LMBs [Figure 9D]. Another way to achieve this result is to enhance the infiltration between lithium metal and electrolyte by introducing a lithiophilic interphase on the anode side of the solid electrolyte. A lithiophilic zinc oxide (ZnO) layer was introduced onto the garnet solid electrolyte surface[108]. ZnO greatly enhances the infiltration of lithium on the electrolyte surface, which fills the gaps in the middle of the garnet with lithium metal [Figure 9E]. The ZnO layer also reduces the interfacial resistance between electrolyte and anode to approximately 20 Ω cm^{-2}, effectively promoting the transmission of Li^+ at the interphase. Duan *et al*. proposed a strategy to enhance the contact between lithium and solid electrolyte by introducing treated copper foam (TCF) into the electrolyte surface [Figure 9F][109]. TCF allows the molten lithium to be fully immersed in the electrolyte and reduces the interfacial resistance to 9.8 Ω cm^2, and the all-solid-state lithium-sulfur battery was able to achieve more than 1,000 cycles. In summary, the introduction of a lithiophilic interphase in solid batteries has great significance in improving the speed of Li^+ transmission, reducing the interfacial resistance, and achieving stable cycling for all-solid LMBs.

Except for optimizing lithium deposition behavior, the introduction of lithiophilic interphase can further improve the interfacial properties. Stable lithiophilic interfaces can not only suppress parasitic reactions between electrolyte and lithium anode, but also inhibit dendrites growth by mechanical strain. This is beneficial to the stability in a long cycle. Table 2 summarizes the electrochemical performance of different lithiophilic interphases.

CONCLUSION AND OUTLOOK

LMBs will play an important role in next-generation batteries that will help meet the increasing demand for electronic devices with high energy density and energy storage systems for renewable energy sources. However, the uncontrollable deposition of lithium can result in the generation of dead lithium and dendrites, which will cause low CE, poor cycle stability and even potential security concerns. The infinite volume changes of lithium anode during cycling will also lead to the repeated destruction/repair of SEI film, thus preventing the interface from stabilizing and further deteriorating the deposition behavior of lithium. To address these problems, the disordered deposition of lithium should be converted to a highly directed process to facilitate the uniform deposition of lithium and stable interphase. According to the heterogeneous nucleation model, the deposition of lithium on substrates is proceeded by nucleation, which will strongly dictate the subsequent growth process and final morphology. Hence, the introduction of lithiophilic materials is proposed as a promising strategy to address the intractable hindrances of practical LMBs because the nucleation of lithium can be converted to a highly induced process by lithiophilic sites. Combined with the rational design of 3D skeleton as hosts and artificial SEI film as interphases, the deposition of lithium can be well modulated for desirable cycle performance and security of lithium metal anode. The implementation of lithiophilic sites can be divided into the following two main points:

Table 2. Electrochemical performance of lithiophilic interphase in symmetric cells

Lithiophilic interphase	Electrolyte	Current density/capacity	Cycle life	Overpotential (last cycle)	Reference
metal Ag	1 M LiTFSI in DOL/DME, with 1 wt% LiNO$_3$	1 mA cm^{-2}, 1 mAh cm^{-2}	425 cycles	10 mV	[82]
metal Au	1 M LiTFSI in DOL/DME, with 2 wt% LiNO$_3$	1 mA cm^{-2}, 1 mAh cm^{-2}	325 cycles	15 mV	[84]
Li-Zn aolly	1 M LiPF$_6$ in EC/DEC, with 5 wt% VC	1 mA cm^{-2}, 2 mAh cm^{-2}	300 cycles	80 mV	[86]
Li-B-C-Al alloy	1 M LiPF$_6$ in EC/EMC/DMC, 1 wt% VC	0.5 mA cm^{-2}, 0.5 mAh cm^{-2}	600 cycles	80.3 mV	[89]
Li-Ag aolly	1 M LiTFSI in DOL/DME, with 2 wt% LiNO$_3$	1 mA cm^{-2}, 1 mAh cm^{-2}	1,000 cycles	10 mV	[91]
Li-Sn aolly	1 M LiTFSI in DOL/DME, with 2 wt% LiNO$_3$	1 mA cm^{-2}, 1 mAh cm^{-2}	450 cycles	12 mV	[92]
carbon nanospheres	1 M LiTFSI in DOL/DME, with 1 wt% LiNO$_3$	1 mA cm^{-2}, 1 mAh cm^{-2}	150 cycles	25 mV	[96]
Li-rGO	1 M LiTFSI in DOL/DME, with 1 wt% LiNO$_3$	1 mA cm^{-2}, 1 mAh cm^{-2}	450 cycles	10 mV	[100]
Li-CNTs	1 M LiTFSI in DOL/DME, with 1 wt% LiNO$_3$	40 mA cm^{-2}, 2 mAh cm^{-2}	2,000 cycles	54 mV	[102]
Li-Ag	LPSCl	0.5 mA cm^{-2}, 1 mAh cm^{-2}	150 cycles	2 mV	[105]
Li-Ag aolly	LLZTO	0.2 mA cm^{-2}, 1 mAh cm^{-2}	300 cycles	20 mV	[106]
Li-BNNS	LLZTO	0.3 mA cm^{-2}, 1.5 mAh cm^{-2}	190 cycles	10 mV	[107]
Li-ZnO	LLZO	0.1 mA cm^{-2}, 0.025 mAh cm^{-2}	100 cycles	10 mV	[108]
Turn copper foam	LLZTO	0.3 mA cm^{-2}, 0.3 mAh cm^{-2}	300 cycles	31 mV	[109]

(1) The employment of lithiophilic 3D substrates. Due to the abundant inner space and high specific surface area of 3D hosts, the deposition of lithium can be accommodated, and the local current density can be dispersed. However, most 3D matrixes have a poor affinity for lithium, which will cause local accumulation on the top of the host, thus failing to utilize the inner space. Commendably, the preferred nucleation of lithium on lithiophilic sites is helpful in inducing the directed growth of lithium with uniform morphology. Therefore, the enhancement of the lithiophilicity can induce the inner deposition of lithium and reduce the nucleation potential, thus facilitating the utilization of lithium in the void of 3D hosts and increasing the stability of interface. Metal-based lithiophilic sites are most widely employed because of their definite solubility in lithium, which can reduce the nucleation overpotential and induce the selective nucleation of lithium. However, the nonuniform distribution of lithiophilic sites could lead to the local accumulation of lithium, and the blocking of dead lithium will cause the failure of lithiophilic center. Hence, the optimized structural design and spatial distribution of metal-based lithiophilic sites for better exposure and stability is the key to application. In addition, enhancing the lithiophilicity of carbon matrixes by atom doping to regulate adsorption energy to lithium atoms is also promising because it can improve the intrinsic property of hosts without the addition of extra materials. However, the over strengthened adsorption energy could contribute to structural collapse during long cycles. Modulating moderate interaction between doping sites and lithium atoms by rational co-doping can promote the employment of lightweight carbon substrates for lithium metal anode. Crystallography modification of substrates also provides an innovative perspective to regulate the crystallizing behavior of lithium by improving the lattice mismatch of the substrate and lithium and adjusting the UPD layers. This enhanced our understanding of lithiophilicity and deposition behavior of lithium. The exploration of lithiophilic materials is helpful to promote the uniform plating/stripping
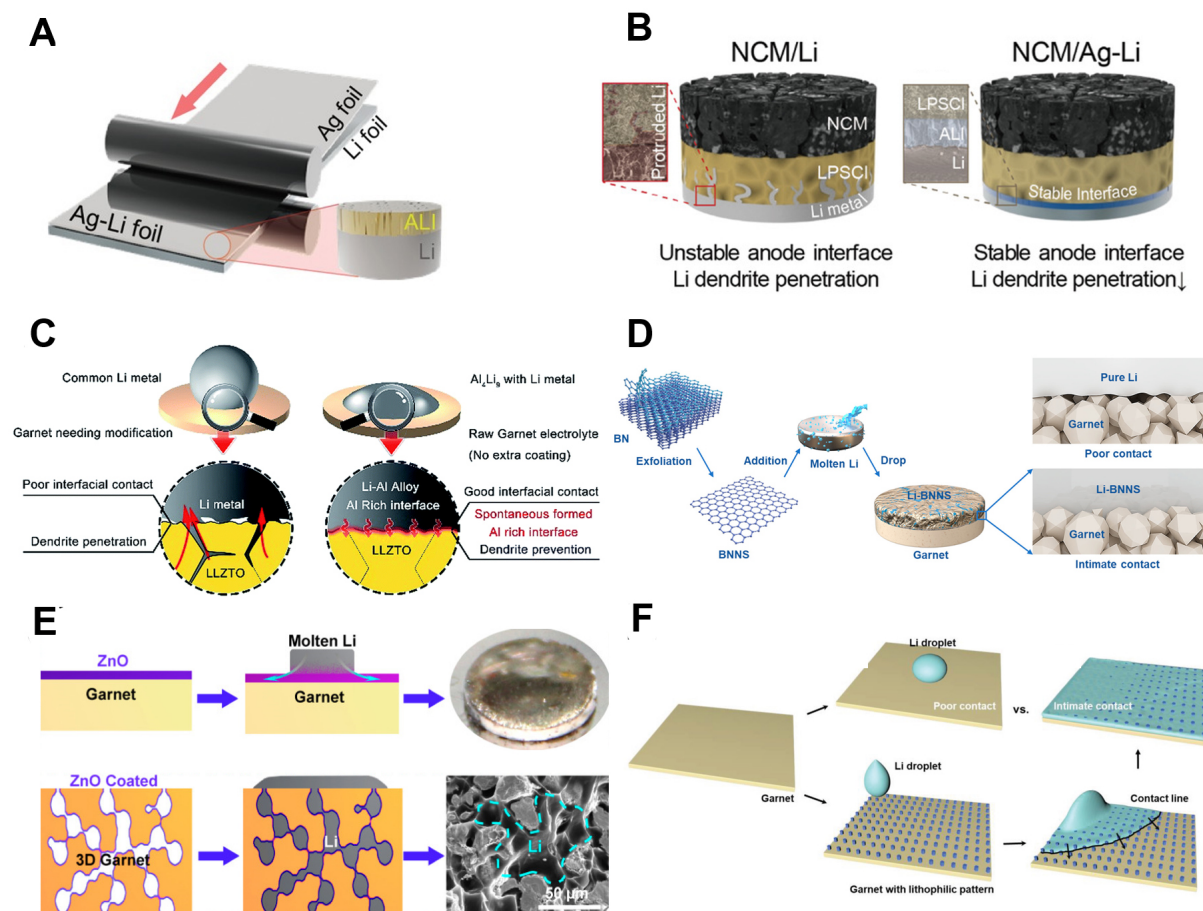
Figure 9. (A) Schematic diagram of the preparation of Ag-Li alloy foil. (B) Schematic illustration of ASSBs with Li metal and Ag-Li alloy after cycling. Reproduced with permission from Ref.[105]. Copyright 2022, Wiley. (C) Schematic diagram of the comparison between the common Li-garnet interface and the Li-Al alloy induced Al-rich interface. Reproduced with permission from Ref.[106]. Copyright 2018, Royal Society of Chemistry. (D) Schematic diagram of the preparation process of BNNS, Li-BNNS composite, and contact comparison between Li-BNNS/garnet and pure Li/garnet interface. Reproduced with permission from Ref.[107]. Copyright 2019, American Chemical Society. (E) Schematic of the contact between Li metal anode and garnet via ZnO lithophilic pattern. Reproduced with permission from Ref.[108]. Copyright 2016, American Chemical Society. (F) Schematic of shaping the contact between Li metal anode and garnet via lithophilic pattern. Reproduced with permission from Ref.[109]. Copyright 2020, Wiley.

behavior during cycling and advance the application of LMBs for high energy density energy storage systems.

(2) The construction of lithiophilic interphases. Because of the high reactivity between lithium and electrolyte, the construction of interphase is crucial to suppress the continuous consumption of electrolyte, optimize the Li+ flux and promote the uniform plating/stripping of lithium. The combination of metal-based materials and carbon materials is effective in stabilizing the interface, thus promoting the application of lithium metal anode. In addition, the accelerated development of solid-state batteries presents a higher requirement for interphase because of the huge interfacial resistance between solid electrolyte and lithium metal anode. The lithiophilic interphase can effectively enhance the compatibility between lithium anode and solid-state electrolyte, accelerate the Li+ transmission between interfaces and improve the interfacial stability. The construction of lithiophilic interphase is indispensable for LMBs with long cycle performance.

The constructure of lithiophilic host and lithiophilic interphase both show great superiority in inducing uniform and compact lithium deposition behaviors, but exhibit unique advantages and applications, respectively. The lithiophilic host can maximize the profit of the abundant inner space of 3D structure to accumulate lithium. In addition, the desirable processing feasibility endows the 3D hosts possibility to design multitudinous lithiophilic sites. The development of lithiophilic 3D hosts is gradually applied to the anode-free LMBs. However, the design of lithiophilic host cannot inhibit the high reactivity of lithium to electrolyte, resulting in continuous electrolyte decomposition. In contrast, the lithiophilic interphase can further improve the interfacial properties, suppressing parasitic reaction, optimizing the Li$^+$ flux, and inhibiting dendrites growth by mechanical strain. However, the lithiophilic interphase is commonly constructed above lithium or lithium alloy anode which restricts its design method. The introduction of lithiophilic interphase on lithium metal anode is crucial to the development of all-solid-state batteries. The flexible combination of lithiophilic 3D hosts and interphases is a promising route to facilitate the lithium metal anode with high energy density, commendable CE and stable cycle performance. However, the commercial application of LMBs is still underexplored, even though the application of lithiophilic materials has made enormous strides. Continuous effort is still necessary to uncover the essence of lithiophilic materials and the mechanism of regulating the deposition behavior of lithium.

(1) How to define lithiophilicity? Although various lithiophilic materials have been proposed, the exact definition is still not decided. In the beginning, the lithiophilicity is analogous to the concept of hydrophilicity to describe the wettability of lithium on different materials in molten lithium test. Later, the concept is extended to describe the preferred nucleation behavior of lithium on different sites and the reduction of nucleation overpotential. Many mechanisms of regulating lithium nucleation are assigned to lithiophilicity, such as alloying process, surface energy, interaction with lithium atoms, and oriented lithium accumulation. This results in confusion regarding the evaluation criteria and essence of lithiophilic materials. To sum up, the lithiophilicity of materials can be summed up as the ordered regulation of lithium deposition. Commonly, the deposition of lithium is a highly disordered process due to the weak lithium bond. However, the lithiophilic sites can convert it to a highly ordered lithium deposition by preferential alloy sites, strong lithium adsorption, low diffusion barrier, matched lattice orientation, and so on. This can be reflected in the lower lithium deposition barrier and faster lithium diffusion on lithiophilic sites. The systematic evaluation methodology should be complemented to qualitatively estimate the lithiophilicity of lithium. The analysis of voltage profiles during galvanostatic testing is an important measure. Nucleation overpotential, which reflects the nucleation barrier, is a key indicator for evaluating the lithiophilicity of materials. In addition, testing the wettability of different materials by molten lithium is another method to assess the affinity to lithium.

(2) How to enrich the concept of lithiophilicity? Lithiophilicity is an inclusive concept with respect to the regulation of the nucleation and growth of lithium. At present, the mechanism of lithiophilic regulation is mainly ascribed to the adjustment of the interaction between lithium and substrates. Furthermore, extensive and systematic exploration could be conducted from other perspectives of multiphysical fields to regard lithiophilicity and enrich the concept of lithiophilicity, thus increasing our options to optimize the plating/stripping behavior of lithium. The understanding of lithiophilicity and regulation of the nucleation and growth of lithium must be based on a comprehensive understanding of the actual deposition behavior. However, the actual mechanisms of nucleation and growth are still hard to characterize due to the sensitivity of lithium, although many hypotheses and models have been proposed. Various in-situ methods such as electrochemical in-situ methods, in-situ electron microscopy, in-situ nuclear magnetic resonance (NMR), and in-situ electron paramagnetic resonance spectroscopy (EPR) ,or *ex-situ* analysis methods, such as electron microscope, scanning probe microscopy (SPM), neutron depth profiling (NDP), X-ray

tomography, and neutron tomography/radiography are indispensable to uncover the specific nucleation and growth process of lithium and the functional mechanism of lithiophilic sites. Furthermore, theoretical calculation and machine learning are also effective methods to analyze the lithiophilic behaviors, simulate the nucleation and growth behavior of lithium and forecast potential lithiophilic candidates. DFT and Molecular dynamics (MD) simulation is an effective method to parse the interaction between lithium and lithiophilic sites which can expand our understanding of lithiophilicity from molecular scale. This is helpful in analyzing the key mechanism behind lithiophilicity and making further predictions and screening of new lithiophilic materials. The comprehensive application of these methods is a promising approach to uncovering and enriching the concept of lithiophilicity.

(3) How can lithiophilic materials be practically employed in lithium metal anode based on our understanding of lithiophilicity? The construction of lithiophilic hosts or interphases as an effective method to optimize the deposition of lithium is incredibly valuable for practical lithium metal anode. The in-depth study of lithiophilic materials can deepen our understanding of the exact deposition behavior, which is the foundation of modification. Additionally, lithiophilic materials also dramatically improve the cycle stability and CE for practical lithium metal anode. However, different from the coin cell test conditions, the commercial application of LMBs sets more stringent requirements for energy density, cycle performance in adverse conditions and security issues. This requires the all-around consideration of the structure and stability of 3D matrixes, distribution and lasting action of lithiophilic sites, combination of the plating and stripping process, compatibility with electrolyte and matching with cathodes such as sulfur cathodes or oxygen cathodes.

The pursuit of energy storage systems with high energy density has accelerated the intensive exploration of LMBs, which deepens our understanding of the deposition behavior of lithium. Based on previous understanding, modification strategies using lithiophilic sites for lithium metal anode is a promising route to facilitate the uniform deposition of lithium and attain long cycle reversibility. LMBs research will also inspire the development of other important metal-based batteries involved in metal deposition processes.

DECLARATIONS
Authors' contributions
Conceived the manuscript: Liu J, Pei N, Zhang P, Zhao J
Wrote the manuscript: Liu J, Pei N
Reviewed the manuscript: Liu J, Pei N, Yang X, Zhang P, Zhao J
Contributed to the discussion of the manuscript: Liu J, Pei N, Yang X, Li R, Hua H, Zhang P, Zhao J

Availability of data and materials
Not applicable.

Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication

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REFERENCES

1. Yan Y, Zeng T, Liu S, Shu C, Zeng Y. Lithium metal stabilization for next-generation lithium-based batteries: from fundamental chemistry to advanced characterization and effective protection. *Energy Mater* 2023;3:300002. DOI
2. Cheng XB, Zhang R, Zhao CZ, Zhang Q. Toward safe lithium metal anode in rechargeable batteries: a review. *Chem Rev* 2017;117:10403-73. DOI PubMed
3. Lin Y, Wen Z, Liu J, Wu D, Zhang P, Zhao J. Constructing a uniform lithium iodide layer for stabilizing lithium metal anode. *J Energy Chem* 2021;55:129-35. DOI
4. Zhang L, Chen Y. Electrolyte solvation structure as a stabilization mechanism for electrodes. *Energy Mater* 2022;1:100004. DOI
5. Zou P, Sui Y, Zhan H, et al. Polymorph evolution mechanisms and regulation strategies of lithium metal anode under multiphysical fields. *Chem Rev* 2021;121:5986-6056. DOI
6. Chen XR, Zhao BC, Yan C, Zhang Q. Review on Li deposition in working batteries: from nucleation to early growth. *Adv Mater* 2021;33:e2004128. DOI
7. Ely DR, García RE. Heterogeneous nucleation and growth of lithium electrodeposits on negative electrodes. *J Electrochem Soc* 2013;160:A662-8. DOI
8. Ling C, Banerjee D, Matsui M. Study of the electrochemical deposition of Mg in the atomic level: why it prefers the non-dendritic morphology. *Electrochim Acta* 2012;76:270-4. DOI
9. Jäckle M, Groß A. Microscopic properties of lithium, sodium, and magnesium battery anode materials related to possible dendrite growth. *J Chem Phys* 2014;141:174710. DOI PubMed
10. Chazalviel J. Electrochemical aspects of the generation of ramified metallic electrodeposits. *Phys Rev A* 1990;42:7355-67. DOI PubMed
11. Chen XR, Yao YX, Yan C, Zhang R, Cheng XB, Zhang Q. A diffusion-reaction competition mechanism to tailor lithium deposition for lithium-metal batteries. *Angew Chem Int Ed* 2020;59:7743-7. DOI
12. Biswal P, Stalin S, Kludze A, Choudhury S, Archer LA. Nucleation and early stage growth of Li electrodeposits. *Nano Lett* 2019;19:8191-200. DOI PubMed
13. Scharifker B, Mostany J. Three-dimensional nucleation with diffusion controlled growth : part I. number density of active sites and nucleation rates per site. *J Electroanal Chem* 1984;177:13-23. DOI
14. Pei A, Zheng G, Shi F, Li Y, Cui Y. Nanoscale nucleation and growth of electrodeposited lithium metal. *Nano Lett* 2017;17:1132-9. DOI PubMed
15. Plieth W. Electrochemistry for materials science. Amsterdam, The Netherlands: Elsevier, 2008.
16. Kashchiev D. On the relation between nucleation work, nucleus size, and nucleation rate. *J Chem Phys* 1982;76:5098-102. DOI
17. Oxtoby DW, Kashchiev D. A general relation between the nucleation work and the size of the nucleus in multicomponent nucleation. *J Chem Phys* 1994;100:7665-71. DOI
18. Han Y, Jie Y, Huang F, et al. Enabling stable lithium metal anode through electrochemical kinetics manipulation. *Adv Funct Mater* 2019;29:1904629. DOI
19. Guo Y, Li D, Xiong R, Li H. Investigation of the temperature-dependent behaviours of Li metal anode. *Chem Commun* 2019;55:9773-6. DOI
20. Fleury V, Chazalviel JN, Rosso M, Sapoval B. The role of the anions in the growth speed of fractal electrodeposits. *J Electroanal Chem* 1990;290:249-55. DOI
21. Wen Z, Wu D, Li H, et al. Ag-modified hydrogen titanate nanowire arrays for stable lithium metal anode in a carbonate-based electrolyte. *J Energy Chem* 2021;54:282-90. DOI
22. Pei N, Liu J, Ma H, Chen Z, Zhang P, Zhao J. Silver copper oxide nanowires by electrodeposition for stable lithium metal anode in carbonate-based electrolytes. *ACS Sustain Chem Eng* 2022;10:7196-204. DOI
23. Liu Y, Sun C, Lu Y, et al. Lamellar-structured anodes based on lithiophilic gradient enable dendrite-free lithium metal batteries with high capacity loading and fast-charging capability. *Chem Eng J* 2023;451:138570. DOI
24. Liu J, Ma H, Wen Z, et al. Layered Ag-graphene films synthesized by Gamma ray irradiation for stable lithium metal anodes in carbonate-based electrolytes. *J Energy Chem* 2022;64:354-63. DOI
25. Chen Q, Wei Y, Zhang X, et al. Vertically aligned MXene nanosheet arrays for high-rate lithium metal anodes. *Adv Energy Mater* 2022;12:2200072. DOI
26. Yan K, Lu Z, Lee H, et al. Selective deposition and stable encapsulation of lithium through heterogeneous seeded growth. *Nat Energy* 2016:1. DOI
27. Feng X, Wu H, Gao B, Świętosławski M, He X, Zhang Q. Lithiophilic N-doped carbon bowls induced Li deposition in layered

graphene film for advanced lithium metal batteries. *Nano Res* 2022;15:352-60.　DOI

28.　Jin C, Sheng O, Luo J, et al. 3D lithium metal embedded within lithiophilic porous matrix for stable lithium metal batteries. *Nano Energy* 2017;37:177-86.　DOI

29.　Shen X, Shi S, Li B, et al. Lithiophilic interphase porous buffer layer toward uniform nucleation in lithium metal anodes. *Adv Funct Mater* 2022;32:2206388.　DOI

30.　Pande V, Viswanathan V. Computational screening of current collectors for enabling anode-free lithium metal batteries. *ACS Energy Lett* 2019;4:2952-9.　DOI

31.　Zhang S, Yang G, Liu Z, et al. Phase diagram determined lithium plating/stripping behaviors on lithiophilic substrates. *ACS Energy Lett* 2021;6:4118-26.　DOI

32.　Jin S, Ye Y, Niu Y, et al. Solid-solution-based metal alloy phase for highly reversible lithium metal anode. *J Am Chem Soc* 2020;142:8818-26.　DOI

33.　Liu Y, Sun J, Hu X, et al. Lithiophilic sites dependency of lithium deposition in Li metal host anodes. *Nano Energy* 2022;94:106883.　DOI

34.　Wu T, Wang Y, Zhang W, et al. Unveiling the role of lithiophilic sites denseness in regulating lithium ion deposition. *J Energy Chem* 2022;71:324-32.　DOI

35.　Zhan Y, Shi P, Ma X, et al. Failure mechanism of lithiophilic sites in composite lithium metal anode under practical conditions. *Adv Energy Mater* 2022;12:2103291.　DOI

36.　Cha E, Yun JH, Ponraj R, Kim DK. A mechanistic review of lithiophilic materials: resolving lithium dendrites and advancing lithium metal-based batteries. *Mater Chem Front* 2021;5:6294-314.　DOI

37.　Duan J, Zheng Y, Luo W, et al. Is graphite lithiophobic or lithiophilic? *Natl Sci Rev* 2020;7:1208-17.　DOI　PubMed　PMC

38.　Yang C, Yao Y, He S, Xie H, Hitz E, Hu L. Ultrafine silver nanoparticles for seeded lithium deposition toward stable lithium metal anode. *Adv Mater* 2017;29:1702714.　DOI

39.　Pu J, Li J, Shen Z, et al. Interlayer lithium plating in Au nanoparticles pillared reduced graphene oxide for lithium metal anodes. *Adv Funct Mater* 2018;28:1804133.　DOI

40.　Ke X, Liang Y, Ou L, et al. Surface engineering of commercial Ni foams for stable Li metal anodes. *Energy Stor Mater* 2019;23:547-55.　DOI

41.　Luan J, Zhang Q, Yuan H, et al. Sn layer decorated copper mesh with superior lithiophilicity for stable lithium metal anode. *Chem Eng J* 2020;395:124922.　DOI

42.　Wang H, Hu P, Liu X, et al. Sowing silver seeds within patterned ditches for dendrite-free lithium metal batteries. *Adv Sci* 2021;8:e2100684.　DOI

43.　Gao L, Sun C, Zhang D, An Y, Yang Y, Bian X. Lithiophilic Zn-doped CuO/ZnO nanoarrays modified 3D scaffold inducing lithium lateral plating achieving highly stable lithium metal anode. *Chem Eng J* 2023;451:138410.　DOI

44.　Huang S, Zhang W, Ming H, Cao G, Fan LZ, Zhang H. Chemical energy release driven lithiophilic layer on 1 m^2 commercial brass mesh toward highly stable lithium metal batteries. *Nano Lett* 2019;19:1832-7.　DOI

45.　Kim JY, Chae OB, Kim G, et al. Spatial control of lithium deposition by controlling the lithiophilicity with copper(I) oxide boundaries. *Energy Environ Mater* 2022.　DOI

46.　Nie Y, Dai X, Wang J, et al. Facile and scalable fabrication of lithiophilic Cu$_x$O enables stable lithium metal anode. *J Energy Chem* 2022;75:285-92.　DOI

47.　Guo C, Guo Y, Tao R, et al. Uniform lithiophilic layers in 3D current collectors enable ultrastable solid electrolyte interphase for high-performance lithium metal batteries. *Nano Energy* 2022;96:107121.　DOI

48.　Tang K, Gao H, Xiao J, et al. Hierarchical Oα-rich Co$_3$O$_4$ nanoarray anchored on Ni foam with superior lithiophilicity enabling ultrastable lithium metal batteries. *Chem Eng J* 2022;436:134698.　DOI

49.　Ding B, An X, Yu J, Lv W, Kang F, He YB. Metal nitride heterostructures capsulated in carbon nanospheres to accommodate lithium metal for constructing a stable composite anode. *Energy Mater* 2022;2:200039.　DOI

50.　Xiong X, Sun R, Yan W, et al. A lithiophilic AlN-modified copper layer for high-performance lithium metal anodes. *J Mater Chem A* 2022;10:13814-20.　DOI

51.　Yu W, Liu F, Zhang L, Liu Z, Wang S, Tong H. Lithiophilic ZnO confined in microscale carbon cubes as a stable host for lithium metal anodes. *Carbon* 2022;196:92-101.　DOI

52.　Wang W, Yang Z, Zhang Y, et al. Highly stable lithium metal anode enabled by lithiophilic and spatial-confined spherical-covalent organic framework. *Energy Stor Mater* 2022;46:374-83.　DOI

53.　Liu Y, Qin X, Zhang S, et al. Oxygen and nitrogen co-doped porous carbon granules enabling dendrite-free lithium metal anode. *Energy Stor Mater* 2019;18:320-7.　DOI

54.　Gao C, Li J, Sun K, et al. Controllable lithium deposition behavior hollow of N, O co-doped carbon nanospheres for practical lithium metal batteries. *Chem Eng J* 2021;412:128721.　DOI

55.　Chen X, Chen XR, Hou TZ, Li BQ, Cheng XB, Zhang R, Zhang Q. Lithiophilicity chemistry of heteroatom-doped carbon to guide uniform lithium nucleation in lithium metal anodes. *Sci Adv* 2019;5:eaau7728.　DOI　PubMed　PMC

56.　Xie Y, Zhang H, Yu J, et al. A novel dendrite-free lithium metal anode via oxygen and boron codoped honeycomb carbon skeleton. *Small* 2022;18:e2104876.　DOI

57.　Zhang R, Chen XR, Chen X, et al. Lithiophilic sites in doped graphene guide uniform lithium nucleation for dendrite-free lithium

metal anodes. *Angew Chem Int Ed* 2017;56:7764-8. DOI

58. Liu L, Yin YX, Li JY, Wang SH, Guo YG, Wan LJ. Uniform lithium nucleation/growth induced by lightweight nitrogen-doped graphitic carbon foams for high-performance lithium metal anodes. *Adv Mater* 2018;30:1706216. DOI PubMed

59. Wen Z, Li H, Liu J, Yang Y, Zhao J. Self-standing N-doped carbonized cellulose fiber as a dual-functional host for lithium metal anodes. *ACS Sustain Chem Eng* 2021;9:2326-37. DOI

60. Li BQ, Chen XR, Chen X, et al. Favorable lithium nucleation on lithiophilic framework porphyrin for dendrite-free lithium metal anodes. *Research* 2019;2019:4608940. DOI PubMed PMC

61. Zhai P, Wang T, Yang W, et al. Uniform lithium deposition assisted by single-atom doping toward high-performance lithium metal anodes. *Adv Energy Mater* 2019;9:1804019. DOI

62. Kaiser SK, Chen Z, Faust Akl D, Mitchell S, Pérez-Ramírez J. Single-atom catalysts across the periodic table. *Chem Rev* 2020;120:11703-809. DOI PubMed

63. Yang Z, Dang Y, Zhai P, et al. Single-atom reversible lithiophilic sites toward stable lithium anodes. *Adv Energy Mater* 2022;12:2103368. DOI

64. Huang W, Liu S, Yu R, Zhou L, Liu Z, Mai L. Single-atom lithiophilic sites confined within ordered porous carbon for ultrastable lithium metal anodes. *Energy Environ Mater* 2022:e12466. DOI

65. Li Y, Pei A, Yan K, et al. Atomic structure of sensitive battery materials and interfaces revealed by cryo-electron microscopy. *Science* 2017;358:506-10. DOI

66. Gu Y, Xu HY, Zhang XG, et al. Lithiophilic faceted Cu(100) surfaces: high utilization of host surface and cavities for lithium metal anodes. *Angew Chem Int Ed* 2019;58:3092-6. DOI

67. Wang D, Zhang W, Zheng W, Cui X, Rojo T, Zhang Q. Towards high-safe lithium metal anodes: suppressing lithium dendrites via tuning surface energy. *Adv Sci* 2017;4:1600168. DOI PubMed PMC

68. Røe IT, Schnell SK. Slow surface diffusion on Cu substrates in Li metal batteries. *J Mater Chem A* 2021;9:11042-8. DOI

69. Obretenov W, Schmidt U, Lorenz WJ, et al. Underpotential deposition and electrocrystallization of metals an atomic view by scanning tunneling microscopy. *J Electrochem Soc* 1993;140:692-703. DOI

70. Vitos L, Ruban A, Skriver H, Kollár J. The surface energy of metals. *Surf Sci* 1998;411:186-202. DOI

71. Bao W, Wang R, Sun K, Qian C, Zhang Y, Li J. Interface crystallographic optimization of crystal plane for stable metallic lithium anode. *ACS Appl Mater Interfaces* 2022;14:38696-705. DOI

72. Kim JY, Chae OB, Wu M, et al. Extraordinary dendrite-free Li deposition on highly uniform facet wrinkled Cu substrates in carbonate electrolytes. *Nano Energy* 2021;82:105736. DOI

73. Mukherjee R, Thomas AV, Datta D, et al. Defect-induced plating of lithium metal within porous graphene networks. *Nat Commun* 2014;5:3710. DOI

74. Chae S, Yi S, Yoon J, et al. Highly defective Ti$_3$CNT-MXene-based fiber membrane anode for lithium metal batteries. *Energy Stor Mater* 2022;52:76-84. DOI

75. Liu W, Xia Y, Wang W, et al. Pristine or highly defective? *Adv Energy Mater* 2019;9:1802918. DOI

76. Zhang H, Huang M, Song J, et al. Effect of the defect densities of reduced graphene oxide network on the stability of lithium-metal anodes. *Mater Today Commun* 2021;27:102276. DOI

77. Zhou B, Bonakdarpour A, Stoševski I, Fang B, Wilkinson DP. Modification of Cu current collectors for lithium metal batteries - a review. *Prog Mater Sci* 2022;130:100996. DOI

78. Li C, Zhang X, Zhu Y, et al. Modulating the lithiophilicity at electrode/electrolyte interface for high-energy Li-metal batteries. *Energy Mater* 2022;1:100017. DOI

79. Cheng XB, Zhang R, Zhao CZ, Wei F, Zhang JG, Zhang Q. A review of solid electrolyte interphases on lithium metal anode. *Adv Sci* 2016;3:1500213. DOI PubMed PMC

80. Kang J, Deng N, Liu Y, et al. Recent advances of anode protection in solid-state lithium metal batteries. *Energy Stor Mater* 2022;52:130-60. DOI

81. Kim S, Lee TK, Kwak SK, Choi N. Solid electrolyte interphase layers by using lithiophilic and electrochemically active ionic additives for lithium metal anodes. *ACS Energy Lett* 2022;7:67-9. DOI

82. Guo F, Wu C, Chen H, et al. Dendrite-free lithium deposition by coating a lithiophilic heterogeneous metal layer on lithium metal anode. *Energy Stor Mater* 2020;24:635-43. DOI

83. Li C, Li Y, Yu Y, et al. One-pot preparation of lithium compensation layer, lithiophilic layer, and artificial solid electrolyte interphase for lean-lithium metal anode. *ACS Appl Mater Interfaces* 2022;14:19437-47. DOI

84. Qian Y, Wei C, Tian Y, et al. Constructing ultrafine lithiophilic layer on MXene paper by sputtering for stable and flexible 3D lithium metal anode. *Chem Eng J* 2021;421:129685. DOI

85. Jin S, Jiang Y, Ji H, Yu Y. Advanced 3D current collectors for lithium-based batteries. *Adv Mater* 2018;30:e1802014. DOI

86. Liu J, Pei N, Hua H, et al. From mosaic-type to heterojunction-type SEI films on the Li anode: decoupling chemical and electrochemical degradation of the electrolyte. *ACS Sustain Chem Eng* 2022;10:9232-41. DOI

87. Lin Y, Wen Z, Yang C, Zhang P, Zhao J. Strengthening dendrite suppression in lithium metal anode by in-situ construction of Li-Zn alloy layer. *Electrochem Commun* 2019;108:106565. DOI

88. Lin L, Liu F, Zhang Y, et al. Adjustable mixed conductive interphase for dendrite-free lithium metal batteries. *ACS Nano* 2022;16:13101-10. DOI

89.   Tang F, Zhang X, Osenberg M, et al. High-performance 3D Li-B-C-Al alloy anode and its twofold Li electrostripping and plating mechanism revealed by synchrotron X-ray tomography. *Energy Environ Mater* 2022:12387. DOI

90.   Ma C, Liu C, Zhang Y, et al. A dual lithiated alloy interphase layer for high-energy-density lithium metal batteries. *Chem Eng J* 2022;434:134637. DOI

91.   Zhong B, Wu J, Ren L, et al. Constructing a lithiophilic and mixed conductive interphase layer in electrolyte with dual-anion solvation sheath for stable lithium metal anode. *Energy Stor Mater* 2022;50:792-801. DOI

92.   Du J, Wang W, Wan M, et al. Doctor-blade casting fabrication of ultrathin Li metal electrode for high-energy-density batteries. *Adv Energy Mater* 2021;11:2102259. DOI

93.   He X, Ji X, Zhang B, et al. Tuning interface lithiophobicity for lithium metal solid-state batteries. *ACS Energy Lett* 2022;7:131-9. DOI

94.   Chen T, Meng F, Zhang Z, et al. Stabilizing lithium metal anode by molecular beam epitaxy grown uniform and ultrathin bismuth film. *Nano Energy* 2020;76:105068. DOI

95.   Wan J, Song YX, Chen WP, et al. Micromechanism in all-solid-state alloy-metal batteries: regulating homogeneous lithium precipitation and flexible solid electrolyte interphase evolution. *J Am Chem Soc* 2021;143:839-48. DOI

96.   Zheng G, Lee SW, Liang Z, et al. Interconnected hollow carbon nanospheres for stable lithium metal anodes. *Nat Nanotechnol* 2014;9:618-23. DOI

97.   Liu Y, Lin D, Liang Z, Zhao J, Yan K, Cui Y. Lithium-coated polymeric matrix as a minimum volume-change and dendrite-free lithium metal anode. *Nat Commun* 2016;7:10992. DOI PubMed PMC

98.   Wang JP, Lan DN, Chen GY, Hu XT, Lin C, Li Q. Built-in stable lithiophilic sites in 3D current collectors for dendrite free Li metal electrode. *Small* 2022;18:e2106718. DOI

99.   Liu H, Di J, Wang P, et al. A novel design of 3D carbon host for stable lithium metal anode. *Carbon Energy* 2022;4:654-64. DOI

100. Lin D, Liu Y, Liang Z, et al. Layered reduced graphene oxide with nanoscale interlayer gaps as a stable host for lithium metal anodes. *Nat Nanotechnol* 2016;11:626-32. DOI

101. Dong L, Nie L, Liu W. Water-stable lithium metal anodes with ultrahigh-rate capability enabled by a hydrophobic graphene architecture. *Adv Mater* 2020;32:e1908494. DOI PubMed

102. Wang ZY, Lu ZX, Guo W, et al. A dendrite-free lithium/carbon nanotube hybrid for lithium-metal batteries. *Adv Mater* 2021;33:e2006702. DOI

103. Kamaya N, Homma K, Yamakawa Y, et al. A lithium superionic conductor. *Nat Mater* 2011;10:682-6. DOI

104. Seino Y, Ota T, Takada K, Hayashi A, Tatsumisago M. A sulphide lithium super ion conductor is superior to liquid ion conductors for use in rechargeable batteries. *Energy Environ Sci* 2014;7:627-31. DOI

105. Choi HJ, Kang DW, Park JW, et al. In situ formed Ag-Li intermetallic layer for stable cycling of all-solid-state lithium batteries. *Adv Sci* 2022;9:e2103826. DOI

106. Lu Y, Huang X, Ruan Y, et al. An *in situ* element permeation constructed high endurance Li-LLZO interface at high current densities. *J Mater Chem A* 2018;6:18853-8. DOI

107. Wen J, Huang Y, Duan J, et al. Highly adhesive Li-BN nanosheet composite anode with excellent interfacial compatibility for solid-state Li metal batteries. *ACS Nano* 2019;13:14549-56. DOI

108. Wang C, Gong Y, Liu B, et al. Conformal, nanoscale ZnO surface modification of garnet-based solid-state electrolyte for lithium metal anodes. *Nano Lett* 2017;17:565-71. DOI

109. Duan J, Huang L, Wang T, et al. Shaping the contact between Li metal anode and solid-state electrolytes. *Adv Funct Mater* 2020;30:1908701. DOI