

Review Article

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A review for modified Li composite anode: Principle, preparation and challenge

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Abstract: As the most common energy storage technology on the market, lithium-ion batteries are widely used in various industries and have a profound impact on our daily lives, with the characteristics of high voltage, high capacity, good safety performance, and long cycle life. Lithium metal was first used in the anode of lithium-ion batteries. However, the inherent growth of lithium dendrites and the instability of the SEI film limit the practical application of lithium metal materials. Despite this, lithium metal is still an ideal anode material to meet the growing demands for electronic equipment and electric vehicles due to its extremely high theoretical specific capacity, low density, and the lowest negative electrochemical potential. With the urgent need to develop new energy storage technologies, the research on lithium metal anodes has once again received extensive attention. In this review, the research progress in the modification of composite lithium metal electrode materials is summarized, including lithium/alloy composite electrode, lithium/carbon-based materials composite electrode and artificial SEI film. The possible directions for future development of lithium metal electrode are also prospected.

Keywords: lithium-ion battery, lithium metal anode, modification

1 Introduction

With the rapid development of human society and technology, the demand for traditional fossil energy is increasing. However, the fossil energy that can be exploited on the earth is limited, so the increase in people's energy demand will lead to the gradual exhaustion of fossil energy. Therefore, there is an urgent need to develop green and efficient new energy and energy storage technologies to meet people's energy demand [1]. Among the existing chemical power sources, which convert chemical energy into electrical energy, lithium-ion batteries have attracted worldwide attention due to the advantages of high voltage, high energy density, good safety performance, and long cycle life [2]. Lithium-ion batteries are mainly composed of a cathode, an anode, an electrolyte, a separator, and a battery casing, which mainly rely on lithium ions to shuttle reversibly between two host structures through the electrolyte. The working principles of typical lithium-ion cells are shown in Figure 1a. During charge, lithium ions diffuse from the cathode into the anode, losing an electron from the cathode in the process to maintain charge balance. Concomitant oxidation and reduction take place at the two electrodes, respectively. The reverse process occurs during discharge.

Lithium metal was first used in the anode of lithium-ion batteries, but frequent accidents brought safety concerns to public attention, thus resulting in limiting the practical application of lithium metal materials. Subsequently, since the commercialization of lithium batteries for several decades, the research on lithium battery anode materials has mainly focused on carbon-based materials, silicon-based materials, and tin-based materials. Commonly used carbon-based anode materials mainly include coke, graphite, MCMB, etc. Silicon is believed to be one of the most promising anode materials because of its high capacity ($4,212 \text{ mA h g}^{-1}$ for $\text{Li}_{4.4}\text{Si}$ at high temperatures), natural abundance, environmental

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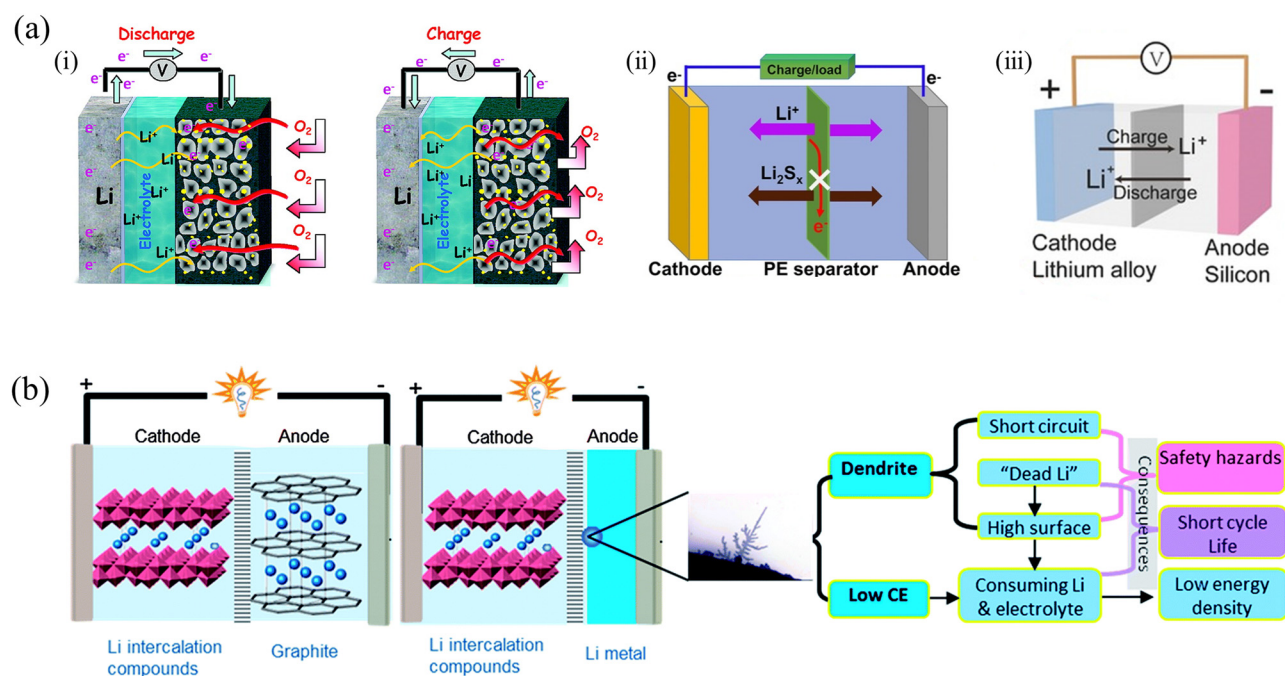


Figure 1: (a) Representative lithium-ion battery structure diagrams of (i) lithium–air battery, reprinted with permission from [11], (ii) lithium–sulfur battery, reprinted with permission from ref. [12], and (iii) lithium–silicon battery, reprinted with permission from ref. [3]; (b) schematic diagrams of lithium metal batteries and the typical morphology of lithium dendrites as well as the main problems, reprinted with permission from ref. [7].

friendliness, and low electrochemical potential, but there is a large volume effect during lithiation and delithiation [3]. Tin and tin-based compounds have a high theoretical specific capacity (994 mA h g^{-1} for $\text{Li}_{22}\text{Sn}_5$), high availability, and high electrical conductivity, but will produce sharp volume changes during lithium ions insertion/extraction [4].

The main barriers to the development of lithium metal batteries are shown in Figure 1b. For one thing, the uneven surface of the lithium metal electrode leads to different electrodeposition rate during charge and discharge processes, which results in the growth of lithium dendrites. The dendritic form in which lithium tends to deposit leads to poor battery cycle performance. In severe cases, the continuous growth of lithium dendrites can even pierce the separator and contact the cathode, which is known as the main reason of safety accidents, thermal runaway, and explosion, caused by internal short circuits [5–7]. For another, lithium metal has high reactivity and can react with almost all electrolytes. After multiple charge and discharge cycles, it will react with the liquid electrolyte to form the solid electrolyte interface film (SEI film). At the same time, originating from the inhomogeneity of lithium deposition, the lithium metal becomes loose and porous, and the surface area is greatly increased, causing the volume of the lithium metal anode to

continue expanding, which results in unstable SEI film, with repeated fracture and regrowth. Then, further plating causes lithium dendrites to shoot out through the cracks, producing isolated lithium and finally forming “dead lithium” [8–10]. As a result, these processes arouse the low Coulombic efficiency, short cycle life, and most importantly, safety hazards.

In recent years, with the urgent demand to develop new energy storage technologies, especially in lithium–sulfur and lithium–air batteries, the research on lithium metal anodes has once again received extensive attention. Lithium metal is regarded as one of the most promising anode materials originating from its high theoretical specific capacity ($3,860 \text{ mA h g}^{-1}$), low density (0.59 g cm^{-3}), and the lowest electrochemical potential (-3.04 V versus the standard hydrogen electrode) [1,7,8]. Therefore, the research on lithium-ion batteries has mainly focused on the modification and protection of lithium electrodes to improve the safety performance and cycle stability. At present, the main improvement strategies focus on electrolyte engineering and interface engineering [8]. The electrolyte engineering is an approach to dendrite prevention through adding additives and adjusting electrolyte components and the interface engineering is usually a commonly adopted approach to stabilize the SEI film by covering a protective layer before cycling on the lithium

surface. In this work, we will review the research progress of the modification of composite lithium metal electrodes and the possible directions for future development of lithium metal electrode.

2 Lithium/alloy composite electrode

Metal is a substance with luster, ductility, easy to conduct electricity, heat conduction, and other properties, so it has been extensively studied [13–16]. Lithium is able to react with lots of metals M (M = Mg, Ca, Al, Si, Ge, Sn, Pb, As, Sb, Bi, Pt, Ag, Au, Zn, Cd, Hg, etc.) at room temperature to form intermetallic compounds. The formation of lithium alloys is usually reversible, so the metals that can form alloys with lithium can theoretically be used as the anode material. Using lithium alloy instead of lithium metal can reduce the reactivity between the anode and the electrolyte and stabilize the electrode/electrolyte interface. At the same time, the three-dimensional structure of the lithium alloy can be used to provide more lithium metal storage sites, thus inhibiting the growth of lithium dendrites. However, in the process of metal forming alloy with lithium, the volume changes greatly, and the repeated insertion and extraction of lithium cause the mechanical stability of the material to gradually decrease [17].

If the pure metal is replaced by intermetallic compounds or composites, the anode cycle performance of the lithium alloy will be significantly improved [18]. This method is that under a certain electrode potential, one or more components in the intermetallic compounds or composites can reversibly store lithium, which can expand/shrink, while other components are relatively inactive, even inert, acting as a cushion for the matrix, thereby maintaining the structural stability of the material. The research mainly focuses on Sn-based, Sb-based, Si-based, and Al-based alloy materials, as well as composites and lithium alloys. The above-mentioned several types of alloy materials can be collectively referred to as lithium storage alloys. Establishing a stable 3D conductive host with lithiophilic nature and adequate Li plating space could not only buffer the volume change of the lithium anode, but also reduce the local current density and control the electrical field distribution to allow uniform Li deposition.

Al is a kind of light metal with abundant reserves and stable structure and easy to form Li–Al alloy.

Simultaneously, lithium is easy to deposit on the Al surface, and the nucleation barrier is low [19]. Among these lithium/alloy composite electrodes, the representative one is Li–Al expanded metal, made by Zaghbi *et al.* [20]. The Li–Al composite electrode was obtained by pressing lithium foil and a sheet of Al expanded metal with 50% void volume covered with a thin film of composite C, which can accommodate lateral expansion to minimize volume changes of the electrode, resulting in better electrochemical properties. Based on the strong bonding force between Al and Li, a Li–LiAl alloy composite is prepared by a thermal infusion strategy [21], shown in Figure 2a. It is found that Li–Al 3D skeleton could be formed to block the formation of lithium dendrites on the surface of the anode, which is extremely crucial to maintain stability and improve the electrochemical performance of the Li–Al composite. This kind of structure not only avoids volume change, but also offers outstanding conductivity and high specific surface area to accommodate Li.

Another representative one is Li–Mg alloy. The kinetically controlled vapor formation and deposition method (KCVD) is used for preparing Li–Mg alloys [22]. The samples display a columnar and porous structure, effectively preventing dendrite formation. Moreover, lithium atoms exhibit a high diffusion coefficient in the composite electrode, improving the cycling ability of the anode and the rechargeability of lithium batteries. As shown in Figure 2b, a strong passivation layer is grown on the surface of the Li–Mg alloy composite [23], making the surface morphology of the anode smoother during cycling. At the same time, a porous skeleton structure is formed after delithiation, which ensure the overall structural integrity of the anode during Li stripping/plating process and the remarkable enhancement on electrochemical performance.

Besides, to suppress the dendrite growth, researchers have also developed Li–Zn composite electrodes [24]. Zhu *et al.* developed Li–Zn composite electrodes by hot-melt mixed coating method instead of Li anode, making the electric field distribution more uniform and improving the electrochemical stability of the electrode [25]. A novel 3D Li–Zn@Cu composite anode is established by electrochemical method, which delivers sufficient space for lithium deposition and low-energy barrier for lithium nucleation, thereby inducing uniform lithium deposition during cycling to achieve dendritic-free deposition behavior [26], shown in Figure 3a.

The schematic in Figure 3b is a composite anode designed by the lithium foil and the copper current collector [27]. As the picture shows, Li will deposit more quickly on the tips of the 2D copper foil because of the

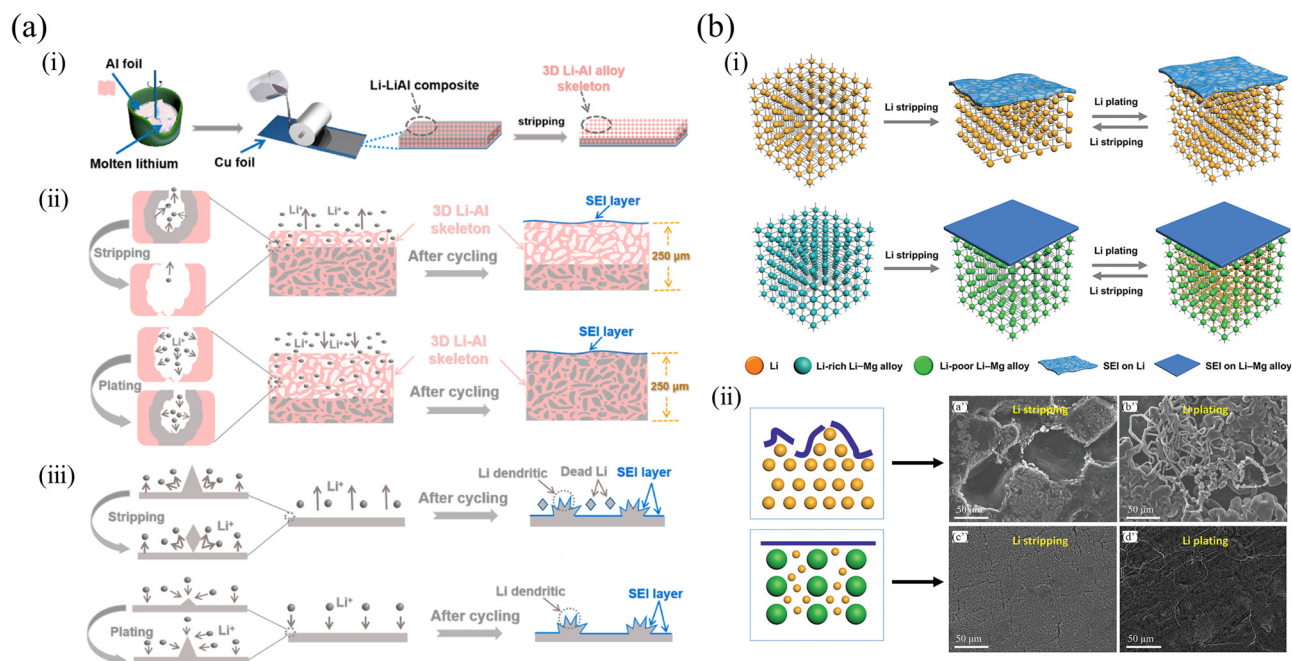


Figure 2: (a) Schematic diagrams of (i) preparation of Li-LiAl composite electrode, (ii) Li stripping/plating of Li-LiAl composite electrode, and (iii) Li stripping/plating of bare Li electrode, reprinted with permission from ref. [21]; (b) schematic structure diagram of (i) in the bulk and at the surface for Li and Li-Mg alloy anodes during Li stripping/plating process, and (ii) SEM images of Li and Li-Mg alloy after (a', c') Li stripping and (b', d') following Li plating at 0.5 mA cm^{-2} for 24 h in Li/Cu and Li-Mg/Cu coin cells, reprinted with permission from ref. [23].

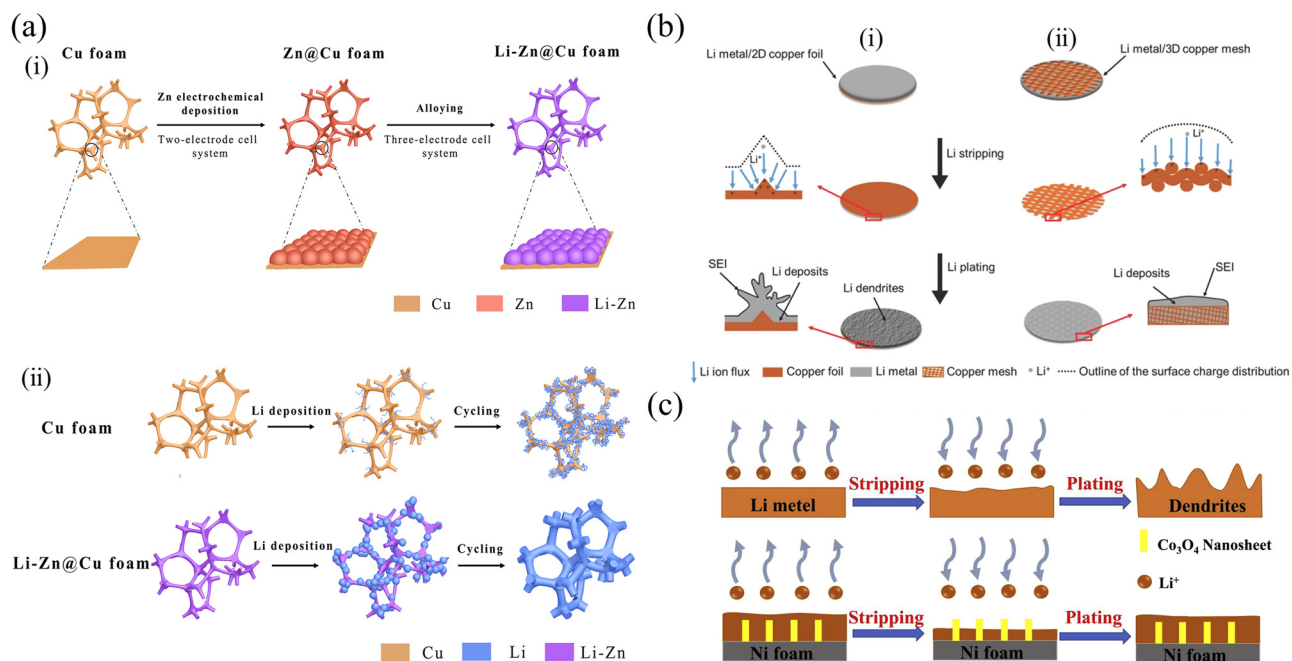


Figure 3: (a) Schematic diagram of (i) the fabrication for 3D Li-Zn@Cu foam, and (ii) Li depositing stage on substrates of Cu foam and 3D Li-Zn@Cu foam, reprinted with permission from ref. [26]; (b) schematic diagrams of the stripping-plating process of (i) the bare Li metal/2D copper film and (ii) Li metal/3D copper mesh, reprinted with permission from ref. [27]; (c) bare Li anode and Li-Co₃O₄/NF composite anode, reprinted with permission from ref. [28].

rough surface, which leads to the concentration of the ion flux. Compared with the 2D copper foil, the Li/Cu current collector anode with a 3D structure can accelerate the charge transfer speed and reduce the interface resistance. At the same time, the larger specific surface area can reduce the local current density, resulting in the uniform charge distribution, and therefore, reducing the growth rate of lithium dendrites. A novel composite lithium anode is prepared by thermal infusion of molten lithium into 3D nickel foam (NF) framework decorated by lithiophilic Co_3O_4 nanosheet arrays [28], shown in Figure 3c. Li- Co_3O_4 /NF composite anode with a large surface area and 3D porous structure is crucial in cutting down the local current density, causing uniform lithium nucleation and deposition, and thus suppressing the dendrites growth.

3 Lithium/carbon-based materials composite electrode

Carbon is a most prolific element in nature, so there has been a lot of research on carbon materials [29–35]. Creating new materials, especially carbon nanomaterials, can achieve efficient energy conversion and storage [36–39]. The commonly used carbon materials are graphite, diamond, buckminsterfullerene C_{60} , single-walled carbon nanotube (SWCNT), and graphene. The commercial development of lithium ion batteries stems from the use of carbon materials as lithium reservoir in the anode, which avoids the problem of lithium dendrite formation and provides great improvements in cycle-ability and safety [40]. However, the theoretical specific capacity of graphite anode is 372 mA h g^{-1} , much lower than lithium metal electrodes [41]. And there is a large capacity loss during the first charge and discharge, resulting in that the energy density of the lithium-ion batteries with graphite anode still cannot meet the needs of the rapidly developing energy demand. Therefore, researchers have set their sights on lithium/carbon-based materials composite electrode.

Coating is a commonly used surface modification method. It is believed that the coated material forms a physical resistance layer on the surface of the substrate. Therefore, researchers used carbon materials to coat the lithium metal so that the lithium ion could have reversible insertion and extraction reactions with the carbon, to form a lithiated carbon. In addition, the carbon film is regarded as a passive layer against the side

reaction between lithium and electrolyte. The carbon-coated lithium (Li/C) electrode is reported widely. Arie *et al.* [42] used magnetron sputtering technology to deposit amorphous carbon coatings on the surface of lithium metal anode [43]. Arie and Lee demonstrated C_{60} and the diamond-like carbon films [44] via vacuum techniques, preventing the growth of lithium dendrites.

The infinite dimension change of Li is originated from its “hostless” nature [45]. Therefore, rational design of a three-dimension scaffold or “host” for lithium metal is necessary [46]. The ideal framework structure for inhibiting lithium dendrites would include high surface area, low density materials with uniform conductive surfaces for lithium deposition. Carbon-based materials are the ideal candidates for lithium anode because carbon owns high surface areas with excellent mechanical strength, especially those emerging carbon materials. At the same time, generally speaking, carbon is stable under the redox environment in lithium batteries.

The combination of lithium and graphite materials to form a three-dimension conductive network has been extensively studied. As shown in Figure 4a, Liu *et al.* [47] used a simple one-step stirring molten method to manufacture lithium-graphite hybrid (LGH) anodes on a large scale. In comparison with bare lithium foil, LGH anode has a stable graphite matrix and can effectively drop the local current density, thereby reducing the formation of dendrites and stabilizing the interface. A composite anode (Li-EG) prepared by pressing and heating a mixture of expanded-graphite (EG) and lithium powder has been reported [48], shown in Figure 4b. The porous and conductive expanded-graphite is uniformly embedded in the lithium metal, offering abundant space for accommodating the lithium metal, thus preventing the nucleation and growth of lithium dendrites.

Reduced graphene oxide (rGO) exhibits high lithophilicity, ensuring uniform lithium infusion and deposition during synthesis and subsequent cycling, so it has also been extensively studied. Lin *et al.* [45] prepared a layered Li-rGO composite anode, made by injecting molten lithium into rGO with uniform nanogaps (Figure 4c). The layered rGO provides a stable support for lithium stripping/plating, significantly reduces the volume change of the electrode layer during the cycle, and provides a mechanically stable passivation layer. By horizontally and centripetally electroplating lithium in the patterned voids of rGO/Li hybrid (P-rGO/Li), the lithium dendrite is fundamentally suppressed [49], shown in Figure 4d. Lithium nucleates at the rough edges of the voids in the patterned anode grow horizontally and centripetally to fill the empty spaces.

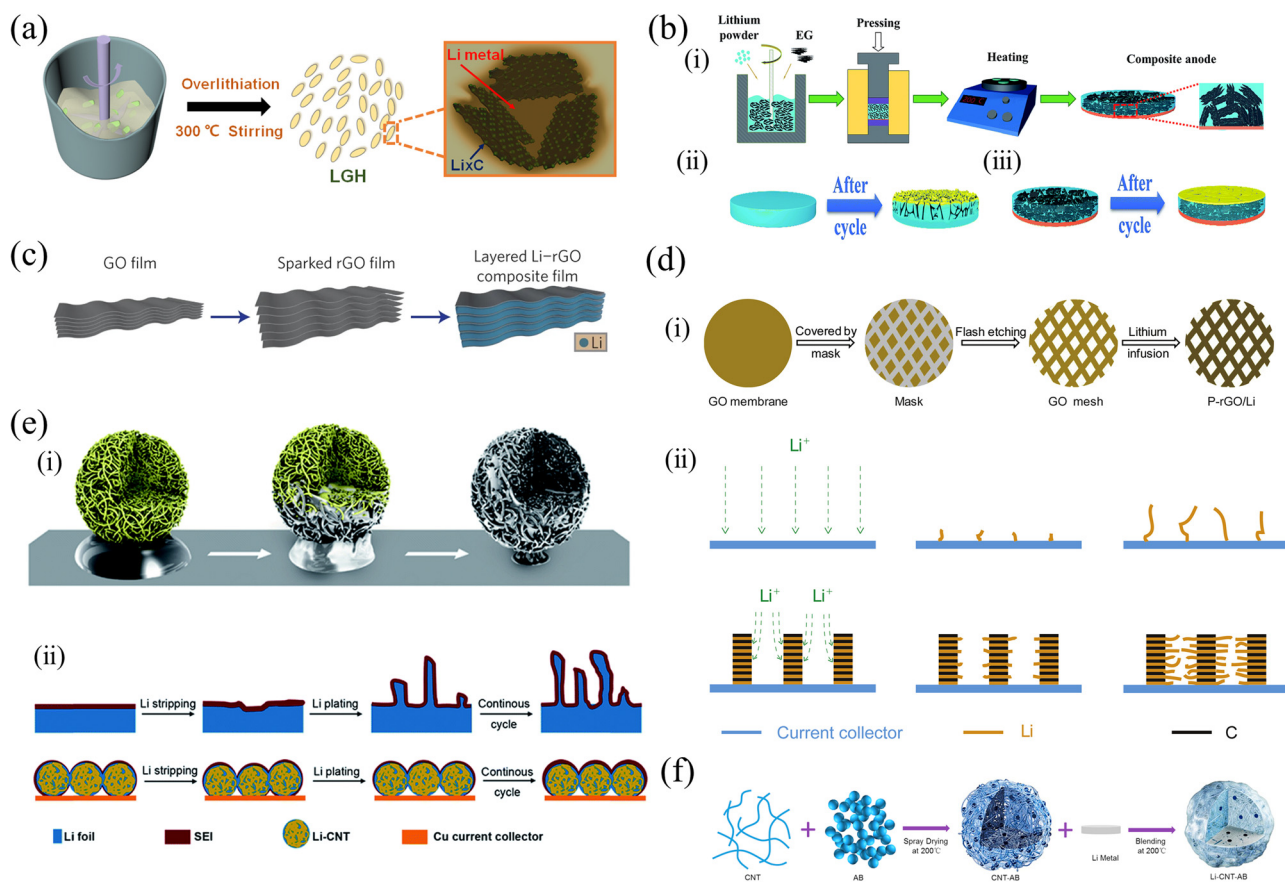


Figure 4: Schematic diagrams of (a) the fabrication process of LGH by the stirring molten method, reprinted with permission from ref. [47]; (b) the Li-EG composite anode fabrication process (i) and the Li plating behavior of the Li foil (ii) and the Li-EG anode (iii), reprinted with permission from ref. [48]; (c) the material design and the consequent synthetic procedures from a GO film (left) to a sparked rGO film (middle) to a layered Li-rGO composite film (right), reprinted with permission from [45]; (d) the preparation process of P-rGO/Li (i) and lithium deposition on planar current collectors and P-rGO/Li electrodes (ii), reprinted with permission from ref. [49]; (e) the molten impregnation preparation of the Li-CNT composite (i) and the morphological evolution during the stripping/plating cycles on Li foil and Li-CNT electrodes (ii), reprinted with permission from ref. [51]; (f) the synthetic procedures of the Li-CNT-AB, reprinted with permission from ref. [52].

Due to the nanostructure of carbon nanotubes (CNTs) and the bonding strength between atoms, these cylindrical carbon molecules have excellent mechanical stiffness and tensile strength. In addition, CNTs also have certain chemical stability and high conductivity [50]. Guo *et al.* [51–53] conducted a series of studies on CNT-modified lithium metal electrodes by a facile and scalable molten impregnation means. As shown in Figure 4e, the Li-CNT composite anode not only exhibits the high specific capacity of lithium metal and the excellent characteristics of low lithium dissolution/deposition potential, but also demonstrates obviously suppressed dendrite formation and good electrochemical performance. In addition, the preparation process of the Li-carbon nanotube-acetylene black (Li-CNT-AB) composite microsphere anode is shown in the schematic illustration in Figure 4f. The lithiophilic

CNTs are used to construct the porous spherical skeleton, and the lithiophilic AB particles uniformly distributed in the spherical skeleton are used to utilize the pore space of the sphere, thereby increasing the lithium concentration of the composite anode and acting as a lithium deposition promoter during battery cycling because of its lower lithium nucleation barrier.

In the recent years, many researchers have used the carbon layer as the substrate to deposit materials with different morphologies on the carbon layer to modify the lithium metal anode [54–56], including, of course, carbon-based materials [57,58]. Among these modifications, the CVD method is widely used. As shown in Figure 5a, sponge carbon deposited on a 3D carbon paper (SCCP) substrate can be used to make the entire lithium metal deposited under the sponge carbon layer, so as to

inhibit the growth of lithium dendrites. The Coulombic efficiencies at 3 mA h cm^{-2} and 4 mA h cm^{-2} are as high as 98–99% with SCCP composite electrode [59]. The stable lithium-framework composite anode (CC/CNT@Li) is established by melting lithium metal into 3D interconnected lithiumphilic CNT on porous carbon cloth (CC), shown in Figure 5b, which reduces the polarization of the electrode and ensures uniform lithium nucleation and continuous smooth lithium electroplating [60]. The CC/CNT can provide enough lithium nucleation sites, reduce the local surface current density, avoid the growth of lithium dendrites, and buffer the volume changes during the plating/stripping process.

4 Artificial SEI film

The chemical composition of the SEI film is related to the electrolyte composition (including salts, solvents, and additives) and strongly affects the lithium morphology and cycling performance of lithium batteries [61]. It's reported that the main components of SEI film include

LiF, Li_2CO_3 , LiOH, Li_2O , etc. [62–66]. It is the existence of this SEI film that hinders the further reaction between lithium metal and electrolyte, ensuring the chemical stability of lithium metal. However, the infinite volume of lithium metal during charge and discharge will cause the SEI film to rupture and regrow, thus leading to “dead lithium” and lithium dendrites [67,68]. An artificial SEI film designed between lithium metal and electrolyte can avoid further consumption of electrolyte and lithium metal, which is caused by the instability of the intrinsic SEI film, and inhibit the formation of lithium dendrites. Ideally, the SEI film should be homogeneous, relatively thin, have compact structure, and possess high ionic conductivity and high elastic strength to mechanically suppress the breakthrough by lithium dendrites [8]. Therefore, the artificial SEI film needs to have the following two conditions [69,70]. For one thing, the artificial SEI film should have good chemical stability and mechanical properties to adapt to the volume change during the charge and discharge cycle of lithium anode and prevent further corrosion of the lithium anode. For another, the artificial SEI film should possess high ionic conductivity, so that the lithium ion can be inserted and extracted quickly.

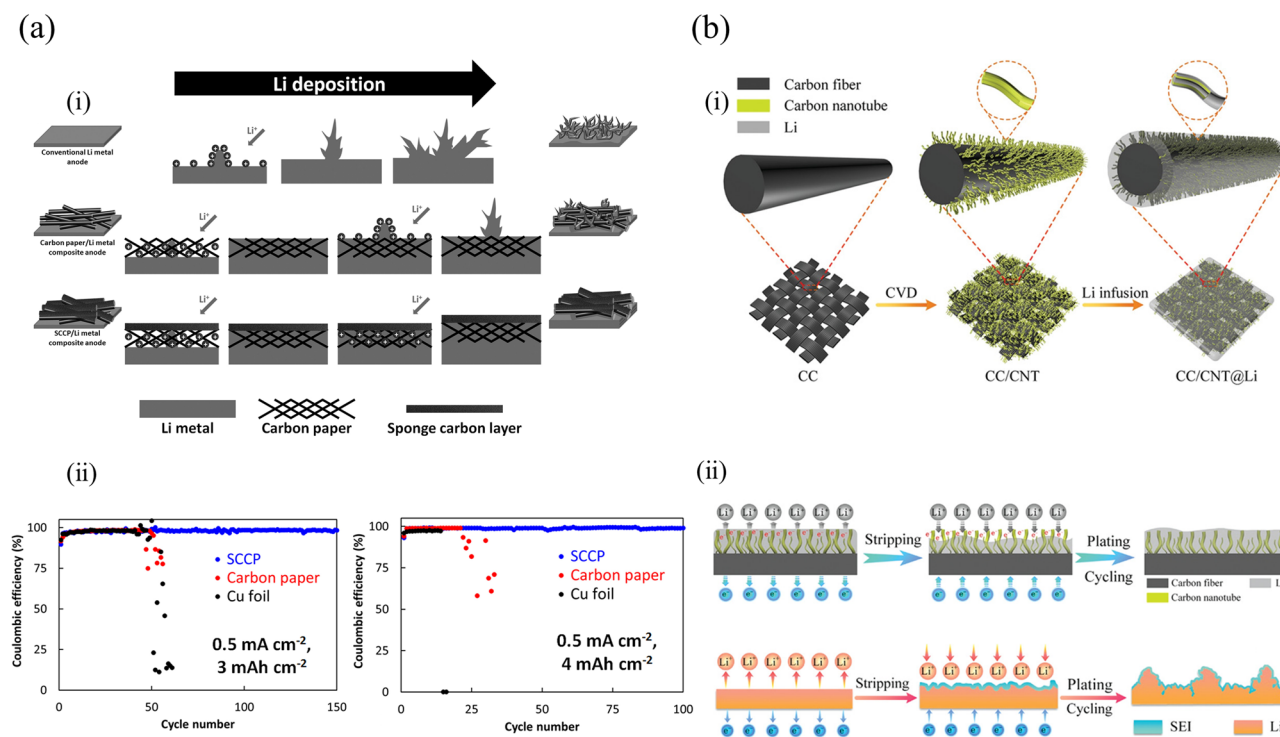


Figure 5: Schematic diagrams of (a) Li metal deposition on planar Li, carbon paper/Li, SCCP/Li surface (i) and coulombic efficiencies for Li plating of 3 and 4 mA h cm^{-2} , at a current density of 0.5 mA cm^{-2} (ii), reprinted with permission from [59]; (b) the synthesis procedures of CC/CNT@Li composite anode (i), morphology evaluations of CC/CNT@Li composite anode and bare Li anode (ii), reprinted with permission from [60].

LiPON is the artificial SEI film with an amorphous structure that has been studied more frequently, originating from its relatively high ionic conductivity (10^{-6} S/cm), relatively low electronic conductivity (10^{-16} – 10^{-14} S/cm), and stable electrochemical performance [71,72]. As shown in Figure 6a, the dense LiPON layer composed of spherical particles is established on lithium electrode by radio frequency (RF) reactive sputtering, with a thickness of $2\mu\text{m}$ [73]. The LiPON layer is stable, which can prevent further reaction between lithium and electrolyte. In low-energy batteries, the LiPON layer can improve the efficiency of lithium-

ion transmission and LiPON@Li composite anode shows higher discharge capacity and higher cycle capacity than bare Li anode. Besides, an effective method to protect the lithium anode is proposed by designing a dense and uniform LiPON coating on the lithium via nitrogen plasma-assisted deposition of electron-beam reaction evaporation [74], shown in Figure 6b. LiPON coating with stable electrochemical, mechanical performance, and high ion conductivity can minimize the corrosion reaction between lithium and electrolyte and prevent the lithium dendrites from growing further.

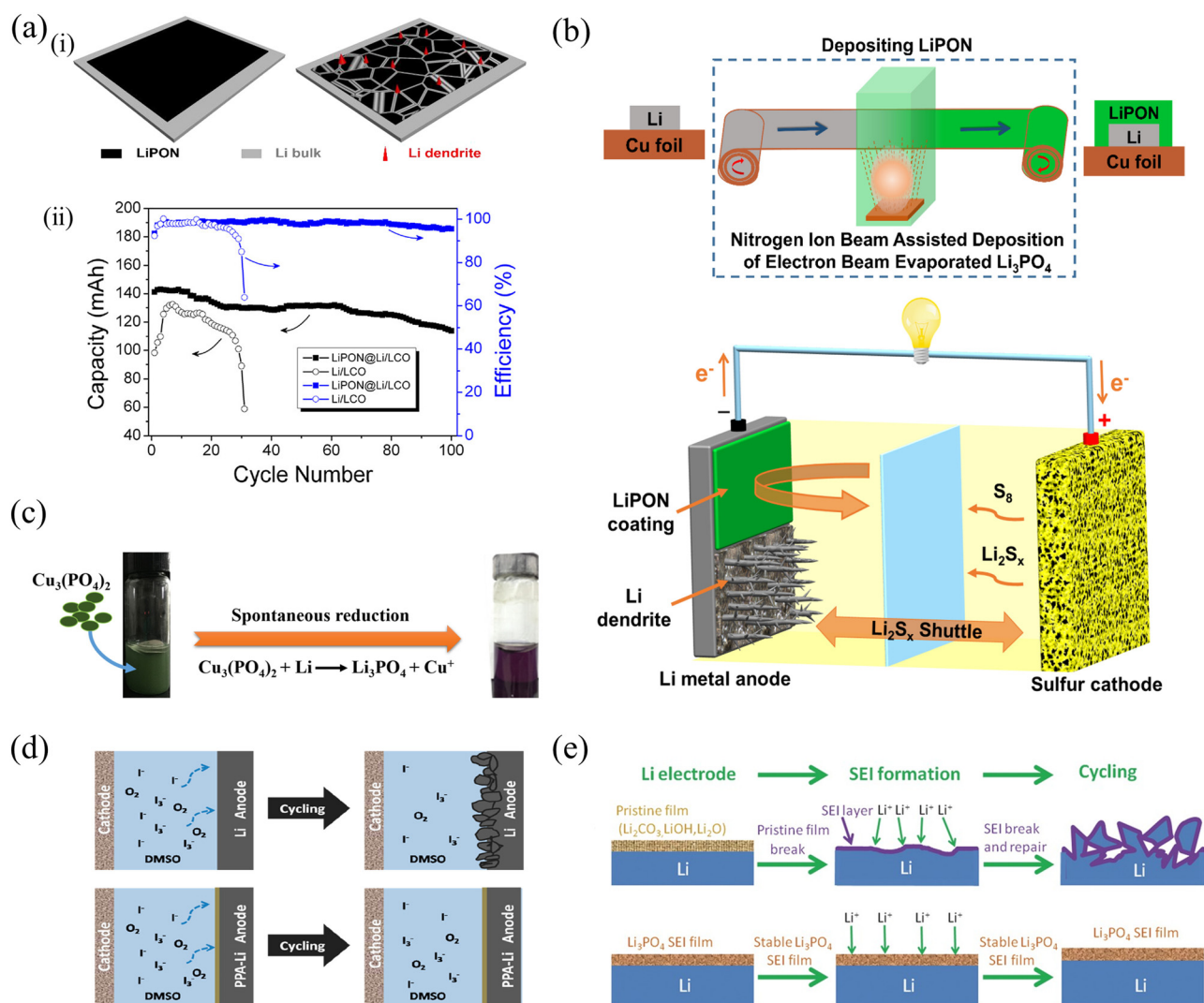


Figure 6: (a) Schematic diagrams of LiPON@Li anodes in pouch cells with low-energy density and ultrahigh energy density after cycles (i) and capacity of cells and efficiencies as a function of cycle number at 0.1C (ii), reprinted with permission from ref. [73]; (b) schematic diagrams of the mass production of LiPON-coated Li metal foils by using a continuous roll-to-roll system and the performance of a LiPON-coated Li metal anode in Li-S battery configurations, reprinted with permission from ref. [74]; (c) the process for the fabrication of the Li₃PO₄-Li anode, reprinted with permission from ref. [75]; (d) schematic structures of the Li-O₂ Cells with Li/LiNO₃/DMSO electrolyte of Li anode and PPA-Li anode, reprinted with permission from ref. [76]; (e) schematics of the general Li metal and Li₃PO₄-modified Li metal anodes during SEI formation and cycling, reprinted with permission from ref. [77].

As shown in Figure 6c, an artificial Li_3PO_4 SEI layer is prepared by the spontaneous redox reaction of the lithium metal and copper phosphate ($\text{Cu}_3(\text{PO}_4)_2$) in tetrahydrofuran (THF) organic solvent at room temperature, which serves as a protective layer to hinder the unfavorable reaction during cycling and the formation of lithium dendrites [75]. Through a simple soaking method, an artificial Li_3PO_4 SEI layer on lithium metal (PPA-Li) is used to prevent the growth of lithium dendrites, shown in Figure 6d, which exhibits excellent stability and brings about a uniform and featureless surface of the lithium anode [76]. Li *et al.* established a uniform artificial Li_3PO_4 SEI layer (Figure 6e), without repeated fracture and regrowth, therefore restraining the further reaction between the Li anode and the electrolyte [77]. Because of its good lithium ion conductivity and high Young's modulus, the lithium dendrites growth can be prohibited.

Based on knowledge of the metal and its oxides [17,78–87], the researchers turned their attention to the artificial SEI film synthesized from metal and its oxide. A facile surface chemistry method to stabilize the lithium metal anode is to synthesize Li-rich composite alloy films *in situ* on the surface of lithium [88]. The authors formed $\text{Li}_{13}\text{In}_3$, LiZn , Li_3Bi films, etc., exhibiting fast lithium diffusion, and at the same time, insulating LiCl is formed as a by-product, inhibiting reduction of lithium ions on the surface. Therefore, the alloy/ LiCl -protected Li foil provides a stable interface for lithium electrodeposition, thus preventing the growth of lithium dendrites, shown in Figure 7a. Another way, utilizing ion-exchange chemistry performed in a carbonate electrolyte, 1 M LiPF_6 in an ethylene carbonate–dimethyl carbonate (EC/DMC) solvent blend containing a second salt, has taken advantage of depositing coatings of Sn onto lithium anode [89]. As shown in Figure 7b, a tri-layer structure is formed, and Sn nanoparticles are uniformly deposited on the surface of lithium. The Sn-protected Li provides an interphase to accommodate volume changes and hinder lithium dendrites formation. Kozen *et al.* [90] established a 14 nm coating of Al_2O_3 via Atomic Layer Deposition (ALD), exhibiting an improved capacity retention for up to 100 cycles compared with bare Li metal anodes, shown in Figure 7c. The Al_2O_3 coating can act as an effective protective barrier to prevent corrosion of lithium metal exposed to air, sulfur, and organic solvents. In addition, a 3D carbon felt coated by petaloid zinc oxide (CFZO) is engineered as a controllable host for prestoring lithium metal through thermal infusion method [91]. The unique structure of the CFZO-Li not only supplies adequate space for lithium deposition, but also decentralizes

partial current density, thus resulting in a uniform lithium deposition behavior. From Figure 7d, we can see that lithium dendrites can be prevented effectively, assembled with bare Li anode and traditional carbon host/Li metal composite anodes. An artificial TiO_2 /lithium *n*-butoxide (ROLi) hybrid SEI layer with an efficient mechanical strength was proposed to improve the stability of lithium metal anodes [92]. As shown in Figure 7e, the TiO_2 /ROLi SEI film promotes the transmission capacity of lithium ions and ensures the long-term cycle stability of lithium metal anodes, thus avoiding the growth of lithium dendrites. Additionally, the TiO_2 /ROLi- LiFePO_4 full cell shows a high-capacity retention rate of ~100% for 200 cycles and a high capacity of 140 mA h g^{-1} at 0.5 C.

The LiF-rich artificial SEI film has been proved to be an effective strategy to inhibit the growth of lithium dendrites [5,68,93]. This is due to the relatively low-energy barrier of Li^+ transport on the LiF surface, compared with Li_2CO_3 , the main component in native SEI film [93,94]. Yuan *et al.* [95] set up “spansules” made of $\text{NaMg}(\text{Mn})\text{F}_3@\text{Core}@shell$ microstructures as the substrate for the lithium metal, which can form a metal layer and a stable LiF-rich SEI. The metal layer is found to be able to lead to uniform Li deposition and the LiF-rich SEI film is considered to be able to stabilize the lithium/electrolyte interface, arousing uniform lithium-ion flux, thus expected to be dendrite-free. Recently, a type of fluorocarbon ($-\text{CF}_x$)-bonded carbon nanoparticles (F-EC300J) transformed from EC300J is developed to establish high-loading lateral Li deposition (Figure 8a) [96]. The abundant $-\text{CF}_x$ bonds on the surface of F-EC300J can produce LiF-rich SEI films during cycling, which provides uniform and stable Li plating/stripping in long-term cycling. In addition, based on its higher surface energy, it induces lateral lithium deposition and high coulombic efficiency under high loading.

Due to its high ionic conductivity 10^{-3} – $10^{-4} \text{ S cm}^{-1}$ [97], Li_3N is widely used as a fast lithium ion conductor, which can effectively protect the surface of Li metal [98–100]. As shown in Figure 8b, an artificial SEI layer Li_3N , from the reaction of Cu_3N nanoparticles attached together by styrene butadiene rubber ($\text{Cu}_3\text{N} + \text{SBR}$) and lithium metal, possesses high mechanical strength and lithium ion conductivity, thus preventing the growth of lithium dendrites [101]. Therefore, the cycling efficiency of the protected lithium anode can be significantly improved. Ma *et al.* [102] built the surface modification of copper (Cu) foil current collector with indium nitride (InN) film (Figure 8c), and then used the same method to modify the surface of lithium metal. After reacting with lithium metal, indium is transformed into Li_3N and Li_xIn_y

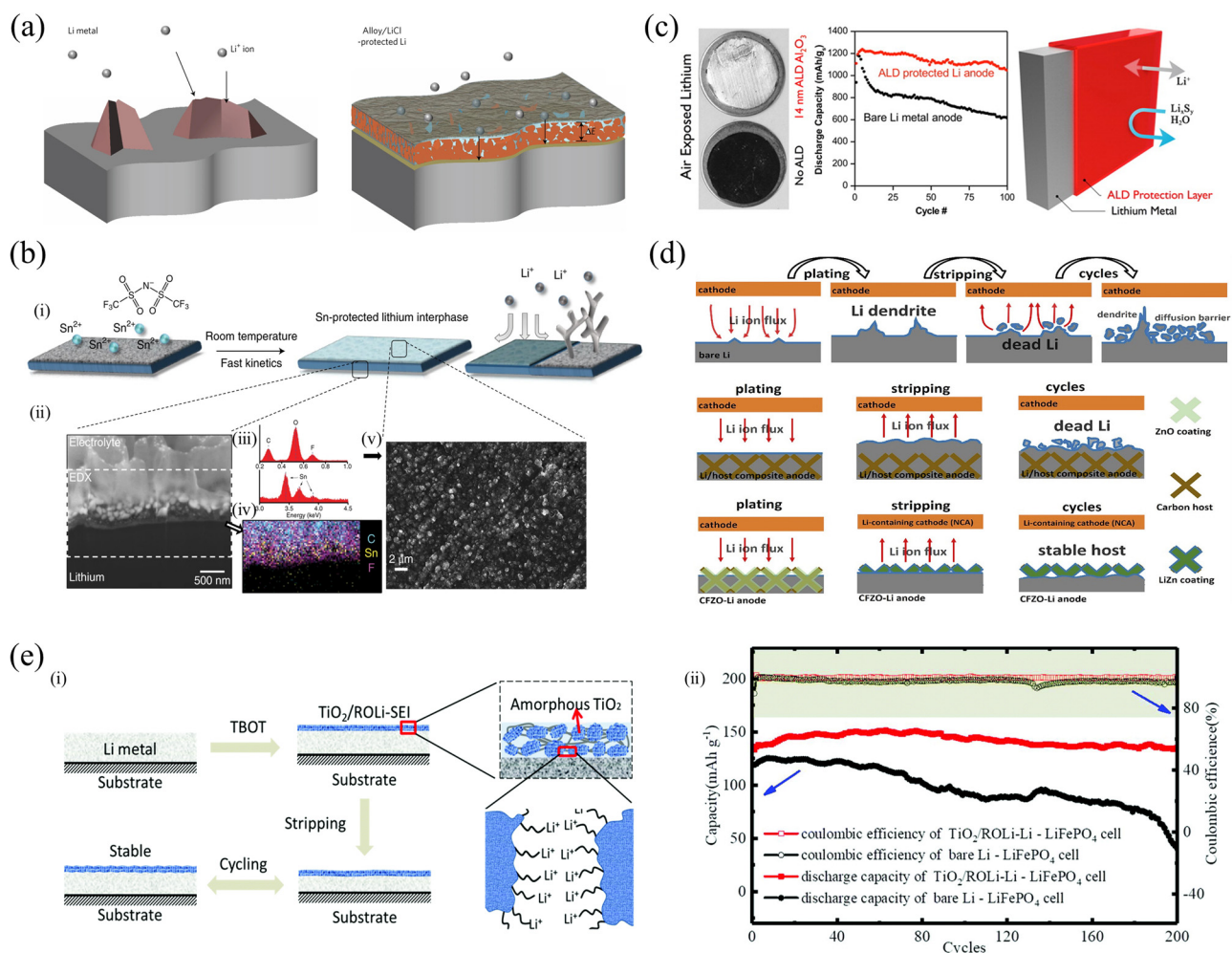


Figure 7: (a) Schematic depicting the function of the alloy-protected lithium foil, reprinted with permission from ref. [88]; (b) hybrid anodes based on facile and fast Sn deposition on reactive metals produced by ion exchange: (i) a schematic illustration of the tin protection on the lithium metal electrode; (ii) a cross-section cryo-FIB-SEM image of the tin-protected lithium, with dashed lines showing the EDX location; (iii) typical EDX spectra of tin-protected lithium; (iv) EDX elemental mapping of fluorine (magenta) and tin (yellow) in the dashed rectangular region; (v) room-temperature field-emission SEM image of the surface morphology of the tin-protected lithium, reprinted with permission from ref. [89]; (c) schematic diagrams of ALD Al_2O_3 -Li metal and discharge capacity of bare Li metal anode and anode protected with 14 nm ALD Al_2O_3 Li-S cells, reprinted with permission from ref. [90]; (d) schematic diagrams of the Li stripping/plating behavior for different Li anodes, including bare Li anode, traditional host/Li metal composite anodes prepared by thermal infusion method, and hierarchical CFZO-Li composite anode compatible for Li-containing cathodes, reprinted with permission from ref. [91]; (e) schematic diagrams of the fabrication of $\text{TiO}_2/\text{ROLi-Li}$ electrodes and the lithium stripping/plating process: (i) and the coulombic efficiency and capacity of full cells composed of TiO_2/ROLi , bare Li, and LiFePO_4 at 0.5 C, reprinted with permission from ref. [92].

to produce an electron-ion mixed protective layer, which provides strong protection to achieve a dendrite-free lithium surface.

Another commonly used coating material is organic polymer. Originating from their high flexibility, they are used as artificial SEI films to alleviate changes in the volume of lithium anode during plating and stripping [103–106]. Copper foil is widely used as a current collector for lithium metal anodes [107]. Liang *et al.* [108] display a novel design via putting a 3D oxidized polyacrylonitrile

nanofiber network on the top of Cu current collector (Figure 8d). As resistance to lithium-ion movement, the polar functional groups on the surface of the polymer fiber are able to guide the uniform deposition of lithium ions. As shown in Figure 8e, the space above the anode is divided into small confinement by the nano-channels with a high aspect ratio, thus resulting in uniform lithium deposition [109]. Compared with the bare electrode, the Coulombic efficiency of modified electrode is greatly improved, and the cycle life is longer.

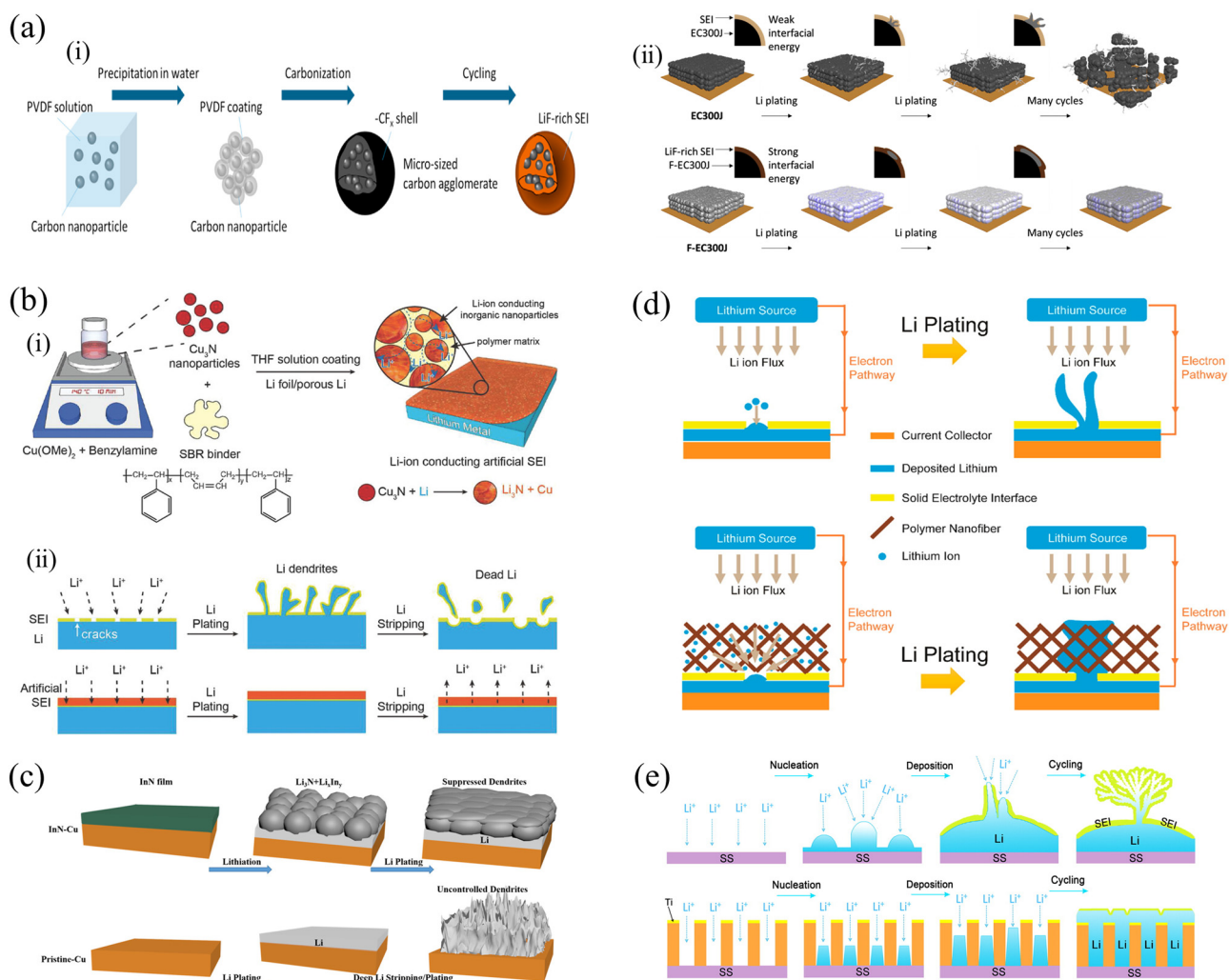


Figure 8: Schematic diagrams: (a) the synthesis and structure of $-CF_x$ bonded carbon nanoparticles (F-EC300J): (i) and Li deposition accommodated in the EC300J, (ii) F-EC300J laminates, reprinted with permission from ref. [96]; (b) (i) the fabrication of the Cu_3N + SBR composite artificial SEI, (ii) the Li-plating/stripping behavior of bare Li, the artificial SEI-protected Li, reprinted with permission from ref. [101]; (c) the InN film *in situ* converted into the mixed lithium metal protective layer, reprinted with permission from ref. [102]; (d) the lithium deposition on bare Cu electrode and modified Cu electrode, reprinted with permission from ref. [108]; (e) the lithium deposition on bare electrode and modified stainless steel (SS) electrode coated with a nano-channel layer, reprinted with permission from ref. [109].

5 Comparison of representative modification approaches

Based on the above discussion, here we compare the three modification approaches from principle and performance improvement. Lithium/metal-based materials composite electrode and lithium/carbon-based materials composite electrode mainly construct 3D conductive skeleton structures, which not only reduce the local current density, thus guiding uniform lithium deposition and inhibiting the growth of lithium dendrites, but also provide more lithium-ion deposition sites and ease the expansion of lithium electrode volume. As a result, the

surface of the lithium composite electrode after cycling is still relatively intact, and the stability of the structure can be maintained. However, the construction of the artificial SEI film is mainly to improve the stability of the SEI film by constructing a film with high mechanical strength and high ionic conductivity on the surface of the lithium electrode in advance, and prevent the puncture of the lithium dendrites in a mechanical manner, and can avoid further reaction between the electrolyte and lithium electrode caused by the rupture of the intrinsic SEI film.

In addition, we compare the performance improvement of typical composite electrodes in the three modification approaches, as shown in Table 1. From the table,

Table 1: Coulombic efficiency improvement comparison of the selected typical composite electrodes tested before and after modification

Typical composite electrodes	Cycles	CE before (%)	CE after (%)	Reference
Li metal/3D copper mesh	70	30.9	97	[27]
Li/expanded-graphite	500	57.3	93.5	[48]
Polymer nanofiber artificial SEI	120	71.3	97.4	[108]

we can see that the best performance improvement is Li/expanded-graphite, which can stably cycle 500 times and still have a coulombic efficiency of 93.5%. This is because expanded-graphite, which is porous and conductive, is uniformly embedded in lithium metal and provides sufficient surface and space for accommodating and attracting lithium metal. The *in situ* lithiation reaction of expanded-graphite and lithium metal forms LiC_6 with good lithophilicity and ionic conductivity, which provides abundant nucleation sites and reduces the nucleation barrier and overpotential of lithium, thereby effectively inhibiting the nucleation and growth of lithium dendrites.

6 Summary and outlook

As we discussed above, there are mainly three types of modification measures for composite lithium metal electrodes including constructing a lithium/alloy composite electrode, a lithium/carbon-based materials composite electrode and an artificial SEI film.

Although a valuable advance has been made in the research of lithium anodes, it's believed that there is still a great progress to be discovered. Here, several possible directions for future lithium anode research are outlined, which may lead to effective practical solutions. First, one may modify the current collector structure. The specific current collector structure can be designed to guide the lithium dendrites to laterally grow within the interior, thereby preventing the vertical growth of lithium dendrites from piercing the SEI film and causing safety accidents. Second, a stabilized lithium metal anode can be developed by using polymer host to alleviate the dendritic growth due to its lithium-ion affinity. Third, nano-structured electrolytes should be applied to stabilize dendritic electrodeposition, such as MOF-based electrolyte, which can achieve uniform lithium-ion transmission.

In short, a single strategy cannot be universally applicable to solve all the problems of lithium anodes. The combined modification method may eventually make

lithium anode a viable technology. As a high-energy power source, lithium metal batteries have great development potential and require more in-depth research in practical applications.

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