Carbon nanomaterials for stabilizing zinc anodes in zinc-ion batteries

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Abstract: Because of their low price, excellent safety and energy storage performance, aqueous zinc-ion batteries (ZIBs) have great potential for use in the power grid and in wearable devices. However, the Zn anode of ZIBs is not stable, for example, Zn dendrite can be formed on the Zn anode accompanied by hydrogen evolution and side reactions, leading to its instability, which has been an obstacle to its use. Carbon nanomaterials have recently been used to improve the performance of Zn anodes due to their unique structure, excellent conductivity and good stability. This review summarizes this recent development for stabilizing zinc anodes. The carbon nanomaterials are used are as hosts, protective coating layers, electrolyte additives and modifiers in the separators to stabilize the Zn electrodes. The problems involved in doing this are presented, and some future developments are outlined.

Key words: Zinc anode; Carbon nanomaterials; Graphene; Carbon nanotubes; Zinc dendrite

1 Introduction

The severe environmental concerns and increasing energy consumption resulting from accelerated industrialization on the global scale have raised the demand for reliable, green, and efficient electrical energy storage devices. The rechargeable battery, as an energy storage device, has attracted extensive attention owing to its high capacity and high energy density[1]. Over the past few decades, lithium-ion batteries (LIBs) have been the most commonly used rechargeable energy storage devices, especially in the field of new energy vehicles. However, safety concerns, high costs, and limited lithium resources on the earth are the main issues for lithium-ion batteries[2–4]. Recently, zinc-ion batteries (ZIBs) have drawn significant attention for application in large-scale grid energy storage systems and wearable electronics. Compared to LIBs, aqueous zinc-based batteries use zinc metal as an electrode which has numerous merits. (1) Zinc is much cheaper than lithium[5]. (2) Zinc anode has an ultra-high theoretical capacity of 820 mAh g^{-1} due to the two-electron transfer mechanism of zinc ions. (3) Zinc has relatively lower redox potential than other metals. (4) The aqueous electrolyte is environmental friendliness and safe, and possesses high ionic conductivity compared to most organic electrolytes[6]. (5) The small radius of hydrated Zn^{2+} ions (8.6 Å) facilitates the rapid intercalation and detachment of hydrated Zn ions in various types of layered cathode materials.

Although zinc anode has many advantages, the practical application of ZIBs is hindered by some serious issues pertaining to the zinc anodes, such as zinc dendrite formation, corrosion, side reactions and hydrogen evolution reactions. These issues seriously affect the stability and lifespan of zinc-ion batteries. For instance, the formation of Zn dendrites can puncture the separation film, causing a short circuit in the cell. Corrosion and other side reactions could produce by-products on the zinc anode, thereby raising the resistance of the batteries and reducing the capacity. Significant effort has been put into designing and fabricating stable zinc anodes by optimizing either host–zinc interface or zinc–electrolyte interface[7]. Introducing some nanomaterials to the hosts, separator or electrolyte is one effective strategy for optimizing the interface and regulating zinc deposition, thereby effectively suppressing dendrite growth and reducing side reactions[8]. For example, graphene/Zn interpenetrated hybrid foils (GiZn) have been reported as electrodes for aqueous ZIBs. The introduction of graphene nanosheets in GiZn not only provides abundant zincophilic sites but also endows the hybrid foil with excellent electrical conductivity and wettability, thus providing dendrite-free and stable anodes for ZIBs[9]. Zn-phosphorus solid solution alloy combined with a

Received date: 2022-12-18; **Revised date:** 2023-04-13

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conductive nitrogen doped carbon framework (ZnP-NC) has been designed as a protecting layer for Zn anode, the synergistic effects of the ZnP and NC enabling long-term dendrite-free plating of zinc anodes[10]. A flexible composite film of expanded graphite and copper particles was reported as a host for a Zn anode without dendrites, because the copper particles acted as zincophilic seeds that reduced Zn nucleation overpotential, and the expanded graphite substrate induced epitaxial electrodeposition of zinc[11]. The materials reported in these literatures all contain carbon nanomaterials.

Carbon nanomaterials have been extensively investigated in the past decades due to their unique structure, high conductivity, excellent mechanical properties and good chemical stability[12]. Carbon nanomaterials have diverse structures, such as zero-dimensional (0D) fullerene or graphene quantum dots, 1D carbon nanotubes (CNTs), 2D graphene and 3D graphene foam. The excellent properties and diverse structures of carbon nanomaterials make them very useful and promising in many fields, including catalysis, energy storage and conversion, environmental science and biomedicine. It is encouraging that carbon nanomaterials have greatly aided the preparation of stable zinc anode[13–14]. Fig. 1a shows the number of publications in the past decade on carbon nanomaterials for stabilizing zinc anodes. The number of articles has increased dramatically in the past two years, which indicated that carbon nanomaterials for stabilizing zinc anodes have attracted increasing attention. Various strategies have been reported to utilize carbon nanomaterials for dendrite-free and stable zinc anodes in high-performance ZIBs (Fig. 1b). Early literatures used carbon nanomaterials as hosts for zinc anode, for example, graphene could be used as a host to regulate the deposition behaviour of Zn^{2+} ions and suppress the growth of dendrites[15–16]. Subsequently, many carbon nanomaterials were reported as protective layers on zinc anode to prevent contact between the anode and the electrolyte and reduce side reactions[17–19]. Recent research has shown that carbon nanomaterials as electrolyte additives can regulate the electric field distribution on the surface of zinc anodes, resulting in a uniform electric field distribution. Carbon nanomaterials as electrolyte additives can also control the deposition of zinc ions, thereby eliminating zinc dendrites[20]. As carbon nanomaterials play such an important role in zinc-ion batteries, there have been some good reviews on carbon nanomaterials in flexible or high-performance zinc-ion batteries[13–14]. However, the role of carbon nanomaterials in stabilizing zinc anodes deserve more attention, therefore, a timely review of this topic is highly desirable.

In this review, we begin with a brief description of the key factors affecting zinc nucleation behaviour and plating quality, as well as the challenges of zinc anodes. Then, four design strategies for stabilizing

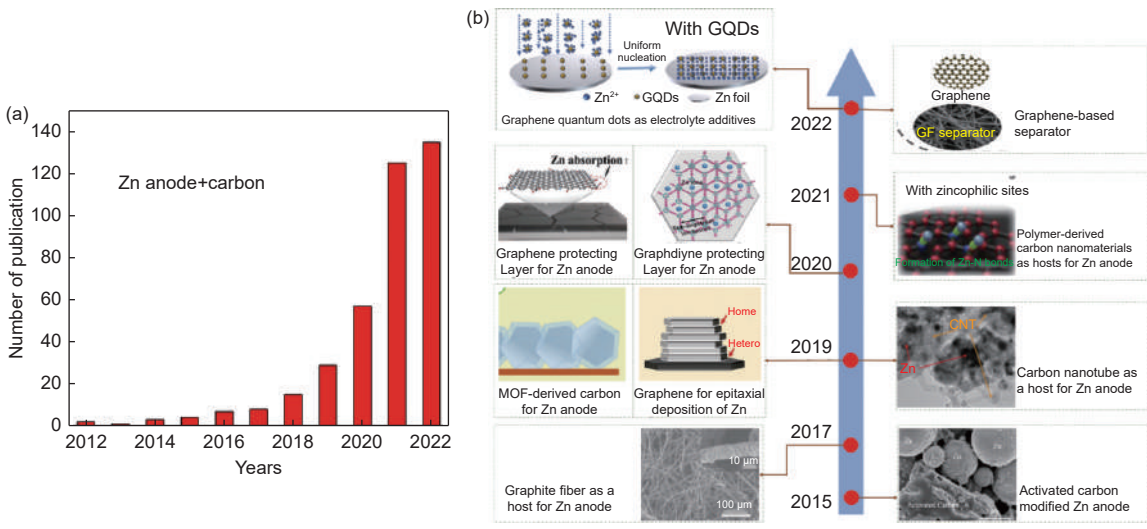

Fig. 1　(a) Number of publications on carbon nanomaterials for stabilizing zinc anode, which was indexed by two topic keywords of ‘‘zinc anode’’ and ‘‘carbon’’ from the Web of Science. (b) Main progress of carbon nanomaterials as hosts, protecting layers, separators and electrolyte additives in aqueous ZIBs

zinc anodes are summarized, including (1) carbon nanomaterials as hosts for zinc deposition, (2) carbon nanomaterials as protecting layers, (3) carbon nanomaterials for separator modification and (4) carbon nanomaterials as electrolyte additives. Finally, we share our views on the challenges and prospects for developing dendrite-free and stable Zn anodes.

2 Issues related to Zn anodes

The energy storage mechanism of Zn anodes is based on the Zn/Zn^{2+} electrochemical redox reaction and reversible cycling of the Zn plating/striping process[21]. However, Zn anodes in aqueous Zn ions currently suffer many challenges, such as dendrite growth, hydrogen evolution reactions, corrosion and passivation (Fig. 2). The irregular zinc plating during battery cycling can lead to severe zinc dendrite growth, resulting in short circuits and poor cycling performance. Another challenge with zinc anodes is the severe hydrogen evolution reactions at the anode/electrolyte interface and the corrosion of zinc, as well as the formation of various by-products. These by-products increase the resistance between the zinc anode and the electrolyte, decreasing the coulombic efficiency and cycle life of the ZIBs. Therefore, the key to protecting the zinc anode is to eliminate dendrites and suppress side reactions.

2.1 Zn dendrites

The formation of Zn dendrites is affected by various factors such as surface energy, Zn ion concentration gradients, excessive overpotential and uneven electric field distribution[22–24]. At the beginning of zinc deposition, Zn^{2+} ions migrate to the Zn anode under the driving force of an electric field and concentration gradient[25]. Since the zinc surface is not smooth, there may be some small tips on the zinc anode. Zn^{2+} ions will preferentially deposit on these tips because of the higher surface charge density of the tip and the higher concentration of Zn^{2+} ions near the tips[26]. The high concentration of zinc can promote the crystallization of the nucleation region, thereby reducing its surface energy. The uneven nucleation and crystallization of zinc metal lead to the formation of zinc dendrites[27]. The dendrites exhibit a needle-like morphology and act as the reaction center for further zinc deposition in the subsequent reactions, leading to further growth of zinc dendrites. In addition, once these brittle straight crystals are fractured, they will be separated from the zinc anode and no longer participate in subsequent electrochemical reactions, resulting in the formation of dead zinc. Zn dendrites may not be affected by the kosher band at low current densities, but high current densities can rapidly damage the battery.

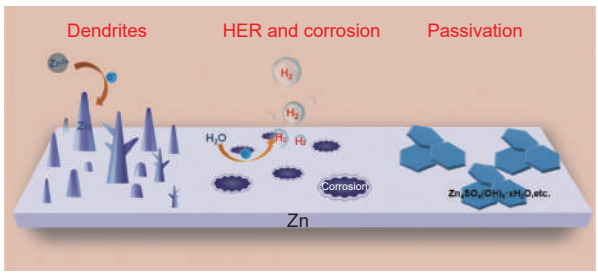

Fig. 2 Schematic illustration of zinc dendrites, HER, corrosion and passivation

2.2 HER and corrosion

Side reactions are another important issue plaguing the Zn anode. One such side reaction is the hydrogen evolution reaction (HER), which is inevitable during the Zn depositing/stripping process[28–29]. HER and the deposition reaction of Zn^{2+} to Zn metals are competitive reactions[30]. The evolution of hydrogen will increase the overall pressure inside the cell, which will cause the whole cell to expand or the electrolyte to leak and finally damage the cell[29]. The release of hydrogen gas by HER will not only decrease the coulombic efficiency of the battery but also increase the local pH value of the electrolyte, which promotes the generation of by-products. These by-products could accumulate on the surface of the Zn anode as an insulating layer and deactivate the electrode[31–32]. The corrosion of Zn is divided into chemical self-corrosion and electrochemical corrosion[6, 21]. Due to the higher reactivity of Zn than hydrogen, the Zn electrode will inevitably self-corrode in an acidic electrolyte. Furthermore, Zn electrode becomes un-

even due to the inhomogeneity of Zn depositing/stripping. The rough surface has higher electrochemical activity, which causes further corrosion of the electrode.

2.3 Zn passivation

Passivation of the zinc anode is another severe issue in aqueous electrolytes. In alkaline electrolytes, some by-products, including ZnO and $Zn(OH)_2$, are produced when the ZIBs are discharged[30, 33]. These insulating by-products attach to the Zn anode, which not only hinders the Zn^{2+} ion transport between the anode and the electrolyte but also increases the resistance of the electrode. This increases the polarization voltage and directly leads to a rapid drop in battery capacity. In weakly acidic electrolytes such as zinc sulfate, basic zinc sulfate is a well-known by-product, which is mainly formed due to the increase of local pH value after hydrogen evolution. The formation of these by-products consumes large amounts of electrolyte and exacerbates battery death. In general, the passivation of Zn affects the depositing/stripping of Zn, hinders the migration of Zn^{2+} ions, and increases the resistance of the Zn anode[34].

3 Carbon materials as hosts

The Zn plating/striping process on zinc film anode is random, which causes dendrites growth. A host material may be used as a structural and conductive substrate with the crucial purpose of guiding the uniform growth of Zn. Therefore, a good host material needs to have some of the following merits: (1) Good conductivity. (2) Large amount of zincophilic sites. (3) Sufficient volume for Zn deposition. (4) Relatively uniform electric field distribution throughout. Carbon nanomaterials have these advantages and are good candidates for host materials. Some typical carbon nanomaterial as hosts will be introduced in this review, such as carbon nanotubes, graphene, carbon nanofibers and polymer-derived carbon materials.

3.1 Carbon nanotubes as hosts

Carbon nanotubes (CNT) can be used as hosts for dendrite-free Zn depositing/stripping. For example, Lu et al. designed a flexible CNT framework as a conductive host for Zn plating to obtain a dendrite-free Zn/CNT electrode for the first time[35]. The CNT framework constructed produced an excellent conductive network and unique porous structure for Zn depositing and stripping (Figs. 3a-b). The large specific surface area of CNTs can significantly reduce the local current density of CNTs and lower the nucleation overpotential of Zn. The good electric conductivity and large surface area make the electric field distribution more uniform and reduce the initial Zn nucleus size and further suppress the growth of Zn dendrites. These merits of the 3D CNT framework can also block the side reactions of electrolytes. A symmetric cell made of Zn/CNT electrode exhibited a low voltage hysteresis of 27 mV at 2 mA cm^{-2} and excellent cycling stability up to 200 h with a high depth of discharge (DOD) of ~28% (Fig. 3c)[35]. Zhou et al. reported a zinc/carbon nanotube (Zn/CNT) foam *via* simple pulse electrodeposition with 3D CNT foams as the hosts. The Zn/CNT foam electrode confined the Zn depositing/stripping in the 3D interconnected network[36]. The 3D structure of the CNT foam provided more volume and accessible sites for Zn plating than planar Zn foils. Therefore, the density of Zn nucleation sites in 3D Zn/CNT foam is much higher than that in plane foil. The symmetric battery assembled with Zn/CNT electrodes showcased 81% depth of discharge (DOD) and an extra-long lifespan of 10 000 min at 3 mA cm^{-2}, which is much larger than that of Zn foil. Furthermore, the full battery composed of Zn/CNT foam anode and MnO_2 cathode demonstrated long stability of 5 000 charge/discharge cycles at 30 C. In addition, Zn nanosheets can also be electrodeposited on multiwall carbon nanotubes (MWCNTs) films to fabricate a good flexible anode of Zn nanoflakes and MWCNTs (Fig. 3d)[37]. The Zn/MWCNTs nanoflakes anode and VO_2(B)-MWCNTs hybrid cathode were assembled into quasi-solid-state aqueous Zn-ion micro-batteries (ZIMB). As expected, the as-prepared ZIMB exhibited a large capacity of 314.7 μAh cm^{-2}, a high energy density of 188.8

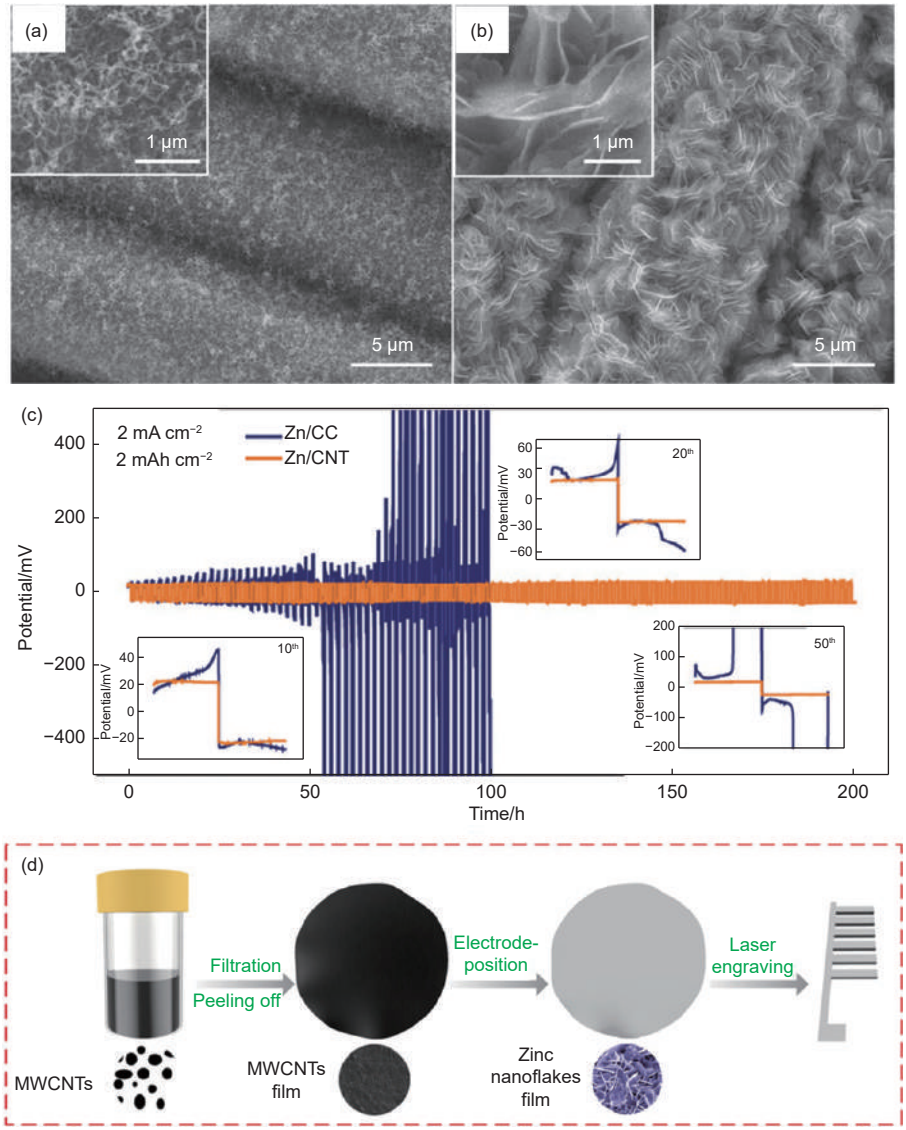

Fig. 3 SEM images of (a) bare CNT and (b) Zn/CNT. (c) The cycling performance of symmetrical batteries based on Zn/CC and Zn/CNT anodes at 2 mA cm^{-2}[35]. (d) The fabrication process of anode using zinc/MWCNTs nanoflakes[37]. Reprinted with permission

μWh cm^{-2} as well as excellent flexibility (the bending angle is up to 150°) and good thermal stability. For carbon nanotubes to become good host materials, it is necessary to construct either a porous and highly conductive network for Zn deposition or a conductive film with lots of zincophilic sites.

3.2 Graphene as hosts

During the electrochemical deposition of Zn metal, the growth of Zn crystals is very strongly related to the structure of the substrate. As shown in Fig. 4a, the growth direction of the Zn crystals can be perpendicular or parallel to the substrate[16]. For example, when Zn was deposited on a stainless steel substrate, the Zn platelets were randomly oriented with some of the Zn platelets perpendicular to the substrate (Fig. 4b). However, graphene can act as a low-lattice-mismatch interface for the epitaxial deposition of Zn. When graphene was coated on the stainless steel substrate, Zn platelets deposited on graphene exhibited a horizontal arrangement, indicating a locked orientation relationship with the graphene. Therefore, the Zn crystal platelets on graphene tend to be parallel to the graphene substrate rather than in random orientation (Fig. 4c). Consequently, the resultant parallel Zn nanosheets on graphene substrate exhibited outstanding thousand cycle reversibility at moderate and high

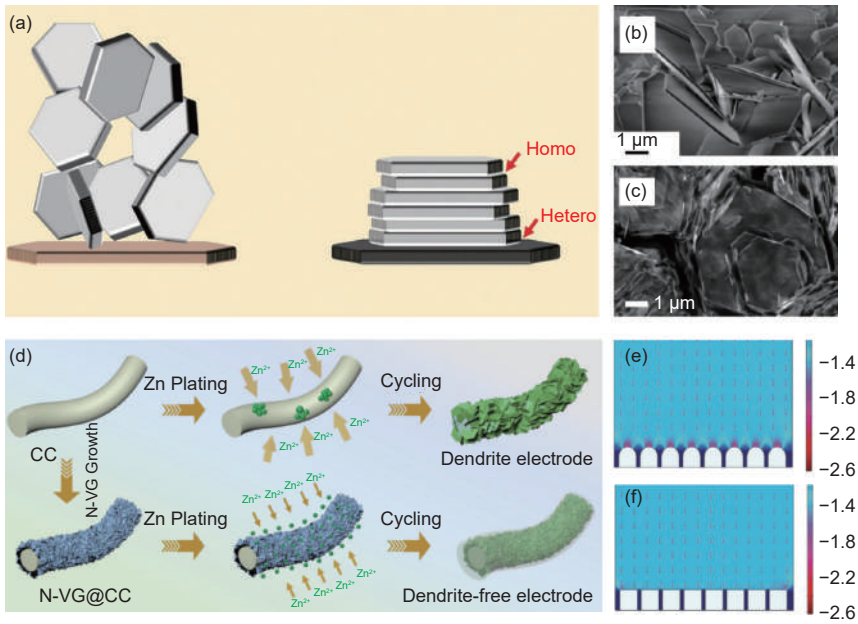

Fig. 4　(a) Scheme illustrating zinc metal crystals grown on a stainless steel substrate and a graphene coated stainless steel substrate. Scanning electron microscopy (SEM) images of Zn electrodeposition on (b) bare stainless steel and (c) graphene-coated stainless steel[16]. (d) The schematic illustrations of Zn deposition processes on CC and N-VG@CC electrodes. Models of the electric field distributions for (e) Zn@CC electrode and (f) Zn@N-VG@CC electrode after Zn nuclei formation[15]. Reprinted with permission

rates, which provided a new pathway toward high-performance ZIBs with good reversibility[16]. This method is based on changing the growth direction of the Zn crystals to avoid the formation of dendrites. As long as the host material has a small lattice mismatch with the Zn lattice plane, the Zn crystals will not grow perpendicular to the substrate to form dendrites but grow parallel to the substrate to form a uniform film.

Heteroatoms in graphene nanosheets and the three-dimensional (3D) architecture of graphene can also facilitate the uniform nucleation and growth of Zn. For example, Cao et al.[15] reported a 3D nitrogen-doped carbon nanomaterial (N-VG@CC) by growing vertical graphene nanosheets on carbon cloth to regulate dendrite-free Zn deposition. Density functional theory (DFT) calculations confirmed that the functional groups containing nitrogen elements in N-VG could decrease the overpotential of Zn nucleation by increasing the interaction between Zn ions and the graphene substrate, resulting in a uniform distribution of Zn nucleation sites. In Fig. 4d, when the current collector was the bare carbon cloth without graphene, Zn^{2+} preferred continuous deposition and growth on the existing Zn nucleus to form Zn dendrites. However, when the N-VG nanosheets were coated on the carbon cloth and acted as the current collector for Zn deposition, metallic Zn was preferentially deposited on the N-VG surface resulting in a uniform, dendrite-free morphology[15]. The electric field distributions for the Zn plating/stripping process are also affected by the substrate, when bare carbon cloth was used as the substrate, the Zn deposition process had an uneven electric field (Fig. 4e), however, the N-VG nanosheets could make electric field streamlines more uniform (Fig. 4f). This work shows that heteroatom doping of the graphene host is another good strategy to suppress the growth of Zn dendrites because heteroatom doping can bring more zincophilic sites and uniform electric field distribution.

The porous 3D graphene structures can provide significant volume change during the Zn reversibly plating/striping process, thereby inhibiting the growth of Zn dendrites. Wu et al. reported two kinds of highly ordered 3D printed graphene arrays (3DGs). As the Zn^{2+} deposition can be regulated by the ordered structure of the 3D graphene, the 3DGs hosts showed con-

siderable columbic efficiencies and a long lifespan[38]. Combining graphene with other materials as a host is another choice for eliminating Zn dendrites. For example, a 3D MXene/graphene aerogel (MGA) was prepared *via* an oriented freezing method and used as a host for Zn deposition[39]. Owing to their abundant zincophilic sites and numerous microporous structures within MGA, Zn can be densely encapsulated inside the 3D MGA host during the Zn electrodeposition process, effectively inhibiting the growth of Zn dendritic. Furthermore, the 3D MXene/graphene scaffold as hosts suppressed hydrogen evolution reactions and passivation. the 3D MXene/graphene/Zn electrode displayed a long-cycling life of more than 1 000 h at 10 mA cm^{-2} and 5 300 dendrite-free cycles in a symmetric cell. Moreover, when employing MGA@Zn, LMO and PVA@MXene as anode, cathode and electrolyte, respectively, a quasi-solid-state and flexible battery was assembled, which demonstrated a high initial capacity and a long cycling lifespan[39]. The 3D structure of the host can provide enough space for Zn deposition, thus avoiding the growth of Zn dendrites, and resulting in good stability and excellent performance of the Zn anode.

From the literatures on graphene as the host of Zn anodes, we may summarize that changing the growth direction of Zn crystals, increasing zincophilic sites through doping, and increasing the space for Zn deposition by designing 3D structures are effective methods for stabilizing Zn anodes.

Furthermore, graphene and carbon nanotubes can also be combined to make 3D graphene-CNTs composites as the hosts, because it is difficult for single carbon nanotube or graphene as hosts to undergo prolonged Zn plating at high current densities without causing large changes in volume. A 3D porous graphene-CNT scaffold was fabricated by combining the nanocomposite gelation strategy and freeze-drying method. Typically, a mixed ink composed of CNTs and graphene oxides was bladed-coated on the substrate and freeze-dried to obtain a porous scaffold. The 3D porous graphene-CNTs scaffold was then decorated with metal-organic framework-derived ZnO/C nanoparticles (3D-ZGC), which was further used as the host for dendrite-free Zn anodes. The 3D-ZGC scaffold host can uniformize electric field distribution and decrease the current density to suppress the growth of Zn dendrites. When tested in a symmetric cell, the 3D-ZGC scaffold anode exhibited an ultrahigh stability of Zn electroplating/stripping at a current density of 20 mA cm^{-2}. It also demonstrated a good cycle stability of 1 500 cycles with a low overpotential of less than 65 mV[40].

3.3 Carbon fibers as hosts

Recently, carbon fibers (CF) have been used as substrates or current collects in various energy storage devices such as supercapacitors and batteries due to their high modulus and strength, outstanding conductivity and excellent stability[41]. However, pristine carbon fibers as the hosts for Zn deposition would result in dendrites growth in the anode. Much effort has been devoted to prepare carbon fiber hosts for stabilizing Zn anodes. For example, Wang et al. used a highly-conductive carbon fiber-graphite felt as the current collector to prepare a self-supported Zn@GF anode through constant voltage electrodeposition of Zn[42]. This carbon fiber-graphite mat with high electrical conductivity provided a larger electroactive area, resulting in faster electron transport, and most Zn crystals grew along the fiber in a relatively compact manner. This carbon fiber-graphite mat anode offered one efficient solution for obtaining a dendrite-free Zn anode. TiO_2 and SiO_2 well-dispersed in carbon fibers (SiO_2/TiO_2/CF) can also promote controllable nucleation and deposition of Zn on carbon fiber hosts. As a result, Zn metal can be smoothly and stably deposited on SiO_2/TiO_2/CF[43]. The as-prepared 3D hollow Zn@SiO_2/TiO_2/CF anode exhibited a long cycle life of more than 2 000 cycles at 20 mA cm^{-2} in a symmetrical cell. N-doped carbon fibers embedded with zincophilic Cu nanoboxes have been reported as a 3D multifunctional host for stable Zn-metal anodes because the zincophilic Cu could act as homogeneous nucleation sites for the uniform deposition of Zn, resulting in a dendrite-free behavior with ultralong cyc-

ling life (450 h)[44]. Yu et al. reported a 3D carbon/Sn hybrid fiber with Sn nanoparticles embedded in a carbon structure (denoted as Sn@NHCF) as a host for Zn deposition using a hard template strategy. The as-synthesized Sn@NHCF host showed high Coulombic efficiency, low voltage hysteresis and dendrite-free cycling stability, because both Sn nanoparticles and pyrrolic nitrogen in the hybrid fiber were strong zincophilic sites for homogeneous Zn deposition[45].

3.4 MOFs derived carbon nanomaterials as hosts

The construction of three-dimensional (3D) heteroatom-doped carbon nanomaterials is a good strategy for designing the host for Zn deposition because the heteroatoms in carbon nanomaterials facilitate Zn deposition. Metal–organic frameworks (MOFs) have periodic nano-porous structures and large surface areas[46–47]. MOFs have been grown on Zn electrodes to protect the Zn anode by preventing dendrite growth, corrosion, and hydrogen evolution[48–49].

Carbon nanomaterials derived from MOFs have attracted a lot of attention due to their high porosity, large surface area, good electrical conductivity and wide range of applications[50–51]. MOF-derived carbon nanomaterials can also be used as the hosts for Zn deposition. For example, N and O co-doped 3D porous carbon architectures on copper foam (NOCA@CF) derived from MOF arrays can be used as a substrate for uniform Zn deposition to suppress the dendrite growth of Zn anode[52]. The NOCA@CF is fabricated *via* a one-pot vacuum carbonization method by using MOF arrays as the precursors. The 3D porous NOCA has a large specific surface area up to 843.4 $m^2\ g^{-1}$, which not only provides a lot of space for Zn deposition but also regulates the electric field distribution during Zn plating.

MOF ZIF-8 derived carbon nanomaterial (ZIF-8-500) annealed at 500 °C has been used as a host material for Zn plating and stripping[53]. ZIF-8-500 electrodes are promising for developing dendrite-free, high-efficient, and high-capacity Zn anodes due to their ordered porous structure. As shown in Fig. 5a, smooth surfaces were observed in all the SEM images of ZIF-8-500 with Zn deposition at areal capacities from 1 to 10 mAh cm^{-2}. The trace amount of Zn in the framework of the ZIF-8-500 electrode provides nucleation sites for Zn plating, resulting in dendrite-free deposition (Fig. 5b). The supercapacitor composed of Zn@ZIF-8-500 anode and carbon cathode exhibited a good energy storage performance. The Zn@ZIF//iodine battery constructed with Zn@ZIF anode and I_2 cathode showed a long cycling life and a good rate capability, which is much better than that of control cells with pure Zn metal anode. Xue et al. combined MOF-derived ZnO/C nanoparticles with a 3D porous graphene/carbon nanotube scaffold (3D-ZGC) and further used it as the host for a Zn-metal composite anode (Fig. 5c)[40]. The MOF-derived ZnO/C nanoparticles are zincophilic and nucleation sites induce homogeneous Zn deposition. Zn plating/stripping behaviors of bare foil and 3D-ZGC composite anode were observed *in situ* by an optical microscope. A fairly rough and uneven Zn electrodeposition with small protrusions appeared on the pure Zn anode after only 10 cycles, and a large number of dendrites appeared after 100 cycles (Fig. 5d). However, the Zn@3D-ZGC composite anode can induce uniform nucleation of Zn, maintaining dendrite-free morphology with a flat surface even after 100 cycles (Fig. 4d). Due to the advantages of 3D-ZGC such as hierarchical porous structure, high specific surface area and good electrical conductivity, the 3D-ZGC composite anode exhibited unprecedented cycle stability for more than 2 000 cycles at a current density of 10 mA cm^{-2} with a fixed capacity of 1 mAh cm^{-2} (Fig. 5e).

Compared to carbon nanotubes and graphene, MOF-derived carbon nanomaterials have more heteroatoms, regular pores and larger specific surface area. But the pores of MOF-derived carbon nanomaterials are very small, which would not provide enough volume for zinc deposition. The issue of small pores in MOF-derived carbon nanomaterials can be overcome by constructing 3D structure of MOF-derived carbon nanomaterials and graphene/carbon nanotubes.

3.5 Polymers-derived carbon nanomaterials as hosts

Polymers have also been used as the precursors

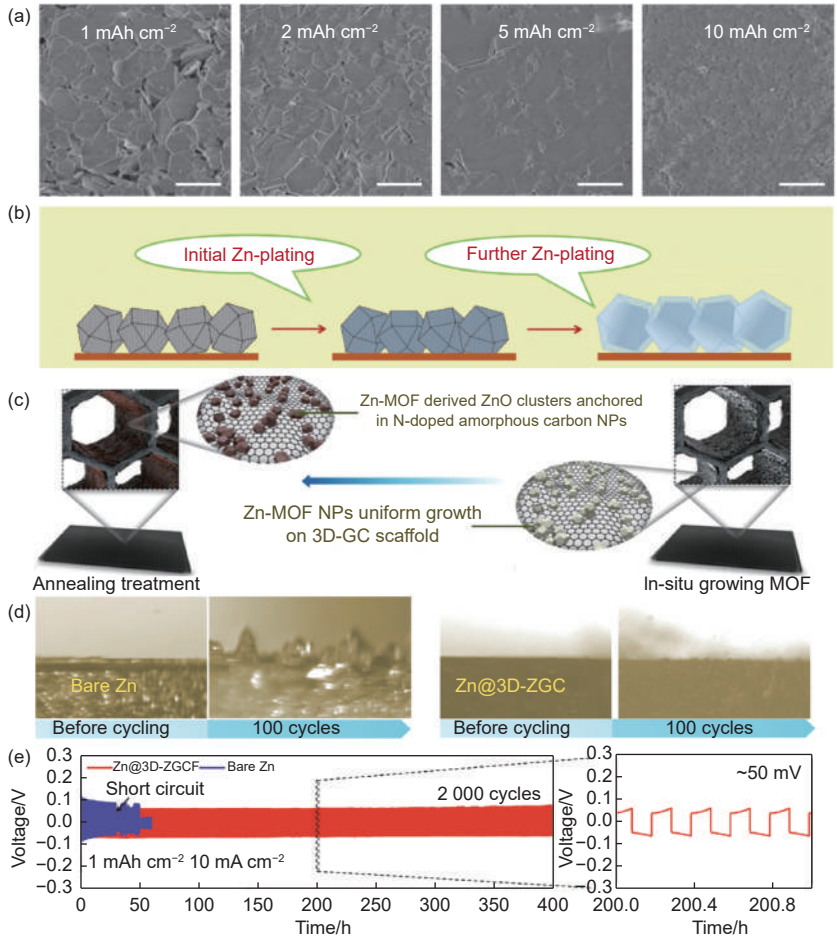

Fig. 5 (a) SEM images of Zn anodes at areal capacities from 1 mAh cm^{-2} to 10 mAh cm^{-2}. Scale bars, 2 mm. (b) Schematics of the Zn metal plating process on Zn@ZIF-8-500 anode[53]. (c) Schematics of the preparing process of the 3D-ZGC host. (d) The optical microscopy images of the Zn plating behavior on bare Zn foil and Zn@3D-ZGC anodes before and after 100 numbers of depositing/stripping cycles. (e) The cycling stability of the whole symmetrical batteries composited of the bare Zn foil (green line) and the Zn@3D-ZGC composite (read line) anodes at 10 mA cm^{-2} with a fixed capacity of 1 mAh cm^{-2}[40]. Reprinted with permission

for the preparation of multifunctional carbon nanomaterials due to their tunable chemical composition, large molecular weight and abundant heteroatoms[54]. Polymer-derived carbon nanomaterials have numerous advantages. For example, pyrolysis of polymers into carbon nanomaterials creates a lot of pores, providing large amount of space for Zn deposition. In addition, most of the heteroatoms in polymer-derived carbon nanomaterials are zincophilic sites, which could reduce Zn nucleation overpotential and regulate Zn deposition. Qiao et al. prepared carbon hollow spheres with several nitrogen dopants by pyrolysis of resorcinol-formaldehyde (RF) polymer spheres[55]. The mechanism of the pro-Zn site was investigated by various *in situ*/*ex situ* techniques and density functional theory (DFT) calculations. The results showed that Zn^{2+} can combine with pyridine N to form Zn-N bonds. This mechanism can promote the formation of spacious nucleation of Zn on carbon hosts. The presence of Zn-loving sites facilitates uniform Zn deposition and enhanced the electrochemical performance at the same time. Wang et al. reported a polyimide-derived oxygen and nitrogen co-doped flower-shaped carbon structure through a combination of polymerization and pyrolysis[56]. The O, N co-doped flower-shaped carbon structure was explored as the host material for ZIBs and supercapacitors. The zincophilic heteroatom dopants (O/N dopants) in the carbon hosts could guide Zn nucleation and Zn crystal growth in a heteroepitaxial mode, resulting in a horizontal plating with the dendrite-free feature. The ether (C—O), carboxyl (—O—C=O—) and pyrrole nitrogen

groups are particularly beneficial to the uniform nucleation of Zn. It can be concluded that pore-rich structures (such as hollow spheres or flower-like structures) and zincophilic dopants are two important factors for designing Zn hosts of polymer-derived carbon nanomaterials. More research efforts need to be devoted into this area, including the effect of other heteroatom dopants on Zn deposition.

Table 1 summarizes the recent literatures on carbon nanomaterials as hosts for Zn anode. The coulombic efficiency of most Zn anodes with carbon nanomaterials as hosts are more than 95%. Heteroatom doping has a great influence on the performance of host materials. For example, Zn@N-VG@CC anode with the N-doped vertical graphene as the host exhibited a voltage hysteresis of about 6 mV, which is the lowest voltage hysteresis in literature (Table 1). The composite hosts show better performance than most hosts with only one type of material. For example, the MGA@Zn anode with the MXene/graphene composite host shows a small voltage hysteresis of 64 mV and an ultralong life span of 1 050 h. Zn@TiO_2/NC anode with MOF-derived N-doped carbon nanomaterials exhibits the longest life span of 1 100 h among all the materials shown in Table 1.

4 Carbon materials as protecting layers

Introducing a protective layer on the Zn foil electrode is another effective strategy to inhibit the dendrite growth of Zn anode. So far, various materials have been coated on the Zn electrode as a protective layer, such as MOFs[60–61], MXene[62], Layered double hydroxides (LDH)[63], polymers[64] and carbon nanomaterials. Carbon nanomaterials show great advantages in Zn electrode protection because of their unique nanostructure, good conductivity, and tunable surface properties. The good conductivity of carbon nanomaterials is beneficial to stabilize the plating/stripping behavior of Zn^{2+}. The pore structure and zincophilic sites on the carbon nanomaterial membrane are propitious for homogenizing the electric field distribution and regulate ion concentration density, thereby inhibiting the growth of dendrites. The excellent mechanical and chemical stability of carbon nanomaterials can separate the Zn anode from the electrolyte, thus hindering side reactions.

4.1 Carbon nanotubes as protecting layers

Carbon nanotubes (CNT) have also been used as the protective layer for stabilizing Zn anode. Dong et al. developed a flexible, freestanding and conductive carbon nanotube scaffold to protect the Zn metal anode[65]. As shown in Figs. 6a-b, this carbon nanotube scaffold was placed on the surface of Zn anode as a protecting layer during the assembly of Zn-based cells. The highly conductive carbon nanotube network stabilized the electric field at the Zn anode, and the depositing/stripping behavior of the Zn anode was significantly improved due to the porous carbon skeleton that regulated the Zn deposition position. The symmetric cell composited of Zn anodes protected by the carbon nanotube scaffolds can stably cycle for 1 800 h at low voltage polarization, which outperform to bare Zn electrodes.

Table 1　Performance of recently reported carbon nanomaterials as hosts for Zn anode

Anode	Carbon nanomaterials	Voltage hysteresis	Life span	Coulombic efficiency	Cycling stability	Ref.
Zn/CNT	CNT	27 mV	200 h (2 mA cm^{-2})	97.9% (5 mA cm^{-2})	88.7% (1000 cycles)	[35]
Zn/CNT foam	CNT foam	143 mV	10000 min (3 mA cm^{-2})	—	82.0% (5000 cycles)	[36]
MGA@Zn	Mxene/ graphene	64 mV	1050 h (10 mA cm^{-2})	99.7% (10 mA cm^{-2})	60 cycles	[39]
Zn@N-VG@CC	N-doped vertical graphene	~ 6 mV	150 h (0.5 mA cm^{-2})	>95.0% (5 mA cm^{-2})	80.0% (300 cycles)	[15]
Zn/GCF	graphene	—	100 h (1mA cm^{-2})	100.0% (0.2 mA cm^{-2})	1000 cycles	[57]
NLSG-Zn	Laser-scribed graphene	18 mV	250 h (1 mA cm^{-2})	99.4% (2 mA cm^{-2})	72.3% (1200 cycles)	[58]
Zn@3D-ZGC	Graphene/carbon nanotube	~ 50 mV	400 h (10 mA cm^{-2})	—	80.8% (6000 cycles)	[40]
Zn@ZIF-8-500	MOFs derived carbon	—	—	98.6% (2.0 mA cm^{-2})	72.0% (20000 cycles)	[53]
Zn@NOCA@CF	CF	—	240 h (1 mA cm^{-2})	95.7% (1 mA cm^{-2})	200 cycles	[52]
Zn@TiO_2/NC	MOFs derived N-doped carbon	~ 60 mV	1100 h (5 mA cm^{-2})	99.4% (2.0 mA cm^{-2})	75.0% (1000 cycles)	[59]
Sn@NHCF	N-doped hollow carbon spheres	21 mV	370 h (1 mA cm^{-2})	99.7% (5.0 mA cm^{-2})	2400 cycles	[45]
HSTF	3D hollow SiO_2/TiO_2/CF	122 mV	600 h (10 mA cm^{-2})	99.5% (20.0 mA cm^{-2})	85.0% (10000cycles)	[43]

Li et al. dip-coated a CNTs protective layer on the Zn anode to prepare a dendrite-free Zn-CNTs anode[66]. The CNTs layers protected the Zn anode from effects of side reactions by limiting them to occur only on the CNTs protective layer, ensuring fast Zn depositing/exfoliating kinetics. Besides, the CNTs network can also act as a charge redistributor to guide the uniform deposition of Zn nanosheets on Zn foil. SEM images confirmed that the Zn nanosheets were uniformly deposited under the CNTs layer without dendrite formation after cycling for 400 h (Figs. 6c-d). The positive effect and mechanism of the CNTs layer in stabilizing Zn anode were also investigated by density functional theory (DFT) calculations. As shown in Figs. 6e-j, the binding energy of the CNTs protective layer and O/S impurity atoms is 3.41/3.40 eV, which is higher than that of Zn foil (2.08/1.37 eV). Due to the stronger adsorption effect of the CNTs layer, side reactions tend to occur on the CNTs protective layer rather than on the surface of the Zn foil. Therefore, the kinetics of Zn deposition/stripping on Zn foil is less affected by side reactions, resulting in good stability and high Coulombic efficiency of this electrode in full cells. For example, the Mn^{2+}/Zn^{2+} hybrid battery assembled with Zn-CNTs anode exhibited an excellent electrochemical performance with 100% capacity retention after 11 000 cycles (Fig. 6k).

4.2 Graphene as protecting layer

Owing to its ultrathin 2D nanostructure, high conductivity, and outstanding mechanical properties, graphene has been considered to a distinguished candidate for the protective layer of Zn electrodes.

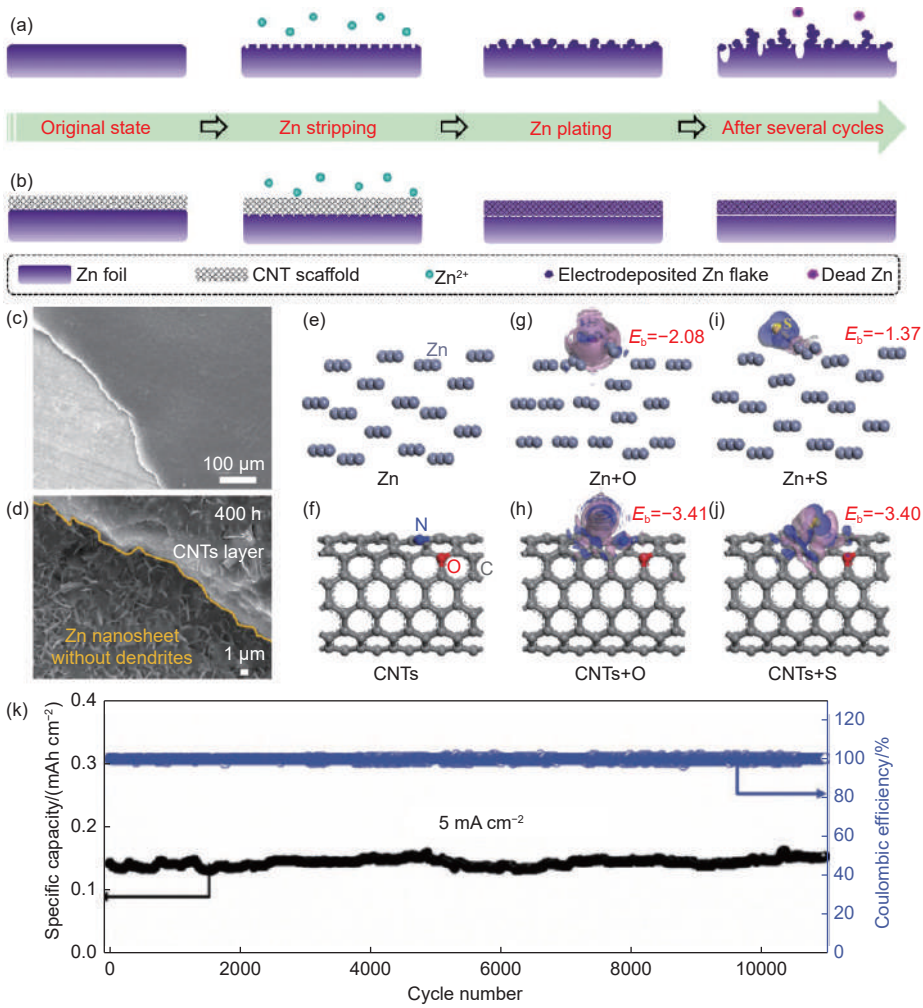

Fig. 6 Schematic illustration of depositing/plating processes of (a) Zn foil electrodes and (b) CNT-stabilized Zn electrodes. SEM images of the carbon nanotubes covered Zn electrode (c) before, and (d) after cycling[65]. (e-j) The stabilized structures and the optimized configurations of Zn planes and CNTs adsorbing O and S. (k) The long-term cycling stability of a Mn^{2+}/Zn^{2+} whole battery[66]. Reprinted with permission

Graphene as a protecting layer can induce a uniform distribution of ions, regulate Zn nucleation and deposition, and inhibit the puncture of the separator by Zn dendrites. For example, Xia et al. have reported a layer-by-layer reduced graphene oxide (rGO) film self-assembled on Zn foil by reducing graphene oxide with Zn metal[17]. The large specific surface area (103.58 $m^2\ g^{-1}$) of the rGO protective layer offered a large number of nucleation sites to induce dendrite-free Zn deposition. An ultrathin interface layer of N-doped graphene oxide (NGO) was introduced on Zn foil by a one-step Langmuir-Blodgett method (Fig. 7a)[18]. The N-doped groups on the protective graphene layer would act as the zincophilic sites for uniform deposition of Zn. As illustrated in Fig. 7b, Zn deposited on bare Zn foil resulted in dendritic morphology, however, NGO-protected Zn electrode (NGO@Zn) achieved a flat deposition morphology. The stability and performance of a full battery is an important for Zn anode. For example, a hybrid pouch cell with the NGO@Zn anode and $LiMn_2O_4$ (LMO) cathode was fabricated, which can easily light up a LED (inset of Fig. 7e). The LMO//NGO@Zn full cell exhibited an excellent cycling stability of over 178 cycles with 80% capacity retention, while maintained a coulombic efficiency of over 98.5%. After ten cycles running of the full battery, the NGO protected Zn anode produces a stable and corrosion-free Zn morphology (Fig. 7c).

Graphene can also be combined with other materials to generate a composite protective layer. Such layers can combine the merits of multiple nanomateri-

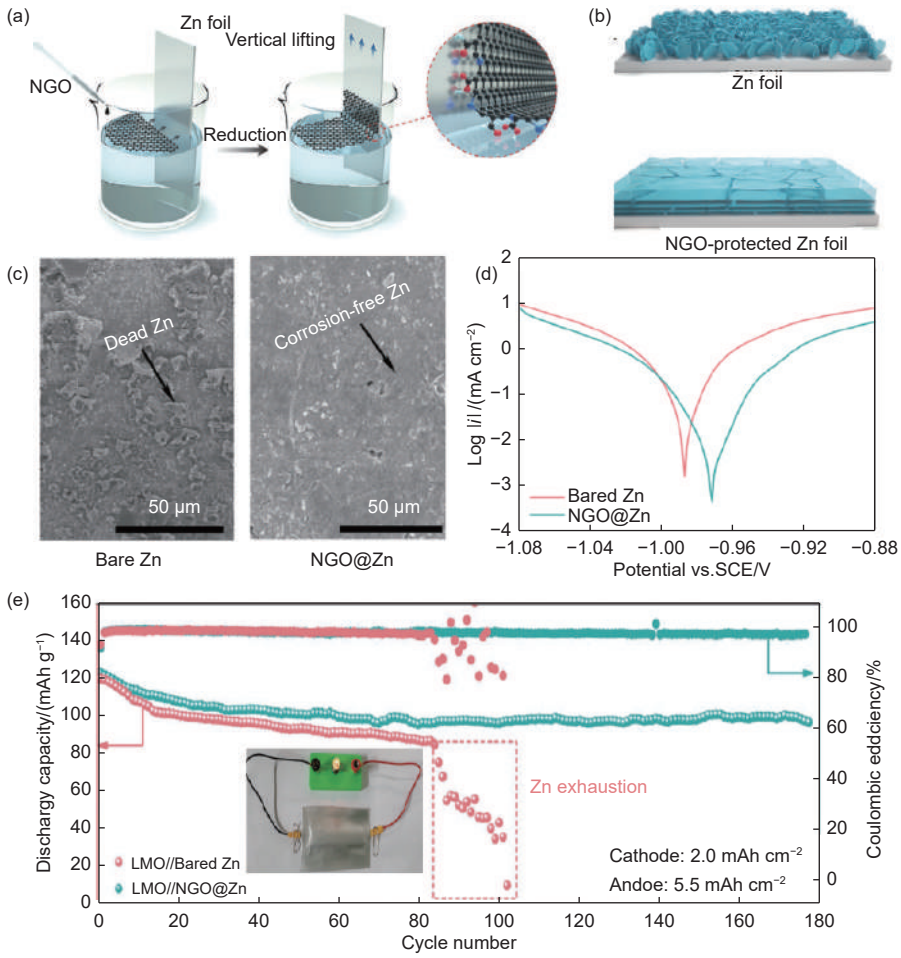

Fig. 7　(a) Schematics of graphene as a protecting layer on the Zn foil. (b) Schematics of Zn plating process on bare Zn foil (upper image) and NGO@Zn electrode (lower image). (c) SEM images of bare Zn (left) and NGO@Zn (right) electrodes after ten cycles. (d) The linear polarization curves of bare Zn and NGO@Zn electrodes. (e) The long-term stability of the whole pouch batteries of LMO//NGO@Zn and LMO//bare Zn, inset is an optical image of the pouch cell with the NGO@Zn anode and LMO cathode[18]. Reprinted with permission

als such as high mechanical strength, excellent conductivity, the adjustable structure of the protective layer and a large amount of homogeneous zincophilic sites. Zhang et al. designed a bifunctional cellulose nanowhisker-graphene(CNG) composite film as a protective layer on the Zn anode[67]. Due to the dual effects of cellulose nanowhisker and graphene on water molecules, the CNG composite film can force $[Zn(H_2O)_6]^{2+}$ to desolvate and isolate the Zn foil from the bulk electrolyte, thereby suppressing Zn anode corrosion. After Zn deposition for 15 min, obvious Zn dendrites appeared on the bare Zn anode, but no dendrites were observed on the Zn anode with a CNG protective layer. The MnO_2/graphene-CNG/Zn whole cell exhibits a long lifespan of over 5 000 cycles with a high capacity retention of 87.8% at 5 C.

Gan et al. reported a composited protective layer (ZGL) consisting of graphene oxide and zeolitic imidazolate framework (ZIF-8)[60]. This material with ordered ZIF-8 particles on graphene oxide could effectively homogenize the flux of Zn^{2+} and significantly reduce the activation energy of Zn^{2+} desolvation. The ZGL-protected Zn anode exhibited an excellent Coulombic efficiency. Fu et al. designed a sandwich layer constructed of graphene nanosheets (GS) and poly(3,4-ethylenedioxythiophene): poly(styrene sulfonic acid) (PEDOT: PSS)[68]. The nanofluidic channels constructed by PEDOT:PSS and GS effectively regulated the Zn^{2+} distribution through their appropriate channel size and functional groups, leading to dendrite-free deposition. The PEDOT:PSS/GS protective layer increased the cycle stability and specific discharge capacity of the Zn anode.

In aqueous ZIBs, side reactions on Zn anode are usually water-induced corrosion reactions. The corrosion-resistant performance of the Zn anode can be measured by linear polarization curves. A higher positive corrosion potential indicates a lower propensity for corrosion reactions, and the lower corrosion current density indicates a lower corrosion rate. For example, the corrosion potential of the NGO-protected Zn anode is −0.972 V, which is more positive than that of bare Zn anode (−0.987 V) (Fig. 7d)[18]. The corrosion potential of the CNG protected Zn anode is −0.98V, which is also more positive than that of bare anode (−1.02 V), and the current density of the CNG protected Zn anode (0.55 mA cm^{-2}) is smaller than that of bare Zn anode (5.75 mA cm^{-2})[67]. These results indicate that the protecting layer can effectively hinder the side reactions.

4.3 Other carbon nanomaterial as protecting layer

As mentioned above, the ordered porous structure and large amount of heteroatom dopants of MOF-derived carbon nanomaterials promote a uniform Zn^{2+} flux. Various MOFs with different heteroatoms may be chosen as the protecting layers for Zn anodes. However, it is still uncertain which metal or heteroatom is good for Zn depositing/stripping. Xu et al. reported a Ti-MOF-derived carbon nanomaterial layer consisting of a mesoporous N-doped carbon framework decorated with TiO_2 nanoparticles (TiO_2/NC)[59]. When TiO_2/NC was coated on Zn foil to form Zn@TiO_2/NC anode, more nuclei were formed under the TiO_2/NC coating, which was beneficial for uniform Zn deposition and inhibiting dendrite growth. The Zn@TiO_2/NC anode exhibited better corrosion resistance, fewer by-products and longer cycle life than that of bare Zn anode.

Graphdiyne (GDY) is a promising 2D carbon nanomaterial with two adjacent carbon atoms linked by "−C≡C−C≡C−" linkages (Fig. 8a). Recently, GDY has attracted much attention due to its narrow bandgap, in-plane porous structure, rich functional groups and high theoretical conductivity. Yang et al. coated a membrane of hydrogen-substituted graphdiyne (HsGDY) on Zn foil to address the dendrite issue of Zn anodes[69]. When HsGDY was grown on Zn foil, its color changed from silver to yellow (Fig. 8a). The sub-Angstrom ion tunnels in the HsGDY layer diverted the inhomogeneously distributed Zn^{2+} from its original migration direction and exhibited homogeneous Zn^{2+} concentration along the HsGDY-Zn interface, fundamentally eliminating dendrite formation on the Zn anode. The HsGDY protective layer increased the lifespan of the Zn electrode in the

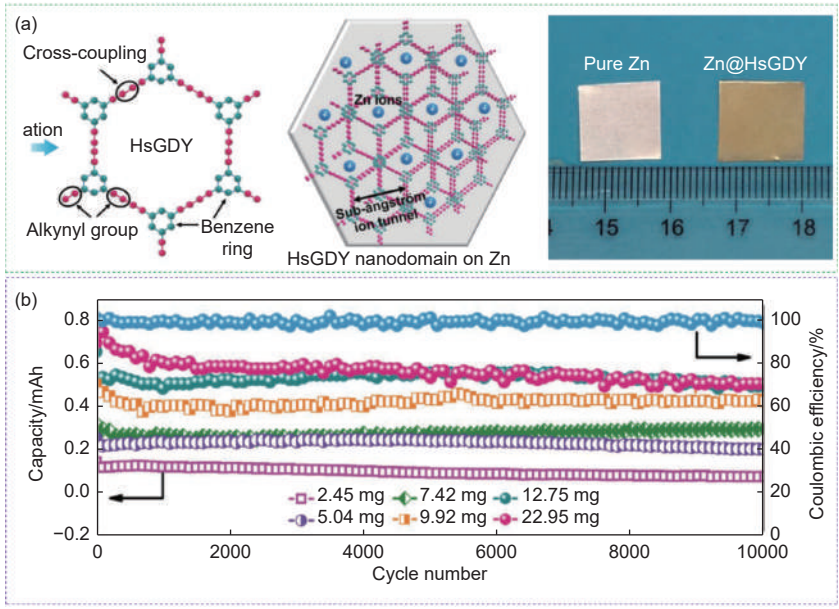

Fig. 8　(a) Structure of HsGDY, schematic illustration of HsGDY on Zn plate and digital images of Zn plate before and after HsGDY growth. (b) The cycling stability of Zn@HsGDY//C full cells with different cathodic loading masses[69]. Reprinted with permission

symmetrical cell from 63 to 2 400 h. Few-layered GDY was synthesized on Zn substrate by a radio frequency (RF) heating method to inhibit the growth of Zn dendrite[70]. Graphdiyne oxide can also be used as a protective layer on Zn metal to prepare a dendrite-free Zn anode with excellent cycling stability[71].

Even in full batteries graphdiyne-protected Zn anode shows excellent stability. For example, the full battery with HsGDY-protected Zn as the anode and N-doped porous carbon as the cathode exhibited an outstanding stability of 10 000 cycles even at a commercial-grade cathode mass loading of up to 22.95 mg cm^{-2} (Fig. 8b).

Table 2 lists the performance of some Zn anode protected by various carbon nanomaterials. The Zn anode protected by N-doped graphene has the lowest voltage hysteresis, which indicates that heteroatom-doped carbon nanomaterials are effective in protecting Zn electrodes. A bifunctional cellulose nanowhisker-graphene composite film (CNG)-protected Zn anode exhibits an ultralong life span of 5 500 h, which is the longest life span in Table 2.

5　Carbon materials for separator modification

As one of the components of the Zn-ion batteries, modification of the separator with carbon nanomaterials is another strategy for stabilizing Zn anode. Cao et al. reported a free-standing cellulose/GO composite (CG) separator by modifying cellulose nanofibers with graphene oxide (GO)[74]. Owing to the low mismatch between the crystallographic orientation (002) planes of Zn and GO, the GO particles on the cellulose/graphene oxide composite separator can effectively manipulate Zn^{2+} to grow on the Zn anode *via* the hexagonal (002) plane. As illustrated in Fig. 9a, the cellulose separator modified with GO could drive the uniform hexagonal Zn deposition with a preferential plane (002), while the pure cellulose separator without GO results in a dendritic plane of (100) or (101). Meanwhile, the CG separator effectively lowered the nucleation overpotential, promoted the uniform nucleation of Zn^{2+}, and inhibited HER and corrosion. The Zn anode with cellulose/graphene oxide composite separator exhibited good coulombic efficiency of 98.69%, and ultralong cycle life (>1 750 h) at 2 mA cm^{-2}. Furthermore, two coin-type Zn||$Zn(CF_3SO_3)_2$||V_2O_5 and Zn||$ZnSO_4$+$MnSO_4$||MnO_2/graphite full batteries with cellulose/graphene oxide composite separators delivered large specific capacity and higher energy density than the batteries with pure cellulose separators.

Table 2 Performance of carbon nanomaterials as protecting layer for Zn anode

Anode	Carbon nanomaterial	Voltage hysteresis	Life span	Coulombic efficiency	Cycling stability	Ref.
Zn@CNTS	CNTs	36 mV	1800 h (0.1 mA cm^{-2})	—	100% (7000 cycles)	[65]
Zn-CNTs	CNTs	80 mV	600 h (0.5 mA cm^{-2})	—	11000 cycles	[66]
Zn/rGO	RGO	—	300 h (1 mA cm^{-2})	—	88.5% (5000 cycles)	[17]
FLG@Zn	Few-layer graphene	—	500 h (1 mA/cm^{-2})	98.0% (1 mA cm^{-2})	97.0% (5000 cycles)	[72]
Zn/rGO	RGO	170 mV	200 h (10 mA cm^{-2})	—	79.0% (1000 cycles)	[73]
CNG-Zn	Bifunctional cellulose nanowhisker-graphene composite	31 mV	5500 h (0.25 cm^{-2})	99.4% (0.5 mA cm^{-2})	87.8% (5000 cycles)	[67]
NGO@Zn	N-doped graphene oxide	17 mV	1200 h (1 mA cm^{-2})	99.5% (5 mA cm^{-2})	94.0% (300 cycles)	[18]
PEDOT:PSS/GS@Zn	PEDOT:PSS/GS	—	500 h (1 mA cm^{-2})	98.0% (1 mA cm^{-2})	8000 cycles	[68]
Zn@HsGDY	Graphdiyne		2400 h (2 mA cm^{-2})	nearly 100%	50000 cycles	[69]

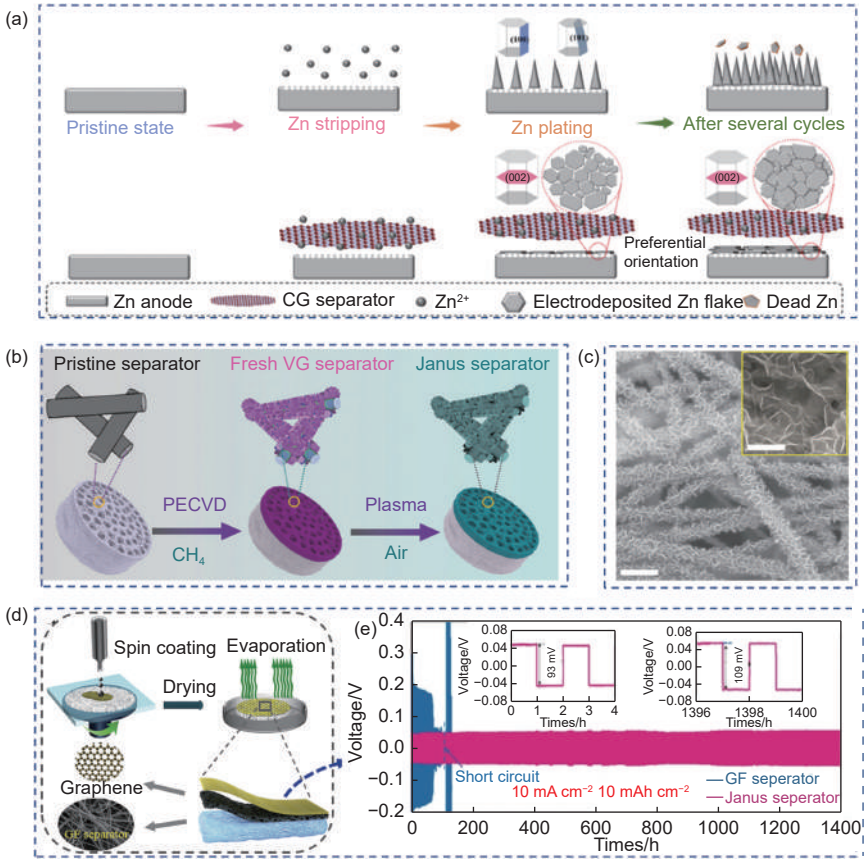

Fig. 9 (a) Schematics of zinc depositing/plating processes with CG separators[74]. (b) Schematic illustration of the preparation process of graphene based Janus separator. (c) SEM image of VG carpet on the Janus separator, Scale bar: 1 μm. Inset: High-magnification SEM image of VG, Scale bar: 100 nm[75]. (d) Schematic illustration of the fabrication process of the Janus separator. (e) Long-term cycling stability of Zn/Zn symmetric cells with the GF separator/Janus separator at 10 mA cm^{-2}[76]. Reprinted with permission

Janus separators composed of carbon nanomaterials and commercial separators have also been investigated. Li et al. fabricated a Janus separator composed of vertical graphene (VG) on one side and a commercial glass fiber membrane on another side (Fig. 9b)[75]. The vertical graphene sheets were observed on the fibers interwoven with each other (Fig. 9c). The O and N heteroatoms were further doped on the vertical graphene *via* plasma treatment. The large surface area and porous structure of the as-prepared O, N co-doped 3D VG scaffold could lower the local current density. Meanwhile, numerous zincophilic sites on the O, N co-doped 3D VG scaffold helped establish a uniform flux of Zn ions. Zn-ion hybrid capacitors with this Janus separator exhibited good capacity retention of 93.7% after 5 000 cycles,

and the V_2O_5//Zn batteries with the Janus separator delivered an excellent energy density of 182 Wh kg^{-1}. Zhang et al. reported another Janus separator by growing parallel graphene adsorbed with sulfonic cellulose on one side of a commercial glass fiber separator by a simple spin-coating strategy (Fig. 9d)[76]. This Janus separator exhibited high chemical stability, excellent mechanical properties and good electrolyte wetting. The sulfonic cellulose on graphene made this Janus separator highly selective, spontaneously repelling sulfate and anchoring hydrogen ions, and allowing only zinc ions to pass through the separator, which greatly suppressed various side reactions. Furthermore, this Janus separator could induce the preferential growth of Zn crystal facets of (002) to suppress dendrites. As a result, even at a high current density of 10 mA cm^{-2}, the Zn symmetric cell with this Janus separator demonstrated an ultralong cycle life of over 1 400 h (Fig. 9e). Besides, the interface pH can also be stabilized by an N-modified graphdiyne on cellulose separator by mediating the desolvation of hydrated Zn^{2+}[77]. Theoretical and experimental results suggested that the pH stabilization and dendrite-free Zn deposition were due to desolvation.

6　Carbon materials as electrolyte additives

Electrolytes also have a strong impact on the stability of Zn anode and the performance of Zn metal batteries. Addition of electrolyte additives is a cost-effective way to stabilize Zn metal anodes which can improve the thermodynamic stability of electrolytes and enhance the cycle life of Zn metal batteries. A small amount of graphene oxide (GO) (0.12% in weight) can be added to the Zn sulfate electrolyte as the electrolyte additive to stabilize the Zn anode[20]. The strong interaction between Zn^{2+} and the polar groups of GO can guide the rapid transfer of Zn^{2+} to the surface of the Zn anode, thereby accelerating the reaction kinetics and promoting uniform Zn deposition (Figs. 10a-c). The cross-section SEM images confirmed that GO additives effectively impeded the

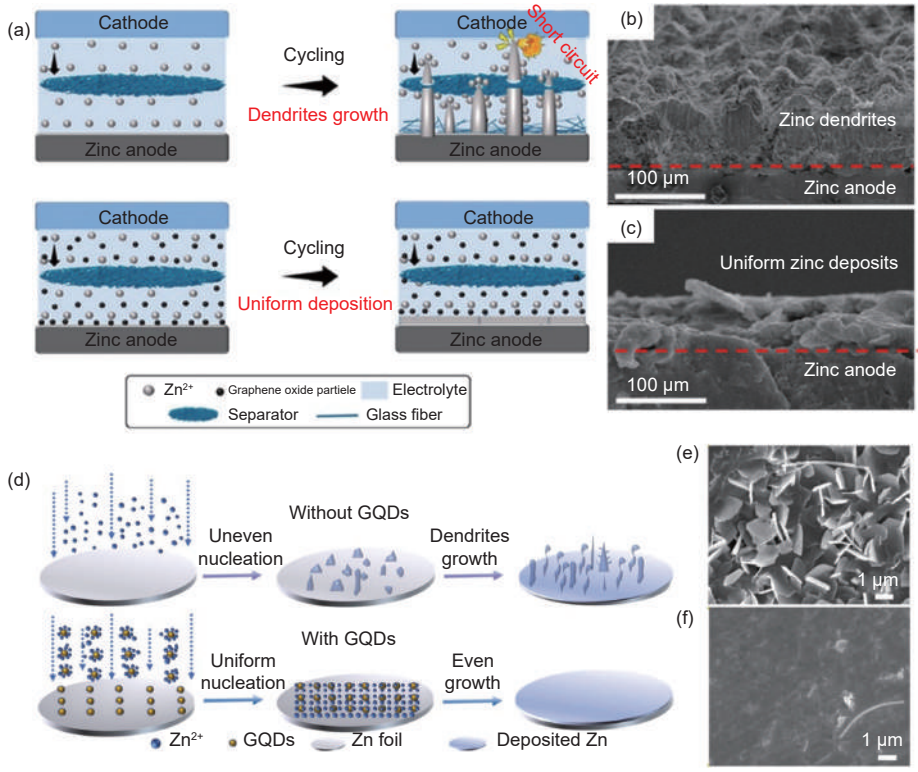

Fig. 10　(a) Schematic illustration of ZIBs with and without GO electrolytes. Cross-section SEM images of the zinc anodes (b) without GO electrolyte additive and (c) with GO electrolyte additive after 200 cycles[20]. (d) Schematic presentation of the effect of GQD additive for suppressing dendrites growth. SEM images of zinc foil after 20 cycles at 0.8 mA cm^{-2} (e) without GQDs and (f) with GQDs[78]. Reprinted with permission

dendrite growth. The remarkable effect of GO additives is also reflected in the energy storage performance of the whole cells. The Zn//MnO_2 cell containing GO additives can provide 93% capacity retention after 250 cycles, which is 40% higher than those without GO.

Graphene quantum dots (GQDs) has been introduced into the electrolyte of ZIBs as the electrolyte additive to achieve an electrochemically stable Zn anode (Fig. 10d)[78]. The lower electronegativity of GQDs increases the binding effect between GQDs and Zn^{2+}, which promote the uniform deposition of Zn, resulting in a robust dendrite-free Zn anode (Fig. 10f). Meanwhile, GQDs with oxygen-containing groups can excite the interfacial hydrogen bonds and alleviate the water-induced side reactions. When the GQD additive was added to the electrolyte, the corrosion currents for the Zn anode decreased from 2.558 to 1.193 mA cm^{-2}, indicating a reduction in corrosion rates. In addition, the Zn symmetric cells with an electrolyte containing GQDs additive show an ultralong cycling lifetime of up to 2 200 h at 0.8 mA cm^{-2} with a low voltage hysteresis of 50 mV. The assembled ZIBs with vanadium cathode, Zn anode, and electrolyte with GQDs additive, demonstrated a high capacity of 164.3 mAh g^{-1} after 600 cycles.

7 Conclusions and prospects

Aqueous ZIBs have broad application prospects in large-scale grid energy storage systems and wearable electronics due to their high safety, environmental friendliness and low cost. However, their practical applications are usually hindered by the instability of the zinc anode.

In this review, we have discussed the role of carbon nanomaterials in stabilizing the anode of aqueous ZIBs. This paper summarizes the recent work from four aspects, including hosts, protective layer, separator and electrolyte. Despite recent impressive achievements of carbon nanomaterials in protecting Zn anodes, there are still many challenges that need to be addressed to promote the large-scale practical applications of ZIBs. Herein, we put forward some opinions and perspectives on carbon nanomaterials for stabilizing zinc anodes.

(1) The usage of carbon nanomaterials as the hosts is the most common strategy to protect Zn anodes. Various carbon nanomaterials have been used as the hosts, and many corresponding mechanisms for explaining their efficacy have appeared in the past literatures. In general, carbon nanomaterials as hosts need to have better electrical conductivity, more uniformly distributed zincophilic sites and sufficient volume space. The zincophilic sites in carbon nanomaterials can increase by nitrogen-dopants, and other heteroatom dopants may also act as the zincophilic sites. A systematic research on carbon nanomaterial hosts doped with various heteroatoms is necessary. In addition, carbon nanomaterials with synergistic effects like 3D structure and heteroatom dopants are possible directions for developing ultra-stable Zn anodes.

(2) The strategy of employing carbon nanomaterials as protective layers is simple and easy to implement. Such carbon-based protective layers can not only inhibit the growth of Zn dendrites but also suppress the side reactions. Surface properties and pore structure are the key factors affecting the performance of protective layers. Carbon-based composite protective layers composed of hydrophilic and hydrophobic materials may be a better choice.

(3) The function of carbon nanomaterials as a separator is similar to a protective layer. The most promising separators may be the carbon-based Janus membranes. Carbon nanomaterials as solution additives are a strategy proposed in the recent literature. If the solution additives can force $[Zn(H_2O)_6]^{2+}$ desolvation and regulate Zn^{2+} distribution during, it may fundamentally solve the problem of Zn dendrites and side reactions on anode. However, the conductivity and weak dispersion of carbon nanomaterials limit its application in solvent additives. A combination of multiple strategies may also be considered in the future.

(4) Large-scale and facile methods to fabricate

carbon nanomaterial-stabilized Zn anode are urgently needed. Although various methods have been reported for stabilizing Zn anodes with carbon nanomaterials, these methods are usually complicated and not suitable for large-scale production. Stable Zn anodes are a necessity for Zn^{2+} batteries in the field of large-scale grid energy storage systems or wearable devices. Therefore, it is particularly important to develop methods to mass-produce these Zn anodes.

Acknowledgements

This work was supported financially by the National Natural Science Foundation of China (52172095), the Natural Science Foundation of Shanghai (19ZR1435000), the Science and Technology Commission of Shanghai Municipality (20060502200), the Innovation Program of Shanghai Municipal Education Commission (2019-01-07-00-07-E00015).

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