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Review

Recent advances in zinc anodes for high-performance aqueous Zn-ion batteries

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ABSTRACT

The zinc ion battery (ZIB) with mild aqueous electrolytes is one of the most promising systems for the large-scale energy storage application due to its high safety, environmental benignity, low cost, and high energy density. It exhibits excellent application potential and has attracted the attention of battery developers for grid energy storage demands in recent years. Compared with the numerous studies on the cathode materials for ZIBs, the research on the enhancement of the electrochemical performance of zinc metal anode is still in its early stage. The current challenges for Zn anodes are their poor cyclability and low Coulombic efficiency (CE) originated from the severe dendrite growth, self-corrosion, and irreversible byproducts formation. To address the intrinsic drawbacks of zinc metal anodes in mild aqueous electrolytes, some effective strategies, including interfacial modification between anode and electrolyte, structural design for Zn anodes and the adoption of novel separators and electrolytes, have been developed recently. This review aims to highlight the recent advances in Zn anode and outline future opportunities for the development of high-performance zinc metal anodes in aqueous ZIBs.

1. Introduction

The energy storage concern has become a serious social issue over the past few decades due to the growing energy demands coupled with the irreversible consumption of fossil fuels, and the corresponding environmental pollution [1–3]. Therefore, the development of advanced electrochemical energy storage devices has been hailed as the panacea for addressing the issues related to safe energy harvesting and storage [4–6]. Among various electrochemical energy storage devices, the battery is a kind of viable technology due to their ability to conserve the intermittent energy converted from renewable resources, such as solar, wind and mechanical energy, which can be quickly released into the power grid when needed [7–9]. This makes the power supply smoother and more predictable. The energy stored in the batteries can also be used in times of peak demands when more electricity is required. Currently, the electrochemical energy-storage landscape is dominated by lithium ion batteries (LIBs) owing to the inherent nature of lithium ion [10,11]. LIBs have incomparable advantages in energy density and power density over any other alternatives [12,13], however, the increasing concerns about cost, safety, contamination and resource limitation for the continuous manufacturing of LIBs have prompted the search for alternative energy storage technologies, such as sodium ion batteries (SIBs), potassium ion batteries (PIBs), aluminum ion batteries (AIBs) and so on [14–17]. Compared with other burgeoning batteries with organic electrolytes, aqueous batteries have attracted special attention in recent years because of the advantages of non-flammability, low cost and good rate performance [18,19]. Their inherent safety and good compatibility with the atmospheric environment make the aqueous batteries possess broad application prospects in advanced stationary grid storage and hence, become a potential competitor to the LIBs in terms of their structural robustness and cost advantage.

For the construction of aqueous energy storage devices, metallic zinc has so far remained the most ideal anode candidate due to its high electrical conductivity, easy processability, high compatibility/stability in water, non-flammability, low toxicity, comparatively low price (*ca.* 2 USD kg^{-1}), and high abundance [20,21]. More importantly, Zn anode

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possesses a high theoretical capacity (820 mAh g^{-1}), suitable redox potential (−0.76 V vs standard hydrogen electrode (SHE)) in aqueous electrolyte, and relatively low polarizability compared with other metallic materials (*e.g.* Mg and Al) [22,23]. All these merits of zinc material portend aqueous zinc ion batteries (ZIBs) as a promising electrochemical energy storage system, and thus trigger a strong research interest in aqueous ZIBs after the millennium. As a result, the number of research reports on aqueous ZIBs has increased dramatically in the past ten years. Although alkaline Zn batteries have already been commercialized, aqueous ZIBs in mild (neutral or slightly acidic) electrolytes hold more promise for future energy storage in the terms of cycle life and safety as free from the corrosivity of the strongly alkaline electrolyte [24]. Different from the anode reaction happened in alkaline electrolyte (*e.g.* $Zn+4OH^- \leftrightarrow Zn(OH)_4^{2+}+2e^-$), the reaction product of zinc electrode in mild aqueous electrolyte is soluble Zn^{2+}, which can inhibit the growth of zinc dendrites to some extent. Therefore, here we will mainly focus on the issues of Zn anode in mild electrolytes.

The current research efforts are mainly focused on exploring high-performance cathode materials of ZIBs, such as manganese-based material [25,26], vanadium-based material [27,28], Prussian blue [29–31] and so on [32,33]. Through a series of mechanism studies and diverse structural optimization, the electrochemical performance, especially cycling stability, of the aforementioned cathodes have been greatly improved [34,35]. It is undeniable that these attempts contribute strongly to the development of aqueous ZIBs, thus making their practical application highly feasible. Nevertheless, the industrialization of zinc anodes is an immature technology still involving from the limited and insufficient understanding of its mechanism, which is a disincentive to improving its performance. Zinc foils are used directly as the anode in most of the current studies about ZIBs, but their electrochemical behaviors do not meet the requirements for the production of industrially scalable devices. Therefore, a review of the recent advances in zinc anodes has a great significance to the development of aqueous ZIBs for future large-scale applications.

It is delightful that more attention has already been paid to zinc anodes as more researchers have begun to notice their importance to the overall performance of ZIBs in the recent five years. Presently, the main challenges of zinc anode include (1) Zn dendrite growth during extended cycles; (2) self-discharge problems by sustained consumption of electrolyte; and (3) formation of irreversible accessory substances (*e.g.,* ZnO). All these drawbacks cause poor reversibility and low Coulombic efficiency (CE) owing to the excessive consumption of Zn and electrolyte by side reactions, similarly to lithium metal anode. As a result, excessive zinc is generally used to maintain a long battery cycle life, but that results in reduced energy density as well as increased cost. In addition, regular replenishing of the electrolyte with water is often required to compensate for the water decomposition. As a consequence, it is essential and urgent to solve these thorny problems of zinc anodes and further improve their electrochemical performance for future practical applications.

In this brief review, we will highlight the issues and solutions of the current zinc anodes for aqueous ZIBs. More importantly, some design strategies for improving the electrochemical performance of zinc anodes as presented in Fig. 1 are specifically discussed, including the interfacial modification, 3D structural design for novel zinc anodes, as well as the development of novel electrolytes and separators. Finally, some prospects for improving the electrochemical performance of zinc anodes for aqueous ZIBs have been constructively proposed.

2. Current challenges of zinc anodes

The reaction mechanism of Zn anode for ZIBs with mild aqueous electrolyte is similar to the conventional rechargeable LIBs, namely the reversible plating/stripping of Zn^{2+} ions in the electrodes [36]. However, for the cathodes, the energy storage mechanism is more complicated [37]. Taking MnO_2-based cathode as an example, Zn^{2+} intercalation reaction, chemical conversion reaction, and a joint H^+/Zn^{2+} insertion/extraction process have been observed in different crystal types of MnO_2 [38]. Generally, the anode reaction for ZIBs in mild electrolytes can be summarized as:

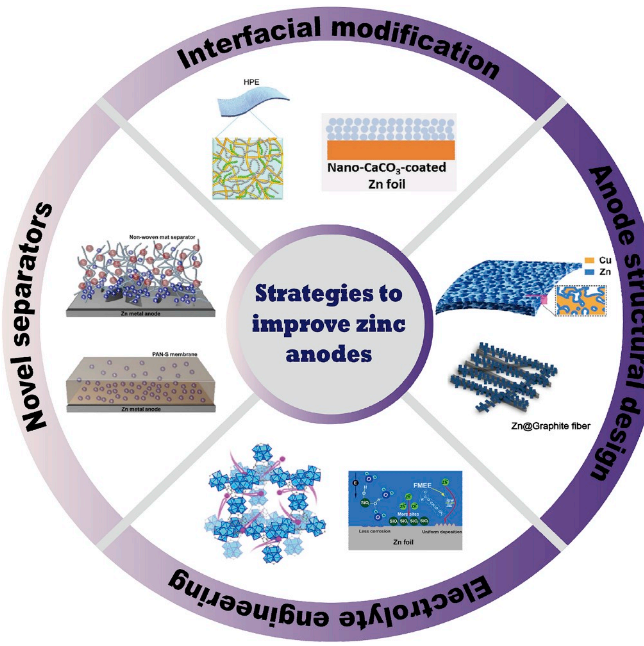

Fig. 1. Strategies to improve zinc anodes for ZIBs.

$$Zn \leftrightarrow Zn^{2+}+2e^- \tag{1}$$

The mass transfer process of the electrode is admirably elucidated by the Nernst-Planck equation [39], in which the diffusion flux, J, could also be analyzed as follows:

$$J = -\frac{qCD}{kT}\frac{dV}{dx} - D\frac{dC}{dx} + Cv_x \tag{2}$$

where q, C, D, k, T, V, x and v_x represent unit charge, concentration, coefficient of diffusion, Boltzmann constant, temperature, electric potential, distance, and convective velocity, respectively. Hence, the Zn ion dissolution-precipitation processes are influenced by three factors, namely potential gradient, concentration gradient, and convection strength. Notably, the coordination shell of Zn^{2+} usually differs with electrolyte ingredients, so the solvation and desolvation of Zn ion is also a nonnegligible factor for Zn redox process. In addition, faster charge transfer in electrolyte boosts the local current density due to the increased transport velocity of Zn ions, and additional electrolyte flow can further assist ion diffusion and greatly reduce the Zn ion concentration gradient [40].

Unfortunately, the zinc plating/stripping are usually inhomogeneous and cause irregular surface appearance and subsequent growth of zinc dendrites, which is also known as the “tip effect” [41]. Specifically, Zn ions prefer to deposit at the districts with high Zn concentration initially and the succeeding Zn nucleation spontaneously grows at the existed protuberances due to their larger surface energy [42]. The partially high electric field and concentrated zinc ions then expedite the nucleation and growth of zinc metal at the local point, which gradually evolves into zinc dendrites. As the cycle number increases, the dendrite growth introduces the surface roughness and strengthens the tip electric field intensity, triggering continuous growth of the harsh zinc dendrites in needle shapes [43]. During repeated battery cycling, the zinc dendrite can pierce the separator and induce internal short circuits with a sudden drop in capacity of the battery [44]. Moreover, compared with the alkaline electrolyte, the decreased pH in the mild aqueous electrolyte induces hydrogen evolution more easily and introduces low plating/stripping CE [45].

To study the dendritic morphology and dendrite growth evolution, some theoretical models for Zn electrodeposition process have been developed. Researchers tried to study the fractal structures of Zn metal by the determination of the fractal dimension during the electrodeposition of zinc by current integration [46,47]. Others selected a phase-field model for the electrochemical process to study the effect of the applied voltage and zinc ion concentration gradient on the dendrite growth [48–50]. These studies indicate that the dendritic morphology of electrodeposited zinc would occur when the overpotential reaches a certain value [40]. The dendrite growth depends on the local overpotential associated with the potential between the anode and the cathode. This means the initiation time of dendrite growth is shorter and the dendrites can grow faster when the overpotential is greater. Although the dendrites can be destroyed by slight overcharging of aqueous batteries as the generated oxygen gas can react with the dendrites, this process consumes the water ingredient from the aqueous electrolyte and causes passivation on Zn surface by producing some oxidized products. Therefore, it is of crucial importance to discover an effective dendrite suppression method.

Self-corrosion of zinc electrode is another problem of current ZIBs [51,52]. Its microcosmic essence can be explained as that the potential of different regions of zinc electrode with a heterogeneous surface is different which constitutes countless corrosion microcells [53,54]. The hydrogen evolution reaction would proceed in some local high-energy areas and bring about OH^-, which would consume finite zinc anode to produce zinc oxide and zincates byproducts. Hence, corrosion makes the battery self-discharge and reduces the utilization and capacity of zinc anodes. Moreover, in the sealed environment, the hydrogen produced by the corrosion process leads to an increase in the internal pressure of the battery. The electrolyte begins to leak after accumulating the pressure to a certain extent. Hence, the low CE of current ZIBs is closely related to the side reactions, such as corrosion and hydrogen evolution. These side reactions consume the Zn anode and the electrolyte, which result in a serious capacity decay.

Furthermore, some byproducts are generated by the side reactions which cause the passivation of zinc electrode. With the presence of byproducts on the electrode surface, the insoluble residue decreases the functional reaction surface area of zinc electrode. Hence, the electrode density will decrease along with the specific surface area of the electrode, causing battery polarization and bringing down the cycling performance.

3. Current strategies for high-performance zinc anodes

The structural and electrochemical features of zinc metal anode have a significant effect on the overall electrochemical performance of the battery system. To complement the native structural features of zinc metal materials, four main design strategies have been developed to enhance their electrochemical performance. These include interfacial modification between anode and electrolyte, structural design for novel zinc anodes, introduction of novel additives for electrolyte and the exploration of functional separators.

3.1. Interfacial modification between anode and electrolyte

Unlike alkali metal anodes (*e.g.*, Li and Na), continuous solid-electrolyte interfaces (SEIs) cannot be generated between the Zn metal anode and aqueous electrolyte [55]. Therefore interfacial modification between the zinc anode and the electrolyte is employed by forming a protective layer. This is one of the most useful methods to enhance the interfacial stability and the cycling stability of Zn electrode. An effective surface coating can avoid direct contact of Zn metal with the electrolyte, block dendrite growth and retard the parasitic reactions, thus leading to a uniform Zn plating.

Carbon has been widely reported to facilitate the cycle stability of Zn anode by the interfacial modification protocol [56]. Kang et al. [57] proposed a novel composite anode via mixing zinc particles with activated carbon to improve the cycle performance of the neutral rechargeable ZIBs (Fig. 2a). The cell exhibits enhanced capacity retention after adding 12 wt% activated carbon in Zn anode compared with the cell using unmodified Zn anode. The improvement is due to the activated carbon that constraining the formation of inactive basic zinc sulfates ($Zn_4SO_4(OH)_6{\cdot}nH_2O$). The well-developed pores of activated carbon could also provide sufficient spaces for accommodating the deposition of Zn dendrites and passivation products brought by side reactions. Afterward, graphene was also utilized to restrain dendrite growth in Zn anodes considering its better mechanical and conductive properties. In this regard, Jiang et al. [58] fabricated a dendrite-free Zn@C anode by facilely coating the Zn foil surface with a porous carbon layer. The coated porous carbon layer served as nucleation sites and reservoirs to capture Zn ions from the electrolyte and homogenize the prioritization of Zn^{2+} ions. Subsequently, Liu's group tried to add acetylene black, carbon nanotube, and active carbon into the porous Zn anode composite and tested their performance in rechargeable aqueous batteries, respectively [59]. It is notable that both cycle span and discharge capacity of the Zn anodes are improved by these carbon additions. Lately, Liu et al. [60] reported the application of a mesoporous hollow carbon spheres coated Zn foil as the anode for Zn-ion hybrid supercapacitor. As expected, this novel carbon coating material also improves the cycle span and discharge capacity by regulating zinc dendrites/protrusions growth.

Similar to the function of the carbon layer, Au nanoparticles are also utilized as heterogeneous seeds to achieve a uniform zinc anode surface by guiding even Zn deposition. Zhi et al. [61] found that decorating Au particles on zinc anode surface by sputtering-deposition method contributes to a homogeneous and stable Zn dissolution/precipitation process on the anodes. In addition, Pan et al. [55] reconstructed an artificial solid-electrolyte interface layer for Zn anode to achieve a well-contacted interface using nanosized metal−organic frameworks (MOFs) and polyvinylidene fluoride (PVDF). The modified anodic interface remarkably decreases the charge-transfer resistance and effectively regulates current flow on the electrode surface, leading to dendrite-free Zn plating/stripping cycling performance.

Some polymer materials have also been reported to improve the interface performance of zinc anodes. For example, Cui et al. [51] attempted to regulate the Zn deposition behavior by a "brightener-inspired'' polyamide coating layer, which effectively elevated the nucleation barrier and restricted Zn ion flux. As schematically illustrated in Fig. 2b, the as-introduced polyamide 6 layer does not only work as a solid-state brightener for harmonizing Zn^{2+} migration with uniform nucleation, but also functions as a water/O_2 inhibitor. Thanks to the unique hydrogen-bonding networks and strong coordinating ability with metal ions of polyamide layer, the as-modified Zn anode could produce a dendrite-free plating/stripping with an ultralong cyclic performance. Subsequently, Mantia et al. [62] explored the influence of layered double hydroxides (LDH) on zinc electrodeposition efficiency. The potential drop at the beginning of the zinc reduction tends to disappear due to the formation of a more compact zinc deposition on LDH. Although the LDH ingredient is reported to generate hydrogen at the beginning of the zinc reduction, the stability and the efficiency of zinc anode have been greatly enhanced for long cycles by restricting local overpotential and reducing hydrogen evolution. Moreover, the copper-doped Zn–Al–CO_3 layered LDH coating was demonstrated to perform a similar function on zinc anode in the same principle [63].

In addition to the polymer coatings, titanium dioxide (TiO_2) has also been found as an available passivation material for metallic zinc anode coating [64]. The corrosion of zinc anode is expressively restrained by the high electrically conductive and conformal TiO_2 layer. The production of harmful gas and non-conductive byproducts is hindered in this electrochemical system. As schematically shown in Fig. 2c, the

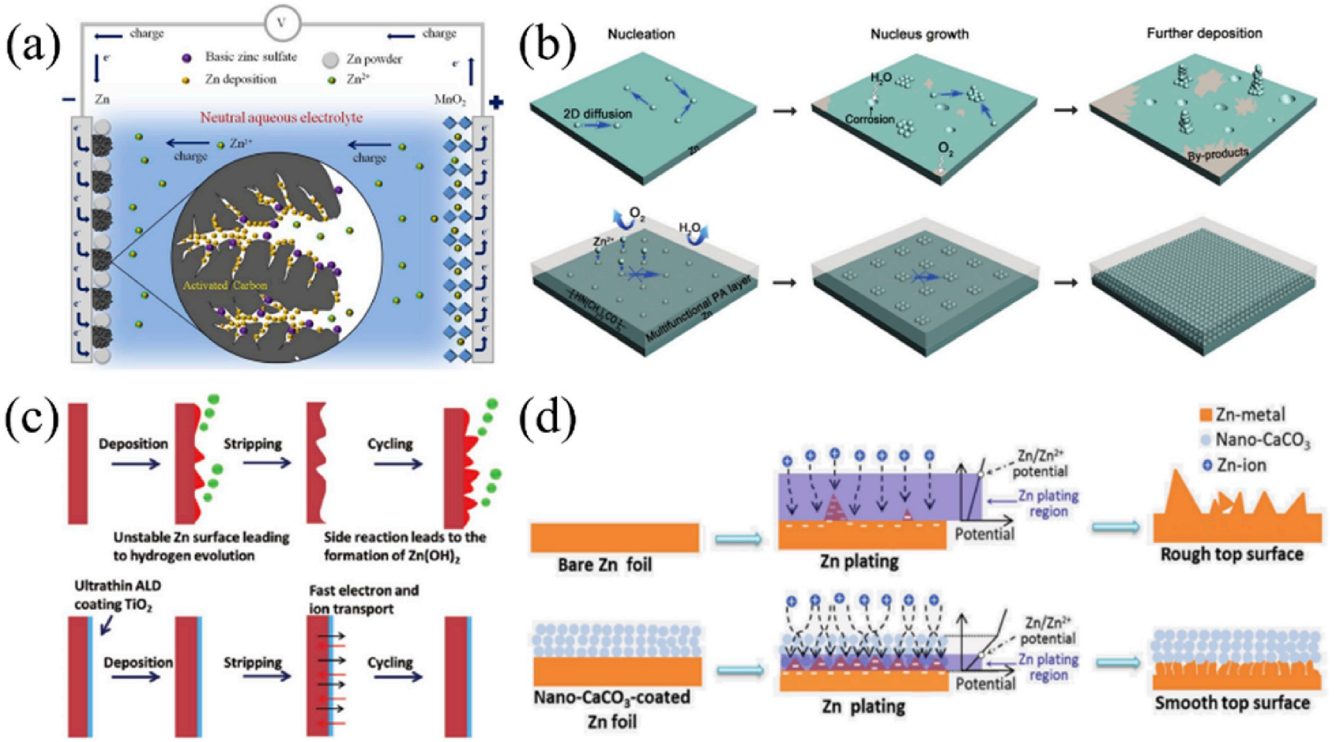

Fig. 2. Typical examples of interfacial modification strategy to improve zinc anode performance. The schematic illustration for (a) the deposition of zinc in activated carbon, (b) the polyamide layer coating on zinc anode, (c) TiO_2 coating for zinc anode, (d) the morphology evolution for bare and nano-$CaCO_3$-coated Zn foils during Zn stripping/plating cycling.

protection layer can prevent direct contact between the electrolyte and electrode, which strongly accelerates the electron and ion transport. This assertion was confirmed when the artificial TiO_2 layer protected Zn anode shows reduced overpotential (72.5 mV) at 1 mA cm^{-2} for Zn–Zn symmetrical cells and extended Zn–MnO_2 battery cycling performance up to 1000 cycles with a super-high capacity retention of 85%. This work demonstrates that introducing the atomic layer is another viable way to improve the lifespan of ZIBs by enhancing electrochemical and chemical stability of Zn anodes.

Exhilaratingly, coatings of other nanoporous materials are also confirmed as an effective strategy for controlling the growth of Zn dendrites and achieving an even Zn stripping/plating surface. As shown in Fig. 2d, the porous nano-$CaCO_3$-layer and nano-SiO_2 layer can enhance Zn plating/stripping evenness and inhibit the growth of dendrites [65]. Specifically, they meliorate the Zn plating reaction to the surface region of Zn foils, which guarantees uniform electrolyte flux and Zn plating rate over the entire Zn foil surface, thus leading to a homogeneous Zn plating ability.

Furthermore, Chen's group explored the fabrication of innovative zinc anode using electroplating with organic additives such as cetyltrimethylammonium bromide, sodium dodecyl sulfate, polyethyleneglycol, and thiourea [43]. The additive produces a significantly different crystalline pattern and surface texture such that when zinc gets into contact with the battery electrolyte, the surface electrochemical activity becomes linearly polarized. The Tafel fitting results of linear polarization data indicate that the corrosion currents decreased 6–30 times after the organic additives were introduced. Moreover, Zn-sodium dodecyl sulfate appeared more suitable for aqueous batteries due to the relatively low corrosion rate, low dendrite growth, low float current, and the significantly high cycling stability.

To conclude, conductive protective layers (such as carbon and metal materials) physically prevent the penetration of Zn dendrites and uniformizes the current flow on the electrode surface. The zinc deposition process also happens in these conductive materials and some zinc dendrites grow from its conductive surface towards the zinc anode. However, it is important to state that the functionalized conductive protective layer does not last long enough since zinc can be equally grown toward the cathode, which might affect the performance of the battery. Non-conductive protective layers (such as TiO_2 and $CaCO_3$) can work as the steady passivation layer to avoid direct contact between the zinc metal and the electrolyte, then effectively suppress the zinc corrosion and hydrogen evolution. However, from the aspect of ion and electron transport, the rate performance of anode would reduce extremely when using these electrochemically inert protection materials. Therefore, it is essential to find a solution to these problems by facilely developing strategies that work beyond the laboratory scale.

3.2. *Structural design for novel zinc anodes*

Structural design for novel zinc anodes is commonly regarded as another effective strategy to tolerate the zinc dendritic growth and diminish the formation of byproducts [66,67]. Usually, some highly conductive 3D porous nanostructured networks are selected to work as an upholder/supporter for consistent Zn distribution and improve the electroactive performance for the attainment of uniform current distribution [68]. For instance, Guo et al. [69] proposed in-situ electrochemical deposition of three-dimensional (3D) zinc anode framework on carbon fiber substrate (Fig. 3a). The 3D Zn@CFs framework has lower charge transfer resistance with larger electroactive areas in promoting the dendrite resistance and corrosion tolerance. Batteries based on the as-prepared 3D zinc framework anode present ultra-steady cycling performances with no dendrite growth after 140 cycles. More noticeably, Lu et al. [70] designed a dendrite-free Zn/CNT anode by depositing Zn on a flexible 3D carbon nanotube (CNT) network (Fig. 3b). Satisfactory CE is achieved due to the lower Zn nucleation overpotential and the uniformly distributed electric fields. Hence, Zn/CNT anode presents appreciably low voltage hysteresis of 27 mV and extraordinary cycling stability for 200 h (Fig. 3c). The efficient rechargeability of the Zn/CNT

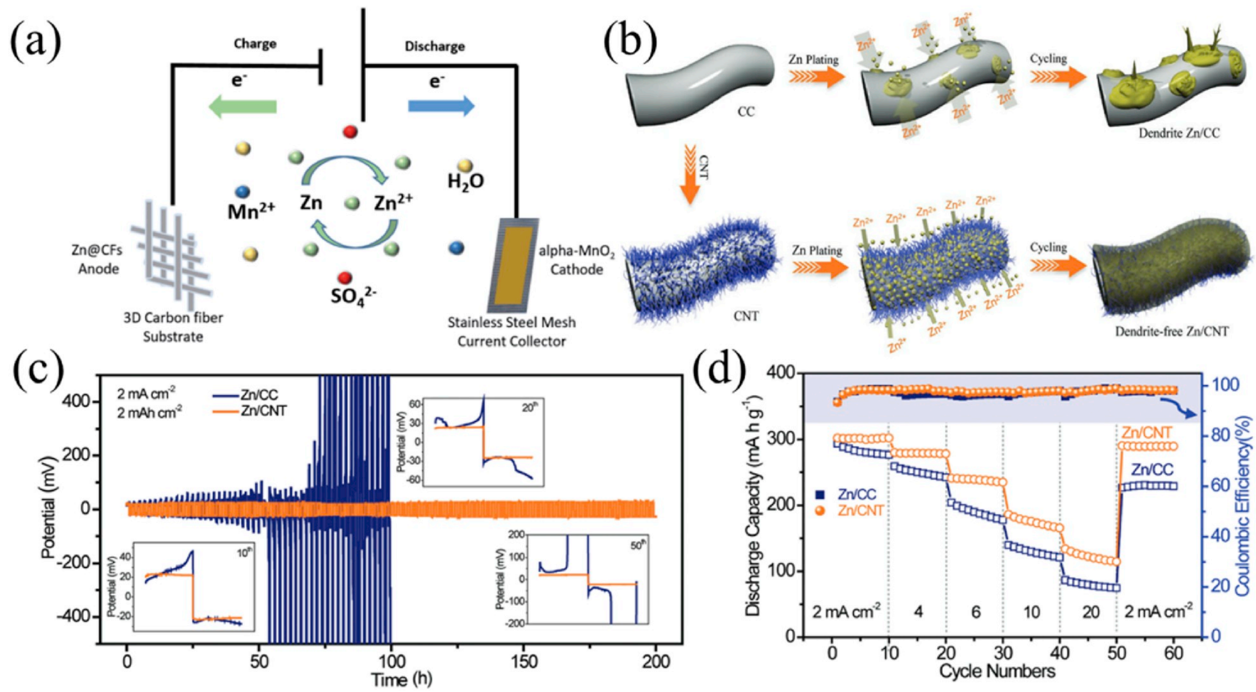

Fig. 3. (a) The schematic description for 3D zinc@carbon fiber composite framework anode for aqueous Zn–MnO_2 batteries. (b) Schematic diagrams for Zn deposition on CC and CNT electrodes. (c) Voltage profiles of symmetric cells based on Zn/CC and Zn/CNT anodes at 2 mA cm^{-2}. (d) Rate performance and CEs of the Zn//MnO_2 batteries with Zn/CC and Zn/CNT anodes.

anode also enables the Zn//MnO_2 battery remarkable stability upon 1000 cycles and superior rate performance as shown in Fig. 3d.

Most impressively, Archer et al. [71] reported an epitaxial mechanism to regulate the nucleation and growth of Zn deposition. They demonstrated that graphene in a low lattice mismatch for Zn can drive Zn deposition with a locked crystallographic orientation relation. The resultant epitaxial Zn anodes possess peculiarly higher reversibility, more stable voltage profiles and longer cycle life than a general zinc foil. This work provides a universal avenue for developing high energy density batteries that use metals as anode.

Literature is replete with the application of carbon bases as a scaffold for Zn plating/stripping, such as carbon cloth [72,73], carbon nanotube paper [74], carbon nanotube yarn [75], graphene fiber [76], graphene composite [77] and 3D graphene foam [78]. Zinc anodes have been demonstrated to be easily prepared by electrochemical deposition of a compact zinc film on these carbon skeletons. The specific electrochemical properties of the zinc anodes combined with carbon materials for ZIBs are listed in Table 1. It is refreshing to note that these enhanced zinc anodes used for ZIBs exhibit durable performance and have great prospects for wearable electronic device applications due to the good flexibility. However, hydrophobic carbon scaffolds usually increase interfacial resistance and their electronic conductivity is lower than pristine Zn, which limits the kinetics of the carbon-based Zn anodes.

Apart from carbon hosts for zinc anode, some metal networks are also widely explored as zinc anode stabilizers. As illustrated in Fig. 4a, Xu et al. [79] fabricated a highly steady 3D Zn anode by electrodeposition of zinc on a chemically etched porous copper skeleton. The high electrical conductivity and open structure of the 3D porous copper skeleton ensure a dendrite-free cycling behavior with nearly 100% CE by accelerating the electrochemical kinetics and reducing polarization. A stable operating status for 350 h was achieved on this novel architecture when evaluated in 3D Zn|3D Zn symmetric cells, which was much longer than a general lifespan of planar Zn foil electrode-based cells plagued by short circuit damage (Fig. 4b). Cu foam was also demonstrated as a superior carrier for the deposition of metallic zinc by reaching a high plating/stripping CE close to 100% [80]. Additionally, Wang et al. [81] reported a synergistic strategy by incorporating Cu–Zn solid solution interface on the copper network, followed by the introduction of polyacrylamide electrolyte additive to modify the zinc anode surface. This protocol powerfully reduces the overpotential of the zinc nucleation and gives a uniform deposition/stripping of Zn. The dendrite-free anodes show a stable cycling performance for 350 h and fast electrochemical kinetics even under a high rate. Moreover, a reticular network made of holey nickel nanotubes was utilized as a zinc anode scaffold in another

Table 1
Electrochemical performance of ZIBs using a carbon-based zinc anode.

Anode	Cathode	Electrolyte	Cyclability/rate capability (mAh g^{-1})	Capacity retention/cycle number	Ref.
Zn@CF	α-MnO_2 nanowire	$ZnSO_4$/$MnSO_4$	275.2@0.33 C/182.0@2 C	86.8%/140	[69]
Zn@CNT	CNT-MnO_x @PEDOT	PVA/LiCl–$ZnCl_2$–$MnSO_4$ gel	300@2 mA cm^{-2}/110@20 mA cm^{-2}	88.7%/1000	[70]
Zn@carbon cloth	MnO_2@PEDOT	PVA/$ZnCl_2$/$MnSO_4$	366.6@0.74 A g^{-1}/143.3 @7.43 A g^{-1}	83.7%/300	[72]
Zn@carbon cloth	[EMIM]PF_6-PEDOT:PSS/Bi_2S_3	$Zn(TFSI)_2$/LiTFSI/PAM gel	302.1@60 mA g^{-1}/117.7@1.5 A g^{-1}	95.3%/5300	[73]
Zn@CNT paper	α-MnO_2 nanorod/CNT	Hierarchical polymer electrolyte	306@62 mA g^{-1}/150@1.85 A g^{-1}	97%/1000	[74]
Zn@CNT fiber	MnO_2@CNT fiber	$ZnSO_4$/$MnSO_4$ PAM hydrogel	264@0.2 A g^{-1}/117@15 A g^{-1}	98.5%/500	[75]
Zn@ graphite fiber	Prussian blue nanocrystals	Na_2SO_4/$ZnSO_4$	81@0.1 A g^{-1}/70@0.5 A g^{-1}	85%/150	[76]
Zn@ graphene	$V_3O{\cdot}H_2O$/rGO	$ZnSO_4$	245@1.5 A g^{-1}/157@12 A g^{-1}	79%/1000	[77]
Zn@graphene foam	Layered zinc orthovanadate	Fumed silica/$ZnSO_4$	250@0.1 A g^{-1}/101@10 A g^{-1}	89%/2000	[78]
Zn@ graphene	α-MnO_2	$ZnSO_4$	0.8 mAh cm^{-2}@8 mA cm^{-2}	62.5%/1000	[71]

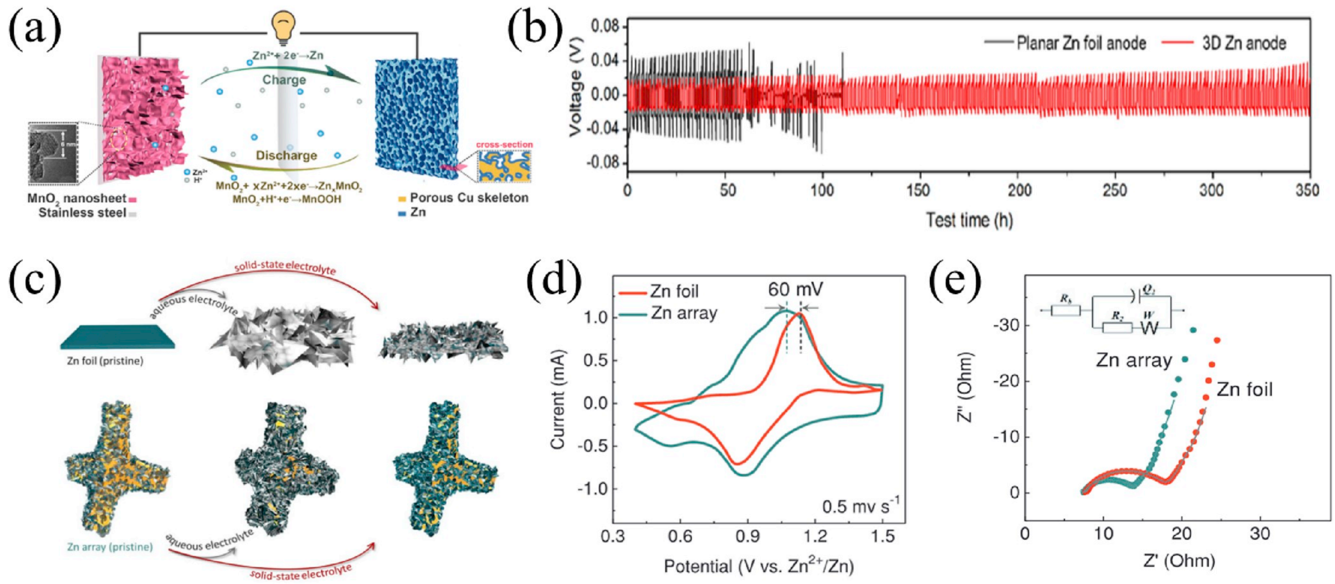

Fig. 4. (a) The schematic illustration for the 3D porous copper skeleton supported Zn anode/MnO_2 nanosheet cathode full cell. (b) Cycling performance at a constant current of 0.5 mA cm^{-2} (the amount of Zn deposited in each cycle is 0.5 mAh cm^{-2}). (c) The schematic illustration of zinc foil and array in aqueous electrolyte and solid-state electrolyte. (d) CV curves comparison of the ZIBs made of zinc orthovanadate cathode and Zn array or foil anode after 5 cycles charge/discharge activation at 0.5 C. (e) Electrochemical impedance spectra of the foregoing Zn array and Zn foil electrodes at the fully charged state.

ZIB research [82]. These metal skeletons are proven as promising solutions to improve cycling performance, but the heavy inactive metal brings down the specific capacity of the whole anode.

Benefiting from the unique layered morphology and excellent conductivity, 2D MXene is regarded as an ideal material to host metal ions and enable rapid ion diffusion as well. A flexible three-dimensional layered $Ti_3C_2T_x$ MXene@Zn paper was prepared as an alternative of Zn metal anode by Qian's group [83]. The $Ti_3C_2T_x$ MXene structure offers fast electron transport channels and obtains relatively even charge distribution, thus leading to a smooth and dendrite-free surface even after long-time cycling. Hence, the as-constructed $Ti_3C_2T_x$ MXene@Zn anode delivers more stable cycling behavior and lower overpotential than a commercial Zn anode during the Zn plating/stripping process due to the enhanced metallic conductivity and hydrophilicity.

Some nanoarray structures have also been reported as an effective way to bypass the issue of poor Zn reversibility and achieve high rate capability. For example, Fan et al. developed a 2D ultrathin layered zinc orthovanadate array cathode to enhance the Zn^{2+} (de)intercalation kinetics and achieved long-cycle stability (Fig. 4c) [78]. In this rational design, Zn array anode is sustained by a highly conductive porous graphene foam and works under a gel electrolyte. As expected, the as-designed ultrathin mesoporous Zn array brings a high surface area with a single-crystalline layered structure to support direct fast ion transfer, which results in an enhanced Zn ion storage performance. Hence, Zn array anode displays higher capacity, smaller polarization and lower charge-transfer resistance than commercial Zn foil as shown in Fig. 4d and e. The full quasi-solid-state ZIB assembled from the novel layered zinc orthovanadate cathode and metallic Zn nanoflake array exhibits an impressively long-standing performance. The rapid electrochemical kinetics and rate capability are highly correlated with the small Zn ion migration barrier and its derived intercalation pseudocapacitive behavior. More notably, no distinct aggregation, pulverization, or dendrite formation can be detected on the Zn anode after cycling.

Furthermore, Long et al. [84] designed a sponge-like zinc anode in a porous, interconnected, three-dimensional (3D) architecture. The unique 3D structure of zinc anode helps control the Zn dissolution/precipitation processes to solve the problems of inefficient zinc utilization and limited rechargeability. Especially, the 3D porous architecture can effectively maintain fully metallic and interconnected pathways at the core of the electrode to sustain a long-range electronic conductivity. Also, the current distribution in the electrode becomes more even due to the amplification of the electrified interface in the 3D structure. More importantly, the confined void-volume elements in the interior of the porous electrode restrains the shape change by accelerating saturation/dehydration of zincate to ZnO. These inherent characteristics in the 3D structure of zinc make it physically difficult to form large-scale dendrites, by averting the conditions required for dendritic formation. The electrochemical properties of all these zinc anodes combined with non-carbon materials for ZIBs are specifically given in Table 2.

The cycling performance of zinc anode has been efficiently improved on the abovementioned conductive bases; however, the current deposition amount of zinc is still limited. The mass load of the deposited zinc on carbon matrix was about 6–8 mg cm^{-2}, while that on metal networks is only around 1 mg cm^{-2}. Moreover, Zn was uncontrollably deposited beyond the conductive base especially at high current densities and dendritic Zn deposition still exists even at very low current densities. Hence, more structural designs for achieving uniform zinc deposition under high active material loadings should be explored.

3.3. Novel electrolytes

Electrolyte is another important factor that determines the electrochemical performance of batteries [85,86]. An eligible electrolyte should keep a good Zn deposition/stripping reversibility and release a broad electrochemical window. The strongly acidic or alkaline electrolyte would cause the severe corrosion problems of the electrode and thus generally lead to a fast capacity fading. Most of the electrolytes for aqueous ZIBs contain one or more soluble zinc salts, such as $ZnSO_4$, $ZnNO_3$ [87,88], $ZnCl_2$ [72,85], $Zn(CH_3COO)_2$ [89], zinc trifluoromethanesulfonate ($Zn(CF_3SO_3)_2$) [90], and zinc bis(trifluoromethanesulfonyl)imide ($Zn(TFSI)_2$) [91]. $ZnCl_2$ and $ZnNO_3$ generally cause a narrow electrochemical window and irreversible Zn dissolution/precipitation processes as a consequence of the instability of Cl^- and NO_3^- [92]. Currently, $ZnSO_4$ and $Zn(CF_3SO_3)_2$ electrolytes are the two most acknowledged electrolytes. Although $Zn(CF_3SO_3)_2$ electrolyte possesses higher invertibility and faster kinetics than $ZnSO_4$ in Zn deposition/dissolution processes, the high price of $Zn(CF_3SO_3)_2$ would

Table 2
Electrochemical performance of ZIBs using a non-carbon-based zinc anode.

Anode	Cathode	Electrolyte	Cyclability/rate capability (mAh g^{-1})	Capacity retention/cycle number	Ref.
Zn@Copper skeleton	MnO_2	$ZnSO_4/MnSO_4$	364@0.1 A g^{-1}/250@0.4 A g^{-1}	69.2%/300	[79]
Zn@Copper foam	β-MnO_2	$ZnSO_4/MnSO_4$	381.2@0.2 A g^{-1}/105.4@5 A g^{-1}	89.1%/600	[80]
Zn@ Copper mesh	MnO_2	$ZnSO_4/MnSO_4$/PAM gel	179.8@0.2 A g^{-1}/92@1 A g^{-1}	87.2%/200	[81]
Zn@ nickel nanotube	MnO_2	$ZnSO_4/MnSO_4$	275.5@0.2 A g^{-1}/192@1 A g^{-1}	145%/500	[82]
$Ti_3C_2T_x$ MXene@Zn paper	$LiMn_2O_4$	$ZnSO_4/Li_2SO_4$	81@1 C/47@3 C	97.69%/600	[83]

severely obstruct its practical application. Therefore, developing novel electrolytes in a facile and inexpensive strategy is essential to enhance the zinc anode behaviors in a long-term application.

Introducing additives into the electrolyte gives them a distinct crystallographic orientation and surface texture, which can strongly inhibit zinc dendritic growth, and thus improve the reversibility and stability of Zn anode [93]. It is widely accepted that the pre-addition of $MnSO_4$ constituent in the $ZnSO_4$ electrolyte can achieve accessible Mn^{2+} ions and thus restrain the Mn ion dissolution from the Mn-based cathode. Recent studies demonstrated this process also has a positive influence on the zinc anode interface under the mild aqueous condition [37]. The surface morphology of the cycled Zn anode tends to be smoother and denser in the electrolyte of 2 M $ZnSO_4$ with 0.1 M $MnSO_4$ than pure 2 M $ZnSO_4$ electrolyte, thanks to the strongly remitted polarization problems. Notably, as Na^+ possesses a lower reduction potential than Zn^{2+}, Na_2SO_4 additive has also been demonstrated to eliminate Zn dendrite growth via an electrostatic shield mechanism in zinc/sodium vanadate batteries [94].

In addition, Wang et al. [95] found that a concentrated aqueous electrolyte based on Zn and lithium salts helps improve CE, blocks the dendrite growth and ensures low water consumption. The fundamental structural studies combined with molecular-scale modeling indicate that the high reversibility of Zn is derived from the unique solvation-sheath structure of Zn^{2+} in the highly concentrated electrolyte. The high population of anions forces the vicinity of Zn^{2+} to form close ion pairs $(Zn\text{-}TFSI)^+$. Then, the Zn of $(Zn\text{-}(H_2O)_6)^{2+}$ can be effectively constrained to reach better reversibility and facilitated kinetics. Hence, this unique electrolyte significantly benefits the application of ZIBs, which not only enables dendrite-free Zn plating/stripping behavior at almost 100% CE, but also significantly manages water consumption in the open atmosphere. In the same way, a "water-in-salt" electrolyte containing 21 m LiTFSI and 1 m $Zn(CF_3SO_3)_2$ enhances the performance of ZIBs in both overpotential and durability, by alleviating the dendrite growth problem [96].

Motivated by the impressive function of diethyl ether (Et_2O) in suppressing lithium dendrites in lithium metal batteries, Wang et al. explored its performance in ZIBs as an electrolyte additive [97]. Notably, an enhanced cycle stability is achieved after adding 2 vol% Et_2O in the aqueous electrolyte. The Et_2O additive can contribute to a uniform zinc deposition by acting as an electrostatic shield layer and enhancing the electrode-electrolyte kinetics. Liu et al. [98] also developed a thickening and homogenizing aqueous electrolyte to stabilize Zn metal upon repeated cycling. As illustrated in Fig. 5a, this new electrolyte system containing a thickening agent (fumed silica, FS) that immobilizes the water molecules and a homogenizing agent (fatty methyl ester ethoxylate, FMEE) that uniformizes the Zn^{2+} cations deposition, which effectively inhibits the decomposition of water and suppresses the Zn dendrite formation. The Zn/Zn symmetric cell in the new electrolyte shows an extraordinary reversibility with a CE of 99.5% and long cycling stability over 1500 h. Small dendrites rather than large dendrites in needle or flask shapes were found from the cycled Zn metal surface as shown in Fig. 5b. Moreover, the Zn–MnO_2 full cell in this work

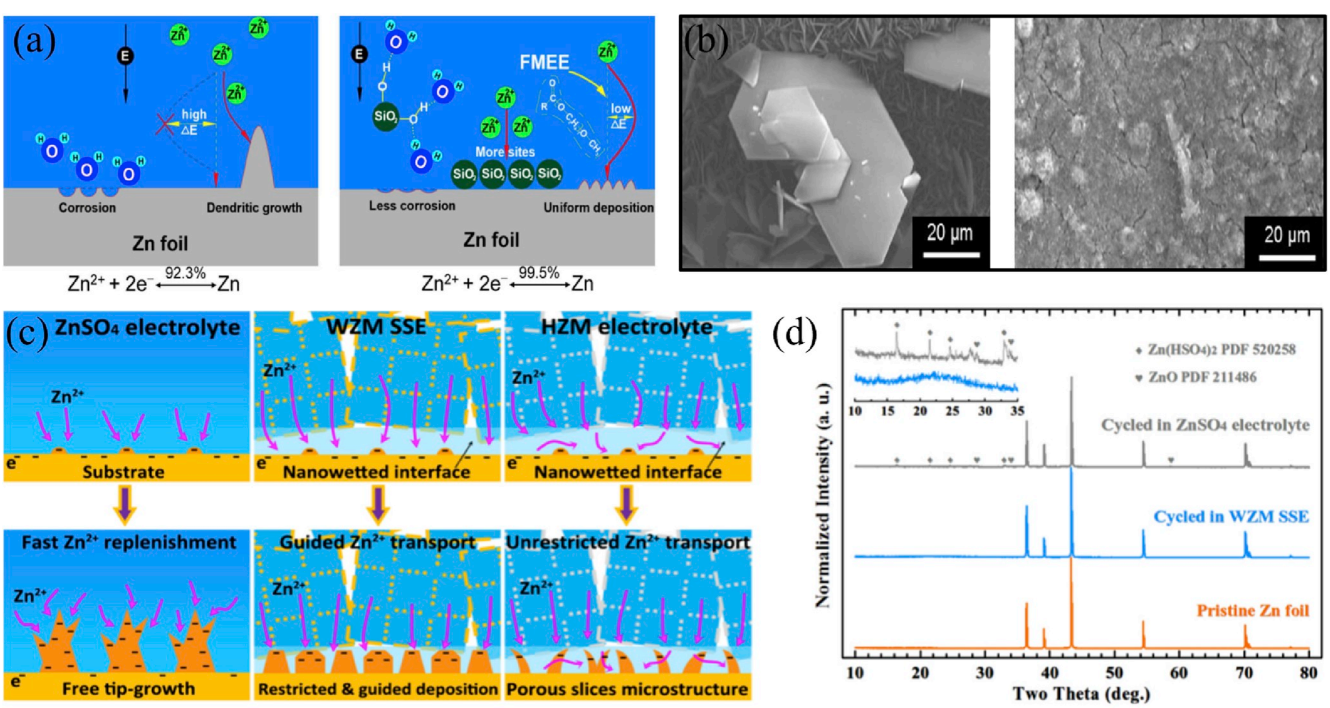

Fig. 5. (a) Illustration of the schemes of the electrochemical processes of Zn metal in the reference $ZnSO_4$ electrolyte and the $ZnSO_4$+FS + FMEE electrolyte. (b) SEM images of Zn metal surface after cycling in $ZnSO_4$ electrolyte (left) and $ZnSO_4$+FS + FMEE electrolyte (right) (c) Proposed mechanism for the different deposition behaviors of $ZnSO_4$ aqueous electrolyte (left column), water@ZnMOF-808 SSE (middle column) and hybrid $ZnSO_4$@MOF-808 electrolyte (right column). (d) XRD patterns of the Zn foils before (orange) and after plating/stripping cycles in water@ZnMOF-808 SSE (blue) and $ZnSO_4$ electrolyte (grey), respectively.

exhibits excellent durability with a low capacity loss of 0.002% per cycle, which is superior to the previously developed Zn metal batteries. Besides, Qian et al. [99] introduced sodium dodecyl sulfate (SDS) to the aqueous electrolyte and found the electrochemical stability window of the electrolyte could be expanded to about 2.5 V. They demonstrated that SDS can alleviate the water-induced corrosion reaction, leading to enhanced cycle life and rate capability. In addition, using PEG as an electrolyte additive can also restrict the zinc anode corrosion and improve the water-retention capability [100]. To be specific, PEG molecules can be attached to the zinc surface during the charging process, which efficiently restrict the lateral 2D diffusion of Zn^{2+} ions from solution near the surface. Limited zinc ion movement leads to a higher numerical density of small dendritic, thus preventing the fugitive growth of the dendritic process and the premature failure of the batteries.

Apart from researching additives for $ZnSO_4$ electrolyte, there are also some breakthroughs on the alternatives for $ZnSO_4$. Notably, Sun et al. [86] found many advantages of $Zn(ClO_4)_2$ in working as electrolyte for ZIBs. The Cl^- containing layer generated by the controlled reduction of ClO_4^- on Zn could effectively inhibit the side reactions and confirm a stable and rapid Zn stripping/plating process.

Gel-based electrolytes have become a recent research hotspot in ZIBs and also greatly promoted the development of flexible and wearable energy storage technologies [73,101,102]. For instance, Zhi et al. [75] successfully fabricated a waterproof and stretchable yarn-type ZIB by double-helix yarn electrodes and a cross-linked polyacrylamide (PAM)-based polymer electrolyte. They demonstrated the PAM electrolyte could act as an efficient separator as well as a good ionic conductor. Subsequently, they designed an extremely safe and wearable solid-state ZIB with a novel gelatin and PAM based hierarchical polymer electrolyte (HPE) [74]. To be specific, this HPE was prepared by grafting polyacrylamide (PAM) onto gelatin chains that are filled in a polyacrylonitrile (PAN) electrospun fiber network. The jointing of PAM into a gelatin hydrogel expressively improves the mechanical strength and zinc ion conductivity, while the PAN network can efficiently reduce the possibility of battery short circuit and further enhance the electrolyte strength. As a consequence of the highly porous 3D architecture and a high level of water retention of HPE, the as-prepared battery exhibits excellent flexibility and safety performance over traditional LIBs and even can work under harsh conditions. Moreover, there are also some progresses on the gel-based electrolyte based on other ingredients such as PVA [34,70,103], borax [104], Starch [105], and fumed silica [78].

Furthermore, the development of solid-state electrolyte (SSE) has been regarded as a fruitful strategy for the new generation of ZIBs, especially for wearable electronics. A strong and durable self-standing gelatin-based SSE was designed and fabricated by Liu's group [106]. This novel SSE system contains less free water compared with general electrolyte systems and possesses a preferable fracture tensile strength. Taking advantage of the SSE, a solid-state ZIB without any toxic chemical fillers is rationally prepared and exhibits impressive cycling stability over 500 cycles. More notably, Pan et al. proposed to fabricate a crystalline single-ion Zn^{2+} SSE derived from a metal–organic framework to achieve the highly efficient utilization of Zn electrode [107]. As schematically illustrated in Fig. 5c, the $Zn(H_2O)_6^{2+}$ ions on the Zn/SSE interface can be uniformly confined to release a more homogeneous and glabrous Zn deposition layer than the zinc anodes in conventional electrolytes. Also, the byproducts, namely $Zn(HSO_4)_2$ and ZnO, can be greatly inhibited as demonstrated by the XRD patterns of the Zn foils before and after plating/stripping cycles shown in Fig. 5d. Hence, the novel SSE provides some incomparable advantages than previous reports, such as high ionic conductivity (2.1×10^{-4} S cm^{-1}), minor activation energy (0.12 eV), high Zn^{2+} transference number (0.93), along with the stable mechanical and electrochemical performance. When used in the VS_2/Zn batteries, the as-prepared SSE delivers high reversible capacities and enhanced rate behaviors. These SSEs offer remarkable possibilities for flexible ZIBs, however, the electrochemical performance of these systems at high current densities still needs to be improved to obtain sufficient power densities in the future applications.

3.4. Novel separators

The separator is another important part of the battery system that controls the ion transport between electrodes. High-performance separators having sufficient chemical and mechanical stability as well as guidance function in Zn^{2+} flux are strongly demanded. In current studies, the separators for ZIBs are the glass fiber membranes made into a few hundred micrometers thick of filter paper due to their high hydrophilicity and tolerance for zinc dendrite. However, it is obvious that the total energy density of battery system on the weight or volume would be seriously reduced upon the use of such thick glass fiber separators [108]. Moreover, glass fiber cannot provide sufficient strength to maintain its structural integrity during the repeated ion transportation processes [109]. Hence, novel and high-performance separators are highly desired to further improve the electrochemical performance of zinc electrode as well as the total battery system.

Remarkably, Liu et al. [110] opened up a new avenue to selecting an ion exchange membrane as a separator for ZIBs to achieve its performance enhancement. Specifically, they reveal that the cross-linked polyacrylonitrile (PAN) based cation exchange membrane (PAN-S membrane) can enhance cation transport and uniform ionic flux distribution when applied as a separator for ZIBs. As shown in Fig. 6a and b, the PAN-S membrane can induce a stronger dendrite growth suppression than conventional separator due to the more homogeneous Zn ion concentration. As expected, the cycled anode surface presents a dendrite-free morphology with the PAN-S membrane instead of the flower-shaped dendrites generally observed when aqueous separators are used (Fig. 6c and d). Further application prospect of the as-prepared separator tested in Zn/Zn battery showed uniform ion flux and efficient cations transport as illustrated in Fig. 6e. This work provides an important insight into the potential improvement in anode performance by separator design.

Researchers have found that the deposition of zinc on the surface of anodes induces two phase crystallographic structure composed of Zn (100) and Zn (002), corresponding to the perpendicular and the parallel phase conformers to the surface. In order to induce the beneficial Zn (002) deposition, the lignin@Nafion composite membranes were innovatively synthesized and utilized as separators for ZIBs by Srinivasan's group [109]. Nafion separators contribute to the form of planar zinc hydroxide sulfate (ZHS) layer parallel to the anode surface as an effective solid electrolyte interface and stimulation of the deposited Zn (002). The advantages of these membranes result from the $–SO_3^-$-Zn^{2+} interaction and the modified Zn ion coordination. In contrast, filter paper separators usually bring the deposited Zn (100) and a loose layer of ZHS protrusion, which leads to a severe capacity fading. The lignin component in the composite membrane facilitates the growth of lateral zinc hydroxide sulfate parallel to the surface and Zn (100) lattice. Higher capacitance and enhanced durability are further demonstrated in β-MnO_2/Zn full battery. Congeneric research also reports the advantage of a Nafion ionomer membrane by stabilizing the anode in a super thin and nanowall-like morphology during repeated cycles [22]. Compared with other conventional porous separators (glass fiber, filter paper, polypropylene, *etc.*), Zn^{2+}-integrated Nafion ionomer membrane possesses a stronger ability in suppressing the growth of bulk/dendritic Zn deposits and provides a high cycling stability for the battery.

4. Summary and outlook

The zinc anode is a salient part of ZIBs that determines their overall electrochemical performance for future applications. Unfortunately, research into the optimization of Zn metal anodes for the enhancement of the electrochemical performance of ZIBs is still at the developing stage. Considering their potentially high efficiency coupled with their

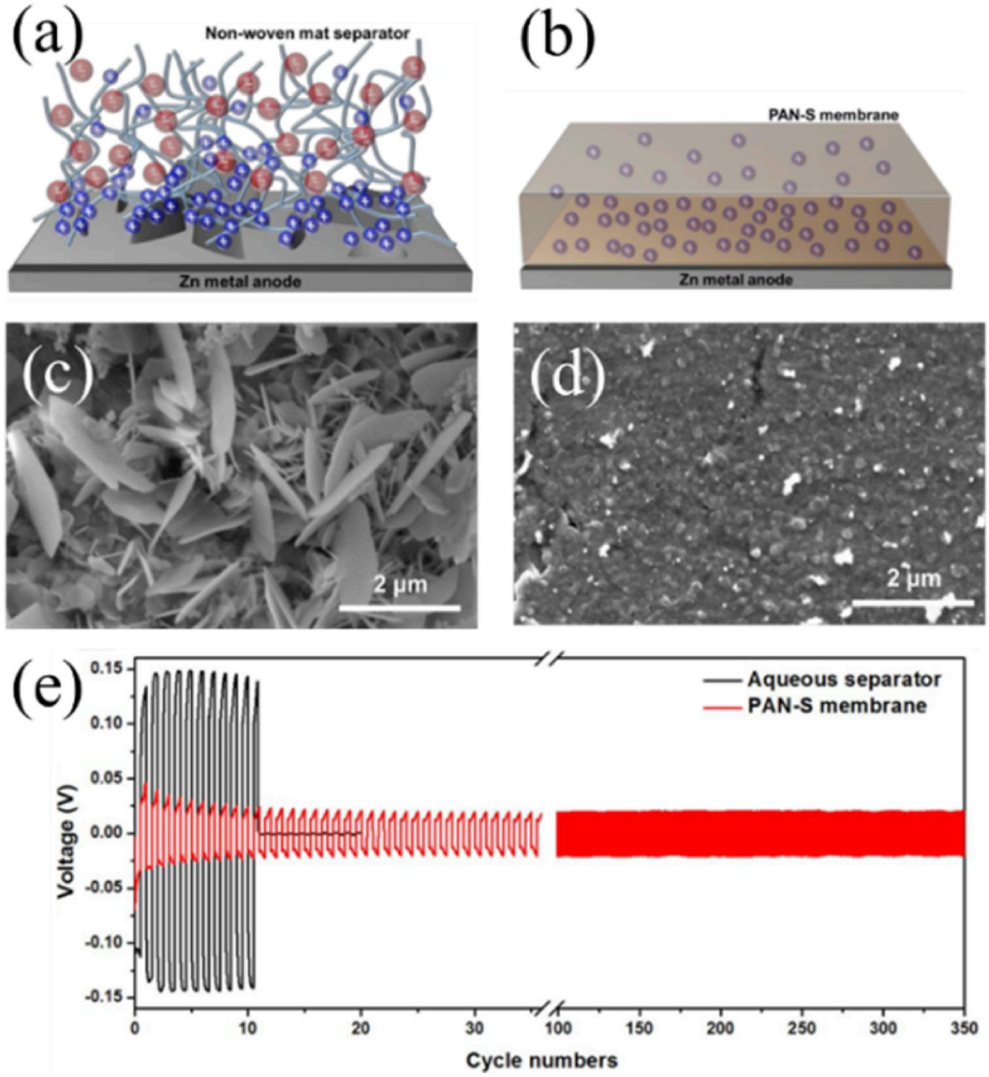

Fig. 6. Schematic descriptions of Zn deposition with (a) conventional separator and (b) single-ion transport PAN-S membrane. SEM images of Zn anode surface from the cells using (c) commercial nonwoven separator and (d) PAN-S membrane, and (e) cycling performance comparison between the conventional separator and PAN-S membrane.

environmental benignity, further researches into high-performance zinc anodes are strongly desired to replace the routine Zn foil anodes, which suffer poor reversibility, low CE, harmful dendrite growth, and severe self-corrosion. It is delightful to note that ZIBs have attracted significant research attention for the past decades. Also, plenty of breakthroughs have been achieved on the optimization of Zn metal anodes with different strategies and their electrochemical behavior in ZIBs has been enhanced. However, the fundamental understanding of the mechanism on Zn dendrite growth and side reaction is still inadequate. Therefore, more research is needed to ensure a complete understanding of the mechanism and the exact role of the zinc plating/stripping with its associated byproduct formation. Based on the unique properties and advantages of zinc metal for batteries, further research is suggested to be geared towards:

1. Strategy to attain a homogeneous Zn nucleation is the key to solving the harsh dendrite and Zn corrosion problems. In this regard, the careful fabrication of artificial solid electrolyte interface layer can induce uniform electrolyte permeation and flatten the zinc ion deposition. Some protective layers can also tolerate the detrimental dendrites growth and withstand the common issue of separator piercing in the ZIBs use phase. It is important to state that industrially scalable techniques are highly desirable for commercial productions. Moreover, these coatings and modification materials should work effectively under high current densities and sufficient loading mass.
2. The design and fabrication of low cost commercially viable novel anodes with excellent structural integrity and self-healing performance are strongly recommended. The self-healing strategy is a promising solution to in situ exclude the already-generated dendrites of the in-service zinc anodes. In this case, it can efficiently elongate the lifetime of electrode materials by ensuring a recoverable morphology of Zn anodes upon repeated cycles and avoid disassembling operations as well as work suspension. More efforts could be devoted to investigating the formation of Zn dendrites under different charge/discharge conditions, and developing some electrohealing strategies to passivate the already-formed Zn dendrites.
3. Optimization of the electrolyte constituents is essential for the development of current liquid ZIBs. The capacity fading of most batteries is due to the depletion of liquid electrolytes, rather than short circuit caused by the zinc dendrites. Hence, future electrolytes are expected to be non-consumable for long term usage. Also, some adverse effects of the additives on cathode performance should be fully considered.

4. Developing solid polymer electrolytes is also a compelling way to enhance the lifespan of the batteries by effectively enhancing the Zn ion transport kinetics and releasing a homogeneous ionic flux. The improvement of electrolyte is also of great significance in alleviating the dissolution of cathode materials. Moreover, the advanced electrolytes which are suitable for the application of flexible and wearable ZIB products are highly anticipated and worth further exploration.
5. Appropriate separators for ZIBs should be developed not only to possess good chemical and mechanical stability but also to be able to guide the ionic flux distribution, thus preventing the self-corrosion and enhancing the cycling stability of electrode materials. Additionally, functionalized separators which can inhibit the zinc dendrites are urgently needed.

It is anticipated that as the aforementioned strategies are being developed for the enhancement in the electrochemical performance and the understanding of the mechanism for ZIBs, similar technologies can be extended to other metallic electrode materials, such as Li, Na, K and Mg metal electrodes. In a nutshell, the obvious advantages of zinc electrodes, including intrinsic safety and good electrochemical performance make ZIBs environmentally friendly and promising energy storage alternatives with huge commercial prospects.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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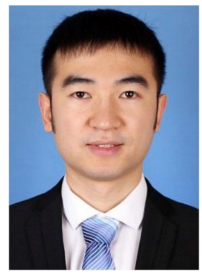

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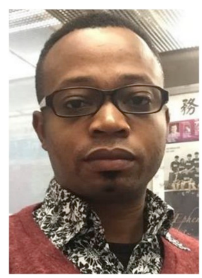

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