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Challenges, mitigation strategies and perspectives in development of zinc-electrode materials and fabrication for rechargeable zinc–air batteries

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As a promising energy storage device, the rechargeable zinc–air battery (RZAB) has attracted increasing attention because of its high energy density, cost-effectiveness, and high safety, and the rich abundance of zinc, as well as its environmental benignity. However, the widespread application of RZABs still faces considerable challenges derived from zinc-electrodes, electrolytes, and air-electrodes. In this paper, specific attention is given to RZAB zinc-electrode materials and fabrication with focus on the fundamental understanding of zinc-electrode reaction mechanisms, technical challenges, mitigation strategies, and perspectives. Particularly, the approaches to overcome the challenges are also presented and analyzed for facilitating further research and development of RZABs.

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Broader context

As competitive electrochemical technologies for energy storage and conversion, electrically rechargeable zinc-based batteries have attracted increasing attention including the zinc-ion battery and zinc–air battery. Compared to the zinc-ion battery, the rechargeable zinc–air battery shows high energy density because of the employment of O₂ as the active material, which deserves to receive much attention. Although important progress has been achieved in the development of the air-cathode, the challenges of the zinc-electrode become a major bottleneck for the future development of the rechargeable zinc–air battery. Therefore, considerable research efforts are required to address the challenges of the zinc-electrode in the zinc–air battery with the aim to meet the demands of its future application.

1. Introduction

With the growing demands for electricity usage in transportation, industry, and daily life, fossil energy such as coal, natural gas and petroleum are depleting more quickly.^{1–5} In view of fossil energy resource limitation, it is highly important to develop sustainable energy sources (solar, wind and so on), as well as associated strategies for energy storage and conversion.

In the past two decades, solar and wind energy sources have attracted much attention for their sustainable energy supply.

Unfortunately, their energy supplies are strongly determined by the weather. Therefore, technologies for energy storage and conversion to compensate for instable solar radiation and wind are necessary. Among many types of novel strategies for energy storage and conversion, batteries have drawn global tremendous attention and are recognized as the most feasible and reliable technologies. Up to now, tremendous efforts have been made to develop different kinds of energy storage batteries, such as lithium ion batteries,⁶ lead–acid batteries,⁷ redox flow batteries,⁸ lithium–air batteries,⁹ zinc–air batteries,¹⁰ sodium ion batteries,¹¹ fuel cells,¹² and supercapacitors.¹³ Among the different batteries mentioned above, metal–air batteries, as listed in Table 1, have attracted great attention due to several advantages such as low-cost, and high energy densities. The metal anodes used in metal–air batteries can be Li, Na, K, Mg, Ca, Zn, Fe and Al.^{14–17} In Table 1, several important properties of various metal–air batteries are presented, including theoretical voltage, specific energy density, and volumetric energy density. Among the metals listed in Table 1, zinc has been widely used as a negative material in metal–air batteries owing to its rich abundance, competitive cost, environmental benignity, high

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Table 1 Comparison of typical aqueous metal–air batteries

Battery systems	Physical properties for various metal anodes			Information for various aqueous metal–air batteries				Ref.
	Reduction potential <i>V</i> (vs. SHE)	Volumetric capacity (mA h cm ^{−3})	Specific capacity (mA h g ^{−1})	Reaction	Voltage (V)	Specific energy density (W h kg ^{−1})	Volumetric energy density (W h dm ^{−3})	
Li–air	−3.0	2062	3861	4Li + O ₂ + 2H ₂ O → 4LiOH	3.45	3582	2234	1–5 and 59–61
Na–air	−2.7	1128	1166	4Na + O ₂ + 2H ₂ O → 4NaOH	3.11	2600	—	
Mg–air	−2.4	3833	2205	2Mg + O ₂ + 2H ₂ O → 2Mg(OH) ₂	3.09	2843	1671	
Zn–air	−0.8	5851	820	2Zn + O ₂ → 2ZnO	1.65	1085	2316	
Al–air	−1.7	8046	2980	4Al + 3O ₂ + 6H ₂ O → 4Al(OH) ₃	2.71	2791	1160	
Fe–air	−0.44	23 376	2974	2Fe + O ₂ + H ₂ O → Fe(OH) ₂	1.28	764	715	

capacity and stability in aqueous electrolyte.^{1,3,15,18} Furthermore, compared with other metal–air batteries, zinc–air batteries (ZABs) hold great prospects for future energy applications in terms of their technology maturity.^{3,14,19–21}

Actually, primary ZABs have been widely used in the field of hearing-aid devices because of their cost effectiveness and high energy density since the late 19th century.²² For rechargeable ZABs, they can be classified into two types: mechanically rechargeable ZABs and electrically rechargeable ZABs. For a mechanically rechargeable ZAB, the exhausted zinc-electrode and electrolyte are replaced by a fresh zinc anode and electrolyte, leaving the air-electrode only operating for the oxygen reduction reaction (ORR).^{3,4} For an electrically rechargeable ZAB, it contains a negative zinc-electrode and a positive air-electrode, which are separated by a separator in an alkaline electrolyte, as shown in Fig. 1.⁴ It should be noticed that the air-electrode of an electrically rechargeable ZAB has two catalytical reactions, one is the ORR during discharging, and the other is the oxygen evolution reaction (OER) during charging. These two reactions can be expressed as the following equations (eqn (1)–(4)):

Zinc-electrode

Air-electrode

Overall reaction

In eqn (1)–(4), the forward arrows mean the discharge reactions, and the backward arrows indicate the reactions for the ZAB charge process. Although the electrically rechargeable ZAB (abbreviated as RZAB in this paper) has attracted increasing attention, the practical application of such technology is still hindered by several challenges, as shown in Table 2. As a vital part of the RZAB, the air-electrode consists of ORR/OER electrocatalysts aiming at promoting the reaction between oxygen and hydroxyl ions (OH[−]). Although noble metal oxides (*e.g.*, IrO₂ and RuO₂) are widely employed as OER electrocatalysts for their high OER catalytic activity and metallic-like electronic conductivity, they are less competitive due to their high cost.²³ Meanwhile, another noble metal, platinum (Pt), encounters similar problems even though it exhibits excellent catalytic activity for the ORR.²⁴ With the rapid development of metal–air batteries, various highly cost-effective electrocatalysts are taken into consideration, such as carbon-based materials and transition metal oxides.^{25–28} What is more, air-electrodes are still facing many challenges, including the catalytic reactivity of electrocatalysts toward ORR/OER reactions, current collectors and gas diffusion layers (GDL).^{29–36} The hydrophobicity of GDL also has a negative influence on the electrical conductivity and gas permeability of a battery, which leads to unfavorable polarization behavior.⁴ In addition, the challenges derived from the current collectors, such as carbon paper, stainless steel mesh and nickel foam, are nonnegligible. The volumetric capacity density on the basis of metal foams is much lower than the theoretical value.^{37–39} Additionally, the electrolyte functions as the medium to promote the transportation of ions, which also plays a crucial role in RZABs. Similar to the air-electrode, the electrolyte faces some technical issues as well, such as ionic conductivity, high dissolution of zinc and electrolyte evaporation, which limit the application of RZABs.^{29,40–43} The high dissolution of zinc in the electrolyte may cause the low utilization of the zinc-electrode, leading to the unsatisfactory electrochemical performance of RZABs.¹⁵ Meanwhile, atmospheric CO₂ could dissolve in the electrolyte, resulting in carbonate precipitation, the reduction of conductivity and the blocking of the air diffusion path in the air-electrode.⁴⁴ All the aforementioned issues may deteriorate the performance of RZABs.^{4,44,45} For zinc-electrodes, one of the

Fig. 1 Schematic of a typical RZAB.

Table 2 The challenges derived from the different components of RZABs

Component	Challenge	Effect	Ref.
Zinc-electrode	Dendrites, corrosion, shape change and passivation	Decrease the effective surface area and utilization of the zinc-electrode, limit cycle life, short-circuiting and capacity loss of the battery	62–72
Air-electrode	ORR/OER activity, materials of ORR/OER catalysts, current collector, gas diffusion layer and carbonate precipitation	Decrease activity of the air cathode, limit energy/power density and energy efficiency	29, 30 and 32–36
Electrolyte	Carbonate precipitation, high dissolution of zinc and electrolyte evaporation	Decrease ionic conductivity, kinetics of chemical reactions and zinc-electrode utilization	5, 29 and 41–43
Separator	Chemical (oxidation) resistance and penetration of zincate ions	Short-circuiting of the battery, decrease the capacity and cycling efficiency of the battery, deteriorate catalytic activity	3, 22, 73 and 74

undesired parasitic reactions, the hydrogen evolution reaction (HER) ($\text{Zn} + 2\text{H}_2\text{O} \rightarrow \text{Zn}(\text{OH})_2 + \text{H}_2$), can lead to the emergence of H_2 on the surface of zinc particles, which can reduce the content of water in the electrolyte and corrode the zinc-electrode during the discharge process, eventually shortening the lifetime of the battery, for example, to less than 400 deep-discharge cycles.⁴⁶ Furthermore, the practical working voltage of aqueous RZABs on discharge is generally less than 1.2 V even the theoretical working voltage is 1.65 V at a reasonable discharge current density, which is mainly caused by overpotentials of the ORR at the air-electrode and zinc oxidation at the zinc-electrode as well as electrolyte resistance.^{5,47,48} Great efforts have been made to increase the discharge potential to over 1.2 V through special designs.^{33,49,50} For example, Li *et al.*³³ fabricated a RZAB using a unique air-electrode containing $\alpha\text{-MnO}_2\text{@XC-72}$ and $\text{Fe}_{0.1}\text{Ni}_{0.9}\text{Co}_2\text{O}_4/\text{Ti}$ as ORR and OER electrocatalysts, which exhibited a discharge and charge voltage of 1.3 and 1.97 V, respectively.³³ Therefore, further performance improvement of RZABs can be achieved through novel designs. Up to now, several review reports with deep insights into the challenges of air-electrodes and electrolytes for RZABs have been provided.^{23,29,30,36,40,51–54} In terms of electrolytes, electrolyte additives are seen as an approach to improve the performances of batteries by depressing Zn dendrite formation at high current densities, including polyamine,⁵⁵ polyoxyethylene nonyl phenyl ether (NP16),⁵⁶ potassium diphosphate (PDP)⁵⁷ and potassium sodium tartrate tetrahydrate (PSTT)⁵⁷ and so on. These electrolyte additives are associate with organic and/or inorganic materials, which are mainly adsorbed on the surface of the zinc-electrode to alleviate ZnO dissolution/deposition and promote uniform dissolution/deposition on the zinc-electrode. So far, there are a series of studies devoted to the challenges and perspectives of the air-electrode and electrolyte, yet only a few studies have been reported on those of the zinc-electrode.^{23,25,27,30,34,52,54,58} Based on the aforementioned background, we mainly focus on the challenges and perspectives of zinc-electrodes.

Herein, a comprehensive overview of the fundamentals of the zinc-electrode for RZABs is provided, with an emphasis on the recent progress and challenges related to the development of zinc-electrodes as well as corresponding future perspectives. Some fundamental understanding and insights that govern the properties of the zinc-electrode for RZABs are also discussed. It is expected that this paper will be inspirational for

facilitating continuing research and development in this field of RZABs.

2. Zinc-electrode challenges and mitigation approaches

2.1. Challenges

The use of zinc-electrodes for RZABs is still facing great challenges including dendrite, corrosion, shape change and passivation. This section will provide some fundamental insights into understanding these challenges.

2.1.1. Dendrite. According to the reaction mechanisms expressed by eqn (1) and (2), when the RZAB is operated in an alkaline electrolyte, zincate ($\text{Zn}(\text{OH})_4^{2-}$) should appear during discharge and completely returns to Zn at the surface of the zinc-electrode during charge. Unfortunately, the zincate concentrations near the electrode and in the electrolyte solution are different, resulting in concentration polarization. In this case, zincate ions tend to diffuse and rapidly deposit on protrusions of the electrode surface. With the cycle continuing, zinc dendrites would accumulate on the zinc-electrode surface. The zinc dendrites are usually observed as sharp, needle-like morphologies (Fig. 2a and e), which pierce the separator with more dendrites formed, leading to electrical short-circuit and catastrophic failure of the battery.^{3,22} With respect to this challenge, significant effort has been made to investigate dendritic formation inside the RZAB. It has been found that the formation of zinc dendrites is mainly controlled by the concentrations of zincate ions and hydroxide ions, the mass transfer process of the electrolyte and current density distributions during charge and discharge.^{75–78} Meanwhile, the morphology, the crystal orientation and the crystal face of zinc dendrites can be changed by the operational current density and electrode overpotential. Despic *et al.*⁷⁵ reported that zinc deposition could lead to the formation of powdered deposits when the current density was larger than a certain critical value. Diggle *et al.*⁷⁶ observed that zinc dendrites were initiated to form in 2 M KOH including 0.01–0.2 M dissolved ZnO at a zinc-electrode overpotential between 85 mV and 140 mV. However, it should be noted that zinc dendrites can also be formed at lower deposition overpotential, as evidenced by the formation of spongy zinc below the overpotential of 85 mV. Considerable research efforts have been made to suppress the formation of dendrites during

Fig. 2 *In situ* optical images of zinc-electrode deposition with different concentrations of PEI additive: (a) 0 ppm; (b) 10 ppm; (c) 50 ppm; and (d) 100 ppm. SEM images of Zn dendrites electrodeposited in (e) an additive-free electrolyte and (f) an electrolyte with 10 ppm PEI. Reproduced with permission.⁶³ Copyright 2015, Elsevier.

zinc-electrode charge and discharge in alkaline electrolytes. For example, Banik *et al.*⁶³ reported the suppression of zinc dendrites using polyethylenimine (PEI) as the electrolyte additive. The dendrite tips in the electrolyte with PEI become smoother compared to the additive-free electrolyte, as displayed in Fig. 2e and f. Their results indicated that the additive of PEI could be considered as an effective

way to address the issue of zinc dendrites. Although considerable progress has been made, further understanding of the mechanisms and controlling the dendrite formation are still required.

2.1.2. Corrosion. As shown in eqn (5) and (6), the standard reduction potential of Zn/ZnO is lower than that of the HER, thus, the HER will inevitably take place during the operation of RZABs, which can result in consumption of the zinc and electrolyte during cycling. Furthermore, the internal pressure of the battery will be increased with the generation of H₂, resulting in battery swell and then shortened life span.^{5,15} The undesired side reaction (eqn (6)) can lead to the decay of the capacity and utilization efficiency of the zinc-electrode. Besides, to investigate the influence of electrolytes with different compositions or concentrations on zinc corrosion, intensive investigations have been carried out. For example, Laska *et al.*⁶⁹ investigated the influence of changing the electrolyte composition over time by dynamic electrolyte exchange and found that a compact precipitation layer was formed in hydrogen carbonate- and chloride-containing electrolytes, which then hindered the surface corrosion of the zinc-electrode. Fig. 3a and c display the cross sections of the zinc-electrode surface in various concentrations of electrolyte. Compared to a low concentration of NaHCO₃ (1 mM), the case at a high concentration (10 mM) presents a dense and less corrosive zinc-electrode, elucidating that an increased concentration of HCO₃[−] could reduce the corrosion of the electrode. From Fig. 3b and d, it can be seen that with increasing the concentration of electrolyte, the dissolution (black line) of Zn²⁺ is obviously decreased to the detection limit ($\sim 1 \times 10^{-7}$ mol L^{−1}).

Fig. 3 SEM images of the precipitation layers and corresponding dissolution profiles in 1 mM NaHCO₃ + 0.1 M NaCl (a and b) and 10 mM NaHCO₃ + 0.1 M NaCl (c and d) after 1000 seconds of pre-corrosion in 0.1 M NaCl. Reproduced with permission.⁶⁹ Copyright 2015, Elsevier.

2.1.3. Shape change. As observed, after many charge-discharge cycles, the thickness and effective specific surface area of the zinc-electrode would be changed, giving rise to the densification and capacity decay of the battery.^{79,80} Therefore, shape change is another challenge of the zinc-electrode induced by the redistribution of active material on the surface of the zinc-electrode.

Based on modeling and mechanistic investigations, it has been shown that the shape change is mainly affected by uneven current distribution in the reaction zones, the concentration of alkaline electrolyte and convective flows when electro-osmotic forces occur.^{71,72,79–82} For example, Einerhand *et al.*⁷⁹ proposed a density gradient model, which indicated that the emergence of electrolyte flow was closely associated with the density gradients in the solution layer near the zinc-electrode and volume variations of the battery. To gain a better understanding of the electrodeposited zinc with various surface morphology, Otani *et al.*⁸³ studied the effects of lead (Pb) and tin (Sn) additives on the generation of electrodeposited zinc. Compared to the Sn additive, the use of Pb could obviously reduce the working potential and showed a superior performance by diminishing the active growth sites during Zn deposition. In addition, the possible mechanism for the formation of layer-like and mossy structures on Zn deposition was proposed in Fig. 4. It can be seen that the deposited structures on the zinc-electrode are different when they are formed at a high and low current density. At the low current density, the mossy structure is ascendant with stacking of microsteps at the initial stage of deposition, suggesting that the mossy structures can be formed through the suppression of microstep growth toward the lateral direction, followed by 2D nucleation on filaments. Besides, locally repeated 2D nucleation is achieved on a wide terrace of the basal plane at high current density, which is considered to be derived from the nonuniform deposition on the surface of the zinc-electrode.

2.1.4. Passivation. During the discharge of the RZAB, the product $\text{Zn}(\text{OH})_4^{2-}$ near the zinc-electrode would reach its limiting solubility, resulting in the initiation of ZnO precipitation onto the zinc-electrode surface, and then forming passivation.⁴ As one of the challenges of alkaline RZABs, passivation can greatly influence the battery performances such as rate capability and cycle life. The key factor causing passivation in RZABs is the surface concentration of the reaction product.^{82,84} During the discharge process, the remaining activity of the electrode is dependent on the available zinc surface for the anodic dissolution process. The underlying densification tends to decrease the active surface area and results in polarization and unsatisfying cycle performances of the batteries, as shown in Fig. 5a.⁸⁵ Great efforts have been made to investigate the origin of passivation in RZABs with focus on the electrolyte flow rate and the presence of specific ionic species in the electrolyte, particularly SiO_3^{2-} and Li^+ .^{84,86–88} For example, Hampson *et al.*⁸⁹ experimentally demonstrated passivation behaviors in various concentrations of KOH electrolyte, as displayed in Fig. 5b. It can be found that the passivation time decreases with increasing both current density and KOH concentration. Fig. 5c indicates that the increased velocity of

Fig. 4 Schematic of the formation of layer-like and mossy structures on the zinc-electrode. Reproduced with permission.⁸³ Copyright 2017, Elsevier.

flow increases the passivation time at constant current density.⁹⁰ Therefore, understanding the factors influencing the passivation behavior is important in reducing the passivation effect of zinc-electrodes in RZABs.

2.1.5. Theoretical investigation. The abovementioned discussion has indicated that the continuous charge/discharge cycles in RZABs can result in several challenges, such as dendrite, corrosion, shape change and passivation. With the aim to better understanding the origin of these phenomena, several different mathematical theories and their associated models have been developed.^{29,75,81,85,91–93} Mainar *et al.*²⁹ gave a summary of the proposed mechanisms for zinc dissolution, which were related to the presence of differently dissolved products and their nature, including the number and type of intermediates, and their states of solvation, absorption and mobility. Although these mechanisms of zinc dissolution are still a matter of debate, it can be proven that zinc dissolution is closely linked to the concentration of OH^- or pH. In fact, there are many vital factors responsible for the issues of zinc-electrodes such as overpotential, electrolyte concentration, electrode thickness, temperature and so on.^{75,91,94} For example, Choi *et al.*⁸¹ described the relationship between current density and the electrode properties by eqn (7):

$$i = \left\{ v_y^n \frac{\partial c_{\text{Zn}}^n}{\partial y} - \frac{\partial}{\partial y} \left(D_{\text{Zn}}^n \varepsilon^n \frac{\partial c_{\text{Zn}}^n}{\partial y} \right) - \frac{L_{zz}}{w_n} c_{\text{Zn}}^p - ak C_{\text{Zn}}^{sn} \right\} \frac{w_n F}{(0.5 - t_{\text{Zn}}^m)} \quad (7)$$

where i , c_{Zn} , ε , and D_{Zn} represent the current density, concentration of Zn^{2+} , electrode porosity and the diffusion coefficient of Zn^{2+} , respectively. Symbol v_y^n is the superficial velocity in the y direction. L_{zz} can be regarded as equal to the diffusion coefficient of Zn^{2+} in the membrane divided by the thickness of the membrane. The symbol t_{Zn}^m represents the transference number of Zn^{2+} for the membrane, which is assumed to have a constant value related to the membrane.

As one of the key factors, the concentration of zincate solution in the electrolyte plays a critical role in the formation of passivation on the zinc-electrode. From the results displayed in Fig. 6, it can be found that three steps are associated with the generation of passivation on the zinc-electrode in alkaline solution.⁸⁵ The OH^- concentration has a great influence on

Fig. 5 (a) Passivation analysis of the zinc-electrode in 7.24 M KOH. Reproduced with permission.⁸⁵ Copyright 1981, The Electrochemical Society. (b) $3(\text{Passivation time})^{-1/2}$ vs. current density in different KOH concentrations. Reproduced with permission.⁸⁹ Copyright 1963, The Electrochemical Society. (c) The relationship between passivation time and current density at different velocities of electrolyte flow. Reproduced with permission.⁹⁰ Copyright 1970, Elsevier.

Fig. 6 Schematic for the evolution of passivation on the zinc-electrode in electrolyte. Reproduced with permission.⁸⁵ Copyright 1981, The Electrochemical Society.

the conversion between Zn and Zn(OH)_4^{2-} .²⁹ In Step 1, OH^- reacts with metallic Zn on the boundary between the zinc-electrode and electrolyte at a low OH^- concentration. After the zincate solution concentration reaches a critical value, ZnO is initiated to deposit on the zinc-electrode surface, giving rise to the formation of passivation (Step 2). Subsequently, the electrolyte becomes saturated by OH^- , and the electrode starts to generate O_2 (Step 3).

To better understand the electrochemical behavior between the electrode and the electrolyte, a schematic for the formation of ZnO film is shown in Fig. 7.⁹⁵ It can be seen that before charge and discharge processes, a layer of electrolyte molecules is adsorbed in the vicinity of the zinc-electrode. With the reactions taking place in the electrolyte, Zn^{2+} and OH^- are transferred to the surface of the zinc-electrode under the force of the electric field and favor to the nucleation, as shown in Fig. 7b–d. With acceleration and nucleation of Zn^{2+} species, zinc oxide densification can be obtained on the surface of the zinc-electrode, which subsequently converts into the zinc oxide film (Fig. 7e and f).

2.2. Recent progress

From the above-mentioned discussion, the main challenges of zinc-electrodes for RZABs are dendrite, corrosion, shape change and passivation. Thus, it is necessary to develop effective solutions to address these challenges. Great efforts have been devoted to enhance the performance of zinc-electrodes, including battery capacity, coulombic efficiency and cycle life. Fig. 8 gives a brief summary of challenges and underlying opportunities for zinc-electrodes in alkaline RZABs. The additive-based solutions including electrode additives and electrolyte additives for

Fig. 7 Schematic of the formation of ZnO film. (a) Quasi-equilibrium state; (b) the exploitation of the transport region; (c) the development of the polymerization region; (d) the nucleation and growth region; (e) ZnO densification; and (f) ZnO film folding. Reproduced with permission.⁹⁵ Copyright 1979, The Electrochemical Society.

Fig. 8 An overview of challenges and multiple opportunities for zinc-electrodes in alkaline RZABs.

improving zinc-electrode performance and the corresponding effects are summarized in Table 3.

2.2.1. Electrode additives. Electrode additives can be used to improve the performance of RZABs through promoting ZnO dissolution/deposition on the zinc-electrodes, increasing the hydrogen overpotential, suppressing formation of dendrites, and reducing corrosion. Currently, electrode additives can be classified into three types: electrode structure additives, inorganic corrosion inhibitors and polymer additives.

Electrode structural additives, such as acetylene black, graphite, activated carbon, carbon black and graphene oxide, are widely used in zinc-electrodes to inhibit the formation of dendrites. For example, Mohamad *et al.*⁹⁶ added Super-P to a porous zinc-electrode and investigated the performance of the assembled RZABs in a 6 M KOH electrolyte. The obtained results indicated that the zinc-electrode with 2 wt% Super-P could give a specific discharge capacity of 776 mA h g⁻¹ and a

power density of 20 mW cm⁻², induced by the arrangement of zinc particles and Super-P powder on the porous zinc-electrode (Fig. 9a and b). Additionally, Li *et al.*⁹⁷ proposed a new approach to enhance the electrochemical performance of a zinc-electrode in a Zn(NO₃)₂ or ZnSO₄ aqueous electrolyte through adding activated carbon. Activated carbon could provide the room for Zn dendrites and other passivation products due to the rich and well-developed pores, ensuring the activity of zinc particles. Similarly, Wang *et al.*⁹⁸ employed highly conductive carbon fiber-graphite felt (GF) as an electronic collector to prepare a self-supported Zn@GF negative electrode (Fig. 9c and d) and a high battery performance was achieved by using such an electrode in 0.5 M Na₂SO₄ and 0.05 M ZnSO₄ (Fig. 9e–g).⁹⁸ Besides adding carbon-based materials, the incorporation of ZnO with a porous zinc-electrode is also considered to be an alternative solution to control the volume change of the zinc-electrode by compensating for the dissolved zinc active material during discharge/charge cycles.^{99,101,103,135}

With the aim of alleviating zinc-electrode corrosion, metal and metal oxide/hydroxide can be added into the electrode as inorganic corrosion inhibitors. Inorganic corrosion inhibitors can not only increase the hydrogen evolution overpotential, but also lower the Zn negative potential. Additionally, the surface of the zinc-electrode can be smoothed through the electrodeposition of those additives. In the early stage, Hg, Pb and their oxides were used to prevent zinc corrosion and suppress hydrogen evolution.¹⁰² Nowadays, they have been replaced by environmentally benign

Table 3 Proposed additive-based solutions for improving zinc-electrode performance and the corresponding effects

Solutions	Effects	Ref.
Electrode additives		
Electrode structure additives	Carbon black, activated carbon, graphite fiber, graphene oxide, ZnO	96–104
Inorganic corrosion inhibitors	In, Bi, Pb, La, Nd, Sn, Ni, Cu, SiO ₂ , PbO, BiO ₃ , Li ₂ O–2B ₂ O ₃ , Al ₂ O ₃ , Bi ₂ O ₃ , Ca(OH) ₂ , In(OH) ₃ , [M ^I _{1-x} M ^{III} _x (OH) ₂] ^{K+} X _{x/n} ⁿ⁻ ·mH ₂ O	65, 67, 83 and 105–116
Polymer additives	Ion-containing polymer, α -hydroxy naphthoic acid, cellulose, agar binder, polyvinyl alcohol (PVA)/poly(diallyldimethylammonium chloride) (PDAA), anion-exchange ionomer	110 and 117–123
Electrolyte additives		
Inorganic additives	LiF, KF, K ₃ BO ₃ , Li ₃ BO ₃ , SnO, K ₂ CO ₃ , Li(TFSI), SiO ₃ ²⁻ , CdO, PbO, Pb ₃ O ₄ , In ₂ O ₃ , Bi ₂ O ₃	124–128
Organic additives	Polyethylene glycol (PEG), perfluorosurfactant, polyoxyethylen alkyl phosphate ester acid (PAPEA), phosphoric acid (PA), tartaric acid (TA), succinic acid (SA), and citric acid (CA), tetra-alkyl ammonium hydroxide (TAAHs), isopropyl alcohol (IP), ethylene glycol (EG), glycerol (GL), <i>meso</i> -erythritol (ER), polyethyleneimine (PEI), polyaniline (PANI), polyacrylic acid (PAA), cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), thiourea (TU)	43, 64 and 129–134

Fig. 9 (a) TEM image of a zinc-electrode containing 2% Super-P; (b) schematic of the microstructure for the porous Zn anode made of Zn and Super-P powder. Reproduced with permission.⁹⁶ Copyright 2013, The Electrochemical Society. SEM images of GF (c) and Zn@GF (d); and galvanostatic discharge/charge voltage profiles (e), rate capability (f) and cycling performance (g) of a full cell. Reproduced with permission.⁹⁸ Copyright 2017, Elsevier.

metals, such as In, Bi, Pb, La, Nd, Sn, Ni and Cu.^{83,105–108} It was reported that the alloy with a composition of 90% zinc, 7.5% nickel and 2.5% indium could give a remarkable inhibiting effect on zinc dendrite formation.¹⁰⁵ In addition to metallic electrode additives, metallic oxides/hydroxides can also improve the electrochemical behaviors of the zinc-electrode. For instance, SiO₂,¹⁰⁹ PbO,¹⁰² Bi₂O₃,^{111,113} Li₂O–2B₂O₃,¹¹² Al₂O₃,^{65,67} Ca(OH)₂,¹¹⁶ La₂O₃/La(OH)₃,¹³⁶ and In(OH)₃¹⁰² were reported as effective additives for zinc-electrodes to enhance the performance of RZABs. As it is well known, an oxide layer (La₂O₃/La(OH)₃) would be formed in an alkaline solution because of the high reactivity of La towards water, which could suppress the corrosion and dendrite growth of zinc in aqueous alkaline solutions. In order to evaluate the effect of La element on the performance of the zinc-electrode,

Yang *et al.*¹³⁶ prepared a Zn_{99.5}La_{0.5} alloy electrode, which suffered less corrosion and exhibited a more stable discharge performance compared to pure Zn, as shown in Fig. 10. Lee *et al.* and Wongrujipairoj *et al.*^{65,67} employed the coating of a thin layer of aluminum oxide (Al₂O₃) on a zinc-electrode to inhibit the self-discharge and improve the electrochemical performance of RZABs. Fig. 11a and b show that the Al, O and Zn elements are detected on the zinc-electrode, meaning that Al₂O₃ has been successfully coated on the electrode. Among three zinc-electrodes mixed with different oxides and pure zinc, the electrode mixed with Al₂O₃ shows a lower working potential as shown in Fig. 11c. Furthermore, an Al₂O₃ layer with an appropriate thickness can effectively improve the stability of RZABs by mitigating the HER and corrosion of the zinc-electrode without sacrificing the battery

Fig. 10 SEM images of pure Zn plate (a) and $\text{Zn}_{99.5}\text{La}_{0.5}$ alloy rod (b) electrodes after polarization; (c) discharge profiles of a $\text{Zn}_{99.5}\text{La}_{0.5}$ alloy electrode at different cycles. Reproduced with permission.¹³⁶ Copyright 2004, The Electrochemical Society.

performance (Fig. 11d and e). Besides, González *et al.*¹¹⁵ increased the efficiency of zinc electrodeposition from 85% to 98% through adding layered double hydroxides (LDH, $[\text{M}_1^{II-x}\text{M}_x^{III}(\text{OH})_2]^{x+} \text{X}_{x/n}^{n-} \cdot m\text{H}_2\text{O}$). According to the results from electrochemical measurements, it can be found that the improvement in efficiency was attributed to the elimination of the potential drop at the initiation of Zn^{2+} reduction and the suppression of H_2 generation during discharge. Similarly, bismuth and calcium oxides were also investigated as electrode additives, and a zinc-electrode with a coating layer of $\text{Bi}_2\text{O}_3\text{-ZnO-CaO}$ was fabricated by Schmid *et al.*¹¹¹ The SEM images of untreated zinc and the zinc-electrode coated with 3.2 wt% $\text{Bi}_2\text{O}_3\text{-ZnO-CaO}$ are shown in Fig. 11f and g. For uncoated zinc, zinc oxide platelets can be obtained during discharge on the surface. In contrast, it is difficult to observe the platelets or dendrites on the coated zinc-electrode after charge. Compared to the untreated zinc, the cyclic stability of the zinc-electrode coated with 3.2 wt% $\text{Bi}_2\text{O}_3\text{-ZnO-CaO}$ is remarkably improved due to the interaction among Bi_2O_3 , ZnO and CaO (Fig. 11h). In addition, the experimental results suggested that the initial utilization of 62% for coated zinc was higher than that of 53% for untreated zinc. Therefore, owing to the immobilization of zincate ions within the coating and the reduction of nonuniform zinc re-deposition, the coating strategy of bismuth can indeed inhibit the morphology change of the zinc-electrode.

As a type of promising candidates, polymer additives are widely used as electrode additives, which can usually adsorb on the surface of an electrode to form a thin film and improve the deposition and dissolution of zinc during charge/discharge cycles, thereby changing the polarization behavior of the zinc-electrode and mitigating the HER. The preferential adsorption

of polymer additives at rapid growth sites can preclude or slow down further growth of dendrites.¹⁵ Previous research has introduced various polymer additives into the electrode systems, including cellulose,¹¹⁰ an ion-containing polymer,¹¹⁷ α -hydroxy naphthoic acid,¹¹⁸ agar binder,¹¹⁹ poly(diallyldimethylammonium chloride),¹²⁰ cetyltrimethyl ammonium bromide,⁶⁴ SDS,⁶⁴ polyethylene glycol,⁶⁴ TU,⁶⁴ PVA,¹³⁷ and anion-exchange ionomers.^{122,123} As it is well known, PVA, a polyhydroxy polymer, has a mass of reactive chemical functions, which facilitates the cross-linking reactions through chemical treatments. A PVA hydrogel obtained by the reaction between PVA and glutaraldehyde in strong acid can provide fast ionic transfer channels and free space. On the other hand, conductive anions (*e.g.* OH^-) as charge carriers can be offered by the PDDA; consequently, Gan *et al.*¹²⁰ synthesized ZnO coated by PVA/PDDA film, which functioned as the polymer matrix and anion charge carriers, respectively. Fig. 12 displays the SEM images of bare Zn and ZnO/PVA/PDDA electrodes, and the corresponding cycle life at 25 and 50 mA cm^{-2} . It is found that the ZnO/PVA/PDDA composite electrode shows fewer dendrites, higher electrochemical activity and longer cycle life than the bare ZnO-electrode. PANI also attracted much attention as a polymer electrode additive. It was reported that a 20PANI@Zn composite material showed a corrosion inhibition efficiency of 85% against a pure zinc-electrode and a capacity retention of 97.81% after 24 hours of storage.¹³⁴

2.2.2. Electrolyte additives. Besides electrode additives, the utilization of electrolyte additives has been intensively explored as an effective strategy to overcome the challenges of zinc-electrodes. According to the nature of additives, electrolyte additives can be classified into two types: one type is inorganic additives, and the other is organic additives, primarily referring to surfactants.

Inorganic additives. Inorganic additives include metal salts, oxides and hydroxides, as well as organic salts. Various inorganic additives such as LiF,¹²⁴ KF,^{124,138} SnO,¹²⁵ CdO,¹³⁹ In_2O_3 ,¹³⁹ BiCl_3 ,¹²⁸ K_3BO_3 ,¹²⁴ PbO,¹³⁹ Li_3BO_3 , K_2CO_3 ,^{124,126,138} and silicate ions^{88,127} have been employed to reduce the dendritic growth on the zinc-electrode. The introduction of the above additives into electrolytes usually leads to the formation of metal ions with a higher reduction potential than Zn. Therefore, during the electrochemical deposition process, the metallic element additives could react with Zn and would influence the morphologies of the zinc-electrode. Previous research showed that the addition of KOH-KF- K_2CO_3 into the electrolyte could alleviate the shape change of the zinc-electrode and the capacity decay of the battery by decreasing the solubility of ZnO in the electrolyte.¹³⁸ As illustrated in Fig. 13, the zinc-electrode of Zn/NiOOH cells with KF in the electrolyte displays less shape change.⁸⁷ Besides, the effect of BiCl_3 as an electrolyte additive was studied by Wang *et al.*¹²⁸ and they found that the addition of Bi^{3+} could inhibit the formation of zinc-electrode dendrites in an alkaline electrolyte both at electrode overpotentials of $\eta = -100$ and -200 mV. Similarly, the surface morphologies of zinc-electrodes after the anodic potentiodynamic test in NaOH solution containing $\text{Na}_2\text{Si}_3\text{O}_7$ at different rotation rates were investigated by

Fig. 11 (a) SEM, TEM and elemental mapping images of the synthesized particles containing 2.0 wt% Al. Reproduced with permission.⁶⁷ Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) SEM and EDS mapping images of an Al₂O₃ coated Zn particle; (c) potential–dynamic polarization curves of Zn gel anodes using different additives on the Zn anodes; and (d) discharge curves and (e) cycling performance of bare Zn, commercialized Zn alloy, and the Al₂O₃ coated zinc–electrode. Reproduced with permission.⁶⁵ Copyright 2013, Elsevier. SEM images of uncoated zinc (f) and coated zinc (g); and (h) cyclic performance of batteries using uncoated zinc and coated zinc. Reproduced with permission.¹¹¹ Copyright 2018, Elsevier.

Diomidis *et al.*⁸⁸ as shown in Fig. 14a and b. It can be seen that increasing rotation rates can lead to a lower potential when the current density is constant (Fig. 14c). Apart from this, Kim *et al.*¹²⁵ effectively suppressed the dendritic growth of zinc electrodeposits by adding SnO to the alkaline solution. As shown in Fig. 14d–g, with increasing the concentration of SnO in the electrolyte, the dendrites on the zinc-electrode are reduced to some extent. Moreover, the increased anodic charge is similar to the increased cathodic charge at a relatively lower concentration of SnO (Fig. 14h).

Regarding organic salts as additives, Wang *et al.*¹ developed a highly reversible zinc-electrode based on a highly concentrated Zn-ion electrolyte (HCZE) with a high concentration of Li(TFSI) (TFSI: bis(trifluoromethanesulfonyl)imide) to address the issues of the unsatisfying coulombic efficiency, undesired dendrite growth during discharge/charge and water consumption. As illustrated in Fig. 15a, the simulated molecular structure in HCZE (Zn(TFSI)₂ + LiTFSI) is obtained by molecular dynamics (MD) studies and density functional theory (DFT) calculations, where Zn(TFSI)₂ and LiTFSI are used as the electrolyte and electrolyte additive, respectively. Unlike the conventional aqueous electrolyte, this HCZE

exhibits unique structures for Zn²⁺ coordination in various concentration of LiTFSI (Fig. 15b). As displayed in Fig. 16c and d, with increasing LiTFSI concentration, the coordination numbers of Zn²⁺–O(TFSI) obviously tend to rise. In contrast, Zn²⁺–O(water) coordination is correspondingly alleviated to some extent. Furthermore, according to Fig. 15c and d, it can be illustrated that the formation of cation–anion aggregates and anion reduction can be achieved with increasing temperatures with 10 m Li(TFSI) + 1 m Zn(TFSI)₂ solution (here, the symbol “m” represents molality, mol kg⁻¹). To better understand the effects of LiTFSI, small-angle neutron scattering (SANS) measurements were carried out to validate the structures in three different concentrations of LiTFSI predicted by MD simulations (Fig. 15e). This HCZE showed an excellent cycle performance (Fig. 15g) at 50 mA g⁻¹, in virtue of the dense and dendrite-free morphology of the zinc-electrode with the absence of ZnO after more than 500 cycles (Fig. 15f).

Organic additives. Different kinds of polymers or surfactants have been reported for organic additives, including PA,¹⁰⁵ TA,¹⁰⁵ SA,¹⁰⁵ CA,¹⁰⁵ ethylene glycol (EG),¹⁰⁵ PEG,¹²⁹ TAAHS,¹³⁰

Fig. 12 SEM images: (a) the bare ZnO electrode, and (c) the ZnO/PVA/PDDA electrode; and the cycle performance of the bare ZnO-electrode and the ZnO/PVA/PDDA composite electrode at (b) 25 mA cm^{-2} and (d) 50 mA cm^{-2} charge/discharge current densities. Reproduced with permission.¹²⁰ Copyright 2015, Elsevier.

Fig. 13 Images of shape change on Zn electrodes of Zn/NiOOH cells in (a) 31 w/o KOH and (b) 3.5 M KOH + 3.3 M KF. Reproduced with permission.⁸⁷ Copyright 1991, The Electrochemical Society.

perfluorosurfactant (including hydrocarbon chain surfactant, CTAB),¹²¹ PAPEA,¹²⁹ branched PEI,¹³³ and PAA.⁴³ Normally, organic additives can be adsorbed on the active sites of the zinc-electrode surface in favor of a uniform deposition of zincate. For instance, Sun *et al.*⁶⁴ investigated the cycling performance of a zinc-electrode with organic additives. Their organic electrode additives were CTAB, SDS, PEG-8000, and TU. SEM images of zinc-electrodes with various organic additives and commercial zinc are shown in Fig. 16a. Owing to the

additive adsorption on the electrode surface, the number of active sites and the nucleation rate are reduced, leading to the regular and uniform deposition of Zn, as evidenced by the morphology of Zn-CTAB, Zn-SDS and Zn-PEG. A similar result was also obtained for Zn-TU ascribed to the production of H_2 on the surface, which blocked the zinc deposition. In the case of the zinc-electrode without additives, the surface contains irregular layer structure, leading to an inferior performance of the battery. Fig. 16b compares the cyclability of RZABs using zinc-electrodes with several additives, and it is indicated that Zn-SDS is the best aqueous battery among all electrodes owing to its decreased corrosion rate, alleviated dendrite generation, low float current and high capacity retention after long cycles. On the other hand, it is reported that dodecyltrimethylammonium bromide (DTAB) is usually employed to suppress the corrosion of carbon steel in well water because of its satisfactory moisture retention and chemical stability.¹⁴⁰ Thereby, Liu *et al.*¹⁴¹ introduced DTAB to 7.0 M KOH solution saturated with ZnO, which could effectively suppress the corrosion of zinc, as proved by both morphology and electrochemical measurements shown in Fig. 16c–g. It can be found that the performance of the zinc-electrode in the electrolyte with 0.07% DTAB is the best among the other three (Fig. 16g). Lan *et al.*¹³⁰ reported that the addition of TAAHs in the zincate solution could significantly suppress the dendritic growth on the

Fig. 14 SEM images of zinc electrode deposition in NaOH containing $\text{Na}_2\text{Si}_2\text{O}_7$ at (a) 400 and (b) 800 rpm; and (c) potential dynamic plots at three different rotation rates in NaOH containing $\text{Na}_2\text{Si}_2\text{O}_7$. Reproduced with permission.⁸⁸ Copyright 2017, The Electrochemical Society. SEM images of Zn electrodeposition in the electrolyte adding (d) 0, (e) 10^{-4} , (f) 10^{-3} , and (g) 3×10^{-3} M SnO; and (h) charge increase vs. SnO content in anodic and cathodic scans. Reproduced with permission.¹²⁵ Copyright 2015, Elsevier.

zinc-electrode if the proper concentration of alkyl groups can be chosen. It was claimed that the ability to suppress dendrites was associated with the size of alkyl group and additive concentration because of the strong blocking effect. Moreover, fluorosurfactant was also verified to be a promising additive to inhibit the growth of zinc dendrites.¹⁴² Similar to fluorosurfactants, perfluorosurfactants could also largely reduce the dendritic growth and mitigate the corrosion of the zinc-electrode by controlling the morphology of ZnO deposition and decreasing the HER rate, respectively.¹²¹ Lee *et al.*¹³¹ compared the hydrogen overpotential and the formation of dendrites among four acid additives (namely TA, SA, PA and CA) in 8.5 M KOH solution, and found that CA showed superior effects in suppressing zinc dendrites. It was also shown that the hydrogen overpotential enormously increased along with decreasing dendrite formation. Except for those fluorosurfactants and acid additives, several other organic additives (e.g. PANI,¹³⁴ PEI¹³³ and PAA⁴³) were also investigated. For instance, Xu *et al.*¹⁴³ developed a RZAB using the electrolyte containing 1-ethyl-3-methylimidazolium dicyanamide (EMI-DCA). Fig. 17a and b show that Zn dendrite formation and growth are observed in the electrolyte containing 9 M KOH and 5 wt% ZnO, whereas a completely different Zn morphology without dendrites is observed by adding EMI-DCA in the electrolyte. Hashemi *et al.*¹³³ investigated the change in the morphology and kinetics of zinc electrodeposition when BPEI was added in 0.5 M ZnSO_4 solution. As shown in Fig. 17e–j, BPEI can adsorb on the surface of the electrode to suppress the kinetics of zinc electrodeposition and

decrease the growth rate of the dendrites, and thus ensure a uniformly deposited layer by current densities with homogeneous distribution. Similarly, compared to the absence of additive, the addition of BPEI leads to a decreased electrode potential and an increased current density of the zinc-electrode, as shown in Fig. 17k.

2.2.3. Other mitigation solutions. Besides the above additive-based solutions, other strategies have also been proposed according to the components of RZABs such as the electrolyte, zinc-electrode, separator and air-electrode, as well as the protocol of charge/discharge.^{14,87,144–153}

The low solubility of zincate is closely related to the improvement of RZAB performance. To overcome this issue, the stationary electrolyte can be replaced by a flowing electrolyte to avoid the accumulation of discharge product zincate.^{87,144,151–153} For instance, Zhang *et al.*^{152,153} increased the average coulombic efficiency and energy efficiency to 96% and 86% of a Zn–Ni battery, respectively, by applying a flowing electrolyte. Zinc dendrites were scarcely observed on the zinc electrode at any current densities using the flowing electrolyte.¹⁵³ Wang *et al.*¹⁴⁷ demonstrated that deposited zinc with uniform morphology could be attained at the conditions of low current, pulsating current or hydrodynamic electrolyte, while a granular morphology could be observed in the case of employing a discrete columnar structure electrode together with a high current and flowing electrolyte. Furthermore, the employment of ionic liquids for RZABs has also been proposed, which facilitates the suppression of self-corrosion of the zinc-electrode, slowing down the

Fig. 15 (a) Schematic of the molecular structure in the RZAB with a HCZE; (b) typical Zn²⁺-solvation structures in electrolytes containing 1 M Zn(TFSI)₂ and three different concentrations of LiTFSI; (c) Zn²⁺-O(TFSI) and (d) Zn²⁺-O(water) coordination numbers; (e) experimental SANS curve (green circles) and the simulated form (black line) for HCZE in D₂O; (f) SEM image of the Zn anode after 500 cycles; and (g) cycle performance of RZAB at 50 mA g⁻¹. Reproduced with permission.¹ Copyright 2018, Nature Publishing Group.

drying-out of the electrolyte and improving the performance of the electrode. Simons *et al.*¹⁵⁴ investigated the deposition/dissolution of ZnO in a 1-ethyl-3-methylimidazolium dicyanamide (EMD) ionic liquid, and indicated that the ZnO deposition in EMD containing 3 wt% H₂O could give uniform and non-dendritic morphologies with a high current density and efficiency. Besides flowing electrolytes and ionic liquids, molten electrolytes have also been used for RZABs in the past few years, which are expected to address the common problems taking place in aqueous electrolytes including H₂ evolution, zinc dendrite formation and carbonate precipitation.¹⁴ To be specific, Liu *et al.* and Cui *et al.*^{14,145} developed a novel RZAB utilizing a molten Li_{0.87}Na_{0.63}K_{0.50}CO₃ eutectic electrolyte containing 3 M NaOH and 1 M ZnO solutions. However, it is noteworthy that the molten electrolyte is usually used at high temperatures, where a special configuration is required when it is used in RZABs (Fig. 18c). From the results displayed in Fig. 18a, b and d, e, it can be seen that the Zn deposition using the molten electrolyte gives rise to a uniform and dendrite-free morphology. Furthermore, the cycle efficiency of the RZAB using the molten electrolyte can be significantly improved (Fig. 18f). Cyclic voltammetry results indicate that the coulombic efficiency of the battery remains at 96.9% after 110 cycles. Morphology control of zinc particles seems to be a valid option for improving

RZAB performance since the large surface of the zinc-electrode can provide more sites for electrochemical reaction. For example, zinc fibers have a great influence on electrochemical performance.¹⁵⁵ As shown in Fig. 18g and h, Zn fibers can be made into a rod or plate form and used as the zinc-electrode. The cycle ability of the RZAB using a Zn fiber electrode is more stable than that employing a commercial one (Fig. 18i), because Zn fibers can provide a larger surface area for the electrochemical redox reaction.

In addition, solid-state electrolytes (SSEs) including inorganic ceramics and polymer electrolytes have been widely used in metal-air batteries, such as the Li-air battery and Na-air battery.^{16,156–158} It has been demonstrated that SSEs are favorable to suppress dendrite growth and avoid penetration of SSEs.¹⁵⁹ Unfortunately, inorganic ceramics are widely used in Li-based batteries and Na-based batteries instead of Zn-based batteries. On the contrary, polymer electrolytes have received increasing attention for their application in RZABs.^{160–170} It has been shown that the employment of a polymer electrolyte is an effective approach to avoid the flooding of the air-electrode in fluid aqueous systems and mitigate the electrode corrosion because of low convection in the polymer electrolyte, thus enhancing the performance of RZABs. As typical polymer electrolytes, PVA-based polymer

Fig. 16 (a) SEM images of prepared anodes by using and without different organic additives and commercialized zinc; and (b) comparison of the cyclability of batteries between the Zn anodes with organic additives and commercialized zinc. Reproduced with permission.⁶⁴ Copyright 2017, American Chemical Society. SEM images of zinc sheets in the electrolyte without (c and d) and with (e and f) DTAB; and (g) Nyquist plots of zinc electrodes in the electrolyte with various percentages of DTAB. Reproduced with permission.¹⁴¹ Copyright 2017, Elsevier.

electrolytes show high chemical stability, hydrophilicity and mechanical strength, and good resistance to alkaline media, and have been widely used in electrochemical energy conversion devices.¹⁷¹ For example, Yan *et al.*¹⁷² developed an all-solid-state ZAB using a mesoporous CoNC nanocrystal-coated graphene framework (GF) (Meso-CoNC@GF)-based air cathode and an alkaline PVA-based gel electrolyte, as displayed in Fig. 19a. When the as-fabricated all-solid-state ZAB operated in ambient air, it displayed a higher open circuit voltage and smaller internal resistance than that using the Pt/C + IrO₂-based air cathode (Fig. 19b and c). A power density of 85.6 mW cm⁻² was obtained at 160 mA cm⁻², and no obvious decay was observed after 70 cycles through a galvanostatic discharge/charge test (Fig. 19d and e). Furthermore, an LED candle was lit by two series-connected as-fabricated all-solid-state ZABs (Fig. 19f). Except for PVA, poly(acrylic acid) and polyethylene oxide, poly(vinylidene fluoride-co-hexafluoro

propylene) (PVdF-HFP) was used to improve the performance of the zinc-electrode. Liu *et al.*¹⁷³ firstly introduced a PVdF-HFP polymer matrix to prepare a polymer gel electrolyte with high ionic conductivity (2.2 mS cm⁻¹) and mechanical stability. Moreover, the polymer gel electrolyte enabled a quasi-reversible zinc deposition/stripping process. Meanwhile, the morphology of the zinc deposits obtained from the polymer gel electrolyte on gold substrates is even smoother without dendrites, as evidenced from Fig. 20. Therefore, polymer electrolytes can be considered as an appealing candidate to address the challenges of the zinc-electrode for RZABs.^{174–176}

To gain a further understanding of the reversibility of zinc/zinc oxide during discharge/charge processes, zinc-electrodes with various morphologies have been reported and applied to RZABs, leading to the enhanced cycling ability of these batteries. For example, Parker *et al.*¹⁴⁶ fabricated a novel three-dimensional

Fig. 17 SEM images of Zn deposited (a) without and (b) with EMI-DCA; and (c) cyclic voltammetry plots and (d) potential–time plots of Zn electrodeposition in the electrolyte without and with EMI-DCA. Reproduced with permission.¹⁴³ Copyright 2015, Elsevier. SEM images of electro-deposited zinc (e–g) without BPEI and (h–j) with BPEI; and (k) the electrical performance of the Zn anode in the electrolyte without and with BPEI at different current densities. Reproduced with permission.¹³³ Copyright 2017, Elsevier.

(3D) aperiodic architected zinc-electrode for RZABs.¹⁴⁶ After extensive cycling up to 188 mA h g^{-1} , a 3D-wired Zn sponge electrode could still remain dendrite-free, which was obviously different from the zinc symmetric cells and Ag–Zn full cells under the same conditions. Fig. 21 displays the schematic of ZnO electrodeposition in an *ad hoc* powder-bed electrode and 3D-wired Zn sponge electrode during charge/discharge. Owing to the 3D structure, the utilization of this 3D sponge zinc-electrode can approach 90% in a primary (single-use) ZAB. This result indicates that the sponge architecture is favorable to preserve long-range conductivity *via* the core/shell structure in which the 3D sponge zinc-electrode and ZnO coating are the core and shell, respectively. The proposed architecture can achieve uniform ZnO deposition within the space and diminish shape change during cycling, and lead to a high utilization of the zinc-electrode. Although the powder-bed electrode has a high surface area, a single particle wrapped by resistive ZnO can break down the long range conductivity, leading to a region of high local current density. As a result, dendritic peaks of the zinc-electrode can be formed and grow long enough to deteriorate the battery performance.

Furthermore, the research results also indicated that low temperature, low zincate, or high KOH concentration and high viscosity could remarkably reduce the minimum dendritic initiation overpotential from 70–90 mV to 20–30 mV.¹⁵⁰ However, Hwang *et al.*¹⁷⁷ found that the employment of low concentration KOH solutions could be more likely to suppress zinc-electrode

corrosion than other electrolytes with high concentrations, indicated by the employment of 4.0 M KOH leading to a sufficiently high current.

Organic membranes, such as a PVA membrane,^{137,166,178,179} polypropylene (PP) membrane,⁷⁴ organic–inorganic film¹⁸⁰ and compound film,¹⁸¹ have been widely used as separators in alkaline electrolytes of RZABs. Recently, separator modifications have been reported to gain a better performance of RZABs. For example, Sheibley *et al.*¹⁷⁹ used a cross-linking method to investigate the effect of a PVA film as the separator on the performance of RZABs. The results indicated that the cross-linked PVA films exhibited superior properties to the commercial separator because the carboxylate functional groups in the cross-linked film were favorable to reduce the resistivity. Additionally, compared to the commercial PP membrane, an increased battery life was obtained by the use of polymerized ionic liquid coated commercial PP membranes as separators.⁷⁴ Fig. 22a and c compare the energy dispersive spectrometer (EDS) mapping of the two membranes after cycling, and illustrate that the poly(1-[(4-ethenylphenyl)methyl]-3-butyl-imidazolium hydroxide)–poly(butyl methacrylate) (PEBIH–PBMA) coated PP membrane can cycle more than 107 cycles than unmodified PP. Besides, to further investigate the detailed mechanisms of cell failure, R_1 and R_3 (R_1 : the contact resistance, R_3 : the charge transfer resistance of the air cathode) resistances were plotted as a function of cycle number, as seen in Fig. 22b and d. Both the PP and PEBIH–PBMA coated PP membranes show similar trends.

Fig. 18 SEM images of Zn deposition at different magnifications (a, b, d, and e); (c) configuration of a RZAB using a molten electrolyte; and (f) the cycle efficiency of the zinc molten battery. Reproduced with permission.¹⁴ Copyright 2017, Elsevier. A rod form (g) and a plate form (h) Zn anode; and (i) discharging curves of a gelled Zn anode and a fibrous Zn anode. Reproduced with permission.¹⁸³ Copyright 2006, Elsevier.

Fig. 19 (a) Schematic of the fabrication of all-solid-state ZABs. (b–d) The comparison of the performance of the batteries using Meso-CoNC@GF and Pt/C + IrO₂-based air cathodes. (e) Cycling performance of the fabricated all-solid-state ZAB. (f) Photograph of an LED candle powered by two connected all-solid-state ZABs. Reproduced with permission.¹⁷² Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fig. 20 SEM images of the zinc deposits on gold substrates: (a) 1 deposition process, (b) 2 deposition processes and 1 stripping process, (c) 5 deposition processes and 4 stripping processes, and (d) 10 deposition processes and 9 stripping processes. Reproduced with permission.¹⁷³ Copyright 2014, Springer-Verlag Berlin Heidelberg.

Fig. 21 Cross-sections of the ZnO electrodeposition in (a) an *ad hoc* powder-bed electrode and (b) a 3D-wired Zn sponge electrode. Reproduced with permission.¹⁴⁶ Copyright 2014, The Royal Society of Chemistry.

Changing the charge/discharge protocol can have effects on the performance of zinc-electrodes and avoid dendrite formation.¹⁸² Normally, the deep discharge process will facilitate the formation of ZnO with poor electrical conductivity, promoting the passivation process. Therefore, the charge/discharge protocol should be optimized. Garcia *et al.*¹⁸² performed systematic research on the effects of pulsed electroplating protocols on Zn dendrite formation, and provided appealing methods to prevent Zn dendrite formation. In their study, uniform and homogenous Zn deposits free of dendrites in Ni-Zn batteries were achieved. Therefore, the employment of pulsed electroplating as the charge protocol is a potential approach to improve the RZAB performance.

3. Conclusion and perspectives

As a promising energy storage device, the RZAB has attracted increasing attention due to its high energy density, safety, rich

abundance and environmental compatibility. However, several challenges are required to be addressed before its practical application, which are mainly from the zinc-electrode, electrolyte and air-electrode. In this review, we overview the challenges and promising multiple solutions of zinc-electrodes for RZABs. From the above discussion, it can be seen that the challenges associated with zinc-electrodes are mainly induced by dendrite, corrosion, shape change and passivation. The appealing strategies for performance-improved zinc-electrodes are primarily concentrated on the aspects of the electrolyte and electrode, as seen in Fig. 23. Thus, it is required to design and prepare novel zinc electrodes. Generally, compared to a planar electrode or a powder electrode, porous zinc-electrodes, typically composed of the conductive material, the current collector, the gelling agent/binder, and the additives, would be desired because they can deliver higher capacity owing to their high accessible area by the electrolyte. The effects of the above four components on the electrochemical properties of the zinc-electrode are nonnegligible. The electrode components should be optimized through innovative design and preparation by combining the effects of electrode structure additives, inorganic corrosion inhibitors and polymer additives on the suppression of the formation of zinc dendrites and the alleviation of Zn corrosion. Therefore, one of the key tasks to achieve long cycle life of zinc-electrodes is to develop a zinc-based composite electrode with proper components and additives through optimized preparation processes. With this in mind, more effective and low-cost inorganic or organic materials should be developed to solve the technical issues in the future. Besides the zinc-electrode, it is worthwhile mentioning that development of the electrolyte is required. A possible strategy is to design and explore new electrolytes with novel electrolyte components and functional additives, such as inorganic and/or organic additives. The ways of changing the electrolyte flow rate and adding specific ionic species in the electrolyte would be able to address the passivation issues. Except for the conventional aqueous electrolytes, nonaqueous electrolytes, such as polymer electrolytes and room temperature ionic liquids, could be used as possible solutions to address the challenges of zinc-electrodes. Meanwhile, it should be noted that further effort is required to improve the solubility of zincate ion products and form a zinc oxide layer in the polymer electrolyte. The utilization of ionic liquids is considered as a facile route to obtain morphology-controllable electrodes by electrodeposition. Accordingly, ionic liquid-based electrolytes are expected not only for zinc-electrodes but also for other metal-based electrodes. In addition, the influence of air-electrodes and separators on the performance of zinc-electrodes also requires some attention. Dendrite growth would be restricted through employing a proper separator. Despite tremendous progress has been achieved, it is noteworthy that there are still some fundamental issues with zinc-electrodes that need to be solved before meeting the commercial requirements of RZABs. There is still room for further development of RZABs, and significant research efforts are still required toward commercialization.

Fig. 22 EDS mapping of zinc-electrodes for RZABs using (a) unmodified PP and (b) PEBIH-PBMA-coated PP separators after cycling. (c) R_1 and (d) R_3 resistance graphs. Reproduced with permission.⁷⁴ Copyright 2016, American Chemical Society.

Fig. 23 Promising strategies for performance-improved zinc-electrodes in alkaline zinc-air batteries.

Conflicts of interest

There are no conflicts of interest to declare.

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