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Electrolyte Salts and Additives Regulation Enables High Performance Aqueous Zinc Ion Batteries: A Mini Review

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Aqueous zinc ion batteries (ZIBs) are regarded as one of the most ideally suited candidates for large-scale energy storage applications owning to their obvious advantages, that is, low cost, high safety, high ionic conductivity, abundant raw material resources, and eco-friendliness. Much effort has been devoted to the exploration of cathode materials design, cathode storage mechanisms, anode protection as well as failure mechanisms, while inadequate attentions are paid on the performance enhancement through modifying the electrolyte salts and additives. Herein, to fulfill a comprehensive aqueous ZIBs research database, a range of recently published electrolyte salts and additives research is reviewed and discussed. Furthermore, the remaining challenges and future directions of electrolytes in aqueous ZIBs are also suggested, which can provide insights to push ZIBs' commercialization.

1. Introduction

Nonaqueous lithium-ion batteries (LIBs) have been dominating the portable electronics and electric/hybrid vehicles market due to their high energy density and long cycle life,[1–5] but the limitation of lithium resources, high-cost, and safety issue,[3,4,6–10] hinder their further development for larger-scale energy storage applications. Nonaqueous sodium-ion batteries (SIBs) and potassium-ion batteries (KIBs) use relatively abundant and low-cost sodium and potassium elements, have become alternatives to LIBs.[1,2,11–14] However, compared to LIBs, they suffer from the lower energy density, higher operating cost and more serious security issues, that is, more explosive,[4,15–19] which leads to the

future is not such bright. Therefore, the drawbacks of these organic-based batteries systems motivate us to explore the alternative battery with low-cost, high safety, and long-cycle-life.[20–23]

Compared to nonaqueous batteries, aqueous batteries have the advantages of low cost, better safety, high ionic conductivity, easy processing, low manufacturing cost, etc., so that they are in a better position for large-scale energy storage applications.[24–28] Among them, the aqueous ZIBs have attracted tremendous attention due to their distinct advantages, that is, high gravimetric and volumetric capacity (820 mAh g^{-1}, 5855 mAh cm^{-3}) offered by Zn metal, low redox potential of zinc (−0.763 V vs a standard hydrogen electrode), good stability of zinc metal in water compared to the extremely active lithium, sodium and potassium metals, as well as its highlighted low cost and natural abundance.[3,29–45]

Nevertheless, aqueous ZIBs still face several challenges that hinder their wider utilization: i) the dissolution of cathode materials and obstacles of intercalating into the host materials;[29,30] ii) the irreversible Zn stripping/plating process caused by formation of Zn dendrites and corrosion on the anode;[31,34,35,37,46] iii) the narrow electrochemical window in aqueous electrolyte;[30,33,36] iv) sluggish transport and solvation/desolvation of Zn^{2+}.[15,36] All of them impact the capacity, life cycle, and rate property of aqueous ZIBs.

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/smll.202104640.

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Till now, plenty of works have reported addressing these issues by designing cathode materials, protecting zinc anode in situ or ex situ. As a result, many excellent general overviews that introduce the cathode materials,[29,40] charge/discharge storage mechanisms,[3,29,30] Zn anode issues and causing factors,[34,35,39] etc., have been concluded by researchers. In these previous reviews, the role of electrolytes has been mentioned frequently but not in-depth to a high professional level. Particularly in the case of the electrolyte salts and additives, there have been few systematical and comprehensive reviews of electrolyte salts and additives in aqueous ZIBs.[33] Thus, in this mini-review, a systematic and comprehensive summary of the types and functions of electrolyte salts and additives for aqueous ZIBs was introduced as shown in **Figure 1**, which will help to improve our comprehensive understanding of zinc-ion electrolyte and have a significant assistance for further development of ZIBs.
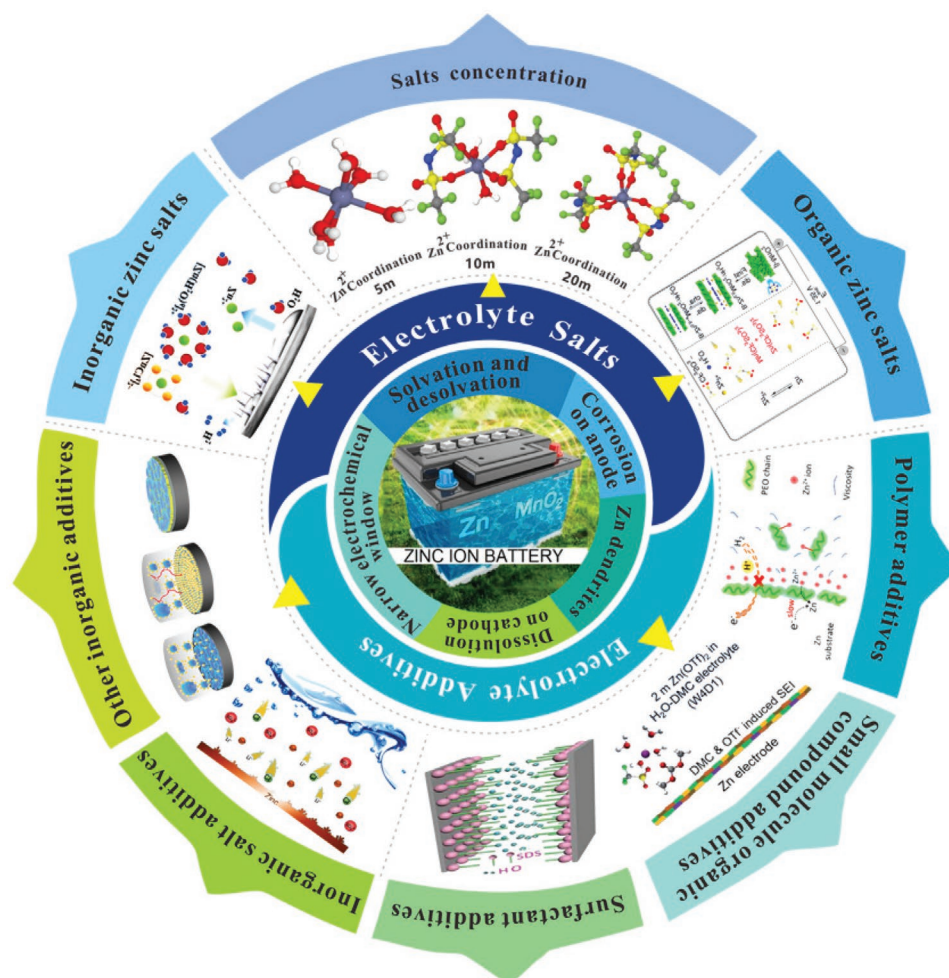
2. Electrolyte Salts

It is well known that early attempts for aqueous ZIBs were made in alkaline electrolytes, but the practical application of ZIBs based on alkaline electrolytes is usually hindered by the low plating/stripping Coulombic efficiency of Zn anode as well as the formation of zinc dendrites and ZnO by-products.[29,33,36,37,40,42,47] Compared with the alkaline electrolyte, a neutral or mild acidic aqueous electrolyte is preferred for ZIBs, thus various kinds of zinc salts, including inorganic and organic zinc salts have been utilized in neutral or mild acidic electrolyte.

2.1. Inorganic Zinc Salts

Until now, a series of inorganic zinc salts have been reported as the electrolyte salts for aqueous ZIBs,[48–56] however, these zinc salts more or less exhibit some drawbacks.[36]

For example, Kasiri et al. reported $Zn(NO_3)_2$, $Zn(ClO_4)_2$, $ZnSO_4$, ZnF_2, as the electrolyte salts for ZIBs.[49] As NO_3^- anions are strongly oxidants and could attack the electrodes, leading to serious corrosions of the Zn foil and copper hexacyanoferrate (CuHCF) cathode, thus the cycle performance was unsatisfactory in the case of using $Zn(NO_3)_2$ electrolyte salt, especially at high-voltage region. If $Zn(NO_3)_2$ is replaced by $Zn(ClO_4)_2$, the CuHCF material in $Zn(ClO_4)_2$ electrolyte possessed a higher reversible specific charge retention than that in $Zn(NO_3)_2$ electrolyte, which is because four O atoms

Figure 1. Types of electrolyte salts and additives for mitigation of the problems in aqueous ZIBs.
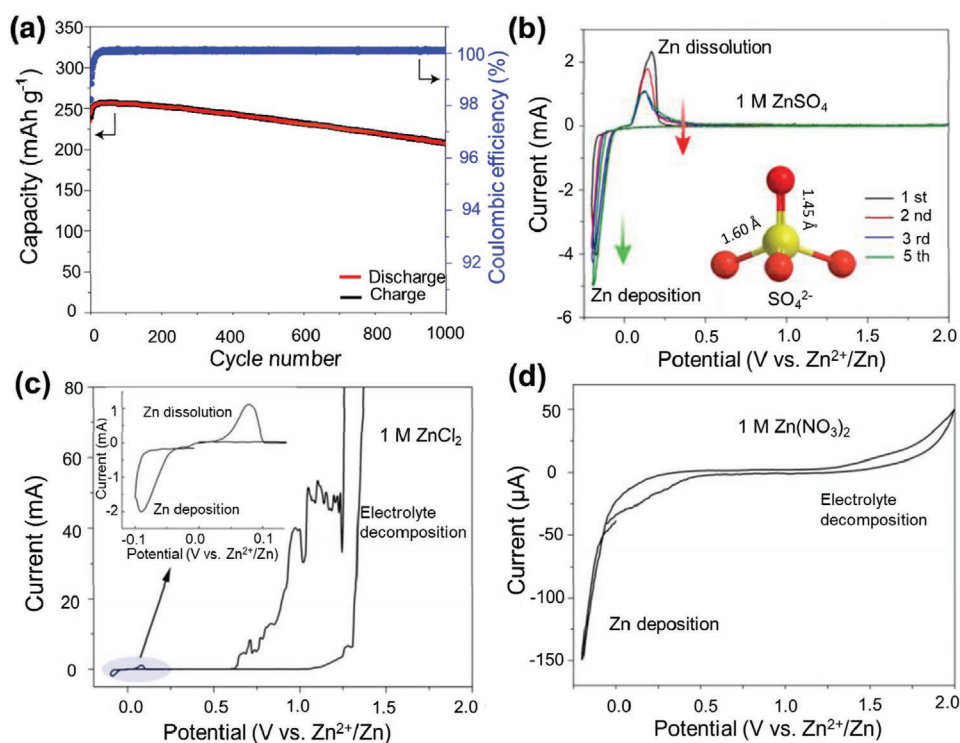
Figure 2. a) Extended cycling performance and the corresponding Coulombic efficiency at 8 C rate (current density: 2400 mA g^{-1}) showing >80% of the capacity retention (with respect to the highest capacity 260 mAh g^{-1}) is maintained after 1000 cycles. Reproduced with permission.[50] Copyright Macmillan Publishers Limited, part of Springer Nature. Cyclic voltammograms of Zn electrode in aqueous electrolyte of b) 1 M $ZnSO_4$, c) 1 M $ZnCl_2$, and d) 1 M $Zn(NO_3)_2$ at the scan rate of 0.5 mV s^{-1} between −0.2 and 2.0 V. Reproduced with permission.[51] Copyright 2016, America Chemical Society.

are tetrahedral coordinated with central Cl atom, resulting in a stable structure and low reaction activity.[49] But $Zn(ClO_4)_2$ based electrolyte is still not suitable as an ideal electrolyte of ZIBs due to high overpotential, which caused by the formation of by-products (e.g., a ZnO thin layer on the Zn foil).[49] Compared with these two oxidative zinc salts, zinc halides (e.g., $ZnCl_2$ and ZnF_2) often show higher compatibility with Zn anode due to minor side reactions with the existence of the low oxidative Cl$^-$ and F$^-$ ions.[49] However, the application of ZnF_2 based electrolyte is restricted by the low solubility and the application of $ZnCl_2$ based electrolyte is restricted narrow anodic electrochemically stable potential window.[43,49] Compared with these mentioned inorganic zinc salts, $ZnSO_4$ based electrolyte could exhibit a wide electrochemical window and better anodic stability.[51] In addition, it features compatibility with electrode materials, low cost, and environmental benefit, thus it is most widely used inorganic salts for aqueous ZIBs.[50–52,54] Nazar's group reported $Zn_{0.25}V_2O_5 \cdot nH_2O$, as the positive electrode, matched with $ZnSO_4$ based electrolyte,[50] exhibited an energy density of ≈450 Wh L^{-1} and a capacity retention of more than 80% over 1000 cycles as shown in **Figure 2**a. And Chen's group also reported using $ZnSO_4$ based electrolyte,[51] the $ZnMn_2O_4$/carbon composite cathode showed a wide electrochemical window (as shown in Figure 2b–d) and the parasitical reactions of O_2 evolution are significantly suppressed, compared to using $ZnCl_2$ and $Zn(NO_3)_2$ based electrolyte.

2.2. Organic Zinc Salts

Traditional inorganic zinc salt electrolytes suffer from their intrinsically limited solubility and low zinc plating/stripping Coulombic efficiency (less than 75%),[20,24,25] therefore, recently, the organic zinc salts have been developed to facilitate ZIBs for the purpose of preforming higher Coulombic efficiency, lower polarization and higher recyclability.

$Zn(CH_3COO)_2$, a most commonly used organic zinc salt with good biodegradability and biocompatibility with environment, has been developed in the V-based ZIBs.[57] Huang's group reported 0.5 mol L^{-1} $Zn(CH_3COO)_2$ solution as electrolyte, the aqueous ZIB delivered a reversible capacity of 97 mA h g^{-1} at 0.5 C and retains 74% of the initial capacity after 100 cycles.[57] Meanwhile, the battery can tolerate charge/discharge process at a high rate up to 10 C. However, the electrochemical performance of such ZIBs is similar to the case with the electrolytes based on inorganic zinc salts.

Thus, several novel organic zinc electrolyte salts were developed.[51,54,58–62] For example, Chen et al., reported $Zn(CF_3SO_3)_2$ as the electrolyte salts,[51] which broadened the electrochemical window and enhanced ZIBs performance with better reversibility and faster kinetics in Zn deposition/dissolution compared to these of using $ZnSO_4$. As shown in **Figure 3**a, a smaller potential separation between plating and a stripping and higher response current can be found for $Zn(CF_3SO_3)_2$, suggesting a better reversibility and faster

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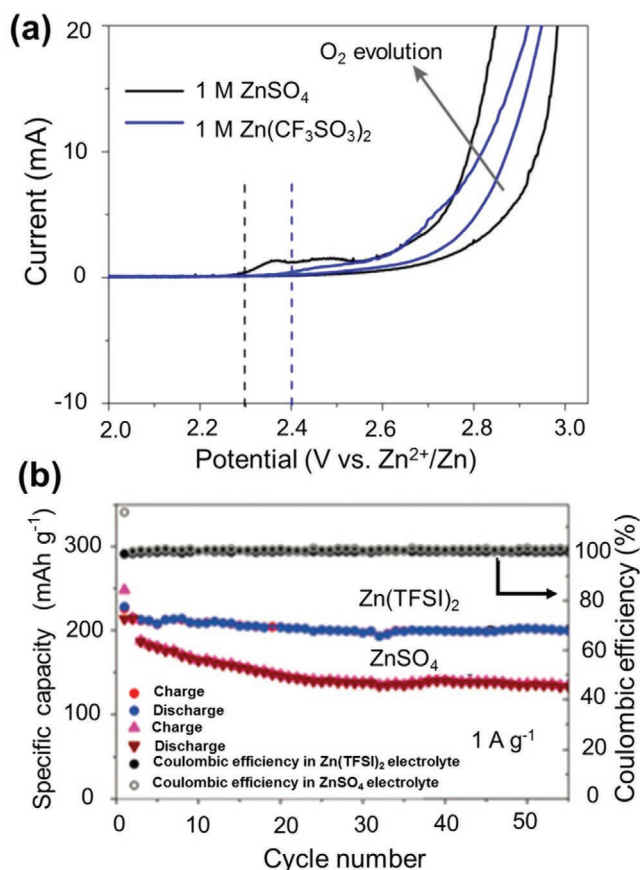
Figure 3. a) Electrochemical stability for ZIBs using $ZnSO_4$ and $Zn(CF_3SO_3)_2$ electrolytes, respectively. The anodic processes for 1 M $ZnSO_4$ and 1 M $Zn(CF_3SO_3)_2$ above 2.3 and 2.4 V can be assigned to the oxygen evolution. Reproduced with permission.[51] Copyright 2016, America Chemical Society. b) Comparison of cycling performances between cells in 0.3 M $Zn(TFSI)_2$ electrolyte and in 1 M $ZnSO_4$ electrolyte, at a current density of 1 A g^{-1}. Reproduced with permission.[61] Copyright 2018, The Royal Society of Chemistry.

kinetics of Zn deposition/dissolution process,[51] because the $CF_3SO_3^-$ anions could decrease the number of water molecules surrounding Zn^{2+} cations and reduce the solvation

effect[], facilitating Zn^{2+} transportation. As a result, the spinel/carbon hybrid exhibits a reversible capacity of 150 mA h g^{-1} and a capacity retention of 94% over 500 cycles at a high rate of 500 mA g^{-1}. Additionally zinc ditrifluoromethane sulfimide $(Zn(TFSI)_2)$ was developed and also exhibited an excellent cycle performance due to the larger $TFSI^-$ anion,[61] which could reduce the solvation effect, resulting in a better electrochemical performance than that of aqueous $ZnSO_4$ electrolyte as shown in Figure 3b.

The advantages and disadvantages of various inorganic zinc salts and organic zinc salts are concluded in **Table 1**. As can be seen, the inorganic zinc salts are cost-effective comparing to the organic zinc salts, but the promotion of zinc anode stability is not as good as organic zinc salts, and organic zinc salts could significantly reduce the solvation effect. Despite the impeccable performance advantages of $Zn(CF_3SO_3)_2$ and $Zn(TFSI)_2$, high cost limits their commercial application. And the organic redox-active groups often suffer from high solubility, leading to the capacity fading in the ZIBs.

2.3. Salts Concentration

Besides type of zinc salt, the concentration also plays an important role influencing on physicochemical property of electrolyte. Commonly, the higher concentration of the salts, the higher plating/stripping Coulombic efficiency of active ions and the better capacity retention could achieve. Such promotion are mainly affected by the solvation and transporting behaviors of cations/anions.[43]

Concentration effect could be more obviously in ultrahigh concentration electrolyte, in other words, "water in salt." This concept is first introduced into LIBs by Wang et al.[63] Soon after they also employed this concept in ZIBs.[54] The highly concentrated aqueous electrolyte (1 M $Zn(TFSI)_2$ + 20 M LiTFSI) enabled Zn anode delivered ultra-high stability and reversibility with no apparent byproducts formed as shown in **Figure 4**a. The pH value increased with the LiTFSI concentration (Figure 4b), indicating effective suppression of interaction between zinc ion and water molecule. In the FTIR spectra, the intensity of hydrogen bonding peak at 3414 cm^{-1} gradually declines with

Table 1. The comparison of characteristics of various electrolyte salts for aqueous ZIBs.

Salts type	Representative advantages	Representative disadvantages	Ref.
ZnF_2	Low oxidative F^-; Low cost	low solubility	[36,49]
$ZnCl_2$	Low oxidative Cl^-; Low cost	Narrow anodic stable potential window; Low anodic stability	[36,49]
$Zn(NO_3)_2$	Low cost	Strong oxidative of NO_3^-, Seriously corrode Zn foil; Low anodic stability	[36,49]
$Zn(ClO_4)_2$	Low reaction activity	High overpotential; Potential safety hazard	[36,49]
$ZnSO_4$	Low cost, Good compatibility with electrode materials; Wide electrochemical window	Easily produced zinc hydroxide sulfate compounds	[36,50,51]
$Zn(CH_3COO)_2$	Good biodegradability and biocompatibility	Weak alkaline	[36,57]
$Zn(CF_3SO_3)_2$	High anodic stability; Weakened solvation effect; Wide electrochemical window	High cost	[36,51]
$Zn(TFSI)_2$	High anodic stability; Weakened solvation effect	High cost	[36,61]
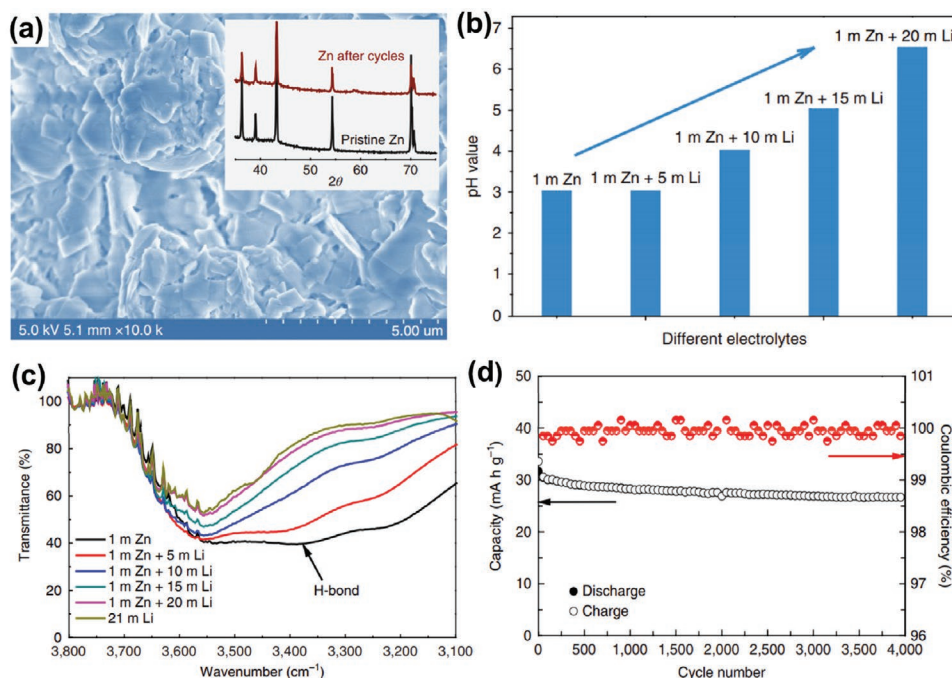
Figure 4. a) SEM image and XRD pattern (inset) of a Zn anode after 500 stripping/plating cycles in high concentrated aqueous electrolyte (1 M Zn(TFSI)$_2$ + 20 M LiTFSI), b) The pH values of the electrolytes with varying LiTFSI concentrations. c) The progression of FTIR spectra with salt concentration between 3800 and 3100 cm^{-1}, d) the cycling stability and Coulombic efficiency of the Zn/LiMn$_2$O$_4$ full cell in high concentrated aqueous electrolyte (1 M Zn(TFSI)$_2$ + 20 M LiTFSI). Reproduced with permission.[54] Copyright 2018, The Royal Society of Chemistry.

the increase in electrolyte concentration, then vanished at a salt concentration of 10 M (Figure 4c), indicating the disruption of water network connected via hydrogen bonding. The reduced water activity and suppressed water-induced side reactions contribute to cycle stability improvement (Figure 4d).

Moreover, Ji and co-workers come up with a 30 M ZnCl$_2$ based electrolyte employed in reverse dual-ion battery,[56] realizing the highest zinc ion insertion potential among all cathode materials reported for ZIBs. Chen's group selected 21 M LiTFSI with 1 M Zn(CF$_3$SO$_3$)$_2$ electrolyte for aqueous Zn/VOPO$_4$ batteries.[62] With using such high concentration electrolyte, oxygen evolution reaction was significantly suppressed up to ≈2.60 V, which is much higher than the theoretical voltage of oxygen oxidation.

These "water in salt" electrolytes feature impeccable performance for both cathode and anode, but such a high concentration has increased its cost and impedes practical application, especially for the salts with intrinsically high cost.[36]

3. Electrolyte Additives

The role of electrolyte additives in aqueous ZIB is also very important. It can improve ionic conductivity, broaden the electrochemical window, inhibit the growth of dendrite, adjust the solvation structure and protect cathode. There are mainly two types of electrolyte additive: inorganic additives and organic additives. Next these electrolyte additives will be introduced accordingly with respect of classification and function.

3.1. Inorganic Salts Additives

Inorganic salt additive is the most popular inorganic additives for aqueous ZIBs due to species diversity and ease of control in the electrolyte solvents. More importantly, inorganic salt additives own versatility for improving the performance of aqueous ZIBs.

First, the inorganic salt additive can enhance the stability of the cathode materials and improve the reversible capacity. For example, the MnSO$_4$ additive was widely used to enhance the manganese oxide cathode material stability.[64–67] In 2016, Lu's group reported addition of tiny amount of 0.01 M MnSO$_4$ into ZnSO$_4$ based electrolyte, the utilization of MnO$_2$ active material has been greatly improved,[65] thus, the resulted ZIBs delivered a higher capacity than that without MnSO$_4$, and the capacity retention could reach 92% after ultra-long 5000 cycles.[65] Such excellent performance is highly likely due to pre-addition of 0.01 mole Mn^{2+} which provided an appropriate equilibrium between Mn^{2+} dissolution. Meanwhile, Na$_2$SO$_4$ additive was introduced to inhibit the vanadium oxide-based cathode dissolution and enhance the stability.[68,69] Niu's group reported Na$_2$SO$_4$ additive limited the continuous dissolution of NaV$_3$O$_8$·1.5H$_2$O via changing the dissolution equilibrium of Na$^+$ from NaV$_3$O$_8$·1.5H$_2$O.[68] Due to the cathode stabilization by adding Na$_2$SO$_4$, the aqueous ZIBs shows excellent reversible capacity of 380 mAh g^{-1} and high-capacity retention of 82% after 1000 cycle as shown in **Figure 5**a. In addition, MgSO$_4$,[70] CoSO$_4$,[52] have also been reported to prevent the corresponding metal oxide cathode dissolution thereby facilitating a stable cycle-life performance for aqueous ZIBs.

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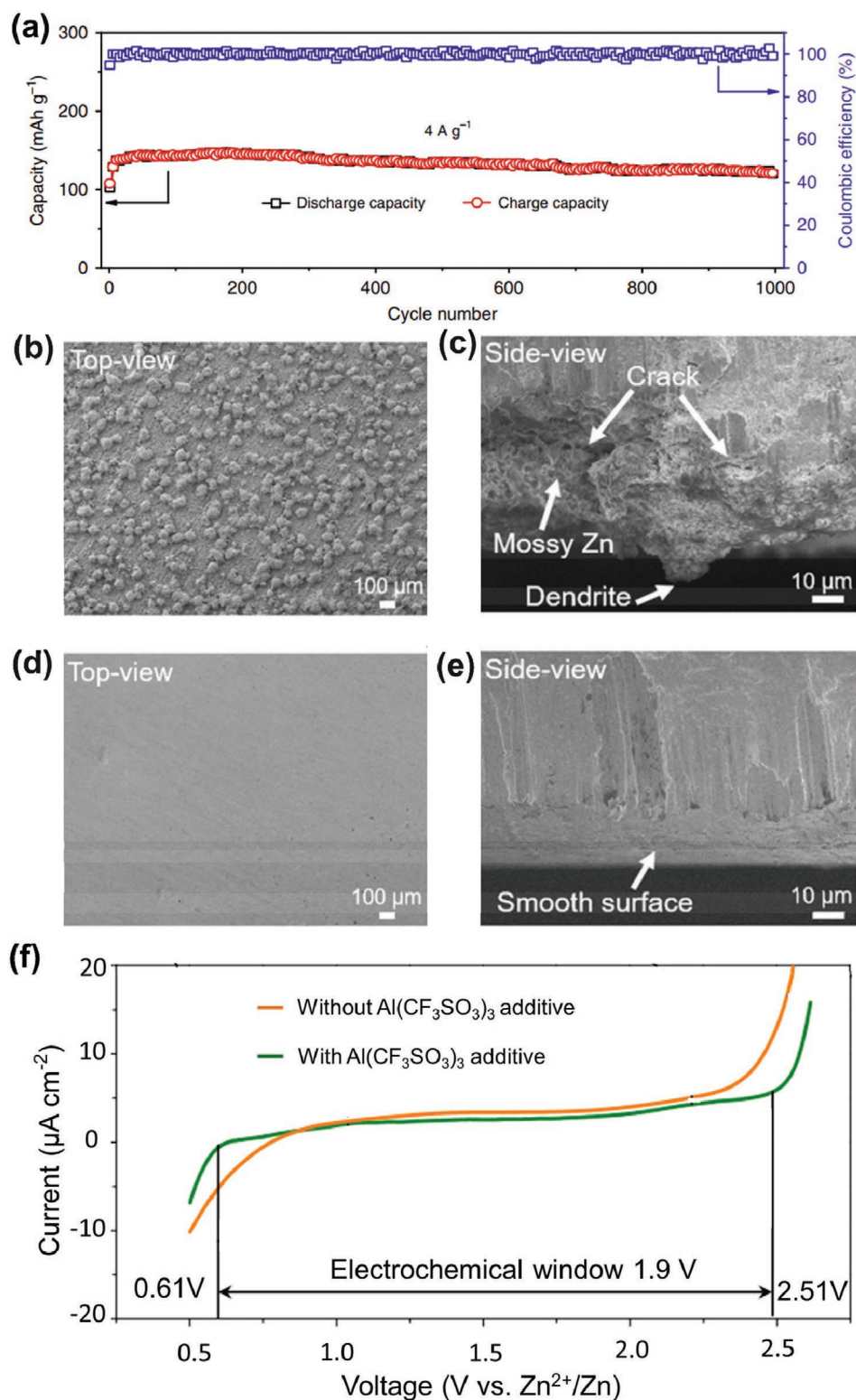
Figure 5. a) Long-term cycle life (4 A g⁻¹) and d rate performance of NaV₃O₈·1.5H₂O electrodes in ZnSO₄/Na₂SO₄ electrolyte, Reproduced with permission.[68] Copyright 2018, The Author(s), Published by Springer Nature. SEM images of Zn electrodes after 20 cycles in the 1 M Zn(CF₃SO₃)₂ b,c) without Zn(H₂PO₄)₂ and d,e) with Zn(H₂PO₄)₂ as electrolyte, respectively. Reproduced with permission.[72] Copyright 2020, American Chemical Society; f) The overall electrochemical windows of electrolyte with and without Al(CF₃SO₃)₃ were evaluated with CV on at scanning rate of 10 mV s⁻¹, Reproduced with permission.[77] Copyright 2021, Wiley-VCH GmbH.

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Second, the inorganic salts additive can also protect the Zn anode via effectively suppressing zinc dendrites. Many research groups reported that the $MnSO_4$ additive not only suppressing dissolution of Mn^{2+} ion from the MnO_2 cathode, but also simultaneously suppressing Zn dendrite.[67,71] Additionally, in recent years, other inorganic salts, that is, $PbSO_4$,[73,74] $NiSO_4$,[74] $CuSO_4$,[74] $NaSO_4$,[75] $LiCl$,[76] etc., have been reported continuously as the electrolyte additive to inhibit the zinc dendrite growth and stabilize the Zn anode. For example, Guo's group reported a small amount of $Zn(H_2PO_4)_2$ salt adding to the conventional aqueous electrolyte (1 M $Zn(CF_3SO_3)_2$).[72] The in situ formed solid-elecrtrolyte interface (SEI) film possessed high interfacial stability and high Zn ion conductivity, which not only restrains the side reactions via isolating the active Zn from the bulk electrolyte, but also ensures uniform and rapid Zn ion transport kinetics for dendrite-free Zn deposition as shown in Figure 5b–e.

Finally, the inorganic salt additive can modulate electrochemical stability window and improve the operating voltage.[77] For example, Li' group reported $Al(CF_3SO_3)_3$ as the electrolyte additive.[77] The Al^{3+} originates from $Al(CF_3SO_3)_3$ not only induced the formation of the Al_xMnO_2 phase that has a high discharge voltage, but also expanded the electrochemical voltage window to match the high discharge voltage. The discharge voltage could increase to 1.7 V, which is ≈0.3 V higher than the value reported earlier. And the electrochemical stability window was expanded from 1.5 to 1.9 V through addition of $Al(CF_3SO_3)_3$ suppressing both hydrogen and oxygen evolution reactions as shown in Figure 5f.

3.2. Other Inorganic Additives

In addition to inorganic salts additive influence, there are new types of inorganic additives have been reported recently.[78–83] For example, our group and Niu's group reported MXene ($Ti_3C_2T_x$) as the electrolyte additives to enhance the electrochemical performances of Zn anodes at almost the same time.[82,83] Our group found MXene nanosheets in the electrolyte dramatically shortened Zn^{2+} diffusion pathways and facilitated their migration, and the abundant functional groups and good conductivity induced uniform nucleation as shown in **Figure 6**a,b.[83] While Niu's group found the MXene layer endowed the Zn anode with a lower Zn nucleation energy barrier and a better homogeneously distributed electric field through the favorable charge redistribution effect in comparison with pure Zn as shown in Figure 6c,d.[82] The multifunctional MXene additive contributed Zn anode exhibiting clearly low voltage hysteresis and excellent cycling stability with dendrite-free behaviors, as well as ensured the high-capacity retention and low polarization potential in ZIBs.

In addition, our group reported another inorganic additive, polyoxometalate, which significantly suppressed zinc dendrites growth.[79] The $[Mo_7O_{24}]^{6-}$ anion clusters in $(NH_4)_6[Mo_7O_{24}]·4H_2O$ bind with massive Zn ions to produce a Zn-rich film, thus ensuring the uniform distribution of Zn ions on the surface of Zn anode, while the NH_4^+ cation can further regulate an even Zn deposition during plating via electrostatic repulsion forces.

To further summaries the role of inorganic electrolyte additives, the electrochemical performances of aqueous ZIBs are compared in **Table 2**. As can be seen, metal sulfate is the most popular additive among all mentioned ZIBs research. The inorganic additives effectively enhance the cycling stability of cathode, but the electrochemical voltage window of ZIBs mainly depends on the cathode materials' type. A part of inorganic salts additives, that is, $CoSO_4$,[52] $In_2(SO_4)_3$,[81] etc., could broaden the electrochemical voltage window to a direction of high voltage, which is beneficial to enhance the energy density. While recently, other inorganic compound (not salts), that is, Mxene and graphene have also received increasing attentions as they illustrates unique advantages for aqueous ZIBs.

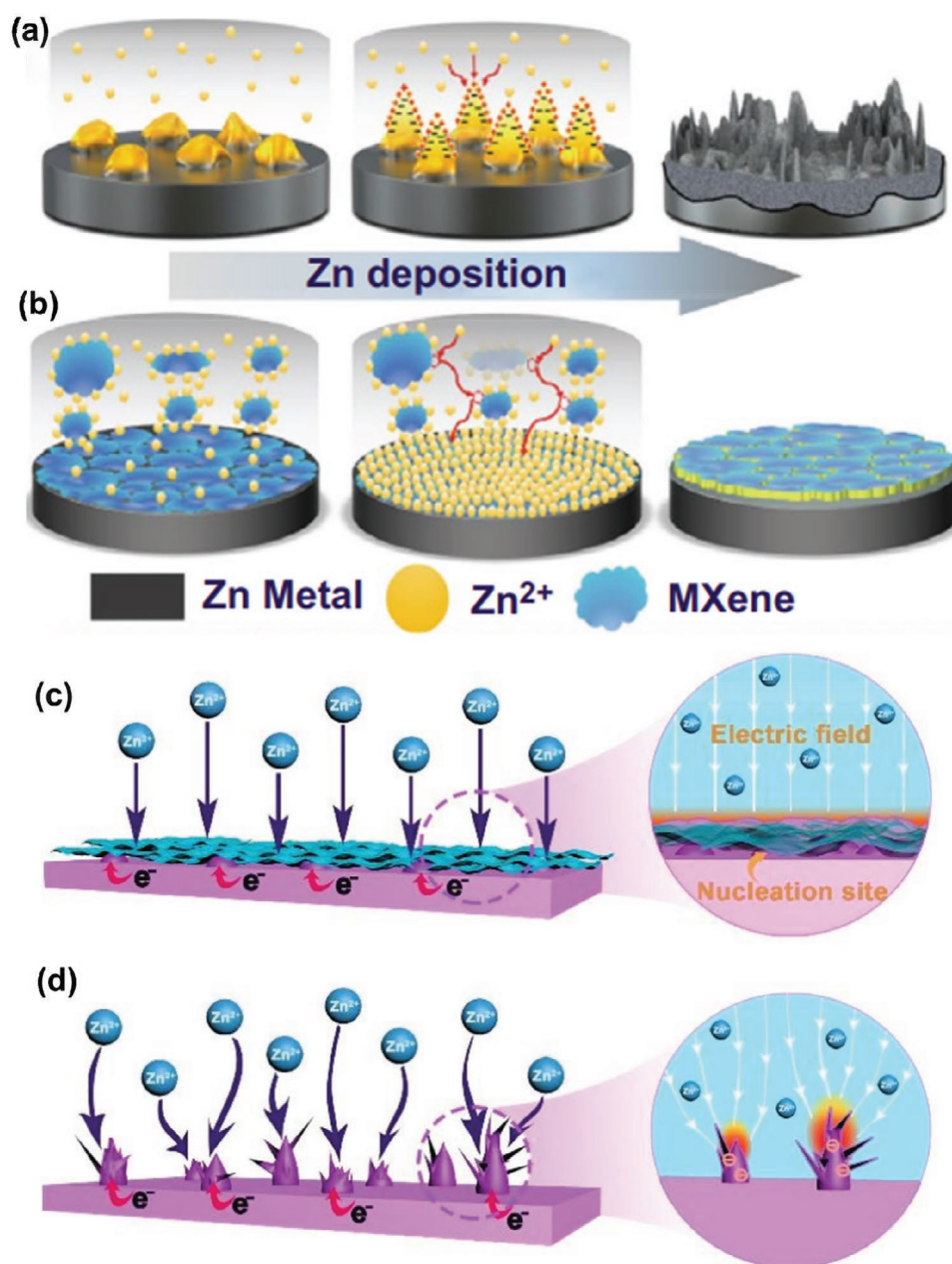### 3.3. Small Molecule Organic Compound Additives

Except the inorganic additives, various kinds of small molecule organic compounds have also been reported as the electrolyte additive to enhance the electrochemical performances of ZIBs.[86–94]

It has been reported that different molecular structure and functional groups play various roles. For example, polar substances electrostatically attached adjacent to the surface of the initial protuberant zinc tips can further hinder zinc ion deposition. Wang's group reported that diethyl ether (Et_2O) molecules is an effective adsorbent on the protrusion tips, which led to the Zn^{2+} deposition readjusted to other areas that flattened the Zn anode surface.[89] The addition of Et_2O yielded a high capacity of 115.9 mAh g^{-1} at 5 A g^{-1} and 97.7% retention of initial capacity after 4000 cycles for Zn-MnO_2 batteries as shown in **Figure 7**a. Chen et al. reported diethyl ether (1%) contributed to the best cyclability at 25 °C, while ethylene glycol additive (30%) resulted in the best electrochemical performance at 0 and –10 °C.[94] These ethers and alcohols additives could decrease the nucleation overpotential of zinc plating, enhance the interfacial stability between the zinc metal and electrolyte, suppress the zinc dendritic growth and side reactions.[94]

Thiourea has been widely demonstrated as an additive in the Cu and Zn electrowinning in sulfate salt system, which can increase the electrolytic efficiency of these metals due to the inhibition of hydrogen evolution.[86] Therefore, for the first time, He and co-workers reported the thiourea as additive into a sulfate-salt contained mixture electrolyte for polishing zinc foil anode.[86] With using the thiourea, the cycling performance of $LiMn_2O_4$/Zn battery increased, and the float charge current density of the battery decreased at room temperature as well as at high temperatures. Recently, Zhu's group adjusted coordination number and geometry of zinc-ligand primary solvation sheath through addition of ligand.[91] Zn^{2+} containing two water and three urea molecules in the first solvation shell desolvated with three urea ligands forming the $[Zn(H_2O)_2]^{2+}$ complex (Figure 7b), performed high reversible intercalation/extraction into/from layered birnessite and helped forming a cathode–electrolyte interphase suppressing Mn dissolution. The $[Zn(H_2O)_2(NH_3)_3]^{2+}$ complex also promoted dendrite-free zinc metal anode. The Zn/birnessite full cell delivered a high energy density of 280 Wh kg^{-1}, and a long cycle life up to 5000 cycles.

Compared with other small molecule organic additives, the ionic liquids (ILs) have regarded as a promising candidate for metal electrodeposition owning to their unique advantages,

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Figure 6. Schematic illustration of the effect of Zn deposition process a) without and b) with MXene. Reproduced with permission.[83] Copyright 2021, The Author(s), Published by Springer; Schematic illustration of Zn plating behavior of c) MXene-coated Zn and d) pure Zn. Reproduced with permission.[82] Copyright 2021, Wiley-VCH GmbH.

that is, good dissolving ability, wide potential window, tailorable structures, low volatility, and non-flammability.[87] Ji's group employed real-time X-ray imaging revealed interfacial dendrites growth, suppression, and dissolution of zinc dendrites dependent on anions of IL additives.[87] The in situ X-ray images (as shown in **Figure 8**) clearly showed that these additives can effectively suppress the initiation and growth of dendritic zinc and improve the formation of compact deposits. In addition, they found the addition of EMI-DCA (1-ethyl-3-methyl-imidazolium dicyanamide) increased the number of dendrite initiation sites, whereas decreased the growth rate of dendrites;

while zinc deposits were easily detached from the substrate in the presence of EMI-Cl (1-ethyl-3-methylimidazolium chloride), EMI-PF$_6$ (1-ethyl-3-methylimidazolium hexafluorophosphate) or EMI-TFSA (1-ethyl-3-methyl-imidazolium bis(trifluoromethane sulfonyl)imide) due to the formation of the loose structure.

3.4. Organic Polymer Additives

Addition of polymeric species to electrolytes has long been revealed as a facile and reliable method to control

Table 2. The electrochemical performances of aqueous ZIBs using various inorganic additives.

Additives	Electrolyte salts	Cathode	Cathode cyclability	Current density	Electrochemical voltage window [V]	Ref.
0.2 M CoSO$_4$	2 M ZnSO$_4$	Co$_3$O$_4$	≈90 mAh g^{-1} at 5000 cycle	4000 mA g^{-1}	0.8–2.2	[52]
0.1 M MnSO$_4$	1 M ZnSO$_4$	ZnMn$_2$O$_4$	48 mAh g^{-1} at 1000 cycle	2000 mA g^{-1}	0.6–1.9	[64]
0.1 M MnSO$_4$	2 M ZnSO$_4$	MnO$_2$	92% capacity retention after 5000 cycles	1540 mA g^{-1}	1–1.8	[65]
0.1 M MnSO$_4$	2 M ZnSO$_4$	MnO$_2$	≈225 mAh g^{-1} at 100 cycle	60 mA g^{-1}	1–1.8	[66]
0.1 M MnSO$_4$	2 M ZnSO$_4$	Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O	≈50 mAh g^{-1} at 4000 cycle	2000 mA g^{-1}	0.8–1.9	[75]
0.1 M MnSO$_4$	2 M ZnSO$_4$	δ-MnO$_2$	≈80 mAh g^{-1} at 100 cycles	200 mA g^{-1}	1–1.8	[84]
0.5 M MnSO$_4$	2 M ZnSO$_4$	δ-MnO$_2$	≈105 mAh g^{-1} at 1000 cycles	200 mA g^{-1}	1–1.8	[84]
1 M MnSO$_4$ + 0.1 M H$_2$SO$_4$	1 M ZnSO$_4$	MnO$_2$	92% capacity retention after 1800 cycles	30 mA cm^{-2}	0.8–2.2	[85]
0.1 M MnSO$_4$ + 0.5 M Na$_2$SO$_4$	2 M ZnSO$_4$	Na$_{0.55}$Mn$_2$O$_4$·1.5H$_2$O	70 mAh g^{-1} at 10 000 cycle	2000 mA g^{-1}	0.8–1.9	[75]
1 M Na$_2$SO$_4$	1 M ZnSO$_4$	NaV$_3$O$_8$·1.5H$_2$O	≈380 mAh g^{-1} at 1000 cycle	4000 mA g^{-1}	0.3–1.25 V	[68]
0.5 M Na$_2$SO$_4$	3 M ZnSO$_4$	Na$_{0.56}$V$_2$O$_5$	≈140 mAh g^{-1} at 1000 cycle	1000 mA g^{-1}	0.4–1.5	[69]
1.26 × 10^{-8} M PbSO$_4$ + 5%fumed silica	1 M Li$_2$SO$_4$ + 2 M ZnSO$_4$	LiMn$_2$O$_4$	74.4% capacity retention after 300 cycles	115 mA g^{-1}	1.4–2.1	[73]
In$_2$(SO$_4$)$_3$	1 M Li$_2$SO$_4$ + 1 M ZnSO$_4$	LiMn$_2$O$_4$	75% capacity retention after 1000 cycles	480 mA g^{-1}	1.4–2.1	[81]
1 M MgSO$_4$	1 M ZnSO$_4$	Mg$_x$V$_2$O$_5$·nH$_2$O	≈85 mAh g^{-1} at 2500 cycle	5000 mA g^{-1}	0.2–1.4	[70]
25 × 10^{-3} M Zn(H$_2$PO$_4$)$_2$	1 M Zn(CF$_3$SO$_3$)$_2$	V$_2$O$_5$	≈115 mAh g^{-1} at 1000 cycle	400 mA g^{-1}	0.2–1.6	[72]
2 M LiCl	3 M ZnSO$_4$	NH$_4$V$_4$O$_{10}$	272.1 mAh g^{-1} at 1000 cycle	500 mA g^{-1}	−0.6–0.6	[76]
1 M Al(CF$_3$SO$_3$)$_3$	1 M Zn(CF$_3$SO$_3$)$_2$	α-MnO$_2$	133 mAh g^{-1} at 1000 cycle	308 mA g^{-1}	0.8–2.1	[77]
Graphene oxide	1 M ZnSO$_4$	MnO$_2$	55 mAh g^{-1} at 250 cycle	2000 mA g^{-1}	0.8–1.8	[78]
6 × 10^{-3} M (NH$_4$)$_6$[Mo$_7$O$_{24}$]·4H$_2$O	1 M ZnSO$_4$	NaV$_3$O$_8$·1.5H$_2$O	122 mAh g^{-1} at 500 cycle	5000 mA g^{-1}	0.2–1.6	[79]
SnO$_2$	1 M Li$_2$SO$_4$ + 1 M ZnSO$_4$	LiMn$_2$O$_4$	82% capacity retention after 1000 cycles	480 mA g^{-1}	1.4–2.1	[81]
H$_3$BO$_3$	1 M Li$_2$SO$_4$ + 1 M ZnSO$_4$	LiMn$_2$O$_4$	78% capacity retention after 1000 cycles	480 mA g^{-1}	1.4–2.1	[81]
8 mg mL^{-1} Ti$_3$C$_2$T$_x$ MXene	2 M ZnSO$_4$	MnO$_2$	205.5 mAh g^{-1} at 500 cycle	1000 mA g^{-1}	1.0–1.8	[82]
0.05 mg mL^{-1} Ti$_3$C$_2$T$_x$ MXene	2 M ZnSO$_4$	V$_2$O$_5$	192.9 mAh g^{-1} at 250 cycle	1000 mA g^{-1}	0.2–1.6	[83]

electrodeposition rate and surface morphology of the electrode.[95] Decades ago, researchers have already reported several polymers additives such as polymethyl methacrylate, polypyrrole, and polyaniline, were employed to prevent dissolution of zinc, manipulation particle size and surface area to improve electrochemical performance.[46,96–98]

Recently, Liu and co-workers reported that long-chain polyethylene oxide (PEO) polymer as the electrolyte additive in ZnSO$_4$ electrolyte.[98] PEO molecules suppress Zn^{2+} ion transfer kinetics and regulate Zn^{2+} ion concentration in adjacent to Zn anodes through interactions between ether groups of PEO and Zn^{2+} ions as shown in **Figure 9**a,b. It can significantly extend cycle life and increase Coulombic efficiency of Zn metal anodes. Accordingly, the resulted Zn ‖ LiMn$_2$O$_4$ full cells also delivered significantly improved cycling stability and higher Coulombic efficiency (99%) in PEO polymer containing electrolytes as shown in Figure 9c. Wang's group reported polyacrylamide electrolyte additive to modify the zinc anode,[46] which can greatly reduce the overpotential of the zinc nucleation and increase the stability of zinc deposition. By using dendrite-free Zn anode, the Zn-MnO$_2$ full

cells showed high-capacity retention of 98.5% capacity after 600 cycles at 1000 mA g^{-1} (Figure 9d).

In addition, the effect of polyethyleneimine, polyethylene glycol, etc., as an electrolyte additive to zinc electrodeposition mechanism in aqueous zinc-ion batteries have also been reported recently.[95,99,100] Compared to the small molecule organic compound additives, the polymer additives own better chemical and thermal stability, low volatility, and non-flammability, etc.

3.5. Surfactant Additives

It is known that the organic surfactants can be subdivided into three categories: cationic surfactants, anionic surfactant and non-ionic surfactants. Protection mechanism of surfactants additives to the Zn anode has been reported by many research groups.[101–109] In general, they are easily adsorbed on the interface between the electrode and the electrolyte due to the influence of surface tension.
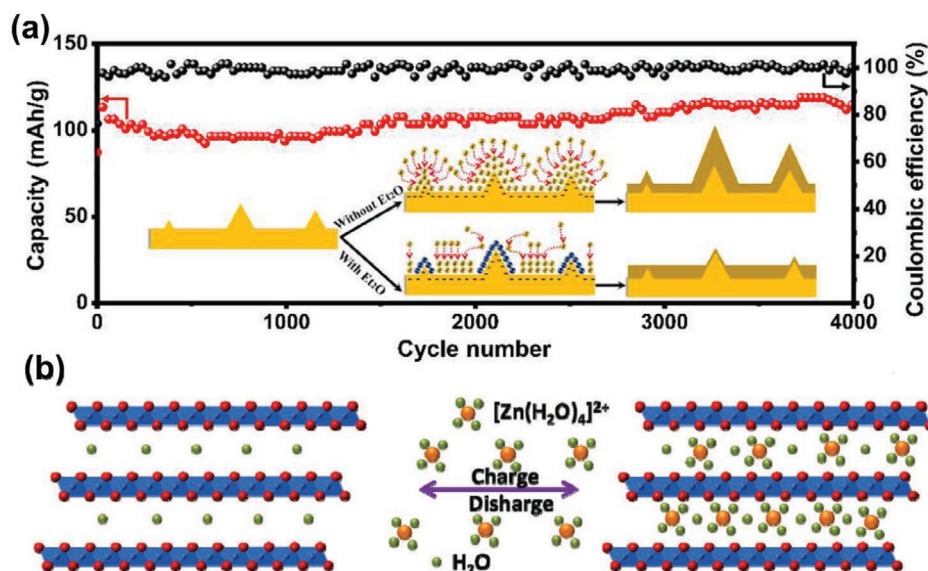
Figure 7. a) Aqueous Zn-MnO$_2$ battery with 2 vol% Et$_2$O electrolyte additive exhibited significantly improved cycling stability, especially at high rates. Reproduced with permission.[89] Copyright 2019, Elsevier Ltd.; b) Charge storage mechanism of the Zn/Na$_{0.1}$MnO$_2$·0.5H$_2$O battery in 1 M ZnSO$_4$ electrolyte. Reproduced with permission.[91] Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
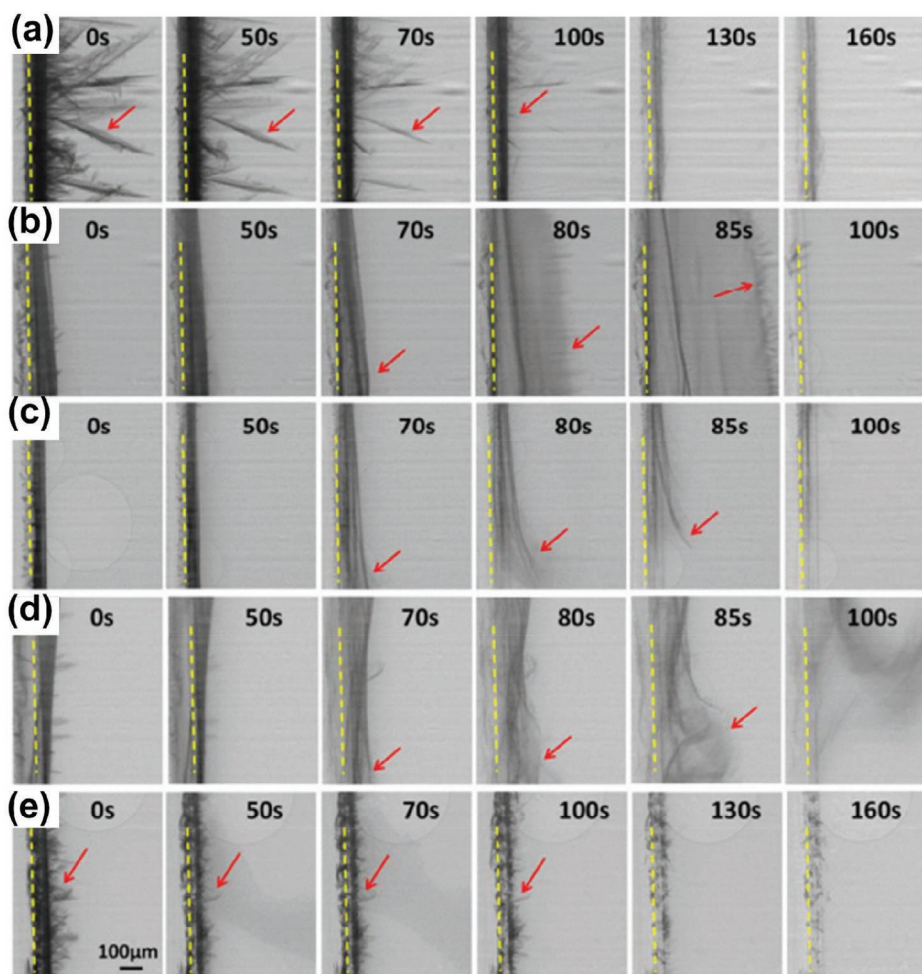
Figure 8. Real-time X-ray images of zinc dissolution at −0.85 V in the electrolytes without additive a) and with imidazolium-based ILs of b) EMI-Cl; c) EMI-PF$_6$; d) EMI-TFSA and e) EMI-DCA. Reproduced with permission.[87] Copyright 2016, American Chemical Society.

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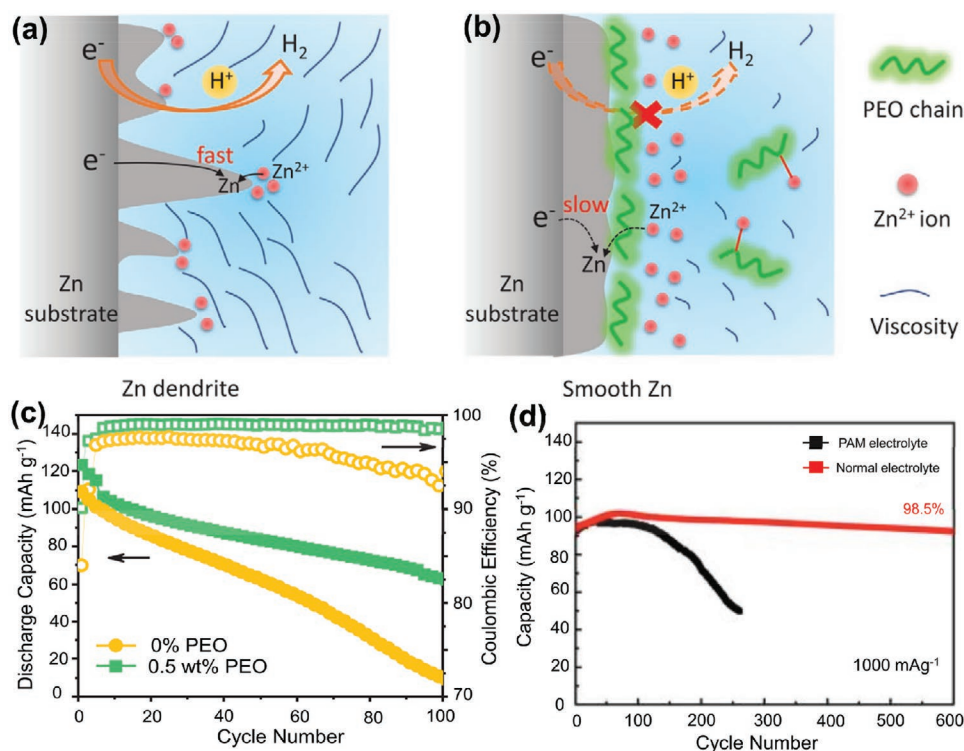
Figure 9. a) Zn deposition with dendritic surfaces and hydrogen evolution, b) PEO polymer molecules stabling Zn anode reactions by slowing down Zn^{2+} ions transfer kinetics, regulating Zn^{2+} ions concentration, and smoothing out the surface chemistry at the vicinity of Zn anode, c) Coulombic efficiency of full cells at 0.5 C in 1 M $ZnSO_4$ + 0.5 M Li_2SO_4 electrolytes with and without PEO additives; Reproduced with permission.[98] Copyright 2019, Wiley-VCH GmbH. d) Cycling performance comparison of the Zn-MnO_2 full cells using the 3D dendrite-free zinc anode and different electrolyte at 1000 mA g^{-1}. Reproduced with permission.[46] Copyright 2020, Wiley-VCH GmbH.

For example, as early as 1998, Kan et al. reported that Triton X-100, a non-ionic surfactant, as the electrolyte additive with low concentration of 0.02 ppm in the electrolyte with pH 4.40, can effectively inhibit zinc-dendrite growth during charge–discharge cycles of the battery and yield longer cycles.[110] Quaternary ammonium surfactant, that is, cetyltrimethyl ammonium bromide, dodecyltrimethylammonium bromide, is typical cationic surfactants, when employed as the electrolyte additive, can inhibit the corrosion of the electrode and prevent the passivation of zinc anode effectively.[104,107] Simultaneously, they can inhibit hydrogen evolution reaction process, which can be adsorbed on the surface of the zinc anode to block the active sites on the zinc surface.[109] Recently, Zhu et al. reported another cationic surfactant-type electrolyte additive, tetrabutyl-ammonium sulfate (TBA₂SO₄),[101] which induced an uniform Zn deposition (as shown in **Figure 10**a,b) via the unique zincophobic repulsion mechanism in both the electrode preparation and the battery charge/discharge process. As a result, the aqueous ZIBs using α-MnO_2 cathode could deliver a lifespan of 300 cycles with 94% capacity retention at a current density of 1 A g^{-1}, significantly higher than that of the control performances in the electrolyte without additive. Sodium dodecyl sulfate (SDS), a typical anionic surfactant, when employed as the additive, can effectively inhibit water decomposition and the corrosion of zinc.[103]

Interestingly, the surfactant additives not only have the function to inhibit the corrosion and delay the passivation of

zinc anode, but also have unique functions on the cathode for aqueous ZIBs. For example, Guo's group reported a Zn/$LiFePO_4$ pouch cell delivered excellent cycling stability over 150 cycles at 1 C (Figure 10c), owning to sodium dodecyl benzene sulfonate (SDBS) additive that improved the wettability of the $LiFePO_4$ cathode, and accelerated the Li-ion diffusion at the $LiFePO_4$ electrode/electrolyte interface.[102] Qian's group also reported that SDS could suppress the Mn dissolution that originated from $Na_2MnFe(CN)_6$ cathode used in ZIBs.[105]

In addition, the surfactant additive also modulates electrochemical stability window. Qian's group not only found the SDS could help protect cathode of ZIBs, but also found the electrochemical stable window of electrolyte used in ZIBs could be expanded to ≈2.5 V by using the SDS additive.[105] The expanded electrochemical stability window of the SDS added electrolyte should allow full and reversible use of sodium storage sites in the $Na_2MnFe(CN)_6$ cathode of ZIBs, corresponding to a high energy density of 170 Wh kg^{-1}.

According to the above conclusions, organic electrolyte additives are in variety with multi-function. The electrochemical performances of aqueous ZIBs using different organic additives are compared in **Table 3**. As it can be seen, the organic additives matched with organic zinc salts or two-component-salts are more beneficial to enhance the electrochemical performances of aqueous ZIBs. Previous researches have reported organic surfactant additives could inhibit the zinc dendrite and stabilize the zinc anode, but not many of them reported the full
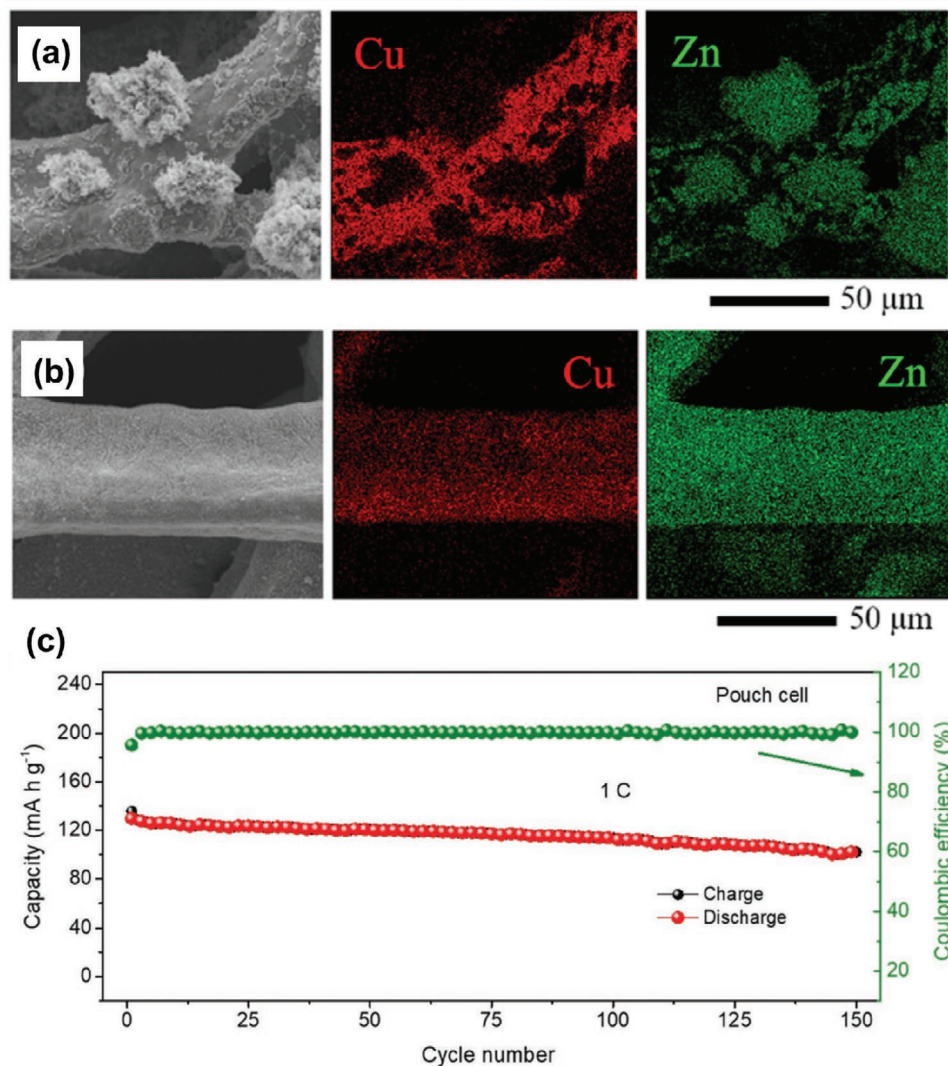
Figure 10. a) SEM images and EDX mapping of Zn anodes synthesized in 2 M ZnSO₄ electrolyte. b) SEM images and EDX mapping of Zn anodes synthesized in 2 M ZnSO₄ electrolyte with 0.05 millimole TBA₂SO₄. Reproduced with permission.[101] Copyright 2020, American Chemical Society; c) Cycling stability of a pouch cell at 1 C with corresponding Coulombic efficiency. Reproduced with permission.[102] Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

ZIBs' cycling performances when using such surfactant additives, thus, it is still questionable whether these organic additives are suitable to the practical ZIBs applications. In addition, extensive use of organic zinc salts to match organic electrolyte additives will significantly increase production costs of ZIBs. Unexpectedly, some of the organic additives, that is, urea, SDS, etc., can greatly broaden the electrochemical windows of aqueous ZIBs, which can further enhance the energy density of ZIBs.

4. Summary and Outlook

This mini review presents the recent development of the electrolyte salts and additives in aqueous ZIBs. The optimization of the electrolyte salts and additives is critical for achieving high-performance aqueous ZIBs.

In case of the salts used for aqueous ZIBs, ZnSO₄ or Zn(CF₃SO₃)₂ are most widely employed in lab research.[36,43] ZnSO₄-based electrolyte could exhibit a wide electrochemical window and high anodic stability compared to other inorganic zinc salts-based electrolytes.[43] Zn(CF₃SO₃)₂ as the electrolyte salt, could further broaden the electrochemical window and contribute ZIBs with better reversibility and faster kinetics in Zn deposition/dissolution,[43] but the cost is higher than ZnSO₄. Therefore, development of new zinc salts with affordable price will be worthwhile to unlock the potential of aqueous ZIBs.

Except the salts categories significantly affecting the performance of aqueous ZIBs, the salts concentration in the electrolyte also affects the performance of aqueous ZIBs remarkably.[32,43,54,56,111] The free water number and water number in the solvation sheath will decrease with increasing salts concentration, thus the activity of water can depress,[36,37] which the Zn anode stability will be improved. And the

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Table 3. The electrochemical performances of aqueous ZIBs using various organic additives.

Additives	Electrolyte salts	Cathode	Cathode cyclability	Current density	Electrochemical voltage window [V]	Ref.
0.14 wt% Thiourea	2 M $ZnSO_4$ + 1 M Li_2SO_4	$LiMn_2O_4$	75% capacity retention after 300 cycles	592 mA g^{-1}	1.4–2.1	[86]
2 vol% Diethyl ether	3 M $Zn(CF_3SO_3)_2$ + 0.1 M $Mn(CF_3SO_3)_2$	MnO_2	115.9 mA h g^{-1} at 4000 cycle	5000 mA g^{-1}	0.8–1.8	[89]
Dimethyl sulfoxide	1.6 M $ZnCl_2$ + 0.1 M $MnCl_2$	MnO_2	150.3 mA h g^{-1} at 500 cycle	2464 mA g^{-1}	0.8–1.9	[90]
Urea	1 M $ZnSO_4$	$Na_{0.1}MnO_2 \cdot 0.5H_2O$	100 mA h g^{-1} at 5000 cycle	3000 mA g^{-1}	1–1.8	[91]
Acetonitrile	3 M $Zn(CF_3SO_3)_2$	V_2O_5	150 mAh g^{-1} at 1700 cycle	589 mA g^{-1}	0.2–1.6	[92]
Dimethyl carbonate	2 M $Zn(CF_3SO_3)_2$	V_2O_5	512.9 mA h g^{-1} at 200 cycle	200 mA g^{-1}	0.3–1.6	[93]
1% Diethyl ether	2 M $ZnSO_4$ + 0.2 M $MnSO_4$	CNT/MnO_2 composite	120 mA h g^{-1} at 500 cycle(25 °C)	3000 mA g^{-1}	1–1.8	[94]
1% Diethyl ether + 30% Ethylene glycol	2 M $ZnSO_4$ + 0.2 M $MnSO_4$	CNT/MnO_2 composite	70 mA h g^{-1} at 500 cycle (−10 °C)	3000 mA g^{-1}	1–1.8	[94]
1 g L^{-1} Polyacrylamide	1 M $ZnSO_4$ + 0.5 M Na_2SO_4	MnO_2	≈100 mAh g^{-1} at 600 cycle	1000 mA g^{-1}	1.0–2.0	[46]
5% Polyacrylamide	0.2 M $MnSO_4$ + 2 M $ZnSO_4$	α-MnO_2/CNT	≈150 mAh g^{-1} at 180 cycle	500 mA g^{-1}	-	[100]
1 vol% Polyethylene Glycol	1 M Li_2SO_4 + 2 M $ZnSO_4$	$LiMn_2O_4$	71.7 mAh g^{-1} at 300 cycles	148 mA g^{-1}	1.4–2.1	[95]
0.5 wt% PEO	0.5 M Li_2SO_4 + 1 M $ZnSO_4$	$LiMn_2O_4$	≈65 mAh g^{-1} at 100 cycle	74 mA g^{-1}	1.3–1.95	[98]
1 mg mL^{-1} SDBS	1 M $Li(SO_3CF_3)$ and 1 M $Zn(SO_3CF_3)_2$	$LiFePO_4$	≈132.2 mAh g^{-1} at 100 cycle	178 mA g^{-1}	0.8–1.5	[102]
SDS	1 M $ZnSO_4$ + 1 M Na_2SO_4	$Na_2MnFe(CN)_6$	≈90 mAh g^{-1} at 2000 cycle	800 mA g^{-1}	1.0–2.5	[105]
0.05×10^{-3} M Tetrabutylammonium sulfate	2 M $ZnSO_4$ + 0.1 M $MnSO_4$	α-MnO_2	≈205 mAh g^{-1} at 300 cycle	1000 mA g^{-1}	0.8–1.9	[101]

electrolyte with high salts concentration is found to broaden the electrochemical window, promote reversible Zn plating/stripping and suppress the dissolution of cathode materials.[54,56] However, the cost and high viscosity leading to sluggish Zn^{2+} transport prevent its widespread utilization.

In terms of the electrolyte additives, different categories have different functions. These additives could suppress side reactions such as corrosion, passivation, and hydrogen evolution; form the electrostatic shield effect; increase the zinc overpotential or limit the Zn^{2+} 2D diffusion,[30,33,36,43] etc. Commonly, inorganic metal ionic additives could stabilize the Zn anode and reduce the solvation effect between water as well as they could form the competitive reaction with water to inhibit the cathode dissolution.[33,36,112] A part of organic additives is stable and can be adsorbed at the electrode interface to from a dense and self-repairable SEI to prevent water penetration onto Zn anode.[33,36,76,113] While some functional redox-active organic additives that are not stable when charge and discharge, could inhibit the decomposition of electrolyte and further broaden the electrochemical windows.

In a word, introduction of additive is an economic and feasible way to handle the problems of the aqueous ZIBs. However, there are still many questions to be solved. For example, with using the additive, many of the reaction mechanisms are still unclear; there is no report about the additive broad applicability for different cathode materials. In addition, the liquid-electrolyte-based ZIBs devices inevitably facing the leakage of harmful electrolyte.[43] Considering flexible ZIBs widely practical applications, the gel electrolyte, which owns the advantages of high physical flexibility, excellent mechanical integrity, and simultaneously serving as separator,[42,43] have therefore been passionately sought after during the past several years and will continue this trend in

the next decades. However, how to overcome the drawbacks of lower ionic conductivity, inferior electrode/electrolyte interfaces, and high overpotential of gel electrolytes is our researchers' efforts in the direction of the future.

Conflict of Interest

The authors declare no conflict of interest.

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