

Mechanistic Perspectives: Integration and Repairing Adaptation of Self-Healing Electrolytes for Zinc Ion Batteries

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Self-healing is a magical function that endows energy storage devices with extraordinary resilience and has become a promising strategy for advancing battery technology. This short review focus on the recent developments made in self-healing chemistry for electrolytes in term of extrinsic and intrinsic dynamical concepts. Firstly, the fundamental mechanism of electrolyte self-healing and repairing adaptation is introduced. The extrinsic self-healing mechanism adopts capsule-vascular networking while intrinsic self-healing lean physical and

chemical routes. The Former healing adaptation, generally follows strong physical networking and covalent linkages, which are more prevalent and practical, compared to the latter case of self-healing. In addition to that, this review also evaluates the estimated healing capabilities and statistics using thermodynamic protocols. Finally, we propose some possible future research directions and development strategies to further apply the self-healing phenomenon for zinc ion batteries.

1. Introduction

The worldwide demand of energy is increasing at an alarming rate owing to population growth and industrial progression. It is therefore critically important to address the recent developments made by scientific community in term of energy. Fossil fuels play a key role in addressing global energy crises.^[1,2] However, conventional methods of generating energy using fossil fuel result substantial emissions of toxic gases, which cause environmental pollution and global warming. Wind mills,^[3] solar panels^[4] and hydroelectricity^[5] are also contribute to bridge the gap between demand and consumption, which is still seems to be insufficient. Therefore, researchers have focused on finding alternative routes for energy generation and storage, which could provide a sustainable energy solution. Among all the alternatives, rechargeable batteries have received immense attention.^[6,7] Rechargeable batteries operate on the principle of reversible ion intercalation, which makes the system electrochemically active. To date, Sodium,^[8] magnesium,^[9] calcium^[10] and aluminum^[11] have been explored as electrode materials in rechargeable battery systems. Nevertheless, Lithium-ion batteries (LIBs) offer satisfactory electrochemical performance and are still preferred for commercial use.^[12] Despite their popularity, LIBs face challenges such as the scarcity and high cost of lithium, as well as environmental and safety concerns. Recently, zinc ion batteries (ZIBs) have gained significant attention as an alternative to LIBs due to their low redox potential (-0.76 V vs. standard hydrogen electrode), high theoretical capacity (820 mAh g^{-1} , and 5854 mAh cm^{-3}), environ-

mental friendliness, and economical cost.^[13] However, zinc anodes face serious problems such as uncontrolled dendrite growth, surface passivation, and by-product formation, which reduce the Columbic efficiency (CE) and restrict large scale applications.^[14] Therefore, the successful development of ZIBs, including 3D hierarchical structural configuration, surface modification, and selection/optimization of electrolytes,^[6] must be considered to align with the current trends and demands of the contemporary world.

The existing challenges of ZIBs are closely related to electrolyte regulation, selection, optimization and repairing. The electrolyte has a central role in the electrochemical operations via facilitation of ions between electrodes. Traditional liquid electrolytes have been widely used for ZIBs, but they come with certain limitations such as leakage, poor electrochemical stability and flammability etc. Unlike liquid electrolytes, gel electrolytes are less prone to leakage, non-flammable and are practiced as an alternatives to traditional liquid electrolytes. The high mechanical stiffness of the gel electrolytes helps to endure the structural integrity cause by dynamic stress during operation. In addition, these electrolytes serves as separators, remarkably simplifying the configurations of the systems. Gel electrolytes could merely be formed by adding stretchable 3D gelation skeletons into the aqueous Zn salt electrolytes,^[15] sometimes even combining with other functions such as self-healing^[16] and anti-freezing^[17,18] etc. The gel electrolytes with self-healing capabilities are the novel class of electrolytes, which have ability to mend themselves when damaged. These self-healing electrolytes tend to prolongs electrochemical performance and longevity of the systems via repeatedly mending aptitude. Designing electrolytes with tailored self-healing properties, makes them an attractive choice for durable and high-performance devices. The Self-healing electrolytes in ZIBs are accredited to large scale applications in actual practice. These electrolytes in ZIBs offer promising benefits across various

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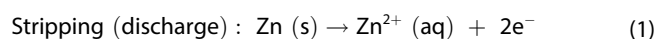
domains, from consumer electronics to industrial applications and energy storage systems. Their ability to enhance safety protocols, durability, consistency, reliability and performance make them a valuable advancement in battery technology. The self-healing adaptation of electrolytes in ZIBs helps to extend the battery life and making them more reliable for long lasting smart phones, wearable and other electronic devices. Similarly, these electrolytic systems have the ability to improve the safety protocols by mitigating electrolyte degradation and leakage which in turn prevent the internal short circuit and thermal runaway in the system. The ZIBs of self healing capabilities are functional despite environmental stress and ensure the consistency and reliability of the systems in the harsh climates. Additionally, they do not need frequent maintenance and replacement which translates to lower operational expenses and overall cost in the market. These feature of self healing, makes the ZIBs attractive to the consumers world wide. Although the self-healing electrolytes are an exciting area of research, still the complex fabrication processes, loses efficacy with repeated use, compatibility issue and robustness are the main challenges for the scientific community.

Research on self-healing electrolytes is ongoing with efforts, focused on conductivity, stability, and overall performance to be improved. New materials are exploring to formulate and optimize the self-healing phenomenon for the better performance of ZIBs. The driven progress, using self-healing approaches are expected to revolutionize and scale up the energy storage industries. This short review is aim to summarize recent developments and advancements pertaining self-healing phenomenon of electrolytes in ZIBs and will help to find conceivable perspectives and contemplations in the future.

2. Basic Working Mechanisms, Existing Issues and Recent Progress

Zn anodes exhibit diverse electrochemistry in different environments, which is highly depends on the nature, concentration, and pH value of electrolytes (Figure 1a).^[19] For instance, Zn anode in alkaline media face serious problems of dendrite growth, electrolyte exhaustion, and by-product formation, leading to intense polarization and inadequate Coulombic efficiency. Conversely, in the neutral or mildly acidic media, Zn^{2+} is fairly stable, which supports the reversible plating and stripping processes.^[20–22]

The stripping and plating reactions in mildly acidic electrolyte are shown in Equation (1) and (2) respectively:



However, achieving uniform nucleation on Zn anodes with high Columbic efficiency and long cycle stability is still challenging. The high Young's modulus and uneven nucleation during stripping can cause a short circuit in a cell.^[23] Moreover, self-corrosion and hydrogen evolution reaction (HER) in weakly acidic media (Figure 1b) can elevate the pH value, leading to the formation of hydroxides or zincates ions, which causes passivation and thus reduces the Columbic efficiency of the system. Therefore, proper selection and optimization of the electrolyte are essential for better performance and long life.

Aqueous ZnSO_4 is the most commonly used electrolyte in ZIBs. However, pH changes during the charge storage process (H_2O decomposition) induce the by-product formation. The possible by-product formation is as follows:



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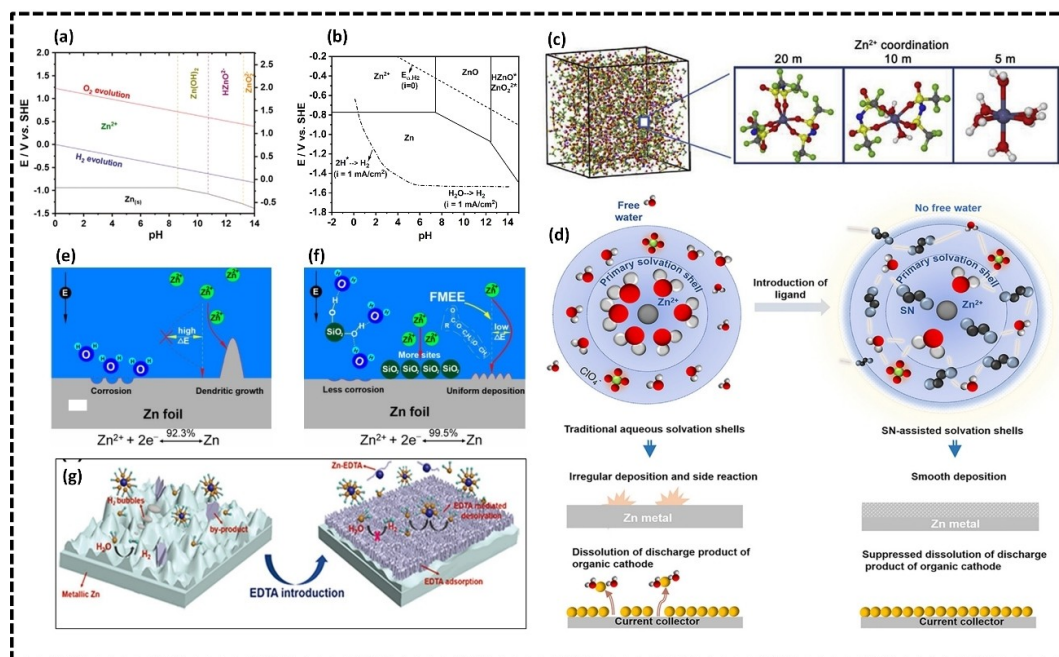
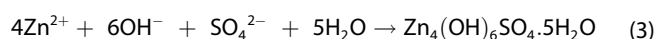
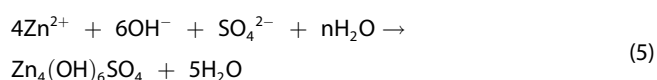
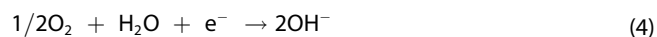


Figure 1. Pourbaix diagram of Zn/H₂O system as a function of pH (a) for 10^{−6} mol/L (b) for 10^{−4} mol/L with HER over-potential considerations. Reproduced from Ref.^[19] Copyright (1991) Elsevier. (c) A simulation cell with Zn²⁺ solvation structures in the electrolytes with 1 M Zn(TFSI)₂ and three concentrations of LiTFSI (5 m, 10 m and 20 m)^[22] Copyright (2018) Springer. (d) Schematic representation of Zn²⁺ solvation structure and its electrochemical behaviors. Reproduced with permission from Ref.^[25] Copyright 2020, Cell Press. (e) Schematic illustration of the electrochemical progression of Zn in ZnSO₄ electrolyte (f) and ZnSO₄ + FS + FMEE electrolyte. Reproduced with permission from Ref.^[26] Copyright 2019, ECS. (g) Schematic of Zn/electrolyte interphase behaviors with the ZnSO₄ and the EDTA-functionalized ZnSO₄ electrolyte during plating.^[27]



It is worth mentioning that such clusters can also form without pH changes based on the following equations:



These by-product and unequal nucleation may result in a relatively narrow voltage window and poor electrochemical reversibility. Therefore, further efforts are needed to explore suitable electrolytes for durable ZIBs. Regarding this, water-in-salt (WIS) electrolytes, such as 1 M Zn(TFSI)₂ and 20 M LiTFSI, have unique physicochemical properties and were found to be quite efficient for durable and reversible Zn-based devices. The solvation sheath around Zn²⁺ is highly coordinated and can be evolved into a stable molecular cluster by electrolytic component and Zn-TFSI—pairs (Figure 1c).^[22] Similarly, an aqueous eutectic electrolyte consisting of zinc salt (Zn(ClO₄)₂·2H₂O) and neutral ligands (succinonitrile SN) is also very useful for Zn²⁺ ion de-solvation and smooth deposition. (Figure 1d).^[25] However, there are still a lot of limitations in actual practice owing to the activity of H₂O in aqueous electrolytes. To overcome these challenges, researchers have added certain functional additives to the aqueous electrolytes. For example, non-ionic fatty methyl ester ethoxylate (FMEE) and fumed silica (SiO₂) based 1 M ZnSO₄ + 0.1 M MnSO₄ electrolyte shows minimal

dendrite growth, incredible cyclic stability (1500 hrs) and high Coulombic efficiency (99.5%) for Zn/Zn symmetrical cell (Figure 1e, f).^[26] Similarly, ethylenediaminetetraacetic acid tetrasodium salt (Na₄EDTA), ZnSO₄-based electrolyte exhibits outstanding adsorption ability over free H₂O and Zn(H₂O)₆²⁺ hydrated ions on the Zn surface and has better rate performance and cycle stability (Figure 1g).^[27]

To further explore this concept, various functional additives such as triethyl phosphate (TEP),^[28] polyacrylamide (PAM),^[29] acetonitrile (AN),^[30] diethyl ether (Et₂O),^[31] and thiourea derivatives,^[32] etc. have been employed to date. These additives were strategically used to formulate electrolytes for high-performance devices as alternatives to traditional aqueous electrolytes. However, cost remains a significant barrier to further development and commercialization. Thus, the design of electrolytes with optimal properties continues to be a crucial and challenging area of research. The self-healing phenomenon plays a pivotal role in the reaction kinetics, significantly mitigating these challenges. This mechanism effectively repairs the structural functionalities of the material autonomously, when damaged. Although limited research has been conducted in this area (Figure 2b), we offer several perspectives to elucidate its potential in energy storage devices.

The electrolyte is a key component that significantly influences the overall battery performance. Its composition and properties can significantly impact energy density, ion transportation, electrode stabilization, voltage and current regulation. As the existing challenges of ZIBs are closely related to electrolyte regulation, the proper selection and optimization of

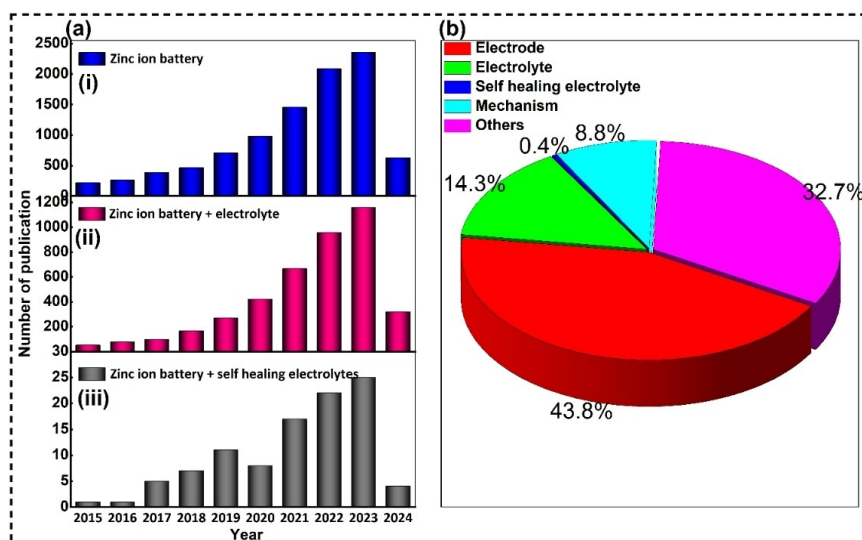


Figure 2. (a) Yearly publication progression based on the keywords (i) zinc-ion battery (ii) zinc-ion battery + electrolyte (iii) zinc-ion battery + self-healing electrolyte (b) A brief statistic of different aspects of ZIBs until May 29, 2024. From the Web of Science.

the electrolyte are essential for improved performance and longevity.^[33] Common electrolytes for ZIBs include aqueous electrolytes (ionic liquid electrolytes, alkaline electrolytes, mildly acidic electrolytes, and neutral electrolytes),^[34] solid-state electrolytes,^[35] quasi-solid and gel-state electrolytes.^[36] Each type is imperfect, therefore solvent design, additive regulation and concentration gradients^[37,38] have to be considered during electrolyte construction. An excellent electrolyte should exhibit high ionic conductivity, stable electrochemical window, easy interface management, good mechanical properties and affordable cost. Additionally, its flexibility, retainability and compatibility further enhance its potential for the state of art battery systems. Its flexibility, durability, and compatibility further enhance its potential for cutting-edge battery systems. Recently, remarkable considerations have been focused on the fabrication and configurations of quasi-solid electrolytes for ZIBs. Accordingly, we present a short overview based on our understanding of such electrolytes with self-healing properties to address the mentioned challenges. Quasi-solid electrolytes typically exhibit semi-solid characteristics, bridging the properties of liquid and solid, such as gel electrolytes (GEs). GEs can serve both as electrolytes and separators, consisting of 3D gelation skeletons fabricated by physical gelation or coagulation of colloidal particles or polymers in a sol or solution.^[39] GEs are prepared by a process called gelation, where a polymer network traps sufficient liquid molecules to form a solid frame that is elastic over time. The gelation may be either physical or chemical cross-linking: in the former case, intermolecular interactions (e.g. hydrogen bonds, electrostatic interactions and helix formation) are responsible for networking, while in the latter case, the three-dimensional structures results from intramolecular interactions (e.g. covalent bonds, Schiff-base reactions and free radical polymerizations) using explicit cross-linkers.^[40,41] As the gel ages, the liquid contents ooze out over time, resulting in the consolidation and shrinking of gel

network, which is a slow process known as syneresis.^[42] The proposed schematic illustration of both gelation and syneresis is shown in Figure 3a, where the wavy blue array represents polymer, and the globular orange circle represents physical cross-linker.^[43] The aging can altered the characteristics of the gel, which leads to efficiency attenuation. Therefore, an adhesive bonding solid polymer electrolytes (ABSPEs) could possibly restrain aging properties. Dong et.al. prepared an anti-aging polymer electrolyte by free radical polymerization for flexible zinc ion batteries using zinc-ion salt in poly(ethylene glycol) diglycidylether (PEGDGE, $M_n=500$) and triethylenetetraamine (TETA $\geq 97\%$) as shown in schematic diagram (Figure 3b). In a typical experimental procedure, propylene carbonate (PC) was used as plasticizer, owing to its hydroxyl group and aromatic rings. The as fabricated homogeneous solid polymer electrolyte exhibits an ionic conductivity of $3.77 \times 10^{-4} \text{ S cm}^{-1}$ with excellent aging stability and surface resistance (R_s) for at least 200 hrs. The optical microscopic image (Figure 3c) of the PEGDGE/TETA/PC/ZnOTf film exhibits light brown color, where crystalline zones are positioned in the amorphous contextual (Figure 3d). The as-fabricated film has good thermal stability (Figure 3e) with only 5% weight loss at 119°C is likely caused by the loss of the plasticizer.^[43]

Furthermore, the gel matrix in GEs reduces the risk of leakage and spoilage of batteries, thereby enhancing the safety of battery system.^[44] Additionally, the GEs impede the dendrite growth on anode surface and mitigate the degradation of cathode active materials by retaining structural integrity.^[45,46] In comparison to liquid and solid-state electrolytes, the gel electrolytes offer high capacity and good cyclic stability by confining the water activity and H^+ insertion/extraction during charge/discharge process, along with high ionic mobility, mechanical stability, light weight, and superior adhesion. These remarkable characteristics endorse GEs suitable for a wide range of applications. Nevertheless, the large-scale application of GEs

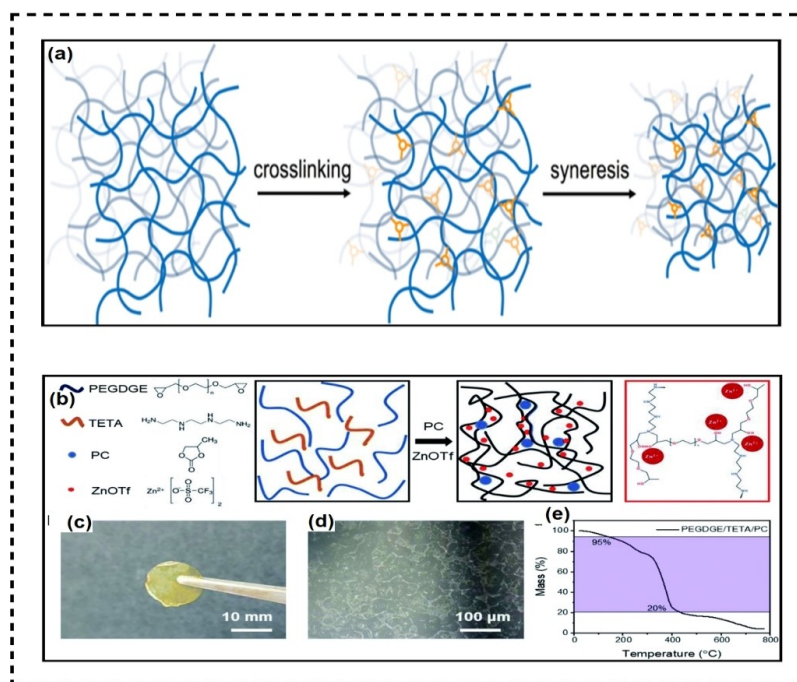


Figure 3. (a) Schematic depiction of the gelation and syneresis. Reproduced from Ref.^[42] Copyright (2019) Springer. (b) Fabrication route of PEGDGE/TETA/PC/ZnOTf polymer electrolyte, (c, d) Optical microscopy of PEGDGE/TETA/PC/ZnOTf film and transparent polymer electrolyte and (e) Thermogram of PEGDGE/TETA/PC/ZnOTf polymer electrolyte. Reproduced from Ref.^[43] Copyright (2020) Royal Society of Chemistry.

for ZIBs is still in its infancy and requires optimization for better performance based on ionic conductivity, flexibility, mechanical and thermal stability, stable electrochemical window, safety and multifunctional integration.^[47] Recently, the universal gel electrolytes (GEs), owing to gelatin with self-healing properties have become a research hotspot for ZIBs.

3. Exploration of Self-healing Electrolytes

The self-healing electrolytes (often polymeric gels) have the ability to repair their structure and functionalities when damaged. Self-healing electrolyte technology is an innovative field within materials science and electrochemistry, aimed at enhancing the longevity and safety of energy storage systems like batteries. This technology focuses on developing electrolytes that can repair themselves after damage, thus improving the performance and lifespan of batteries. The idea of self-healing came into existence in the late 20th century, with research focused on polymers and coatings that repaired themselves after damage. This research laid the groundwork for the application of similar concepts to electrolytes. Researchers began to develop self-healing electrolytes for lithium-ion batteries in 2011. This gel contained a network of polymer chains that could reassemble after damage, maintaining electrolyte functionality. Later on, the development of gel and solid-state self-healing electrolytes marked a significant milestone, combining high ionic conductivity and healing ability in batteries.

The self-healing ability can be achieved through reversible ionic, covalent and H-bonding which are not only attributing to improve the stability and lifespan of the electronic devices but also contribute to limit the resource wastes and trim down the overall cost. Developing self-healing electrolytes can greatly enhance the application of ZIBs by providing support in terms of recharging, flexibility and others. Nevertheless, ZIBs impede their electrochemical performance by threshold twisting, bending and deformation. Interestingly, the self-healing phenomenon of electrolytes help stumble blocks of the ZIBs. However, ZIBs with self-healing electrolytes plagued some other issues of oppressive agglomeration, uneven curling and self-crimping which thus results deprived mechanical stability and low dispersion. To overcome the forgoing pickles, Liqiang Mai et al. introduced an ultrafast self-healing of electrolytes through steric molecular combing strategy, where they fabricated a steric molecular comb of guar gum/ZnSO₄/glycerol, demonstrating ultrafast self-healable impact for quasi solid ZIBs. The ultrafast self-healing capability facilitates dendrite-free, stable and dense deposition of Zn metal during repeated Zn plating and stripping cycles (Figure 4a). In the guar gum/ZnSO₄ system, Zn anode and quasi-solid state electrolyte depicts enormous cracks (Figure 4b) after cycling, which are ascribed by a firm interface and tip effect. The interface resistance may cause large dendritic flakes and finally cellular failure (Figure 4c). In contrast, the guar gum/ZnSO₄/glycerol system demonstrates a robust effect by ultrafast healing approach, effectively regenerating the damaged interface (Figure 4d). The smooth and flat surface morphology (Figure 4e) signifies uniform Zn deposition with no

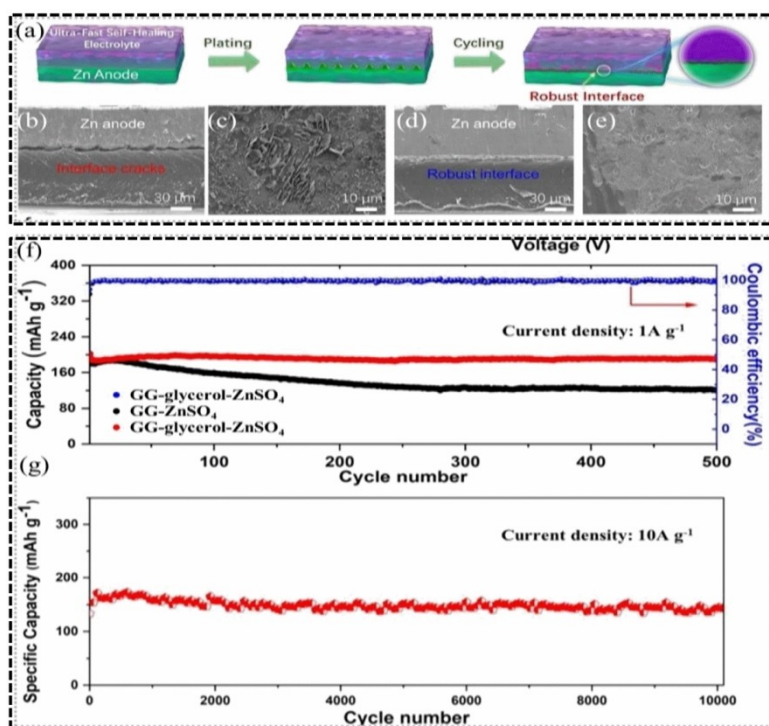


Figure 4. (a) Self-healing and dendrite inhibition interface on Zn anode, (b, c) Micrographs of Zn anodes in the guar gum/ZnSO₄ and (d, e) in guar gum/ZnSO₄/glycerol electrolytes after 250 cycles, (f, g) Long-term cycling performance at 1 A g⁻¹ and 10 A g⁻¹ respectively. Adapted from Ref.^[48] Copyright (2022) ACS Energy Letter.

byproducts observed during the entire process in the guar gum/ZnSO₄/glycerol system.

The self-healing effect is realized by assembling hydrogen bonds among the active sites of glycerol and guar gum system via crosslinking. The prepared electrolyte represent enhanced mechanical strength with the durable network structure. The assembled ZIBs deliver a specific capacity of 200 mAh g⁻¹ at 1 A g⁻¹ after 500 cycles with a retention capacity of 98.5% after 10,000 cycles at 10 A g⁻¹ (Figures 4f and g).^[48]

There are several strategies (Figure 5a) to achieve the self-healing property in aqueous ZIBs, including dynamic covalent bonding, metal-ligand coordination, hydrogen bonding, electrostatic interaction, host-guest interaction and ion-dipole interaction etc. For instance, combining the ionic conduction healing of electrolyte and the electronic conduction healing of electrodes, ZIBs based on PVA/Zn(CF₃SO₃)₂ hydrogel show an outstanding self-healing ability, as shown in Figure 5b. The Self-healing materials may either be active self-healing materials or non-active self-healing materials. The active self-healing materials can realize the self-healing process without the triggering of external stimuli (similar to the wound healing) while the non-active self-healing materials could realize the healing construction based on external stimuli, such as light, heat, pH, etc. The active and non-active self-healing is also name as intrinsic and extrinsic self healing respectively which are discussed in Sections 3.1 and 3.2 in detail.

3.1 Extrinsic Self-healing Mechanism

The self-healing mechanism can be categorized as extrinsic or intrinsic, depending upon the embedded pattern and the binding nature of electrolyte network. Extrinsic self-healing utilizes vascular networks pre-embedded in fabrication^[51] and is laden by specific liquids (healing agents). The liquids are usually added externally on the substrate surface which flow to the damaged area to enable healing. This protocol of self-healing is cropped up in three steps: triggering, transportation and repairing (Figure 6a). The response of the healing agents is initiated during triggering and are transported toward damaged surface to repair. The extrinsic self-healing is further categorized into capsule and vascular base pattern of healing. The extrinsic self-healing electrolytes involve the capillary action to integrate a microencapsulated healing agent and a catalyst on the cracked surface to prevent further rupturing. Microencapsulation involves covering a healing agent that polymerizes with an embedded catalyst to heal the cracks (Figure 6b).^[52] Carolyn Dry^[53] first presented the concept of a liquid repair system within a brittle-walled container using microencapsulation technique. Initially studied for the repair of cracks in concrete, this system uses three-part methyl methacrylate as a liquid resin (Figure 6c). Upon fracturing, the liquids flow directly into the damage areas where it subsequently cures. Various monomers, polymers, and liquid metal alloys have also been applied as healing agents to achieve significant advances. Similarly, Figure 6d–f illustrate the autonomic healing concept, where healing is accomplished by incorporating a microencapsulated

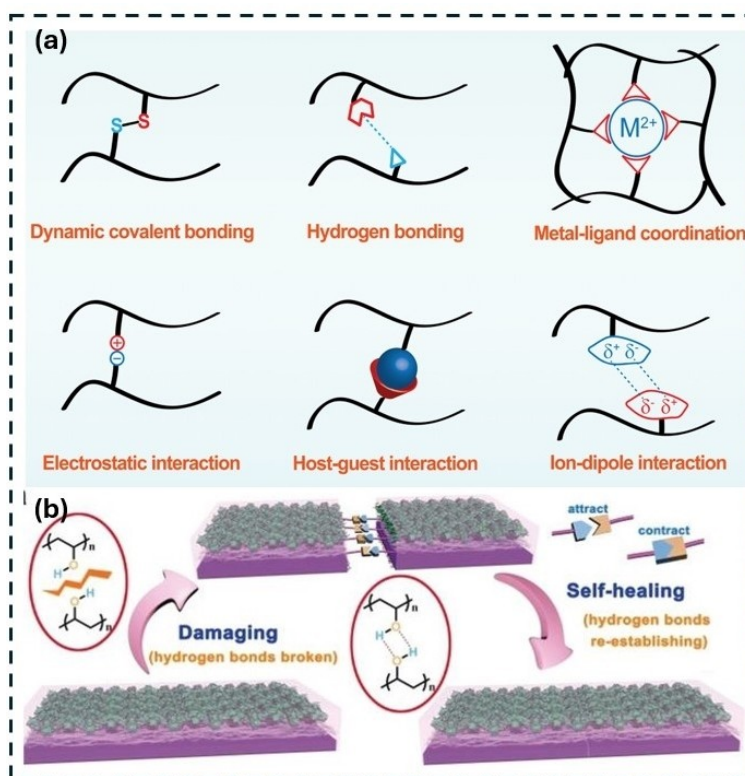


Figure 5. (a) Self-healing materials based on the physical/chemical reaction mechanisms, including the covalent bonding, hydrogen bonding, metal-ligand coordination, electrostatic interaction, host-guest interaction, and ion-dipole interaction. Adapted from Ref.^[49] Copyright (2024) advance sciences. Mechanism of healing on electrode surface (b) Illustration of the structure of self-healing integrated all-in one ZIBs. Adapted from Ref.^[50] copyright GDCh Wiley.

healing agent, triggered by a catalyst within an epoxy matrix. The damage-induced triggering mechanism provides site-specific autonomic control via polymerization. An additional unique feature of this concept is the use of living polymerization catalysts (i.e., catalysts with unterminated chain-ends), enabling multiple healing events. Caruso et al.^[54] asserted 100% healing efficiency of EPON 828 epoxy monomer (Figure 6g) encapsulated with solvents onto an epoxy matrix. Similarly, a favorable healing mechanism was proposed by Meng et al.^[55] using glycidyl methacrylate (GMA) as the encapsulated healing agent (Figure 6h, i). The GMA has both epoxides and alkene (C=C) functional groups, thus the nucleophilic addition and ring-opening reactions occur between GMA and residual amine groups during healing. As most of the organic species tend to enable nucleophilic addition, still the application of nucleophilic addition is not yet been reported as a healing measure, so it is believed that the free expansion of the self-healing agent might lead to repair the rupture area.

A number of encapsulation techniques can be used depending upon the size, properties, permeability and efficiency of the capsule, core material, shell, and encapsulation respectively. The extrinsic self-healing performance is projected from the correlation between liberated quantity of healing agents, diameter of the capsule and damage area, as described by Equation (6).

$$m_t = \rho_s \phi d_c \quad (6)$$

Where, m_t represents the total mass of healing agents, ρ_s is the density of the material, ϕ is the mass fraction and d_c is the diameter of the capsules. The factors effecting on healing performance are structural and dynamic. The overall performance of structural factors can be enhanced by thinning the capsule shell and enlargement of the shell size while higher pressure and temperature and the healing timing, boost the healing performance of dynamic factors (Table 1). The vascular self-healing systems comprise the vascular channels and

Table 1. Factors affecting capsule and vascular based self-healing performance. ^[58]			
Capsule based		Vascular based	
Structural factors	Dynamic factors	Structural factors	Dynamic factors
Capsule size	Temperature	Vessel size and roughness	Temperature
Capsule thickness	Pressure	Vascular network pattern	healing time
Roughness	Healing time	Share parts of a healing system	hydraulic pressure
Dispersion of capsule	Aging and fatigue		mixing process
The ratio of different parts of a healing mechanism			

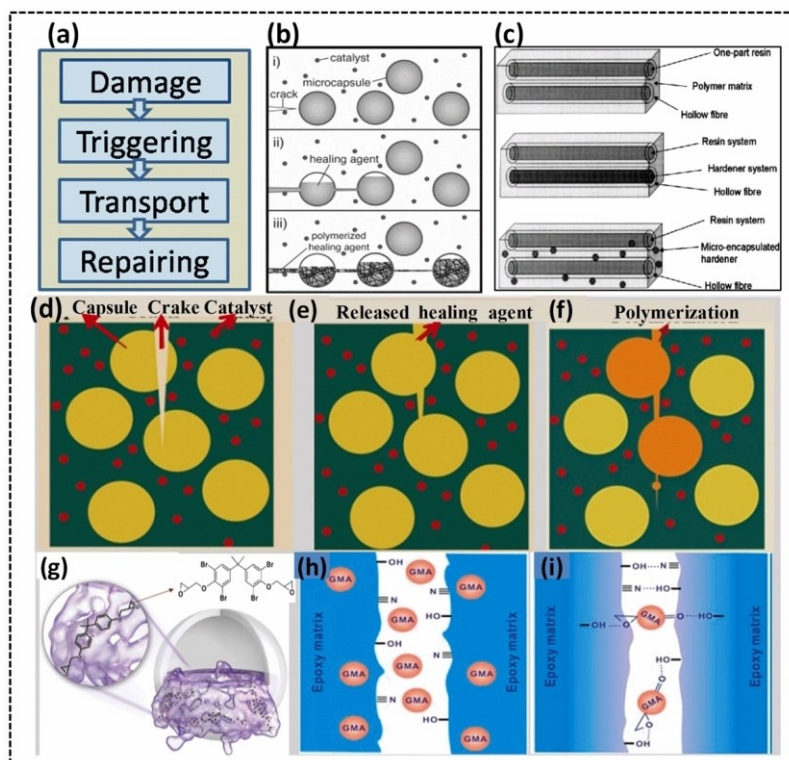


Figure 6. (a) Self-healing protocol through embedded healing agents, (b) The self-healing concept. A microencapsulated healing agent, embedded in a structural composite matrix having catalyst to polymerize healing agent. (i) Cracks formation at damage area. (ii) Crack rupturing, releasing healing agent into the crack plane through capillary action. (iii) The healing agent contacts the catalyst, triggering polymerization that bonds the crack faces closed. Adapted from Ref.^[50] Copyright (2001) Springer Nature. (c) Smart repair concepts of vascular self-healing considered for polymer matrix composites. Adapted from Ref.^[56] Copyright 2001, Elsevier. (d–f) Capsules and microcapsules based healing progression. Adapted from Ref.^[57] Copyright (2019) Wiley. (g) 3D depiction of polymeric microcapsule releasing epoxy monomer EPON 828 as the healing agent. The chemical structure is displayed in the inset. Reproduced from Ref.^[54] Copyright (2008) Wiley-VCH, (h) Dispatched GMA from the epoxy matrix to the damaged region. (i) Hydrogen bonding between the cracked faces. Reproduced with permission.^[55] Copyright (2010) Royal Society of Chemistry.

healing resins with polymeric matrix. The channels deliver the resins for healing in a supplementary manner and reinforce the structural features. These systems rely on the processes of triggering, healing and mechanical manipulation of the channels to achieve effective repair.^[59]

3.2 Intrinsic Self-healing Mechanism

The Intrinsic self-healing electrolytes (often GPEs) inherently possess materials that can heal the damage surface upon activation. Intrinsic self-healing is a reversible, which depends upon the physical (non-covalent bonds) and chemical routes (dynamic covalent bonds). The physical routes are based on the molecular interaction, ionic and coordination bonds while the chemical routes depend on structural composition, reaction mechanism (condensation, addition reactions) and exchange rate of damaging and healing.^[60] The non-covalent bonding system do not need external stimulus for activation because of low bond energy therefore, thus it generally has significant healing function compared to dynamic covalent bonding systems. Moreover, the non-covalent bonding system attains the repairing equilibrium through migration, identification and recombination of molecular chain. Polymeric chains can easily

be cross-restructured via dynamic reversible non-covalently bonding, where the chain diffusion interface is considered to be the key driving force for healing.^[61]

In this context, a quasi-solid electrolytes was constructed through cross linking ureidopyrimidinone(UPy)-telechelic and poly(ethyleneglycol)diacrylate (PEGDA) networks by Davino et al. via in situ free radical polymerization (Figure 7a). This electrolyte demonstrates significant self-healing capability and better specific capacity (150 mAhg^{-1}). The ionic conductivity is observed to drop upon the formation of deep cracks in the PEGDA-UPy film but rapidly recovered to its pristine value at 40°C .^[62]

Similarly, a dynamically healable gelatin-based hydrogel electrolyte was designed by Wang et al., which forms a conformal electrode-electrolyte and solid-solid interface by reversible sol-gel transition and in situ solidification. The unique helical gelatin chain structure provides uniform channel for zinc ion transport by the bridging effect of sulfate groups, enabling repeated repairing of anode-electrolyte interfacial interspaces and long-lasting protection for sustainable zinc-ion batteries. The assembled practical cartridge cells are well stable with total capacity of 22.5 mAh and 100% capacity retention after 240 cycles.^[36]

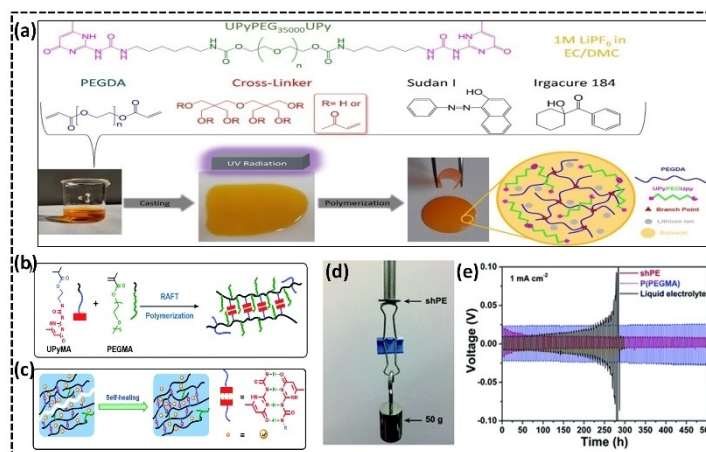


Figure 7. (a) in situ photopolymerization of PEGDA-UPy X cross-linked gel electrolyte (X = 50 and 67 wt %). Adapted from Ref.^[62] Copyright (2022) American Chemical Society. (b) Polymerization depiction of brush-like copolymer, (c) Fabrication of self-healing polymer electrolyte and healing mechanism (shPE), (d) flexibility and stretchability test of shPE, (e) Galvanostatic stability of Li/shPE/Li and Li/liquid electrolyte/Li symmetrical cells at a current density of 1 mA cm^{-2} at 60°C . Adapted from Ref.^[63] Copyright (2018) Royal Society of Chemistry.

Furthermore, Zhou et al. fabricated a brush like flexible (2000% strain), fast self-healing copolymer electrolytes via physically cross-linking of ureidopyrimidinone (UPy) containing monomers and poly(ethylene glycol) methyl ether methacrylate (PEGMA). The designed electrolytes has favorable adhesive strength (2.74 kPa) high capacity (152 mAh g^{-1}), stability (500 hrs) and columbic efficiency (99.2%) (Figure 7b–e).^[63] its, synergy can be attributed to high binding capability of quaternary hydrogen bonds which provide intrinsic healing efficiency and elasticity to the electrolyte.

In contrast to dynamic non-covalent bonds, the dynamic covalent networks are the immense healable protocol for thermosetting, robusting and repairing processes. A self-healable dynamic poly(urea-urethane) gel electrolyte membrane was synthesized by Federico et al. The charge/discharge

ability of HUB-PU network and Celgard® 2500 membrane was compared at C/5 rate. After initial cycling, both the cells were cut deeply and were put in a glovebox for a while (Figure 8a, b), which gives charge/discharge succession repeatedly (during first 10 cycles) with the ratio of 100 cycles (after cutting) at 5/C rate. After the entire surface damaging, the capacity was been dropped to 159 mAh g^{-1} (Figure 8c) which is nearly closed to pristine material (161 mAh g^{-1}). After the cutting, the HUB-PU network showed satisfactory result for another 50 cycles with 94.78% retention at the 50th cycle with respect to the 10th cycle. This performance surpasses that of the commercial Celgard® 2500 membrane (Figure 8d) which shows its failure to recover from the cut with 27% retention and the discharge capacity of 39 mAh g^{-1} .^[64] Moreover, Deng et al. presented dynamical concept for the covalently bonded networks of

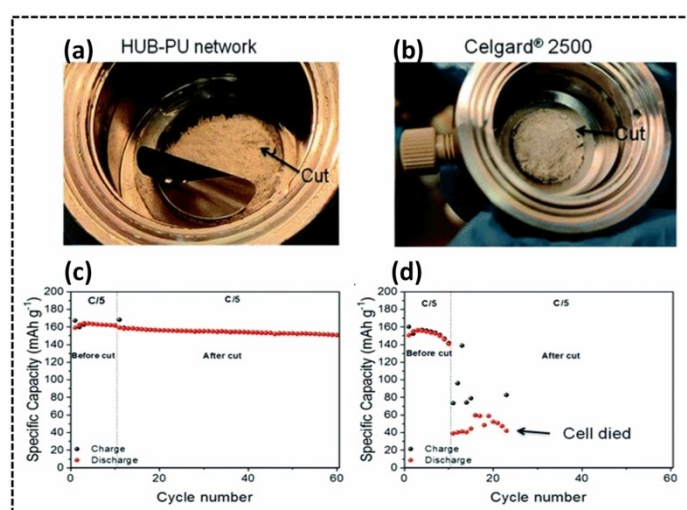


Figure 8. Optical proof of the cut carried out inside the glove box on both the self-healable HUB-PU network and Celgard® 2500 membrane after 10 cycles at C/5 rate. (a, b) Specific capacity (mAh g^{-1}) vs. Cycle number at C/5 rate for the HUB-PU network (c) and Celgard® 2500 membrane (d), respectively. Adapted from Ref.^[64] Copyright (2022) Royal Society of Chemistry.

poly(ethylene glycol) diamine and benzene-1,3,5-tricarbaldehyde gel by Schiff-base reaction. This gel exhibited an ionic conductivity of $4.79 \times 10^{-3} \text{ Scm}^{-1}$ at 30°C , discharge capability of 118.2 mAhg^{-1} at 5/C rate and good cycling performance of 97.8% over 125 cycles.^[65] Borate based self-healing gel electrolyte has also been reported by Zhao et al which has 156.2 mAhg^{-1} discharge capacity at 0.1/C rate and excellent columbic efficiency (CE) of 99.4%.^[66]

Furthermore, Lin and his group introduced a new type of polymeric ionic electrolyte with self-healing capacity by grafting ionic liquid chain units into polymeric backbones. The designed electrolyte benefiting a reconstructing dendrite induced defects and fatigue cracks growth with high initial discharge capacity of 134.7 mAhg^{-1} , rendering a capacity retention of 91.2% after 206 cycles at room temperature.^[67]

Likewise, a flexible and self-healing ionic gel electrolyte was prepared by Chen et al. using zwitterion solvent-assisted method. The synergistic ionic interaction in the electrolyte system endowed remarkable self-healing ability, ionic conductivity ($9.06 \times 10^{-4} \text{ Scm}^{-1}$) and capacity retention (96%) after 155 cycles at 60°C .^[68] Moreover, a redox-mediated double network polyacrylic acid/polyisodecyl methacrylate/ $\text{K}_3[\text{Fe}(\text{CN})_6]$ gel polymer electrolyte (GPE) endow ionic conductivity of 3.76 S/m with 95.3% capacitance retention rate after 10 cutting/healing cycles. Even at severe deformations, the durability is retained which is ascribed to the strong electrode/electrolyte coordination and reversible redox reactions of $\text{Fe}^{+2}/\text{Fe}^{+3}$ ions.^[69] The electrochemical performance of self-healing electrolytes at different conditions is summarized in the given Table 2 below.

Regarding polymeric electrolytes, the self-healing involves five stages, i.e. segmental surface rearrangements, surface approach, wetting, diffusion and randomization. During the network damaging, two main events occur: chain cleavage and/or chain slippage. The former generates reactive groups while the latter may lead to conformational changes. For the autonomous repair of damage networks, the interplay of healing reactions and chain rearrangements is critical.

From thermodynamic point of view, a chemical process (healing) proceeds spontaneously if the total energy of the process, $\Delta G (= \Delta H - T\Delta S) < 0$. Considering inter-macromolecular interactions is zero, ΔG for free chains will be given as:

$$\Delta G = -T\Delta S = -nRT\{\ln N + \ln(z/2e) + (N-2)\ln[1/(1-f)e]\} \quad (7)$$

This approach is useful to estimate the self-healing capabilities by calculating the energy changes in the self-healing lattice of dangling chains. Here, T is the absolute temperature, n is the number of polymer chains, $\ln N$ is the probability of finding one end of each chain, z is the coordination number of the lattice unit, N is the number of segments in a chain and f is the Flory's flexibility parameter. The Flory's flexibility parameter (f) is defined as the probability of two successive bonds to be not collinear and are subject to rotations. If $\ln N = 0$. Thus, Equation (2) can be expressed as:

$$\Delta G = -T\Delta S = -nRT\{\ln(z/2e) + (N-2)\ln[1/(1-f)e]\} \quad (8)$$

The threshold value for f is critical in this approach and is given as K (Boltzmann constant). When $f = K$, then $\Delta G = 0$. According to Equations (7) and (8) when $f > K$, $\Delta G < 0$ and the chains will be able to move spontaneously. On the other hand, when $f < K$, $\Delta G > 0$, then the chains will be too rigid to undergo conformational changes for self-healing and needs an external energy inputs to overcome kinetic barriers.

The healing efficiency $R(\sigma)$ can be estimated from the extent of the recovery with respect to its initial post-damage state as the ratio of fracture before (σ initial) and after healing (σ healed)

$$R(\sigma) = \frac{\sigma \text{ healed}}{\sigma \text{ initial}} \quad (9)^{[61]}$$

Self-healing mechanisms, both extrinsic and intrinsic, are vital in various fields. Each type has its own set of advantages

Table 2. Summary of self-healing electrolytes.

Electrolyte	Operating temperature ($^\circ\text{C}$)	ρ (mAcmm^{-2})/ σ (Scm^{-1})	Cycles/capacity retention (%)	Reference
PBPE (BTA-PEG)	25	$2/4.79 \times 10^{-3}$	125/97.8	[65]
shPE (UPyMA-PEGMA)	25	$2/2.1 \times 10^{-4}$	100/91.1	[63]
Ionogel-3.5 (PIL-UPy)	25	$0.5/1.57 \times 10^{-3}$	120/88.7	[70]
DSP (UPyMA-PETEA)	25	$0.5/1.79 \times 10^{-3}$	200/86.2	[71]
PVA + methanesulfonic acid	25	$2/8.8 \times 10^{-3}$	500/92.7	[72]
FDHE	-10	$5/2.1 \times 10^{-2}$	1000/96	[73]
Guar gum/ ZnSO_4 /glycerol	25	$10/1 \times 10^{-3}$	10000/98.5	[48]
ZnCl_2 + xanthan gum	-20	$0.5/13.8 \times 10^{-3}$	450/83	[74]
Borax-PVA/G	-35	$2/10.1 \times 10^{-3}$	2000/90	[75]
EG-waPUA/PAM	-20	$2.4/1.6 \times 10^{-2}$	600/81.6	[76]
EMIM/PMMA	25	$0.2/1.76 \times 10^{-4}$	206/91.2	[67]
EMIMTFSI/LiTFSI	60	$0.1/9.06 \times 10^{-4}$	155/96	[68]
PAI/Fe GPE	30	$1/3.76 \times 10^{-2}$	4000/95.3	[69]
PAM/ β -CD/EMIMBF ₄	80	$0.2/5.8 \times 10^{-2}$	5000/82.9	[77]

and disadvantages, depending on the context in which it is applied. The extrinsic self-healing mechanisms offer control, quick and predictable healing but come with higher costs and dependencies on external factors. On the other hand the intrinsic mechanisms provide autonomy and cost-effectiveness but may be limited by material properties and slower healing rates. The choice between them depends on the specific requirements and constraints for the practical use.

Considering the self-healing importance of electrolytes, a number of articles have been published in the recent past, the dynamical concepts of non-covalent and covalent networking, linkages and repairing adaptations of the electrolytes.

Currently, Qin et al formulated robust electrical double layer (EDL) and self-electrolyte interphase (SEI) for practical ZIBs, demonstrating remarkable insights.^[78] Similarly the self-adhesive polyelectrolyte electrolytes assembled in ZIBs, exhibit excellent electrochemical performance and long lasting.^[79] Additionally, mastering the phenomena of conversion, reconstructing and decoupling manifest a milestone accomplishment regarding quasi-eutectic electrolytes/electrode zinc ion battery system.^[80–82] However, considerable progress remains to be achieved to pursue the self-healing phenomenon for excellent productivity for commercialization.

4. Summary and Future Perspectives

This article summarized the forefront progress of self-healing electrolytes for zinc ion batteries and other electronic devices. We discussed the self-healing mechanisms, encompassing definitions, techniques, and both extrinsic and intrinsic self-healing processing in terms of composition, design, properties and the choice of electrolyte. Table 2 summarizes the electrochemical performance of self-healing electrolytes at different operational conditions. While self-healing electrolytes and electrode materials can mitigate the stumbling blocks (dendrite growth, surface passivation and by-products) of the ZIBs, other issues are introduced including oppressive agglomeration, uneven curling and self-crimping, which results deprived mechanical stability and durability. Therefore, novel designs and strategies are required to sustain chemical and mechanical properties for long life. The selection of additives, binders, cross-linkers and electrolytes play a key role for better performance. Moreover, the use of electrochemical active materials such as carbon nanotubes, graphene etc. should be encouraged to provide conductive framework for easy electrons mobility. Additionally, the self-healing materials should have salvation capability and high dielectric constant value to facilitate salt dissociation and ionic conductivity during operation. Similarly the integration of self-healing electrolytes with advanced materials and technologies could possibly be leads to the development of next-generation energy storage systems, which potentially be offering higher energy densities and better performance. Future research on self-healing electrolytes for ZIBs should focus on advancing material science, and addressing of practical implementation. On the other hand, a multi-disciplinary approach and collaboration with industry stake-

holders are crucial for translating these advancements into commercial technologies.

Overall, the cited investigations recommended, the augmented capacity, cyclic ability and durability of energy storage devices, using self-healing phenomenon. Despite, the designing and developments are still in infancy, which needs a lot of progress for practical applications.

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Conflict of Interests

The authors declare no conflict of interest.

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