

Review

The Gel-State Electrolytes in Zinc-Ion Batteries

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Abstract: Zinc-ion batteries (ZIBs) are receiving increasing research attention due to their high energy density, resource abundance, low-cost, intrinsic high-safety properties, and the appropriate plating/stripping voltage. Gel-state electrolytes possess merits of having a wide electrochemical window, good flexibility, superior water retainability, and excellent compatibility with aqueous electrolytes, which makes them potential candidates for flexible batteries. However, the practical applications of ZIBs with gel-state electrolytes still have some issues of water content easily dropping, poor mechanical stability, and the interface problem. Therefore, the application of hydrogel-based, self-healing gel, gel polymer, thermos-reversible, and other additional functions of gel electrolytes in ZIBs are discussed in this review. Following that, the design of multi-functional gel-state electrolytes for ZIBs is proposed. Finally, the prospect and the challenges of this type of battery are described.

Keywords: gel-state electrolytes; zinc-ion batteries; self-healing; thermoreversible



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1. Introduction

In pursuit of rechargeable flexible/wearable battery for grid-scale electrochemical energy storage and conversion systems, metal-ion batteries are drawing much attention [1–6]. As the most extreme application of electrical energy storage devices, lithium-ion batteries (LIBs) [7–13] not only have the high energy density, but also show long charge/discharge life cycles [14]. Nevertheless, some inherent issues hinder its widespread application, such as the safety problems, lithium metal extrusion, dendrite growth, and the high cost, together with the limited resources of lithium metal [15]. The zinc-ion battery (ZIB) [16–21], one of the next-generation batteries, is a promising candidate to circumvent some of the above problems, due to their high theoretical capacity, low cost, high abundance, low potential, high energy density, and intrinsic safety. In addition, batteries are mainly composed of electrodes, electrolytes, and current collectors, which holistically determine battery performance. The environment for metal-ion transfers between the two electrode terminals in the battery is provided by the electrolytes, which also judges the electrochemical window, ionic conductivity, and the reversibility of the zinc plating/stripping [22]. Therefore, it is necessary to review the application of electrolytes in ZIBs.

Three main types of electrolytes are included in batteries: liquid-state, solid-state, and gel-state (Figure 1). The aqueous ZIBs with liquid-state electrolytes are usually considered as ultra-intrinsic batteries [23,24]. Nevertheless, various side reactions of dendrite growth [25], oxygen evolution reaction, hydrogen evolution reaction, [26], and metal Zn corrosion and passivation [27] impede Zn-ion batteries' application. However, solid-state electrolytes (SSEs) are an effective strategy to free one from the above issues [28,29]. Meanwhile, the high security, excellent flexibility, good mechanical stability, and no risk of electrolyte leakage merits of SSEs show enormous potential to solve the problems of liquid-state-solution-based batteries [30]. The SSEs can be divided into solid polymer electrolytes (SPEs) [31,32] and inorganic ceramic electrolytes (ICEs) [33]. Frustratingly, the

high crystalline of SSEs at room temperature will lead to ionic diffusion kinetics, low ionic conductivity, and low elastic modulus, which further increase the interfacial resistance between electrode and electrolyte, as well as high polarization voltage. On the other hand, most cathode materials of ZIBs require H^+ insertion/extraction, which stems from H_2O molecules of electrolytes. For ZIB systems, gel-state electrolytes containing amounts of liquid-state electrolytes have attracted extensive attention, such as hydrogel, self-healing gel, gel polymer, and thermos-reversible gel electrolytes. Compared with liquid-state electrolytes, the gel-state electrolytes can confine the activity of water, which can extend the electrochemical stability window and provide good flexibility; whereas, compared with all-solid-state electrolytes, the gel-state electrolyte can offer H^+ insertion/extraction during charge/discharge process for high capacity and good cyclic stability.

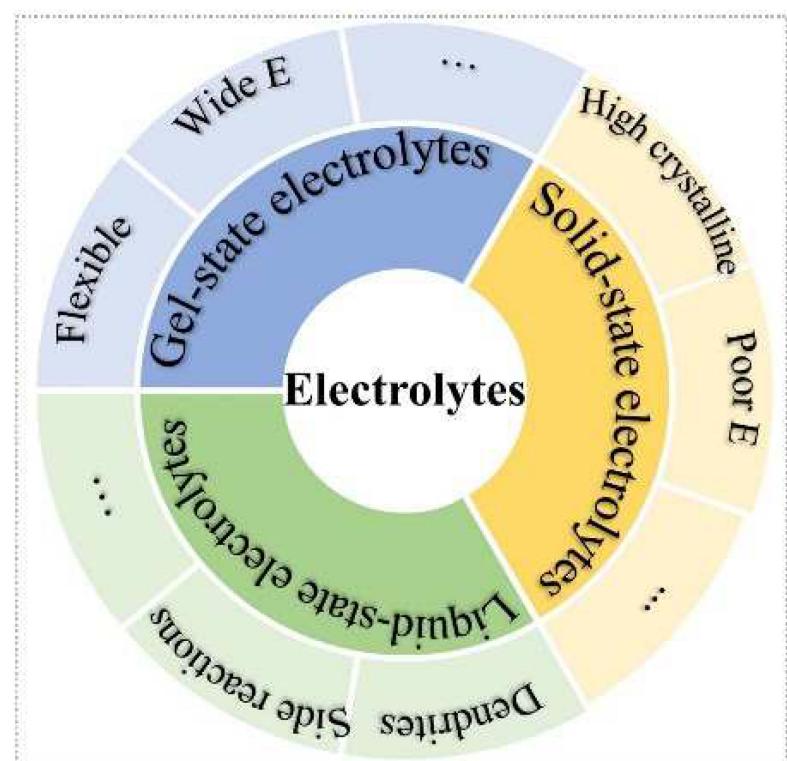


Figure 1. Schematic illustration of three types of electrolytes.

Despite the above advantages of gel-state electrolytes, there are still some problems in practical applications. As a result, it is necessary to further research the development of ZIB gel-state electrolytes. This review summarizes the state-of-the-art progress of gel-state electrolytes in ZIBs. Firstly, the working principle and mechanism of ZIBs are introduced briefly with an overview focused on the gel-state electrolytes. Secondly, the applications of hydrogel-based, self-healing gel, gel polymer, and thermos-reversible gel as well as multifunctional electrolytes are systematically discussed. Following that, challenges and prospects in ZIB research are provided. Finally, the conclusion is presented.

2. Working Principle and Mechanism of Gel-Electrolyte-Based ZIBs

The structure and working principle of ZIBs are similar to those of LIBs, which include three main parts: cathode, anode, and electrolyte. The cathode materials include manganese-based materials, Prussian blue-based materials, vanadium-based materials, organic-based materials, etc., while the anode is metal Zn. After the ZIBs are assembled, there will be a certain potential difference between the two poles of the battery, and a redox reaction will occur between the positive and negative electrodes during the charging and discharging process of the battery. As shown in Figure 2 [34], the charge shuttles through

the movement of Zn ions between the two electrodes. Upon charging the battery, the Zn^{2+} ions on the anode side obtains electrons and are reduced to Zn metal, and the inserted Zn^{2+} ions are extracted from cathode materials. While in the discharging process, the process is completely reversed.

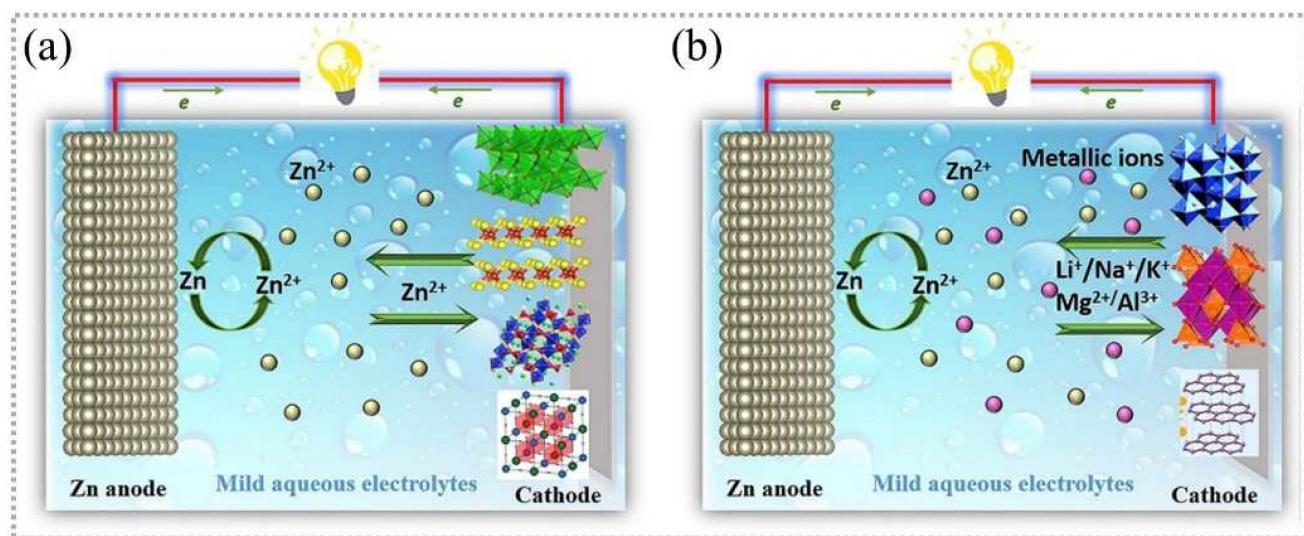


Figure 2. Schematic illustrations of the principles of (a) aqueous Zn-ion batteries (AZIBs) and (b) aqueous Zn hybrid batteries (AZHBs). Adapted with permission from Ref. [34]. Copyright 2019, Energy Storage Materials.

On the other hand, Zn metal easily reacts with the electrolyte to form a solid electrolyte interface (SEI) film on the metal surface, which conducts electricity at the ionic level and insulates at the electronic level. Moreover, the usually formed SEI film is uneven, so that the surface of Zn metal cannot be fully passivated, which eventually leads to continuous side reactions between the Zn metal and the electrolyte. Therefore, it is very important to study the electrolyte of ZIB battery and solve the above problems by ion doping.

3. Gel-State Electrolytes

The gel-state electrolytes with liquid solution contained and good flexibility can play the dual role of electrolyte and separator. They are usually formed by the coagulation of colloidal particles or polymers in a sol or solution under certain conditions. The formation of a spatial network structure enables them to maintain the original structure even with liquid solutions absorbed. Gel-state electrolytes tend to exhibit semi-solid electrolyte characteristics between liquid and solid, which usually have high ionic mobility, mechanical flexibility, light weight, and good adhesion. The superior flexibility and good adhesion properties promote gel-state electrolytes to be used in flexible wearable electronics. However, the commercial application of gel-state-electrolytes-based ZIBs is still in its infancy, so the gel-state electrolytes for ZIBs still need to be continually developed and optimized. High-performance gel-state electrolytes should possess high ionic conductivity, flexibility, mechanical stability, certain electrochemical stability, environmental friendliness, and multifunctional integration. Therefore, the universal gel-state electrolytes—such as polyacrylamide (PAM) [35], poly(ethylene oxide) (PEO) [36], polyvinyl alcohol (PVA) [37], poly(acrylic acid) (PAA) [38], poly(vinyl chloride) (PVC) [39], PCDF, poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) [40], poly(ethylene glycol) diglycidylether (PEGDGE) [41], and tetraethylene glycol diacrylate (TEGDA) [42]—have become a research hotspot for the majority of scientific researchers.

3.1. Hydrogel Electrolytes

The hydrogels are one of the most typical gel-state electrolytes, which could synthesize by crosslinking, dual-network crosslinking, and self-assembly. According to different sources, hydrogels can be divided into synthetic polymer hydrogels and natural polymer hydrogels. For natural polymer hydrogels, they can be directly obtained from nature, which show good biocompatibility and abundant reserves. Discouragingly, they always have poor mechanical properties and instability. In sharp comparison, the synthetic polymer hydrogels have good stability and designability due to controllable physical or chemical procedure utilized. The current synthetic methods for synthesizing hydrogels include physical and chemical monomer crosslinking. When the hydrogel is synthesized through increasing the degree of crosslinking, the modulus and the stretch ability will be increased and decreased, respectively. Additionally, the hydrogel with good solubility to salts and the liquid-like flow ability stem from a superior water absorbency. Nevertheless, physical crosslinking is formed mainly through intermolecular interactions, which will form a cluster structure where ineffective and uniform crosslinking defects exist. Chemical crosslinking, on the other hand, will form certain covalent bonds and possess certain thermal stability.

The hydrogel with special three-dimensional network structure for abundant adsorption sites can contain a large amount of water (normally 300 w%) [29] and improve the ionic conductivity of electrolytes. Up to now, the hydrogel electrolyte has been one of the most promising electrolytes for ZIB systems, based on their excellent flexibility and high ionic conductivity compared with all-solid-state electrolytes for ZIBs as well as their low cost properties, while the problem of mechanical deficiencies remains a challenge, and the battery will fail due to dehydration. Herein, extensive efforts have been expended for the modification of hydrogel electrolytes. For example, Shim and co-workers have developed flexible, fiber-shaped, quasi-solid-state Zn-polyaniline batteries (Fs-ZPBs) which are fabricated using PVA-based gel-type electrolyte with methanesulfonic acid-doping [43]. The special electrolyte could suppress polyaniline degradation and Zn corrosion. As shown in Figure 3a, the battery shows 92.7% and 88.1% capacity retention after 500 bending cycles at 2.5 mm bending radius and 2000 cycles, respectively. In addition, Liu et al. reports a sandwich-type flexible soft pouch battery using a functional double-network hydrogel electrolyte (FDHE), displaying excellent cycling stability of the battery at -10°C and a cyclic stability equal to 1000 charge–discharge cycles with 96% capacity retention [44]. The double-network hydrogel electrolyte (DHE) is fabricated by a two-step method, in which the DHE cloud suppresses the Zn dendrite growth compared with the aqueous zinc sulfate (ZnSO_4) electrolyte (Figure 3b). This method also could improve the mechanical strength and could sustain a compression stress up to 20 times compared with the method of a single network structure. Slide-ring hydrogels and nanocomposite hydrogels are developed to suppress the issue of fragility in the traditional hydrogels. Therefore, hydrogel ZIBs are very promising to drive social development and progress.

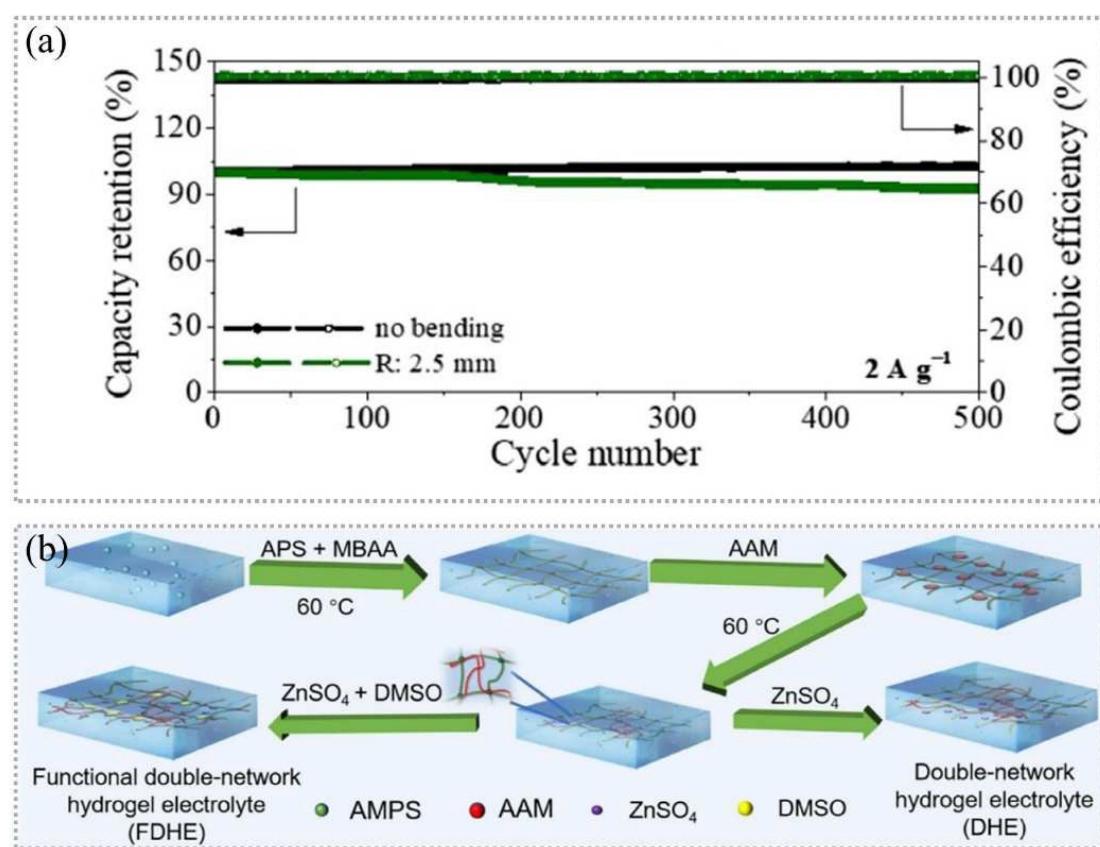


Figure 3. (a) Long-term cycling at 2 A g^{-1} upon bending at a curvature radius of 2.5 mm. Adapted with permission from Ref. [43]. Copyright 2021 Energy Storage Materials. (b) Schematic diagram of the synthesis of PAMPS/PAAM dual-network hydrogel. Adapted with permission from Ref. [44]. Copyright 2022 Chemical Engineering Journal.

3.2. Self-Healing Gel Electrolytes

Self-healing, as the magical additional function of the hydrogel, could be realized by introducing reversible weak interactions into electrolytes, such as reversible ionic bonding, covalent bonding, H-bonding, etc. The self-healing functional could not only achieve the ZIBs automatic repair to improve the stability and lifespan but also increase the social benefits and reduce waste of resources. Therefore, developing ZIBs with self-healing and additional functions, such as rechargeability, high-energy, flexibility for wearable applications, and others, may potentially boost the application to electronic devices.

Although ZIBs can withstand a certain degree of bending or tensile deformation, they also face the problem of battery damage or degradation of electrochemical performance when the deformation is too large, such as electrical shorts between electrodes due to poor mechanical strength. Fortunately, this problem can be mitigated or eliminated with self-healing gel-state electrolytes, in which the self-healing function is similar to the self-healing function of human skin. Some studies have shown that by using this electrolyte, damaged electrolytes can be restored to their original state, or the performance degradation of batteries can be minimized. Not only can the durability and lifespan of ZIBs be improved, but also electronic waste and cost can be reduced. However, the development of ZIBs of self-healing gel electrolytes have been plagued by the issues of severe agglomeration, irregular curling, and self-crimping, which will lead to poor mechanical and low dispersion. Fortunately, ultrafast self-healing electrolytes by means of the steric molecular combing strategy can effectively solve the above problems [45]. They prepare a self-healable ZIB based on guar gum/ZnSO₄/glycerol electrolyte gel electrolyte, as shown in Figure 4. The steric molecular comb is constructed by introducing glycerol into the guar gum system, and forming the hydrogen-bonding between them, which is beneficial to inhibiting the

formation of the carbon–carbon single bond. The alcoholic hydroxyl active sites will be exposed to crosslinking with borate to realize the function of ultrafast self-healing. Furthermore, the binding energy between active water molecules and the system will be stronger. The number of water molecules in the primary solvation shell of Zn^{2+} decreased by 2.2. The assembled ZIBs with this electrolyte could be merged into one piece within 30 s after being cut into two pieces, and it can deliver a specific capacity of 200 mA h g^{-1} at 1 A g^{-1} , even after 500 cycles. Moreover, the battery had an outstanding capacity retention of 98.5% after 10,000 cycles at 10 A g^{-1} . In addition, the hierarchical hydrogen bonding moieties in polymer backbones could realize self-healing function [46]. Meanwhile, these formed H-bonds will enhance mechanical strength with the durable network structure.

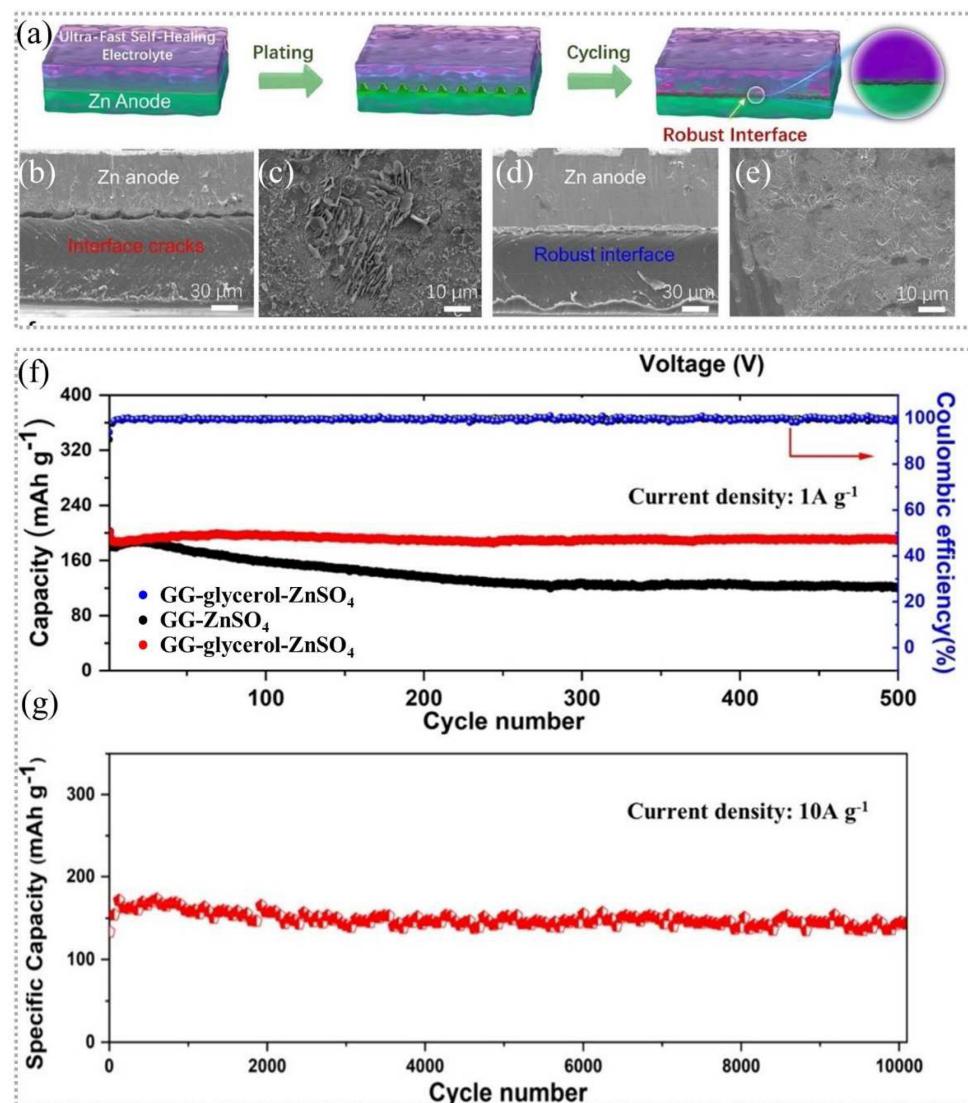


Figure 4. Characterizations of self-healing and self-adaptive interface. (a) Schematic diagram of the dendrite inhibition. (b,c) SEM images of Zn anodes after 250 cycles in the guar gum/ZnSO₄ electrolyte. (d,e) SEM images of Zn anodes after 250 cycles in guar gum/ZnSO₄/glycerol electrolyte. (f) Long-term cycling performance at 1 A g^{-1} . (g) Long-term cycling performance at 10 A g^{-1} . Adapted with permission from Ref. [45]. Copyright 2022 ACS Energy Letter.

The healable gel electrolyte can be divided into two categories. One is the extrinsic healing, and the other is the intrinsic healing. Regarding the first category, this relies on the preliminarily embedded microcapsules or vascular networks, while its wide application is limited by self-healing times. Interestingly, intrinsic healing occurs by some reversible inter-

actions, such as ionic interactions, hydrogen bonding, and so on. In this way, it can not only realize self-healing function but also enhanced mechanical properties. As shown in Figure 5, a self-healing flexible ZIB consists of a PVA/Zn(CH₃COO)₂/Mn(CH₃COO)₂ (named PVA-Zn/Mn) hydrogel electrolyte, a flexible all-in-one cathode (VS₂ nanosheets growing on carbon cloth), and fiber-shaped anodes (electrochemically deposited Zn nanowires) [47]. The PVA-Zn/Mn hydrogel electrolyte has a large amount of –OH group on the PVA chain, which can easily form hydrogen bonds and achieve self-healing functions. Based on the all-in-one cathode and the PVA-Zn/Mn hydrogel electrolyte of the ZIBs, this battery exhibits remarkable electrochemical and mechanical properties, including flexibility and self-healing function. Even after being bent at 60, 90, and 180 degrees, the capacity of ZIBs maintains 110, 121, and 106 mAh g⁻¹, respectively, after 30th cycles, and it delivered a specific capacity of 123 mAh g⁻¹ at 200 mA g⁻¹, even after 40 cycles. Surprisingly, even if the battery is divided into six pieces, it can still self-heal quickly, costing only a little performance loss. In addition, Dang et al. reported the fabrication of ionic conductors by α-lipoic acid (LA) via a solvent-free one-step polymerization method, achieving a re-healable capacity of up to 86% (mechanical and electrical healing efficiencies of 86% and 96%, respectively) [48].

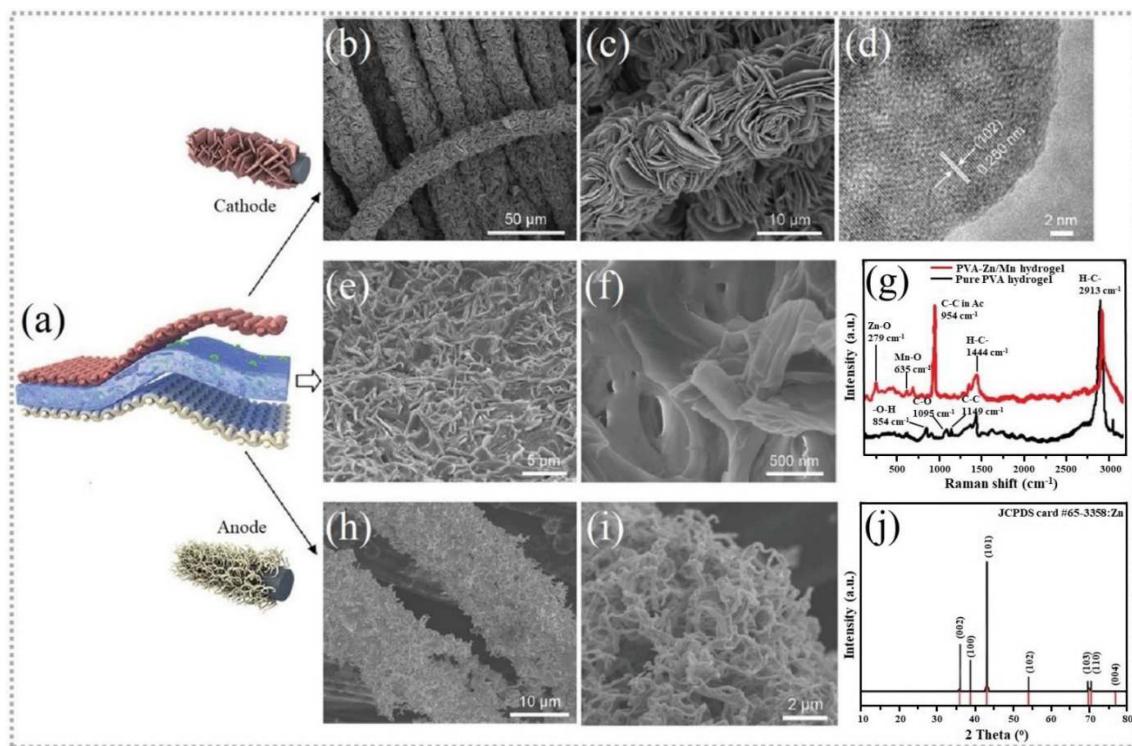


Figure 5. (a) Illustration of the self-healing flexible Zn-ion battery. (b) Low- and (c) high-magnification SEM images of the VS₂ nanosheets/CC cathode. (d) HRTEM image of a VS₂ nanosheet. The lines at the bottom indicate the standard peak position. (e) Low- and (f) high-magnification SEM images of the PVA–Zn/Mn hydrogel electrolyte. (g) Raman shift of PVA–Zn/Mn hydrogel and the pure PVA hydrogel. (h) Low- and (i) high-magnification SEM images of the Zn nanowires/CC anode. (j) XRD pattern of the Zn/CC anode. Reprinted from Ref. [47].

3.3. Gel Polymer Electrolytes

Gel polymer electrolyte (GPE) is an electrolyte material that forms a stable gel by a metal salt medium, a solvent, a liquid plasticizer, and a polymer host matrix. The polymer and plasticizer are both continuous phases. The GPE reduces the production safety problems such as electrode corrosion and oxidative combustion caused by the leakage of liquid electrolytes. Up to now, GPEs have become one of the development trends in the commercial application

of metal-ion batteries. The phase existence state of the GPE is complex and consists of three phases: crystalline phase, amorphous phase, and liquid phase. The crystalline phase consists of the crystalline part of the polymer, the amorphous phase consists of the amorphous part of the polymer swollen by the plasticizer, and the liquid phase consists of the plasticizer and metal salts in the polymer pores. GPE polymers are in a crosslinked state, similar to hydrogel electrolytes with two ways of physical and chemical crosslinking. The commonly used gel polymers in ZIB batteries include polyvinylidene fluoride (PVDF), vinylidene fluoride hexafluoropropylene copolymer [P(VDFHFP)], PEO, polyacrylonitrile (PAN), polymethacrylic acid Methyl ester (PMMA), and so on. A carboxymethyl cellulose/Zn salts (CMC/ZnSs) complex-based GPE is fabricated by dissolving the Zn salts into CMC with a mass ratio ranging within 0–30 wt% in 1 wt%, in which the Zn salts include zinc acetate (ZnA), zinc sulphate (ZnS), and zinc triflate (ZnT) [49]. The mechanical properties of the GPE change with different zinc salt concentrations. With the zinc salts content of 15%, the tensile strength is 46.7, 58.9, and 68 MPa for CMC compared with ZnA, ZnS, and ZnT, respectively, (Figure 6a), which is higher than the 35.6 MPa for CMC. When the mass ratio of ZnA is equal to 15 wt%, the GPE achieved a maximum ionic conductivity of 2.10 mS cm^{-1} . When the above GPE used, the symmetric Zn//Zn cell shows a stable plating/stripping process at $0.5\text{--}10 \text{ mA cm}^{-2}$ and the small overpotential from 45 to 175 mV without any damage over 225 h. A zinc–nickel battery is fabricated by the potassium polyacrylate (PAAK)-KON highly hydrophilic GPE, Zn anode, and the Ni(OH)_2 cathode [50]. This has the merits of the high elastic modulus and limited content of free water, which could inhibit a series of critical problems, such as dendrite formation, corrosion, and the shape change of the Zn anode during the charge–discharge progress (Figure 6b–e). The PAAK-KON GPE is prepared by stirring 0.643 g PAAK and 10 g KOH aqueous electrolyte fusion for one hour, and then allowing the mixed electrolyte to stand for 10 h. The high water content of the PAAK-KOH GPE could improve the ionic conductivity, while the freeze-dried PAAK-KOH GPE are equipped with a highly porous matrix, which could contain amounts of water, both for free water and bound water. As a result, the PAAK-KON GPE exhibits a prolonged lifetime of approximately 776 h and an excellent shelf life of more than 431 h. It even has an excellent cycling performance after floating charge for over 400 h at 60°C .

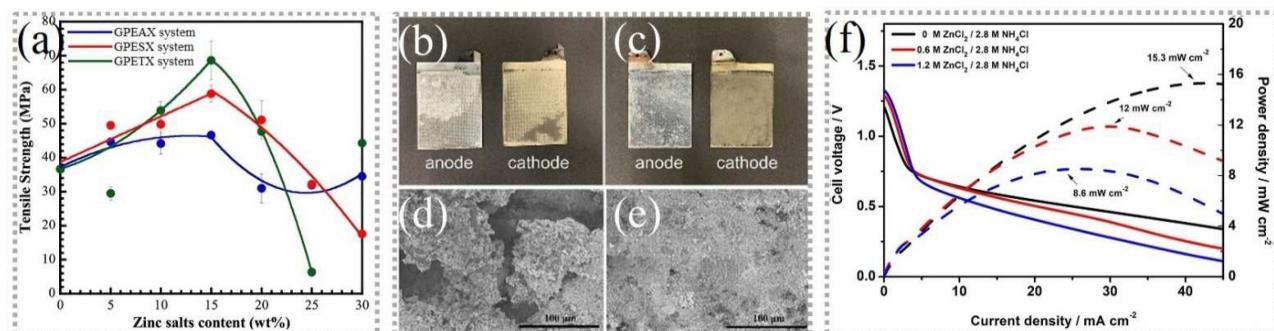


Figure 6. (a) Tensile strength of CMC with different zinc salts and concentration. (Blue) GPEAx system, (red) GPESx system, and (green) GPETx system. Adapted with permission from Ref. [49]. Copyright 2021 Scientific Reports. (b) After 368 h in KOH aqueous electrolytes and (c) 431 h in PAAK–KOH GPE. SEM image of Zn anode after standing for (d) 368 h in KOH aqueous electrolyte and (e) 431 h in PAAK–KOH GPE. Adapted with permission from Ref. [50]. Copyright 2022 ACS Applied Materials & Interfaces. (f) The galvanodynamic discharge curves and the corresponding power density plots of FZABs with the GPEs soaked in the electrolytes containing 2.8 M NH_4Cl and (1) 0, (2) 0.6, and (3) 1.2 M ZnCl_2 . Adapted with permission from Ref. [51]. Copyright 2022 Electrochemistry Communications.

GEP not only has a good application in ZIBs but also has made some breakthroughs in zinc–air batteries (ZABs). The near-neutral electrolytes using chloride-based GEP have the advantages of long-term cycling stability and safe environment compared with alkaline

electrolytes, such as those that could inhibit dendrite growth, ORR, and OER [51]. The chloride-based GEPs are prepared by immersing a quasi-solid PVA gel in a chlorine-based electrolyte ($\text{ZnCl}_2/\text{NH}_4\text{Cl}$) for 48 h, in which the PVA is prepared by freezing–thawing methods. According to the content of ZnCl_2 , three types GPEs are constructed, namely 0 M $\text{ZnCl}_2/2.8$ M NH_4Cl , 0.6 M $\text{ZnCl}_2/2.8$ M NH_4Cl , and 1.2 M $\text{ZnCl}_2/2.8$ M NH_4Cl . The results show that the concentration of ZnCl_2 has a certain regulating effect on the performance of the battery. After ZABs are fabricated, the ZABs with a GPE containing 0.6 M $\text{ZnCl}_2/2.8$ M NH_4Cl exhibits an excellent power density of 12 mW cm^{-2} under the condition of a large current density of 10 mA cm^{-2} and a bending angle of 90 degrees (Figure 6f).

3.4. Thermoreversible Gel Electrolytes

Recently, high energy and high-power densities for the batteries have been obstructed by the problem of thermal runaway. Meanwhile, the batteries may cause a series of safety problems in the process of rapid charging and discharging, such as catching fire or exploding. While the application of fusible switches, extinguishing agents, and shut-off current collectors can combat the above issues, these measures do not allow the battery to return to its original state after cooling. Fortunately, this defect can be well-resolved by the application of thermos-reversible gel electrolytes.

Thermoreversible gel electrolytes can be prepared from various polymers and high-temperature solvents by gel casting [52], such as PVDF/dimerhylformamide (DMF), poly(ethylene terephthalate) (PET)/N-methyl-1,2-pyrrolidinone (NMP), poly(hydroxybutyric acid) (PHBA)/N,N-dimethylacetamide (DMA), and so on. Each of above exhibits excellent ionic conductivity, even at -20°C (up to 10^{-3} Scm^{-1}) and storage modulus (approximately 105 Pa) [53]. These electrolytes are usually liquid below room temperature and can quickly transform into solid gels once heated above a critical temperature. Encouragingly, this phase transition is reversible and shows the excellent temperature sensitivity due to their physical entanglement and non-covalent interactions of laterally associating polymer helices in extended junction regions. Therefore, thermos-reversible gel electrolytes may be good candidate material for designing advanced batteries with intelligent thermal loading. The ploy(ethyleneoxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) and poly(N-isopropylacrylamide-acrylamide) (PNIPAM/AM) have the properties of thermos-reversible properties, which were treated as smart materials. For instance, Zhao et al. [54] reported a smart flexible ZIB with cooling recovery ability using thermos-reversible gel electrolytes, which are prepared by adjusting an aqueous solution with 0.25 M $\text{ZnSO}_4/0.25$ M Li_2SO_4 and mass of PEO-PPO-PEO. These electrolytes transfer from hydrophobic gel state to hydrated sol state when the temperature changes from 25°C to -5°C . Two types of ZIBs are assembled by using $\text{Zn}/\text{LiFePO}_4$ (Zn/LFP)- or $\text{Zn}/\text{LiMn}_2\text{O}_4$ (Zn/LMO)-based electrodes. They could be recovered within five minutes with gel–sol reversibility and without sacrificing ZIB performance. Furthermore, a temperature-sensitive sol–gel transition-state electrolyte of proton-state polymer (N-isopropylacrylamide-co-acrylic acid) (PNA) is used in a rechargeable $\text{Zn}/\alpha\text{-MnO}_2$ battery system [55]. After heating above the lower critical temperature (20°C), the gelation process occurs in the sol–gel electrolyte containing PNA, which inhibits the migration of zinc ions and thus shuts down the battery. After the battery cools, the electrolyte turns into a liquid state, and Zn ions can shuttle through the electrolyte, restoring the battery's original electrochemical performance (Figure 7). Unlike conventional strategies, the sol–gel electrolyte endows the thermally responsive battery with dynamic charge–discharge rate performance at different temperatures, thereby enabling “smart” thermal control of the battery.

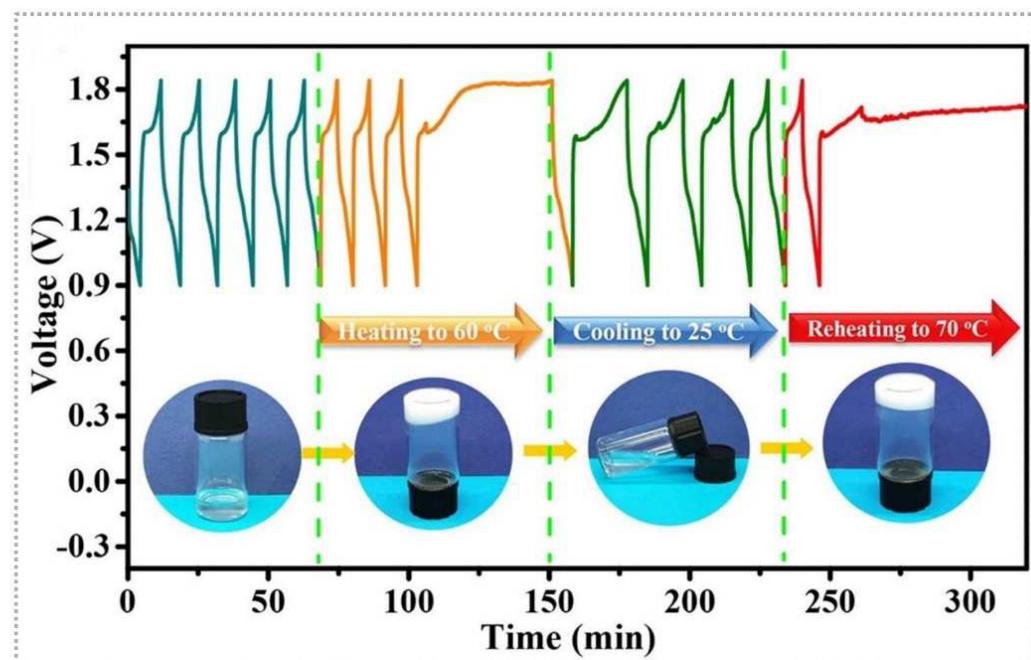


Figure 7. Charge-discharge cycles of the Zn/α-MnO₂ battery with PNA sol-gel electrolyte at different temperatures, and the digital photos of reversible sol-gel transition. Adapted with permission from Ref. [55]. Copyright 2018, Science Bulletin.

3.5. Additional Functions of Gel-State Electrolytes

In recent years, ZIBs have received great research attention, while it still faces many challenges under some extreme conditions. The additional functions of ZIBs are one direction for battery research. One of the proven ways is to develop multifunctional electrolytes with special functions. Thus, Zn-based electrolytes with special functions will be discussed in this section.

3.5.1. Antifreeze Gel Electrolytes

Conventional GPEs inevitably freeze at low temperatures and lose their elasticity, which seriously affects the electrochemical performance of ZIBs and their practical applications in extremely cold environments. Therefore, it is necessary to develop antifreeze GPEs to adapt to low-temperature scenarios [56]. The ideal antifreeze GPE needs to meet the requirements of having a low freezing point, being non-toxic and harmless, and possessing excellent ionic conductivity and mechanical properties. For example, hydrogel electrolytes, as typical gel electrolytes, can be divided into the following three types according to their bound water content: (1) strongly bound water (SBW), (2) weakly bound water, and (3) non-bound water (NBW). As the water will be frozen at 0 °C, the freezing temperature of NBW is 0 °C. However, the SBW have a lower freezing temperature (approximately –100 °C) compared with NBW, due to little free water content. Three strategies are proposed to address the problem of the freezing temperature of gel electrolytes. One of most effective methods to lower the freezing point is introducing salt solutions into electrolytes. This is similar to using sodium chloride (NaCl) to solve the problem of road icing. For example, high-concentration zinc salts (ZnCl₂) are mixed with xanthan gum to prepare new quasi-solid-state electrolytes for ZIBs (Figure 8a), which could depress its freezing point to –20 °C [57]. On the basis of this electrolyte, the ZIBs exhibits a discharge capacity of 119 mAh g^{–1} at –20 °C (Figure 8b), and maintains 83% of the initial capacity after 450 cycles at 0.5 A g^{–1} at the same temperature of –20 °C.

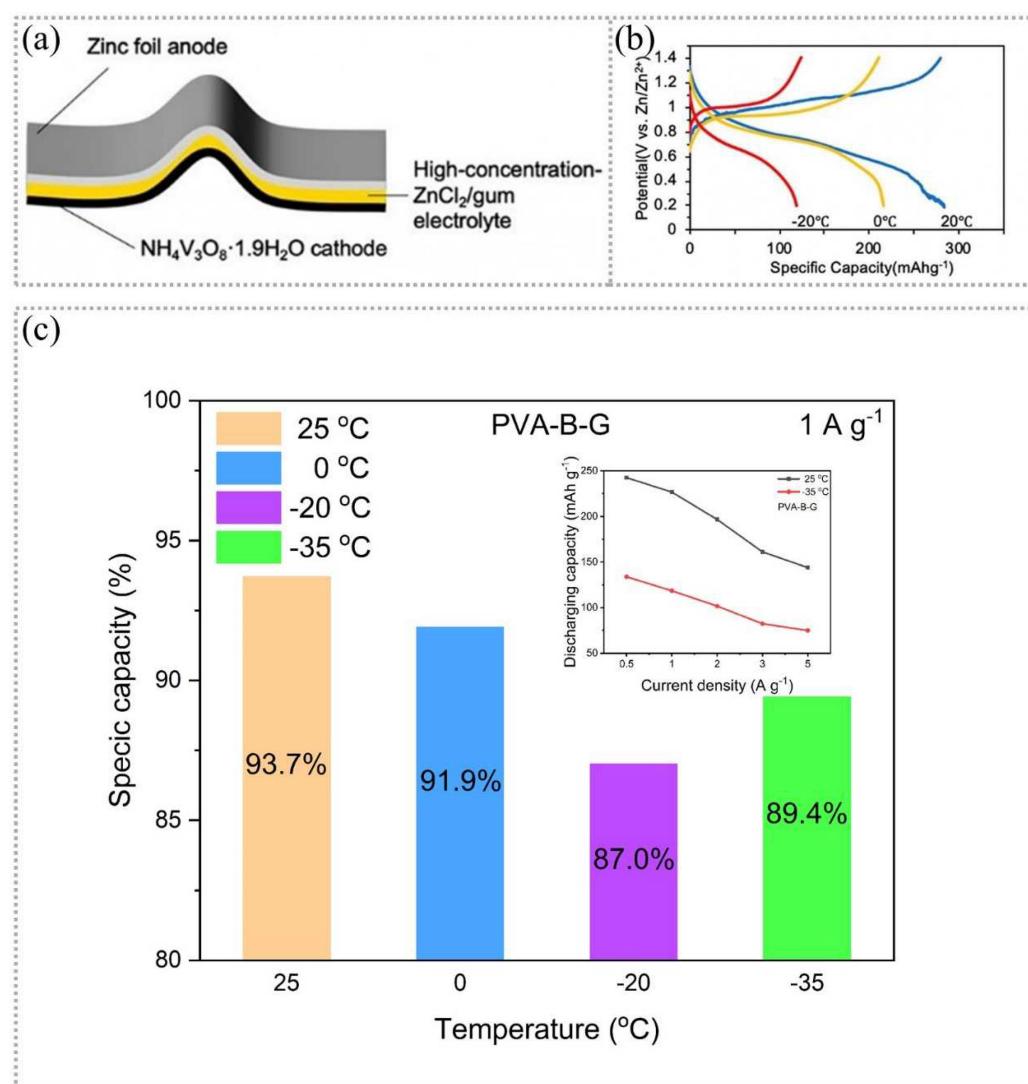


Figure 8. (a) Schematic illustration showing the cross-section view of a HCSE battery with zinc foil anode, high-concentration ZnCl_2 /xanthan gum electrolyte, and the $\text{NH}_4\text{V}_3\text{O}_8 \cdot 1.9\text{H}_2\text{O}$ cathode sandwiched together. (b) Galvanostatic discharge/charge curves of the HCSE battery cycled under 0.2 A g^{-1} at 20 , 0 , and -20 $^{\circ}\text{C}$, respectively. Adapted with permission from Ref. [57]. Copyright 2020 ACS Applied Energy Materials (c) After 2000 cycling performances of the PVA-B-G battery at 1 A g^{-1} at different temperatures, compared with the 1st cycle at 25 , 0 , -20 , and -35 $^{\circ}\text{C}$, respectively. The inset of the figure presents the rate performances of PVA-B-G at 20 and -35 $^{\circ}\text{C}$ [58].

The introduction of polyol solvent is another way to realize the antifreeze function of the gel electrolyte. Low-molecular-weight alcohols, such as glycerol (G) and ethylene glycol (EG), are well-known non-toxic antifreeze agents that are widely used as engine coolants in industry. The freezing point is lowered due to the fact that in the alcohol–water binary solution, alcohols and water molecules form stable molecular clusters to compete with the hydrogen bonds in water in the process. As a result, the saturated vapor pressure of water is reduced, and the formation of ice crystal lattices is destructed. However, due to the low molecular weight of alcohols and the absence of double bonds, the hydrogels prepared by traditional polymerization methods have poor stability and mechanical properties. In order to meet the practical application of antifreeze GPE under extremely cold conditions, Chen et al. designed a PVA-B-G (borax denoted as B) antifreeze hydrogel electrolyte, in which G can strongly interact with PVA, and the freezing point of this gel-state electrolyte is under -60 $^{\circ}\text{C}$. This ZIB battery could work at -35 $^{\circ}\text{C}$ with a high ionic conductivity of

10.1 mS cm⁻¹ and a high energy density (25.8 mW h cm⁻³). It still exhibited approximately 90% initial capacity retention after more than 2000 cycles when the temperature was equal to -35 °C (Figure 8c) [58].

Gel network modification is another excellent strategy to decrease the freeze point. For example, Mo et al. [59] synthesized a special hydrogel electrolyte, which is copolymerized EG-based waterborne anionic polyurethane acrylates (EG-waPUA) and acrylamide (AM) through a free radical polymerization (FRP) method. These EG-waPUA/PAM hydrogel electrolytes present the strong H-bonding interactions among themselves and water, which could realize the function of anti-freezing at subzero temperatures. Benefiting from the covalent interaction of the laterally associated EG-waPUA polymer chains and the PAM polymer chains with sufficient intramolecular hydrogen bonding, this double crosslinked structure endows the hydrogel with excellent mechanical properties and good low-temperature electrochemical performance. The antifreeze battery Zn//MnO₂ battery delivers an 80% room temperature capacity and ~100% Coulombic efficiencies at -20 °C.

In addition to these strategies, frost resistance of natural-polymer-based GPEs provides new ideas. The nano-confinement method separates and confines water in hydrogels to the nanoscale through polymer networks, which can effectively inhibit the formation of hydrogen bonds between water molecules, resulting in supercooling of water in hydrogels. The supramolecular hydrogel of dimethylacrylamide (DMA) and 2-(N-ethylperfluorooctane sulfonamido)ethyl acrylate (FOSA) copolymers is employed to partially inhibit crystallization due to hydrophobicity water confinement (<2 nm) between FOSA nanodomains. Consequently, the hydrogel displays a stronger supercooling effect, which is able to keep 45% of the water in the hydrogel from freezing at -68 °C [60]. Therefore, the nanoconfinement effect for anti-freeze gel electrolytes is capable of ZIB operation under extreme conditions. The CO₂-derived cyclic carbonate crosslinked with potassium polyacrylate/PAM fabricated by a replacement method, also demonstrates good anti-freezing properties and excellent flexibility at low temperatures [61]. It displayed high flexibility and good specific capacity up to 80.4% at -20 °C. Thus, the antifreeze replacement method is to controllably replace the water in the hydrogel with an organic antifreeze, which not only directly reduces the water content in the hydrogel, but also directly reduces the hydrogen bond energy formed between the water molecules and the antifreeze molecules. The interaction between the polymer network in the gel and the mixed solvent further limits the crystallization of water molecules. With the same method, the anti-freeze composite GPE with high ionic conductivity (6.19 mS/cm) is prepared by introducing antifreeze EG into guar gum (GG)/sodium alginate (SA) hydrogel. The assembled ZIBs employing this anti-freezing electrolyte deliver high specific capacity of 181.5 mAh g⁻¹ at 0.1 A g⁻¹ and good cyclic stability, with 80.39% initial capacity retained over 100 cycles at -20 °C [62].

In the future development of antifreeze gel electrolytes, the combination of two/multiple antifreeze strategies in the preparation of antifreeze electrolytes can exert a synergistic effect, combining the advantages of antifreeze and electrical conductivity. Meanwhile, the electrolyte with high mechanical strength and flexibility and relatively high ionic conductivity maintained at low temperature plays an important role in smart wearable devices that can be used in extreme conditions.

3.5.2. Self-Protected Gel Electrolytes

Most batteries could explode under hazardous conditions, such as overpressure and overheating. To dissipate the heat accumulated during battery operation, many studies have adopted physical safety designs, such as fuse circuit breakers and fire-extinguishing agents to prevent safety issues. Unfortunately, these methods only provide one-time protection and cannot achieve reversible recovery. Advanced methods for developing dehydration-resistant gel-state electrolyte and thermally stable energy storage devices have a view to providing new ideas for developing ZIBs at extreme high temperatures. Similar to the method of antifreeze GPEs, this can also be achieved by adding salt and polyol and modifying the network of gel. This method can effectively reduce the presence of free

water, which, in turn, reduces the evaporation of free water inside the battery. Introducing inorganic particles into electrolyte is also regarded as an effective approach for reducing dehydration. For example, adding silica (SiO_2) into PVA can effectively alleviate free water from dehydration [63]. In addition, a temperature-responsive poly(N-isopropylacrylamide-co-N-methacrylic acid propylene amide) (PNIPAM/NMAM) GPE that is solid at room temperature is designed to avoid liquid leakage [64]. As the temperature increases, hydrogen bonds are gradually formed between the PNIPAM/NMAM molecular chains, which cut off the ion transport channels inside the electrolyte and spread on the surface of the electrolyte (as shown in Figure 9). The upper surface changes from hydrophilic to hydrophobic, which limits the movement of free ions. This temperature-responsive GPE can resist thermal runaway and achieve reversible protection.

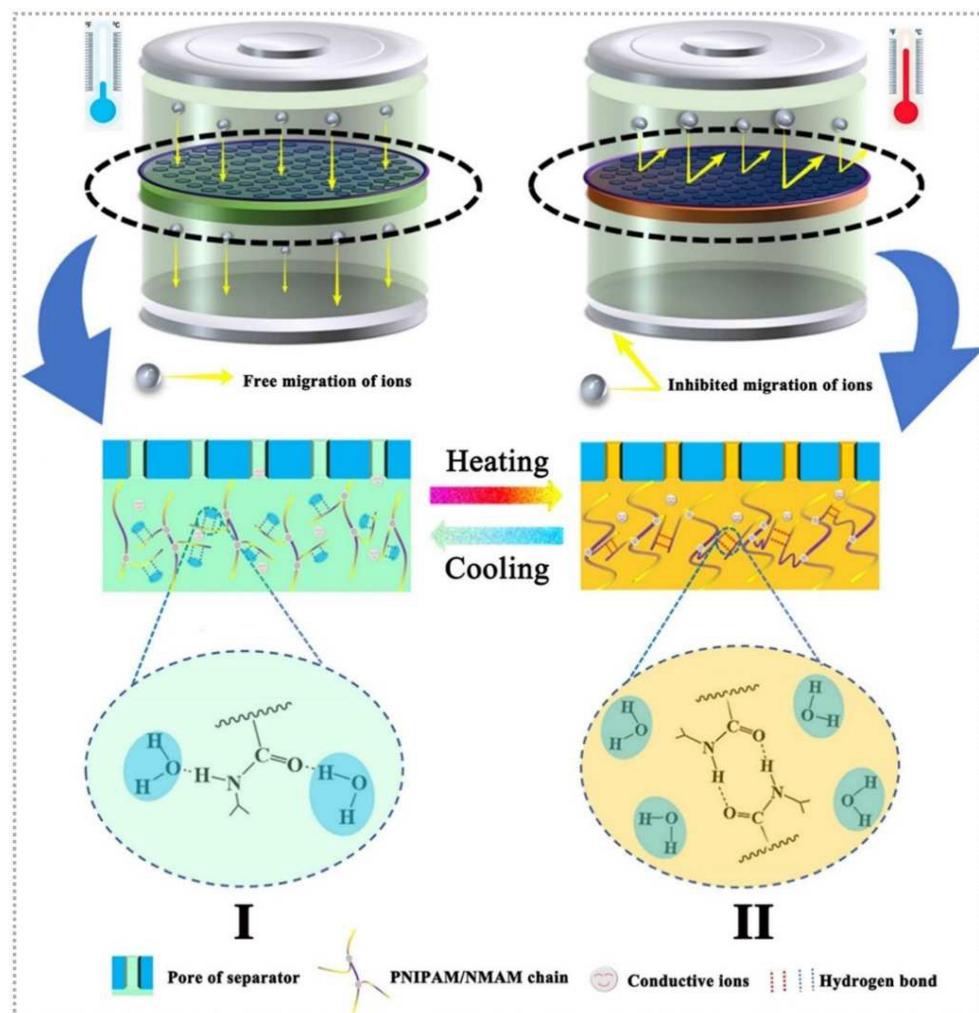


Figure 9. Schematic illustration of the self-protection/thermal-switching function enabled by PNIPAM-co-NMAM polyelectrolytes in the energy storage devices. Thermal-responsive self-protection mechanism of the PNIPAM-co-NMAM polyelectrolyte at low temperature (I) and high temperature (HT) (II). Reprinted with permission from Ref. [64]. Copyright 2021 ACS Applied Energy Materials.

The performance of ZINs by using different gel-state electrolytes is presented in Table 1. In addition, the application of these gel electrolytes can effectively improve the performance of the battery. In this way, the maximum energy density of ZINs mentioned in this review is as high as 481.0 Wh kg^{-1} at 0.211 kW kg^{-1} and maintained approximately 182.6 Wh kg^{-1} at 8.016 kW kg^{-1} [62]. The higher volumetric energy density is up to 127 Wh L^{-1} for the batteries, which is based on the PAAK-KOH gel [50]. For the current battery electric

vehicles (BEVs), such as Nissan and Tesla Model S, the pack-level energy densities are equal to 90 Wh L^{-1} (70 Wh kg^{-1}) and 210 Wh L^{-1} (130 Wh kg^{-1}), respectively [65]. Considering that in practical applications, the energy density of these ZINs may decline, the gel-state ZINs are still expected to be applied to the field of BEVs. The gel-state electrolytes demonstrate excellent properties in diversified aspects of alleviated dendrite growth, electrode materials dissolution, high elastic modulus, self-healing, anti-freezing, and self-protection. Although tremendous efforts have been made to develop gel-state electrolytes in ZIBs, many challenges still exist in the current research as follows:

1. Compared with water solutions, the ionic conductivity of gel-state electrolyte is insufficient, which is mainly due to the easy crystallization of gel electrolytes at room temperature. For example, PEO is a semi-crystalline polymer at room temperature, and its segmental kinetics in the crystalline region are weak, resulting in poor ionic conductivity ($10^{-8} \sim 10^{-5} \text{ s/cm}$) and small ion mobility numbers;
2. The thermal stability and electrochemical stability need to be further improved. GPE with poor thermal stability will affect the safety of ZIBs, to a certain extent. For example, water in the electrolyte vaporizes at high temperatures, increasing the pressure inside the battery. On the other hand, GPE will absorb more water in an aqueous environment, leading to poor electrochemical performance of the batteries;
3. Mechanical stability of gel-state electrolyte needs to be further improved. Although single-component polymer electrolytes can exhibit high ionic conductivity, the mechanical strength still needs to be enhanced. Multicomponent gel electrolytes are expected to solve the durability challenges, for which the formation of composite structures or hierarchical structures by chemical bonds or the combination of polymer networks and gel electrolytes provides a good basis for improving mechanical stability;
4. For high-performance ZIB construction, especially for flexible batteries, it is necessary to enhance the durability of the Zn metal anode, such as strengthening the mechanism of stabilizing the anode and improving the performance of electrode materials;
5. The wider electrochemical potential window of gel-state electrolytes should be developed to adapt the using for high-voltage aqueous flexible batteries;
6. The interface problem between electrode and electrolyte needs to be optimized. This is mainly because the gel electrolyte is in solid-solid interface contact. Although there is liquid solution in the network of the polymer matrix, the liquid content is relatively small, and the contact is not as good as for a liquid solution;
7. Although the current ZIBs based on gel electrolytes have various breakthroughs in some respects, the development and design of multifunctional gel electrolytes are still challenging.

Although the above problems can be solved by adding zinc salts/fillers, developing multi-component/composite SPE, exploring ionic liquid-based polymer electrolytes, and other strategies, they are currently not enough to meet the commercialization standards. Based on the above problems and discussion, there are some prospects of gel-state electrolytes that ZIBs displayed. Gel-state electrolytes in ZIBs may become a breakthrough point for flexible electronic energy storage devices due to their unique properties. In other words, gel-state electrolytes could be used in other metal-ion batteries, such as aluminum-ion batteries (AIBs), which could overcome some shortcoming of ZIBs, and the application of multifunctional batteries could be realized. Conversely, this method may also effectively promote the development of ZINs. With the in-depth research, we hope to usher in this development someday when it is commercialized.

Table 1. The performance of ZINs by using diffident gel-state electrolyte.

Electrolyte	Condition	Function	Reference
PVA + methanesulfonic acid	Current density (A g^{-1})/cycles 2/500	Capacity retention 92.7%	[43]
	-/2000	88.1%	
	Temperature ($^{\circ}\text{C}$)/cycles -10/1000	Capacity retention 96%	
Guar gum/ZnSO ₄ /glycerol	Current density (A g^{-1})/cycles 10/10,000	Capacity retention/Capacity (mAh g^{-1}) 98.5%/-	[45]
	1/5000	-/200	
	Bending/current density (A g^{-1})/cycles 60/-/30	Capacity (mAh g^{-1}) 110	
PVA-Zn/Mn	90/-/30	121	[47]
	180/-/30	106	
	-/200/40	123	
	condition 0.5–10 mA cm^{-2}	State	
CMC/ZnSs	Overpotential:45–175 mv/225 h	Plating/stripping stability No damage	[49]
	Temperature ($^{\circ}\text{C}$)/Time (h) 60/400	State Excellent cycling performance	
PEO-PPO-PEO + 0.5 M ZnSO ₄ /0.25 M Li ₂ SO ₄	Temperature changing ($^{\circ}\text{C}$) 25–5	State Gel–sol reversibility	[54]
PNA	Temperature changing ($^{\circ}\text{C}$) 20–70	State Gel–sol reversibility	[55]
ZnCl ₂ + xanthan gum	Temperature/current density (A g^{-1})/cycles -20/-/-	Capacity retention/Capacity (mAh g^{-1}) -/83%	[57]
	-/0.5/450	119/-	
	Temperature ($^{\circ}\text{C}$)/cycles -35/2000	Capacity retention 90%	
EG-waPUA/PAM	Temperature ($^{\circ}\text{C}$) -20	Capacity retention 80%	[59]

4. Conclusions

In this paper, a comprehensive review of gel-state electrolytes and their applications in ZIBs is presented. Meanwhile, the challenges faced in their development are summarized and analyzed, and prospects are also put forward. Although the application of gel-state electrolyte in ZIBs is still in its infancy, its advantages allow for an improved application scenario for ZIBs. With the development and application of multifunctional gel electrolytes and the continual optimization and development of corresponding electrode materials, we believe that ZIBs will shine in the fields of large-scale energy storage and smart flexibility in the future.

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