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Review Article

Advancements in the Exploration of Gel Electrolytes for Aqueous Zinc Ion Batteries

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Abstract

Aqueous zinc-ion batteries (ZIBs) are seen as a superior substitute for lithium-ion batteries (LIBs) due to their excellent safety, low cost, and eco-friendliness. However, problems such as zinc dendrite growth, hydrogen evolution reaction and electrode corrosion hinder the commercialization of batteries. Electrolyte as a link to other parts of the battery, has been widely concerned. Hydrogel is a kind of cross-linked product filled with water, which has the advantages of high theoretical capacity, good flexibility, good water retention and good mechanical properties, and becomes a potential candidate for ZIBs. By summarizing the development of hydrogel electrolytes, the cross-linking types of gel electrolytes and their applications in ZIBs were reviewed in this paper. Finally, the application of gel electrolyte in ZIBs is summarized and prospected, which brings a meaningful reference for the development of ZIBs.

Keywords: Aqueous zinc ion battery; gel electrolyte; Zinc dendrite; Corrosion

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1. Introduction

With the swift expansion of the worldwide economy, the utilization of energy is increasing day by day. Energy and its environmental problems have gradually become the focus of human social development. The traditional energy we use now, such as oil, coal, etc., will produce low capacity utilization, environmental pollution and high cost problems [1]. As a result, researchers are focusing on renewable, sustainable low-carbon energy sources such as tidal, solar, wind and biofuel [2]. However, because these clean energy sources are easily affected by external factors such as seasons and weather, rechargeable batteries with stable energy storage become the optimal solution for current energy supply among these intermittent energy sources [3-5].

Lithium metal battery is the most commonly used battery. It has the advantages of high specific capacity (3860 mAh.g^{-1}), very low electrode potential (-3.04 V vs standard hydrogen electrode), high energy density, etc., which makes it a perfect choice for the negative electrode material in batteries with high voltage and high energy capabilities [6]. Lithium-ion batteries have been effectively marketed and are extensively

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utilized in electric vehicles and portable electronic devices. However, there are still many problems to be solved in LIBs: (i) the resource; reserves of lithium metal on Earth are scarce; (ii) The materials required for lithium-ion battery assembly are expensive; (iii) The natural electrolytes employed in lithium batteries are highly susceptible to moisture and oxygen in the atmosphere, and are flammable and explosive, which to a large extent hinder the further promotion and application of lithium batteries, especially in large-scale power grid energy storage and wearable device applications [7]. Therefore, the development of alternative multivalent metal rechargeable batteries has become particularly urgent. Metal ion batteries, such as Zn^{2+} [8,9], Ca^{2+} [10,11], Mg^{2+} [12,13] and Al^{3+} [14,15], all have high capacity and energy density, but the electrochemical REDOX voltage of metal ions, such as Ca^{2+}, Mg^{2+}, and Al^{3+}, exceeds the stable potential of water (Figure 1a) [16]. Only zinc metal can be directly used as the negative electrode of aqueous electrolyte, which limits the application of metal ion batteries other than zinc. Based on this, people favor the development of high energy density, high capacity and low cost energy storage systems based on zinc metal.

The earliest rechargeable water-based zinc-ion battery (ZIB) can be traced back to the $Zn/ZnSO_4/MnO_2$ system first developed by Yamamoto et al in 1986. In comparison to other metal ion batteries, Zn ion batteries possess the benefits of a substantial theoretical capacity (820 mAh.g^{-1}, 5854 mAh.cm^{-3}), a low reoxidation-reduction potential (-0.763 V vs standard hydrogen electrode SHE), non-harmful nature, plentiful reserves (300 times greater than lithium). and other advantages. It has stable thermodynamic properties in water medium[16-18]. In addition, zinc metal has a good tolerance to oxygen and moisture in the air compared to other active metals. So far, the research on ZIBs has achieved rich results [16,19,20].

However, there are still some problems and challenges with ZIBs (Figure 1b). For example: (i) zinc dendrites are generated in a liquid elec-

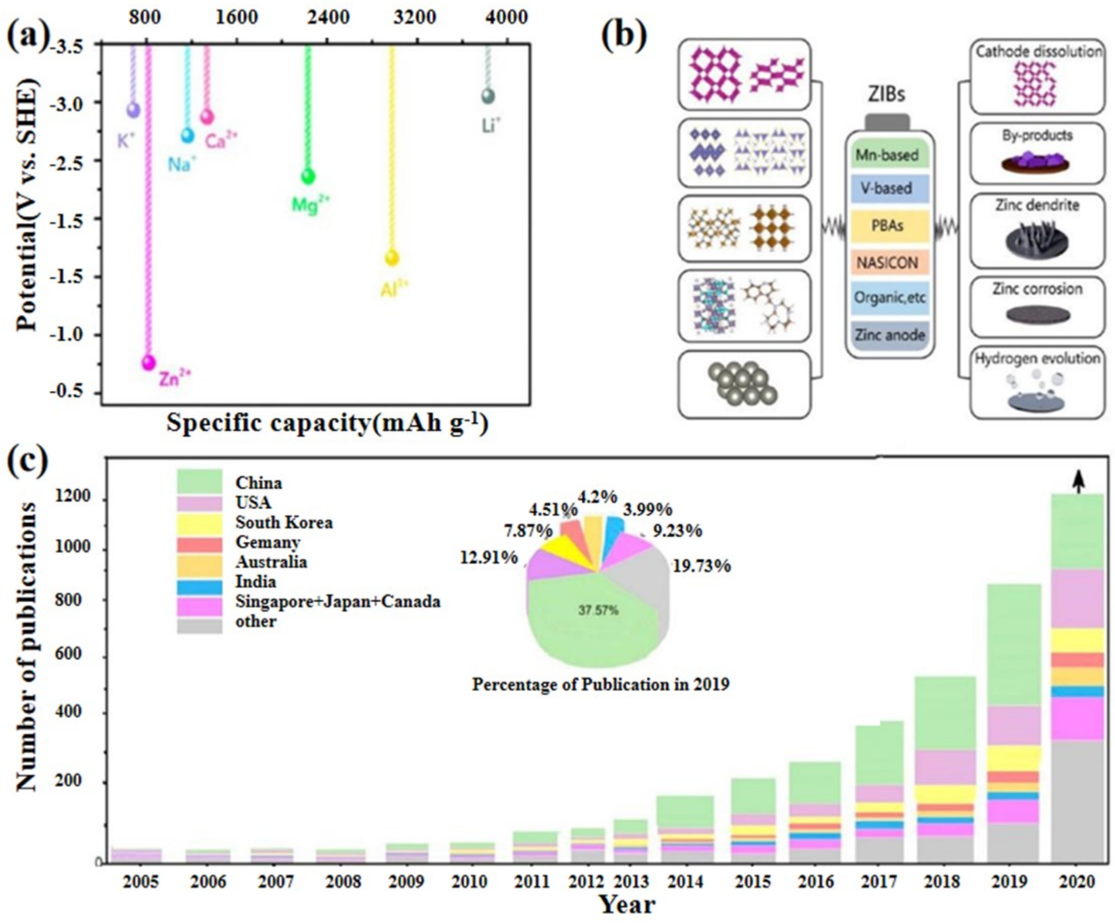


Figure 1. (a) Comparison of standard electrode potentials and theoretical capacities of various metal anodes[16]. (b) The main electrode materials of ZIB and their problems. (c) Comparison of the number of publications on ZIBs until December of 2020 [28].

trolyte environment, which can penetrate the diaphragm and result in a disruption of the battery's electrical flow; (ii) During the cycle, hydrogen evolution reaction will inevitably occur, and the hydrogen generated will expand the volume of the battery and lead to short circuit; (iii) Some positive electrode materials of zinc-based batteries will dissolve in aqueous solution to varying degrees, leading to a gradual decrease in battery efficiency [13,15]. The results show that these problems can be solved by hydrogel electrolyte. Firstly, saturated hydrogels can disintegrate different salt ions, which can deliver ion conduction necessary for electrochemical reactions. Secondly, the hydrogel electrolyte has unique quasi-solid characteristics, which combines the benefits of liquid electrolyte and solid electrolyte, which can not just efficiently stop the escape of fluid, but also restrain the development of Zn dendrites to some degree. A certain mechanical strength also makes the hydrogel electrolyte can alleviate the hydrogen evolution reaction produced by the water-based zinc ion battery, and reduce the volume change of the battery during the cycle. In addition, the hydrogel electrolyte can be tightly fitted to the electrode due to its soft and wet interface. Thanks to the above advantages, the combined application of hydrogel electrolyte and water zinc-ion battery shows good potential.

In recent years, the utilization of hydrogel electrolyte in ZBIs has made many breakthrough progress (Figure 1c). The continuous development of its functions enables the battery to have other practical functions in addition to the original energy storage function, such as extreme deformation tolerance [21,22] and environmental flexibility involving prevention of freezing and prevention of dehydration [23,24]. Through the meticulous creation of functional hydrogel materials based on polymer chemistry and polymer engineering technology, external stimulus responsiveness such as thermal responsiveness and self-healing has been achieved [25-27], and these breakthroughs provide a broader space for the development of multi-functional energy storage systems. Different gel electrolytes have different applications according to different designs, so it is necessary to study the gel electrolytes in more detail.

The purpose of this review is to clarify the working principle and challenges of ZIB. Gel electrolytes are divided into non-crosslinked, physical crosslinked and chemical crosslinked by cross-linking types. Finally, the application of gel electrolytes in ZIBs is summarized and prospected. It provides important significance for the optimization and modification of gel electrolyte.

2. Principles and problems of water zinc-ion batteries

2.1. Reaction Mechanism

Aqueous zinc-ion batteries (ZIBs) usually use the solution containing Zn^{2+} as the electrolyte, and the cathode materials are primarily tunnel architectures with numerous ion channels or stratified architectures with significant layer spacing, such as V_2O_5, MnO_2, etc. According to the different mechanism of charge and discharge process, anode materials can be divided into two categories: (1) Zn is the anode material (Figure 2a), Zn^{2+} is embedded and de-embedded from the electrode surface, and (2) anode materials with Zn^{2+} intercalation (such as Mo_6S_8, Figure 2b) [29].

(1) The reaction mechanism of Zn as a material for the anode is as follows:
(a) in neutral or weakly acidic electrolytes:

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

(b) in alkaline electrolytes:

$$Zn + 4OH^- \leftrightarrow Zn(OH)_4^{2-} + 2e^-$$

$$Zn(OH)_4^{2-} \leftrightarrow ZnO + 2OH^- + H_2O$$

(2) The reaction mechanism of anode material with Zn^{2+} intercalation is as follows: Zn^{2+} intercalation has a reversible ion channel to facilitate the insertion of Zn^{2+}, which does not contain zinc metal. According to different materials, the reaction mechanism is different. Take Mo_6S_8 as an example:

$$Zn^{2+} + Mo_6S_8 + 2e^- \rightarrow ZnMo_6S_8$$

$$Zn^{2+} + ZnMo_6S_8 + 2e^- \rightarrow Zn_2Mo_6S_8$$

2.2 Problems caused by water zinc batteries

Although zinc has the advantages of high theoretical capacity, low potential, safety and so on, it is considered to be the ideal negative electrode material for water-based batteries, but in practical application, there have been a variety of problems, such as: low Coulomb Efficiency (CE), zinc dendrite formation, hydrogen release reaction, corrosion of zinc electrode, and similar phenomena [30].The specific analysis is described as follows:

2.2.1 Growth of zinc dendrites

In the cycle of zinc battery, the growth of zinc dendrites has an important effect on the stability and life of the battery. In alkaline solution, the growth of zinc dendrites will be more serious because of its high electrochemical activity [31]. The occurrence of zinc dendrites is primarily due to the spreading of $Zn(OH)_4^{2-}$ in the electrolyte to the protrusion on the surface of the Zn electrode. The regional flow intensity in the protrusion is greater than that in other areas, leading to an uneven distribution of current on the electrode. Therefore, under the action of the tip effect, Zn accelerates deposition at the tip of the electrode. Further attracting more $Zn(OH)_4^{2-}$ accumulates and gradually forms dendrites during the cycle [32]. As shown in Figure 2c, the zinc dendrites are bifurcated branches, which easily puncture the diaphragm and cause a short circuit of the battery [33].

2.2.2 Hydrogen evolution reaction

The reduction process of Zn/ZnO electrodes and the principle of hydrogen evolution reaction are as follows:

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$

Since the standard reduction potential of Zn/ZnO is −1.26 V and the standard reduction potential of hydrogen evolution is −0.83 V, the hydrogen evolution reaction is more favorable thermodynamically, so hydrogen evolution reaction is inevitable during the cycle of the aqueous zinc battery [34]. However, the hydrogen evolution reaction will have an adverse effect on the electrode, electrolyte and battery. The process of hydrogen production will deplete the electrolyte and diminish the CE of the battery. The hydrogen produced will break the closed structure of the battery, causing the battery to rupture [35]. In addition, the hydrogen evolution reaction not only produces hydrogen, but also increases the concentration of OH^-, which severely corrodes the Zn electrode, and produces $Zn(OH)_4^{2-}$ or ZnO byproducts, especially zinc dendrites [36].

2.2.3 Zinc passivation

When the battery is discharged, the OH^- and Zn^{2+} in the alkaline electrolyte form $Zn(OH)_4^{2-}$, which is decomposed into ZnO after saturation. ZnO is covered on the zinc elec-

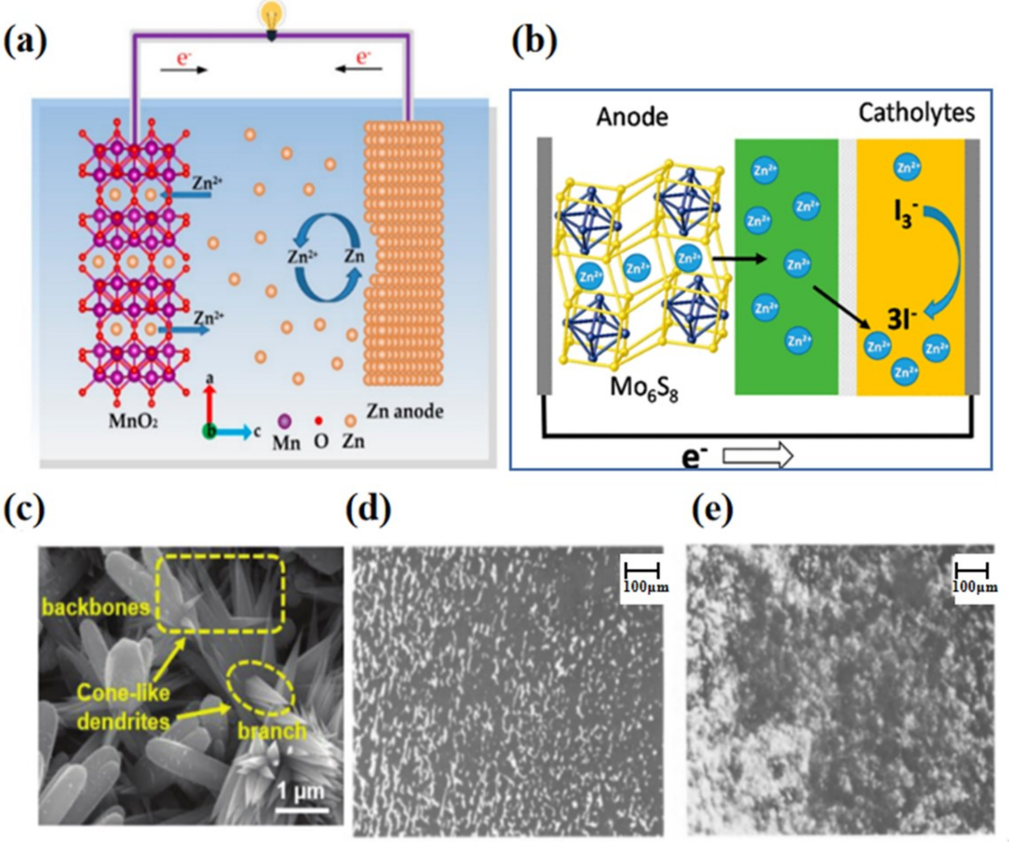


Figure 2. (a) Reaction schematic diagram of zinc anode material [29]. (b) a reaction schematic diagram of the material having the intercalation of Zn^{2+} [39]. (c) SEM diagram of zinc dendrite [33]. (d) Type I ZnO thin film; (E) Type II ZnO thin film [40].

trode, resulting in a decrease in the pore size of the zinc electrode. With the increasing concentration of $Zn(OH)_4^{2-}$, the remaining pore volume will be completely blocked, resulting in passivation of the zinc electrode, thus hindering the movement of ions. The utilization rate of zinc is low. ZnO is not conductive, which will increase the inherent impedance of the zinc electrode, which will also result in voltage drop during discharge and voltage rise during charging [32,37].

ZnO films are divided into two categories (Figure 2d and 2e). One is type I, which, according to the solution-precipitation model, only forms a soluble ZnO. This variety of zinc oxide layer is commonly porous and will limit OH^- to the surface of Zn. As a result, the concentration of OH^- at the electrode and electrolyte interface is reduced.. The other is Type II, which causes a change in the interface pH, resulting in a denser/thicker irreversible layer with stronger adhesion [38].

3. Hydrogel Formation Mechanism

The liquid in hydrogels can be categorized as bonded liquid, middle liquid, and unrestricted liquid. The structure and fluidity of free water is resembling that of fluid H_2O, whereas confined water is physically attached to polymer chains via hydrogen bonds. Between liberated and tethered water, the middle water interacts faintly with the polymer chain and the nearby liberated water molecules. In recent years, the understanding of water-water interaction and water-polymer interaction in hydrogels have been significantly expanded, and the fundamental characteristics of these water molecules and polymer chains will dictate the environmental and electrochemical durability of hydrogels, which is essential in electrolyte applications [41,42].

Hydrogel electrolyte is a type of functional polymer created through a process of crosslinking, resulting in a gel-like substance where water acts as the dispersing agent. In contrast to conventional electrolytes, it enhances electrical conductivity and mechanical durability, making it suitable for use as an electrolyte material in solid or quasi-solid zinc batteries. Common hydrogels have crosslinked, physical crosslinked and chemical crosslinked hydrogels. The polymer is easily soluble in water, and through simple dissolution in salt solution, the free radicals on the polymer chain segments combine with the hydrogen bonds on the water molecules to form a non-crosslinked hydrogel electrolyte. Alternatively, one can integrate water-repellent and water-attracting components into the polymer that dissolves in water, and it possesses a networked composition. The hydrophilic groups can also bond with water molecules and link them to the inner part of the network, while the hydrophobic groups can swell upon contact with water, leading to the formation of crosslinked polymers through either physical or chemical crosslinking mechanisms [43].

A hydrogel with both softness and toughness can be achieved by introducing two overlapping polymer networks, one of which is inflexible and fragile and the other is pliable and adaptable. Macroscopically, hydrogels resemble both solid and liquid, and can be regarded as a semi-solid substance between liquid and solid. The high water content makes the hydrogel's morphological properties similar to that of liquid water, including its permeability to various chemicals and transparency to light. On the contrary, because of the limitations of the polymer network, the water molecules within the hydrogel are unable to move as easily as liquid water. As a result, hydrogels can preserve a specific form, like a solid, which is the basis for their application in water zinc battery electrolytes to prevent volume changes caused by corrosion reactions [44].

4. Application of Gel Electrolyte in Aqueous Zinc-ion Batteries

Electrolyte is an important part of ion migration in batteries, and the properties of electrolyte are related to the electrochemical performance, energy storage mechanism and service life of batteries. The most commonly used electrolyte today is the liquid electrolyte, which has a high ionic conductivity (10^{-3}–10^{-1} $S.cm^{-1}$) [45], and a good contact with the electrode. However, the liquid electrolyte will lead to dendrite growth, zinc electrode passivation, corrosion and other problems, which has a great impact on the performance of the battery and hinders the practical application [46,47]. The solid electrolyte without liquid can avoid dendrite growth, but the solid electrolyte has low ionic conductivity, poor mechanical properties and poor self-healing ability, and is prone to rupture in the cycle, which affects the battery cycle [48]. A gel electrolyte is a substance between a liquid and a solid, containing both liquid and solid shapes. Compared with liquid electrolyte, gel electrolyte has limited free water, which can prevent the formation of dendrites and other unwanted reactions, and also avoid the risk of liquid electrolyte leakage. In comparison to all-solid electrolytes, gel electrolytes exhibits greater ionic conductivity, and can provide better flexibility, higher capacity and better cycling stability [49,50]. The gel electrolyte can not only be used as the separator of the battery, but also as the binder of the battery, making the battery chemical performance more stable [49].

Under certain conditions, when colloidal particles or polymers are hardened in the sol or solution, gel electrolytes can be divided into non-crosslinked, physical crosslinked and chemical crosslinked according to cross-linking conditions [49]. Table 1 has drawn a conclusion on common gel electrolytes and their properties.

4.1 Non-crosslinked Gel Electrolyte

Non-crosslinked gel electrolytes are viscous and fluid, prone to damage or deformation, and have no crosslinking points [60]. Polymers commonly used in non-crosslinked gel electrolytes include xanthan gum (XG), sodium carboxymethyl cellulose (CMC), and gas phase silicon dioxide [47].

XG has high viscosity, acid and alkali resistance and salt resistance, and can be used in gel electrolytes [61]. Chen *et al.* [62] designed a high-concentration $ZnCl_2$/XG antifreeze electrolyte, and then assembled a $Zn//NH_4V_3O_8 \cdot 1.9H_2O$ flexible battery (Figure 3a). The ionic conductivity of $ZnCl_2$/XG electrolyte was 13.8 $mS.cm^{-1}$ at 20 °C. After 800 cycles at 0 °C and 20 °C, respectively, the assembled batteries had capacity retention rates of 90.7% and 90.3% (Figure 3b). CMC is also widely used in the synthesis of zinc-ion battery gel electrolytes to improve battery performance. For example, Li *et al.* [63] designed a CMC-$ZnCl_2$ gel electrolyte as the electrolyte and diaphragm, and assembled a Zn//KVO battery, which had good electrochemical performance and a capacity retent ion rate of up to 97.35% even after 2800 cycles. Furthermore, Zhang *et al.* [64] developed a novel variant of a pliable and high-voltage coaxial fiber water-rechargeable zinc-ion battery (Figure 3c), which not only exhibited a substantial capacity of 100.2 $mAh.cm^{-3}$ and a remarkable energy density of 195.39 $mWh.cm^{-3}$, but also had a small coaxial contact resistance and good mechanical flexibility and stability. At the same time, it maintained high performance after long-term bending. Fumed silica can also be used to reduce the formation of dendrites in aqueous zinc ion batteries. Therefore, fumed silicon dioxide-based gel electrolyte can en-

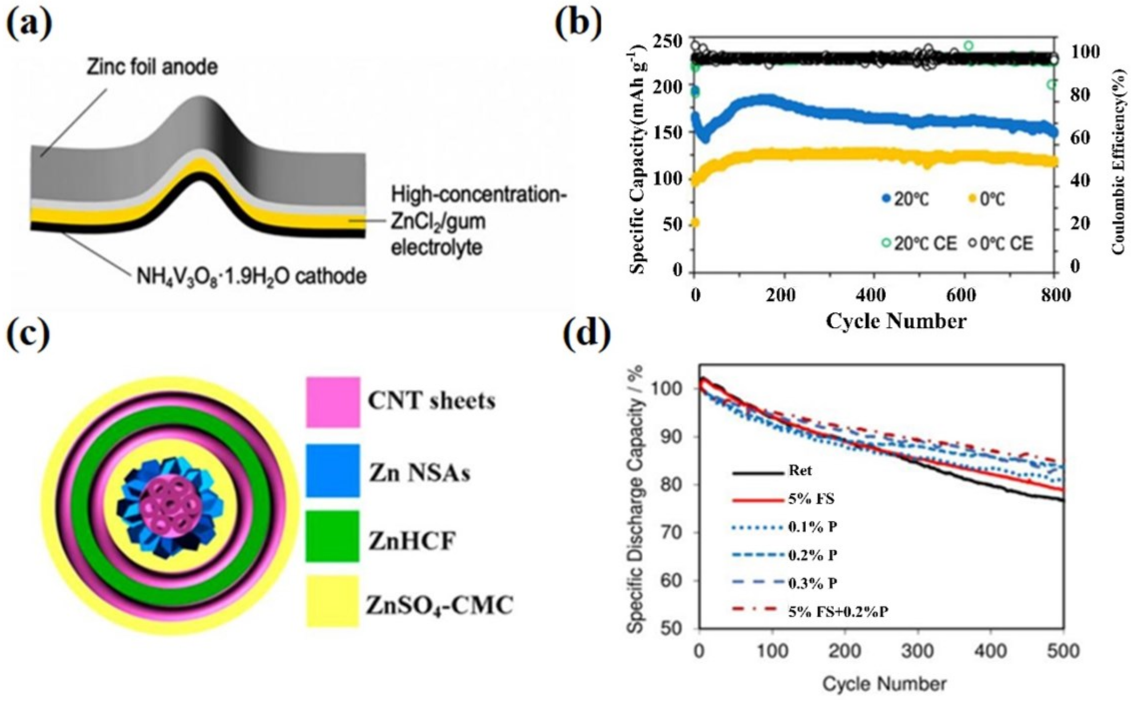
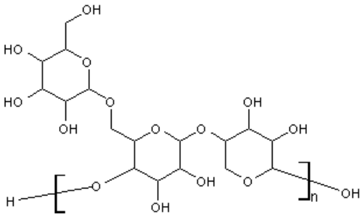
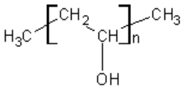
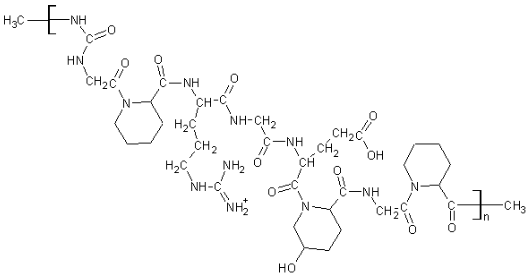
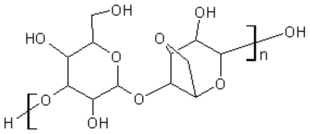
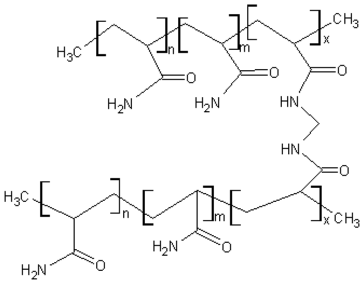
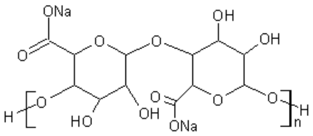
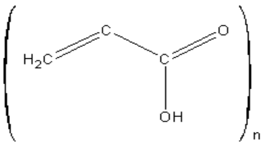
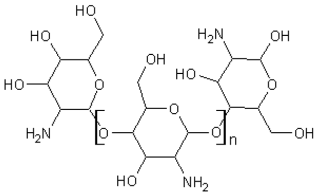
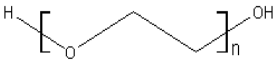


Figure 3. (a) $Zn//NH_4V_3O_8 \cdot 1.9H_2O$ battery cross-sectional diagram zinc. (b) The discharge efficiency and CE as a function of the number of cycles at 20 ℃ and 0 ℃, respectively, at 1.5 $A.g^{-1}$ [62]. (c) A schematic cross-sectional view of the cell [64]. (d) Cycle performance diagram of gel electrolyte with fumed silica, pyrazole and fumed silica pyrazole at 4 C [65].

hance the efficiency of zinc batteries. Nevertheless, the gaseous silicon dioxide gel electrolyte

Table 1. Common gel electrolytes and their properties

Gel electrolyte	Molecule structure	Ionic conductivity ($mS.cm^{-1}$)	Ref.
Guar gum		10.7	[51]
Polyvinyl alcohol		6.1	[52]
Gelatin		6.15	[53]
Agar		30.5	[54]
Polyacrylamide		28.8	[55]
Sodium alginate		11.44	[56]
Polyacrylic acid		175	[57]
Chitosan		18.6	[58]
Polyethylene glycol		22.4	[59]

exhibits a slightly greater level of corrosion on the surface of zinc. T.K.A. Hoang *et al.* [65] introduced pyrazole as a corrosion inhibitor and assembled Zn//$LiMn_2O_4$ batteries. Electrochemical tests of the gel electrolyte containing fumed silica (5% FS) and the gel electrolyte containing the addition of pyrazole (5% FS+0.2% P) showed little difference at the beginning, but the difference became apparent after about 300 cycles (Figure 3d). After 500 cycles, the capacity retention rate of 5% FS was 78.9% and that of 5% FS+0.2% P was 85.2%.

Although the non-crosslinked gel electrolyte has a certain viscosity, its mechanical properties are often unsatisfactory because there is no crosslinking point. If there is additional force, the non-crosslinked gel electrolyte is vulnerable to damage.

4.2 Physical Crosslinked Gel Electrolyte

Physical crosslinked electrolyte has a high self-healing ability, which is primarily composed of intermolecular forces, such as electrostatic attraction, hydrogen bonding and chain winding. These physical forces are non-permanent, and it can be dissolved by heating [36,66,67].

Currently commonly used physical cross-linked electrolyte polymers include gelatin, polyvinyl alcohol (PVA), etc. [53]. Gelatin is abundant in nature and environmentally friendly. Gelatin is hydrophile, and the hydrogen bond between the chains is formed by a triple helix structure, which is entangled with each other, and the structure is stable. However, due to thermal reversibility, gelatin gel will be unstable at a certain temperature or above. When the temperature is higher than 40 ℃, the hydrogen bond will be destroyed, and the gelatin will be reduced to a gelatinous shape after cooling; however, if the heating time is too long, the gelatin will denature and will not be reduced after cooling (Figure 4a) [68]. Gelatin contains -NH, -OH, -CO groups, and these different types of hydrogen bond interactions can provide physical cross-linking points. Han *et al.* [69] prepared a gel electrolyte using gelatin powder dissolved in aqueous solutions of Li_2SO_4 and $ZnSO_4$ (Figure 4b). The gelatin electrolyte had a large porosity and therefore it had a high ionic (6.15×10^{-3} S.cm^{-1}) (Figure 4c). It can be seen from Figure 4d that some 10 mm long flake particles, namely Zn dendrites, were grown in the non-gelatin battery, which were unevenly distributed on the surface of Zn. On the other hand, the Zn electrode's surface in the gelatin electrolyte battery was even and sleek, and gelatin effectively prevents the development of Zn dendrites.

PVA molecular structure contains hydroxyl group, strong polarity, easy to form hydrogen bonds with polar molecules (such as water molecules), can improve water absorption and conductivity, and has high viscosity and flexibility, therefore, PVA is commonly used in gel electrolytes [70]. Chen *et al.* [71] prepared self-healing PVA/$Zn(CF_3SO_3)_2$ hydrogel electrolytes by freezing/thawing. When the PVA/$Zn(CF_3SO_3)_2$ hydrogel is cut into two segments and contacted, the loosely mobile PVA chains will draw each other in through hydrogen bonds. With the rise of contact duration, additional uncrystallized PVA chains will migrate towards the break, restore additional hydrogen bonds, and ultimately accomplish full self-repair (Figure 4e). Zhou *et al.* [72] prepared Zn///δ-MgVO batteries assembled by PVA/G gel electrolyte mixed with PVA, $Zn(CF_3SO_3)_2$ and glycerol. The PVA/G gel electrolyte has high freezing resistance and tensile strength (44.8 kPa). At −30 ℃, the ionic conductivity is 10.7 mS.cm^{-1} and the discharge capacity is 256.3 mAh.g^{-1} (current density is 0.1 A.g^{-1}).

Wang *et al.* [73] used polyacrylamide (PAM) and glycerol (Gly) as raw materials, and used the hydrogen bond between polyacrylamide or glycerol and water to avoid crystallization of the gel electrolyte at low temperatures. At −40 ℃, the gel electrolyte still had good chemical properties, and the ionic conductivity was 9.65×10^{-5} S.cm^{-1}. The outstanding mechanical characteristics and ionic conduction bestow PAM-H_2O-Gly hydrogel with the capacity to function as the electrolyte of flexible ZIBs (Figure 4f). To demonstrate this, flexible aqueous ZIBs were created using the PAM-H_2O-Gly electrolyte, with SWCNTs/PANI functioning as cathodes and Zn foil serving as anodes. Remarkably, due to the exceptional ability to resist freezing and high conductivity of ions in the PAM-H_2O-Gly-20% electrolyte, the ZIBs still maintain a specific capacity of 52 mAh.g^{-1} at −40 °C. As illustrated in Figure 4g, when the ZIBs were curved into cylinders and subsequently flattened during the cycling process at −40 °C, their capacities remained nearly unchanged compared to the initial state. This suggests that the flexible ZIBs with anti-freezing properties hold significant potential for practical use in cold environments.

The physical crosslinked gel electrolyte is formed by intermolecular force such as hydrogen bond. Therefore, its production method is relatively simple, and it has the advantages of stretchability, self-healing ability, anti-freezing property, etc., which can effectively improve the electrochemical stability of the zinc negative electrode, as shown in Table 2.

4.3 Chemical Crosslinked Gel Electrolyte

Physical crosslinked gel electrolytes generally have poor structural stability, poor thermal stability and can only withstand small deformation, which will bring adverse consequences for zinc batteries involved in the corrosion hydrogen evolution reaction, so today's chemical crosslinked hydrogels have greater research potential. The polymers frequently employed for the production of hydrogel electrolytes are polyethylene glycol (PVA), polyacrylic acid (PAA) and polyacrylamide (PAM), which possess ample hydrophilic moieties on their lateral chains: hydroxyl, carboxyl and amide groups [77]. The hydrogel matrix crosslinking networks formed by these three polymer hosts are different. For instance, PVA can be crosslinked by chemical crosslinking agents like glutaraldehyde and borax, and the original rigid PVA hydrogels have excellent tensile properties through interaction [78].

In contrast, PAA and PAM hydrogels are often chemically cross-linked through double bonds produced by radical polymerization. Furthermore, the copious carbonyl and hydroxyl moieties on the polymer side chain make the monomer have a large hydrogen bonding gel potential and have a good affinity with water electrolyte [79,80]. Polyacrylamide-based hydrogels with chemical crosslinking are the

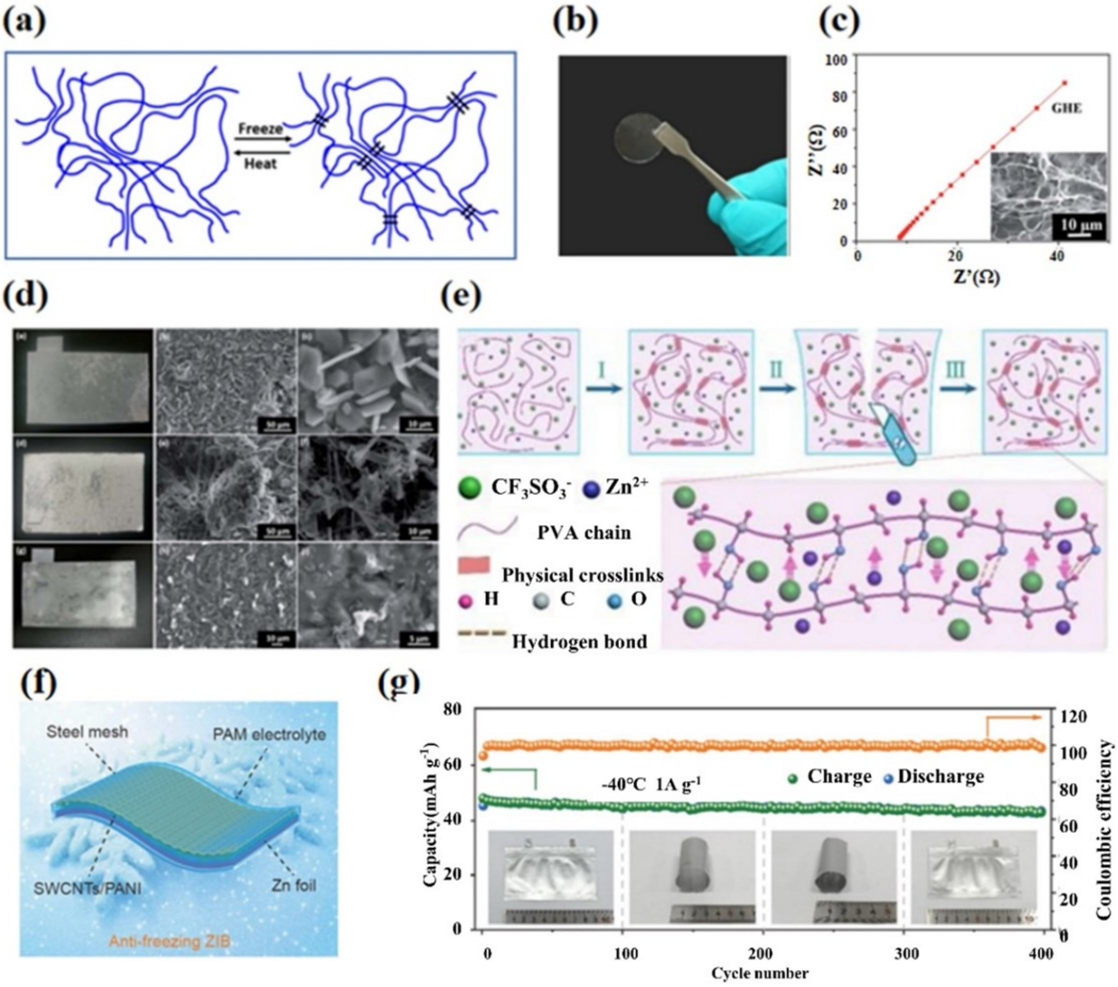


Figure 4. (a) Changes of gelatin before and after heating [68]. (b) The gelatin produced. (c) EIS diagram of the gel electrolyte. (d) An optical image of the battery module after symmetrical cell cycles [69]. (e) Schematic diagram of preparation process of self-healing electrolyte and schematic diagram of self-healing [71]. (f) The configuration of flexible anti-freezing ZIBs. (g) Cycling performance of flexible anti-freezing ZIBs at different bending states under −40 ℃ at 1 A.g⁻¹. The insets are the optical images of flexible anti-freezing ZIBs at different bending states [73].

most promising chemical crosslinking gel electrolytes at present. For example, in the report of Yang *et al.*, a prehydrogel solution of 2-acrylamide-2-methyl-1-propane-sulfonate sodium salt (AMPS) as sulfonic acid base source and acrylamide (AM) as neutral monomer was applied on the surface of Zn and polymerized to form a negatively charged -SO_3^- group polyanionic hydrogel on the surface of Zn [81]. The preparation principle of Zn-SHn is shown in Figure 5a. Based on the enhanced adsorption model of Zn^{2+} on the PAM chain, with or without -SO_3^- (Figure 5b and 5c), the binding energy (−1.4 eV) generated by the sulfonated PAM unit through the Zn-O interaction on Zn^{2+} is much stronger than that of the unsulfonated PAM unit (−0.08 eV). The results show that polyanionic hydrogels have high zincophilic properties. Combined with the three-dimensional interconnected water-rich hydrogel skeleton, Zn^{2+} can be strongly trapped and smoothly transported to Zn metal through the hydrogel layer. At the same time, the negatively charged -SO_3^- group can repel SO_4^{2-} ions and hinder the transport of water molecules, which is conducive to the rapid diffusion and uniform nucleation of Zn ions (Figure 5d). The results show that in the PAM hydrogel matrix, there are cross-linking points between all the chain segments, forming a highly cross-linked porous framework, and there are a lot of Zn^{2+} solution in the porous PAM framework. Their porous structure facilitates the transport of electrolyte ions [82].

In addition, Xanthan gum (XG) contains ample polar entities, robust covalent connections, and intermolecular hydrogen bonds, which can form interpenetrating three-

Table 2. Electrochemical properties of zinc anode in physical crosslinked gel electrolyte

Physical crosslinked gel electrolyte	Charge/Discharge current (mA.cm^{-1})	Cycle time (h)	Ref.
Sodium alginate	1.77	250	[74]
Polyvinyl alcohol	2	500	[72]
Agar	0.5	2000	[54]
gelatin	0.2	800	[69]
Polyacrylamide/carboxymethyl chitosan	0.5	1200	[75]
Polyvinyl alcohol/Glycerin	0.1	800	[71]
Sodium alginate	2	1400	[76]

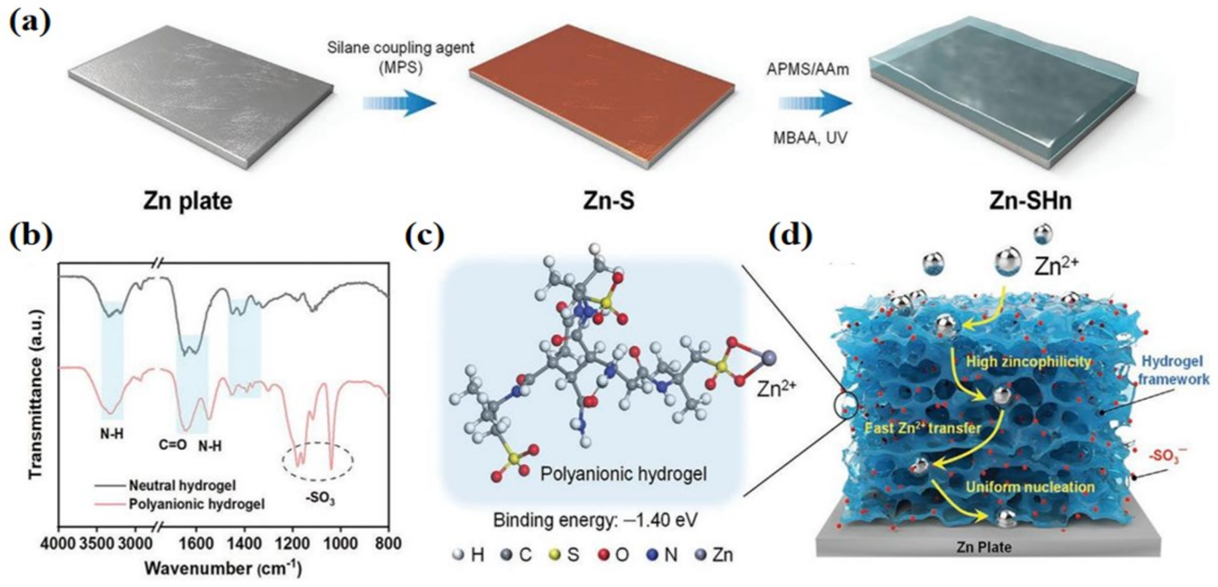


Figure 5. Preparation and characterization of Zn-SHn (S is silane coupling agent, H is hydrogel, and n is negatively charged). (a) Schematic diagram of Zn-SHn preparation. (b) FTIR spectra of Zn-SH and Zn-SHn. (c) Optimal configuration of Zn^{2+} adsorbed on -SO_3^- group. (d) Transport diagram of Zn^{2+} in SEI layer of polyanionic hydrogel [81].

dimensional networks through chemical crosslinking to promote ion transport and absorption. For example, ammonium persulfate (APS) generates a free radical site on the main chain of Xanthan gum (XG) and reacts with AM to form graft copolymer Xanthan gum- polyacrylamide (XG-PAM). Because of the plentiful hydroxyl and carboxyl functional groups in the strands of cotton cellulose nanofiber (CNF) and copolymer XG-PAM, physical effects such as hydrogen bonding and entanglement can be created between XG-PAM and CNF chains [55]. The usual production method of XG-PAM/CNF hydrogel electrolyte is illustrated in Figure 6a. Because of the plentiful hydroxyl and carboxyl functional groups in the chains of CNF and copolymer XG-PAM, physical effects such as hydrogen bonding and entanglement can be established between XG-PAM and CNF chains (Figure 6b), thereby guaranteeing excellent flexibility, reduced rigidity, and superior elasticity during deformation. Ultimately, it is soaked in an electrolyte (2 mol.L^{-1} $ZnSO_4$ and 0.1 mol.L^{-1} $MnSO_4$) for 24 hours. After 4 days, XG-PAM/CNF hydrogel electrolyte was obtained (Figure 6c). As a result, these hydrogel monomers are easily transformed into hydrogel states, thus playing the role of quasi-solid hydrogel electrolytes in energy storage applications.

Therefore, compared with the physical crosslinked gel electrolyte, the chemical crosslinked gel electrolyte has a more stable network structure, can withstand larger deformation and better ionic conductivity, and can effectively stabilize the electrochemical stability of the zinc negative electrode in the water zinc ion battery. Table 3 summarizes the cycling stability of the zinc negative electrode in various chemical gel electrolytes.

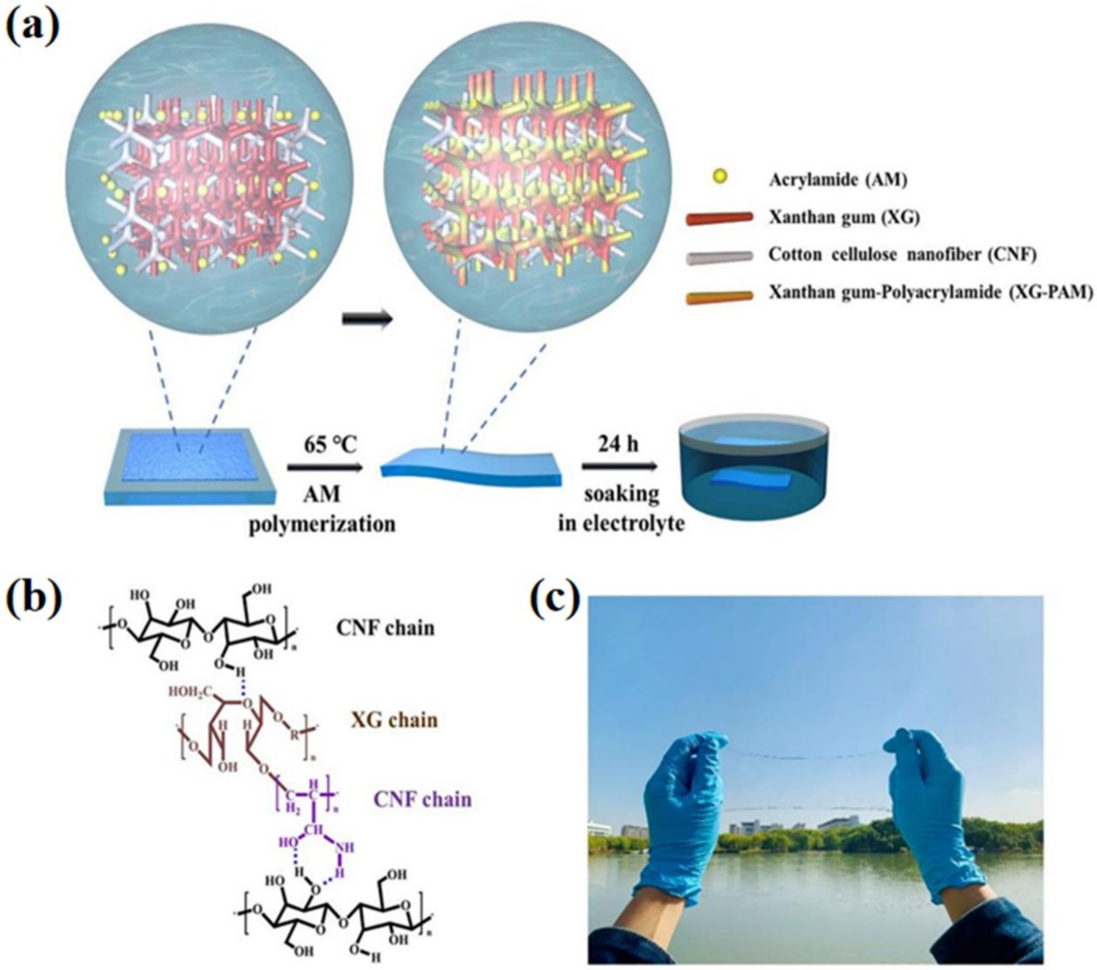


Figure 6. (a) Schematic diagram of XG-PAM/CNF hydrogel electrolyte film prepared by simple free radical polymerization method; (b) Chemical structure of XG-PAM/CNF hydrogel; (c) Optical image of XG-PAM/CNF hydrogel electrolyte film [55].

5. Summary and Outlook

ZIBs hold great potential in real-world uses like storing energy for power grids on a large scale and powering wearable devices. Nonetheless, their practical application is impeded by a range of issues including dendrite formation, the hydrogen evolution reaction, and electrode passivation. Here, this paper focuses on the existing electrolyte-based solution, gel electrolyte, to solve the related problems. We categorize them into non-crosslinked, physical crosslinked, and chemical crosslinked categories and explore the operational principles involved in this procedure.

Although the electrochemical performance of water-based zinc batteries can be improved by using gel electrolytes, there are still many problems that need to be solved in some aspects, such as:

(1) The scalability of zinc batteries is a big challenge. Due to its unique quasi-solid properties, hydrogel electrolytes can effectively alleviate hydrogen evolution reaction (HER) in gentle electrolyte systems, but due to its relatively low mechanical strength, the inhibition effect on dendrites is usually not ideal. The interconnected network structure of hydrogels is the foundation of their mechanical properties. Hydrogel electrolytes need to have a certain degree of mechanical toughness to deal with the problem of hydrogen generated by HER during the zinc battery cycle. Despite the conventional hydrogel electrolyte possessing specific mechanical characteristics, its flexibility and malleability are not up to par, significantly constraining its potential applications. Hence, enhancing the network architecture can enhance the mechanical properties of electrolytes. The establishment of a dual network architecture is a viable approach to enhance the pliability of hydrogel electrolytes. The mechanical robustness of the monolayer structure is constrained, but the mechanical robustness of the hydrogel electrolyte can be significantly enhanced following the cross-linking of the dual-layer lattice architecture, and it can even have the deformation ability of stretching and bending. Nanoparticles and nanostructures can additionally enhance the mechanical characteristics of hydrogel electrolytes. In future investigations, the enhancement of mechanical durability of hydrogel electrolyte will be examined through optimizing the internal network structure of hydrogel and enhancing external additives [94];

(2) Due to the high water content inside the hydrogel, the ecological flexibility of the hydrogel electrolyte is extremely crucial. Numerous elements in the surroundings can impact the efficiency of hydrogel electrolytes, such as temperature, moisture, and so on. In extremely cold temperatures, the hydrogel electrolyte's surface will start to solidify prior to the internal structure of the hydrogel, leading to inadequate connection between the electrode and the electrolyte interface.[95]. At present, some studies have shown that adding modifiers can reduce the freezing point of hydrogels, improve

Table 3. Electrochemical properties of zinc anode in chemically crosslinked gel electrolyte

Chemical crosslinked gel electrolyte	Charge/Discharge current (mA·cm^{-1})	Cycle time (h)	Ref.
Poly (3-(1- vinyl-3 - imidazole) propyl sulfonate	5	500	[83]
ADN/$Zn(ClO_4)_2 \cdot 6H_2O$	0.5	1000	[84]
Polyacrylic acid	0.5	600	[85]
Polyacrylamide/Gelatin/Methacryloxyethyl-N, N-dimethylpropanesulfonate	1	400	[86]
Cellulose/Tetraethyl orthosilicate/Glycerin	2	800	[87]
Carrageenan/Wool keratin	0.5	1900	[88]
Tetracarboxylic acid/4-hydroxypyridine	1	2300	[89]
Lignocellulosic/$ZnSO_4$	1	2000	[90]
Polyacrylamide/Sodium alginate	1	1000	[91]
Polyacrylamide/Stearyl methacrylate	2	400	[92]
Carboxymethyl chitosan / $ZnSO_4$	1.25	1300	[93]

the water holding capacity of hydrogels, and enhance the stability of electrolytes in the surroundings. Nevertheless, the effectiveness at colder temperatures will still be somewhat compromised in comparison to the standard temperature condition, leading to a decrease in lifespan. Furthermore, additional enhancements are required to optimize the water retention capabilities. In addition, gases such as carbon dioxide in the air permeate the inside of the battery, causing problems with electrolyte deterioration. It is feasible to improve the viscosity of the outer surface of the hydrogel to adsorb the harmful gas and prevent its diffusion to protect the hydrogel electrolyte;

(3) The conductive strength of the electrolyte depends on the movement and migration of ions, and the ionic conductivity is an important indicator reflecting the performance of the electrolyte. The hydrogel electrolyte not only has the ability to take in and retain a significant amount of conducting ions, but its internal porous structure also creates an environment that facilitates the movement of ions. Therefore, enhancing the internal arrangement of hydrogel is crucial for enhancing the conductivity of hydrogel electrolytes. Currently, the investigation and enhancement of hydrogel electrolytes primarily rely on the conventional method, which involves incorporating modifiers or additives to facilitate the internal cross-linking reaction. and by increasing the transmission channel and the number of ions to improve the conductivity. Nonetheless, the creation and alteration of hydrogel electrolytes are comparatively uncomplicated and devoid of significant advancements. Furthermore, finding a way to attain a heightened electrical conductivity and sustain this level for an extended duration without deterioration is also an exceedingly crucial issue. As such, it becomes imperative to innovate hydrogel substances and procedures in order to enhance ionic conductivity.

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CRediT Author Statement

Author contributions: Y. Xiong and L. Kuang were responsible for collecting the data and writing the draft; J. Dai, X. Li, and X. Gu conceived the idea, and discussed and revised the manuscript. All authors have read and agreed to the published version of the manuscript.

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