Multi-functional hydrogels for flexible zinc-based batteries working under extreme conditions

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Abstract

Zinc-based batteries are potential candidates for flexible energy storage due to their high capacity, low cost, and intrinsic safety. Hydrogel electrolytes with saturated aqueous solvents can provide remarkable electrochemical performances while retaining satisfactory flexibility for zinc-based batteries. The past decades have witnessed their fast growing. However, the study of zinc-based batteries with hydrogel electrolyte under extreme conditions is still in the early stage and many technical issues remain to be addressed. In this review, the physical and chemical properties of hydrogel electrolytes are discussed for application in zinc-based batteries. Strategies towards hydrogel electrolytes and flexible zinc-based batteries under extremely high/low temperatures or under deformation conditions and their behaviors are reviewed and analyzed. Moreover, designing strategies for all-around hydrogel electrolyte towards all these extreme conditions are proposed. A perspective discussing the challenges and future directions of hydrogel electrolyte for zinc-based batteries is provided.

Keywords: zinc battery, flexible battery, hydrogel electrolyte, anti-freezing, anti-dehydration, mechanical strength

1. Introduction

Flexible batteries with high performance and stretching/bending capabilities have received great interest in recent years to support the development of flexible electronics such as wearable sensors for health monitoring[1-4]. At present, Li-ion batteries have been widely used in different realms ranging from smartphones to electric vehicles and have dominated the market due to their high voltage, good cycle stability, and mature manufacturing technologies.[5-8] Also, flexible Li-ion batteries with various structures are expected to meet diverse application requirements in the future.[9-11] However, Li-ion batteries may catch fire or even explode under certain working conditions. Besides, lithium reserve is limited, leading to the high cost of lithium metal. Therefore, it is significant to develop althernative batteries with low cost, high safety, and high energy density.[12, 13] Zinc-based batteries are regarded as potential substitutions of Li-ion batteries and have captured great attention for their multiple advantages. First, the commonly used aqueous electrolytes guarantee the intrinsic safety of zinc-based batteries.[14, 15] Secondly, the worldwide abundant zinc reserves leads to low cost of zinc-based batteries. Finally, the theoretical capacity of metallic zinc is up to 820 mAh g^{-1} (or 5854 mAh cm^{-3}).[16]

Soft electrolytes and electrodes with good compatibility with each other are critical for the development of high performance flexible zinc-based batteries[17-20]. Though there are extensive research efforts to develop flexible electrodes, research activities on flexible electrolytes are limited[21-23]. The development of flexible electrolyte is even more important for flexible batteries as the ionic resistance of the flexible electrolyte could be significant[24, 25]. Among various flexible electrolytes, hydrogels are very promising for flexible zinc-based batteries due to their high ionic conductivity and good flexibility. Their natural water-saturated polymeric networks facilitate ionic transport leading to high ionic conductivity (normally 1-2 orders of magnitude higher than that of Li-ion batteries);[26, 27] soft and moist hydrogel interfaces guarantee the intimate contact with electrodes;[28, 29] meanwhile, their ductile properties create the possibility of wide application for flexible zinc-based batteries.[30, 31]

Therefore, over the years, efforts have been made to develop soft hydrogel electrolytes for flexible zinc-based batteries [32-34]. For example, additives like SiO_2 and graphene oxide (GO) have been employed to promote ionic conductivity of hydrogel electrolytes[35, 36], and new strategies like sol-gel transition have been applied to obtain an intimate electrode/electrolyte interface.[37] Recent progress about the hydrogel materials for flexible zinc-based batteries has also been comprehensively summarized.[38-41] These reports mainly discussed strategies for improving battery performance under room temperature and undisturbed situations. However, the effects of extreme working conditions on the performance and durability of the battery have not been discussed yet, which are critical for practical application of flexible zince-based batteries. The hydrogel electrolyte is more environmentally sensitive in the flexible zinc-based battery system for its fragile nature and water-saturated body compared to electrodes.[42, 43] In particular, nullification of hydrogel electrolytes under extreme temperature (-20 °C and 50 °C) and various deformation still remain issues for flexible zinc-based batteries: 1) at extremely low temperature (-20 °C), the ionic conductivity of hydrogel electrolyte decreases significantly and water in the hydrogel electrolyte freezes.[44] 2) at extremely high temperature (50 °C), the facile dehydration of hydrogel causes structural deformation, salts crystallization, and decreased ionic conductivity.[45] Besides, the risk of thermal shock is also not negligible.[46] 3) during daily use, the flexible battery inevitably suffers from local stress and various deformations, including stretching, bending, and rolling.[47] The aforementioned extreme situations may lead to battery performance degradation or even battery failure. Therefore, it is of great importance to develop advanced hydrogel electrolytes to deal with these issues and further facilitate their application under extreme working conditions.

Few studies have focused on the effects of the extreme working conditions on the hydrogel electrolytes for flexible zinc-based batteries before the year 2019.[48, 49] Although this research vacancy has gradually been filled by recent emerging studies,[50-52] recent progress and design strategies have not been systematically discussed and summarized yet Also, there is a lack of guidance for constructing all-around hydrogel electrolytes that can withstand these extreme conditions. In this review, recent progress and strategies towards various extreme working conditions, including low (-20 °C) and high temperature (50 °C), and mechanical deformations, are summarized. Moreover, we propose a promising combination strategy for realizing all-around extreme-condition tolerance ability. Finally, current challenges and future research directions are discussed for further development.

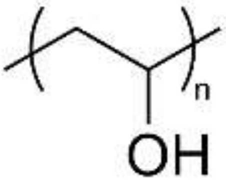
2. Fundamentals of hydrogel electrolytes

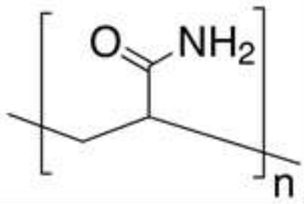
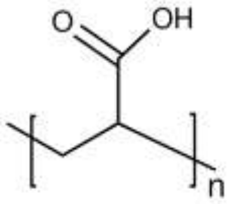
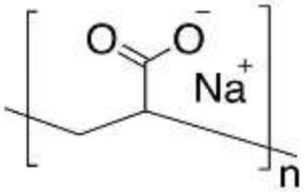
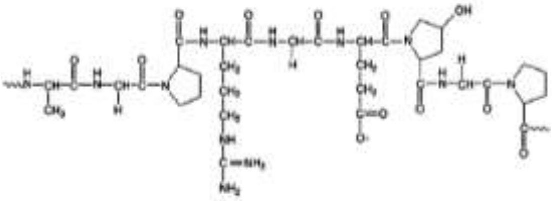
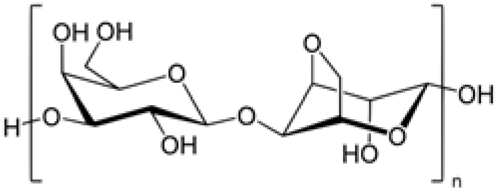
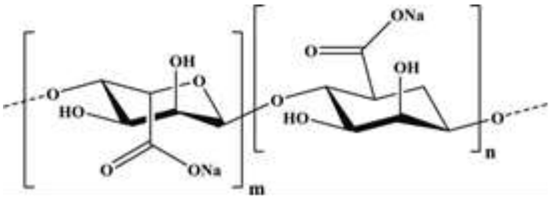
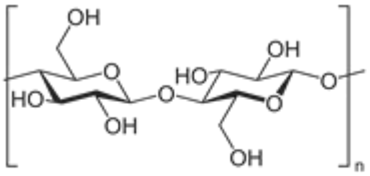
Hydrogels are polymeric materials with three-dimensional (3D) network structures comprised of crosslinked polymer chains and inner enclosed water.[53] Based on the existing research, it is believed that these two key components determine the hydrogel properties. Hydrogel networks with different degrees of crosslinking are formed through covalent chemical bonding or physical bonding.[54] The well-crosslinked hydrogel networks provide sufficient place for water, and further various hydrophilic functional groups (e.g., hydroxyl, amino, and carboxyl groups) on the polymer chains interact intimately with water molecules and trap them in the hydrogel networks. Moreover, modifications like grafting and copolymerization can be applied to the polymers to realize anticipated function.[55] The crosslinking degree of hydrogels is also crucial in affecting the hydrogel properties. Typically, high degree crosslinking will enhance the mechanical strength of hydrogels but impair their elasticity, because the increased crosslinking points reinforce the interaction among polymer chains but also restrict their free stretching at the same time.[56] Besides, the water absorption of hydrogels will also decrease within the crowded polymer networks.[57] On the contrary, hydrogels with low crosslinking degree possess opposite properties. Insufficient crosslinking may even lead to the dissolution of polymer chains in water.[58]

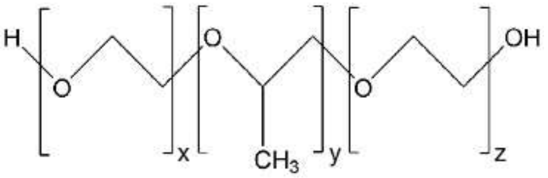
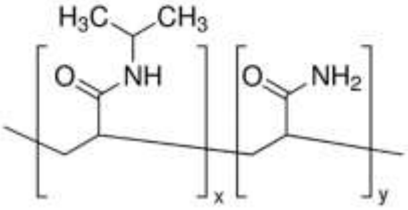
Water is hosted in the hydrogel networks. Meanwhile, the water also serves as the host of multiple ions, which equip hydrogels with various functionalities. For example, hydrogels containing acid (H^+) or alkaline (OH^-) solutions have been widely applied as electrolytes to flexible batteries and supercapacitors.[24] The 3D interconnected network provides unblocked pathways for ion transport, which is further facilitated by the rich water content. As a result, the ionic conductivity of hydrogel electrolytes can be comparable with some liquid electrolytes.[59] Besides, ions like Fe^{3+} can endow hydrogels with extra self-healing capacity by ionic bonding.[60] Not only salt ions, but also nanoparticles (e.g., silica (SiO_2), graphene oxide (GO), and carbon nanotube (CNT)) can disperse uniformly in the water for synthesizing nanocomposite hydrogels, which generally possess an enhanced mechanical property.[61, 62] On the other hand, the solvent in hydrogels is not limited to water but can also be organic solvents like polyols and dimethyl sulfoxide (DMSO). For example, by immersing the hydrogel in the ethylene glycol (EG), the water in the hydrogel can be partially or totally replaced.[63]

Due to their tailorable properties and high ionic conductivity, hydrogel electrolytes received significant attention in the recent research of flexible zinc-based batteries.[64] The commonly used hydrogel electrolytes and their features are summarized in **Table 1**. Among them, polyvinyl alcohol (PVA), polyacrylic acid (PAA), and Polyacrylamide (PAM) hydrogels are representative homopolymers. They distinguish from each other by their different hydrophilic functional groups.[65] Typically, PVA hydrogel is synthesized using the in-situ polymerization method through physically crosslinked (hydrogen bonding), while the PAA and PAM hydrogels are crosslinked through chemical bonding (chemical crosslinker). It is worth mentioning that these homopolymers can freely combine with each other by chemical bonding to form copolymers, which exhibit superior chemical/physical properties than the homopolymers.[36] Moreover, biopolymers like gelatin, agarose, alginate, and cellulose have also obtained great attention due to their environmental-friendly nature in recent years.[66-69] The abundant hydrophilic groups affiliated to polymer chains endow the biopolymers with good water compatibility. As for the recently emerged block polymers such as poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) and poly(Nisopropylacrylamide-acrylamide) (PNIPAM/AM),[70, 71] they are treated as smart materials due to thermo-reversible properties. When applied as electrolytes, hydrogels containing salt solutions with higher concentration will acquire a higher ionic conductivity. However, the salt tolerance capacities of various hydrogels are quite different. For example, PVA can in-situ polymerize in 1.8 M KOH solution, while the gelatin can only tolerate 0.1 M KOH solution with the same synthesis method.[66, 72] Besides, fabrication methods of the hydrogel electrolyte are also crucial. For instance, the as-synthesized pure PVA hydrogel can withstand 6 M KOH solution through post-absorbing, much higher than the in-situ polymerized PVA hydrogel.[35]

Table 1. The widely used hydrogel substrates for zinc-based batteries.

Name	Molecular structure	Functional groups	Features	Crosslinking
Polyvinyl alcohol (PVA)[73]		Hydroxyl	Flexible Self-healable	Physical Chemical

Polyacrylamide (PAM)[33]		Amide	Flexible reusable	Chemical
Polyacrylic acid (PAA)[74]		Carboxyl	Flexible Self-healable	Physical (Self-healing) Chemical
Sodium polyacrylate (PANa)[27]		Sodium carboxylate	Flexible Self-healable	Physical (Self-healing) Chemical
Gelatin[66]		Peptides	Flexible Salt-unstable Biodegradable	Physical
Agarose[75]		Hydroxyl	Flexible Biodegradable	Physical
Sodium alginate[76]		Sodium carboxylate Hydroxyl	Flexible Biodegradable	Physical
Cellulose[77]		Hydroxyl	Flexible reusable Biodegradable	Physical Chemical

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO)[37]		Hydroxyl	Thermo-responsive	Micellization
Poly(Nisopropylacrylamide-acrylamide) (PNIPAM/AM)[78]		Amide Isopropyl acrylamide	Thermo-responsive	Chemical

Although flexible zinc-based batteries display satisfactory performances at the lab level, they still face challenges towards practical applications, partly owing to the unsatisfied performance of hydrogel electrolyte under extreme conditions (e.g., < -20 ℃, > 50 ℃ environment, and deformations). This time, water and polymer chains may inversely prohibit the normal hydrogel functions. **Figure 1** further demonstrates these extreme working conditions in detail.

As a flexible energy storage device, zinc-based batteries inevitably undergo stretching, bending, folding, or twisting multiple times during daily use. Over time, delamination occurs in the battery, causing poor contact between the electrode and the hydrogel, which in turn result in battery performance degradation.[79] Even worse, when suffering from local stress, the fragile hydrogel will facilely break up and directly lead to battery failure.[80]

The excellent water storage capability enables hydrogel electrolytes liquid-like properties. However, its freezing temperature of 0 ℃ remains an obstacle for application of hydrogel electrolytes at a low temperature.[81] Once the water in the hydrogel freeze, the hydrogel's inner network structure collapses, leading to loss of elasticity and softness. The initial conformal hydrogel electrolyte/electrode interface will be interrupted since the frozen hydrogel is no longer shape-adapted.[48] Meanwhile, water solubility decreases significantly at a low temperature, resulting in salt precipitation and a decrease in hydrogel ionic conductivity.

Moreover, the hydrogel properties will be severely affected as the water gradually evaporates from the hydrogel. Especially at a high temperature (e.g., 50 ℃), the water loss is accelerated, leading to hydrogel shrinkage and structural deformation. When applied in the zinc-based battery system, the poor contact between the contracted hydrogel electrolyte and the electrode can result in high interfacial resistance. Furthermore, salt precipitate while water evaporation, accompanied with a decline in the ionic conductivity.[34] Obviously, the aforementioned hydrogel deterioration will finally harm battery performance and limit the range of battery operation conditions. It is indispensable to resolve this long-lasting hydrogel issue and further improve flexible zinc-based batteries' operational capability under extreme working conditions.

On the other hand, heat accumulates rapidly during the battery ultrafast charge/discharge processes or extreme conditions like internal short-circuiting, which may cause severe thermal shock and even battery explosion. Although the zinc-based batteries with hydrogel electrolytes are praised for their high safety due to the intrinsic aqueous nature, their safety issues under extremely high temperatures (e.g., > 70 ℃) cannot be neglected.

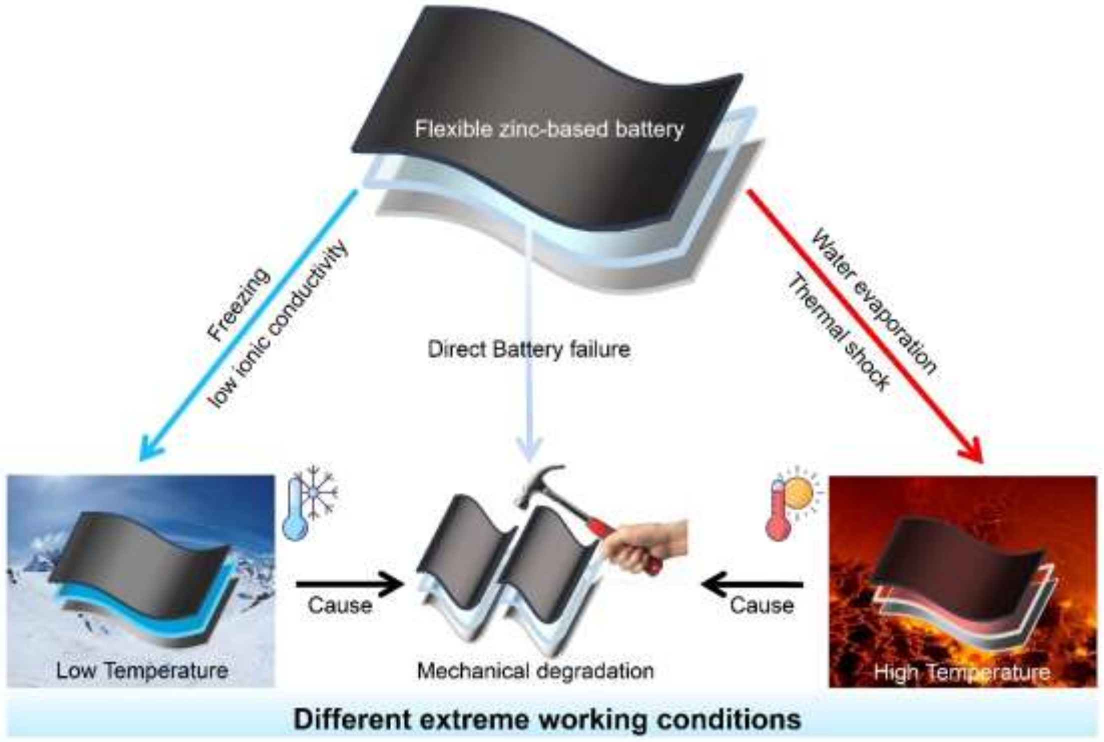


Figure 1. Flexible zinc-based batteries with hydrogel electrolytes working under different extreme conditions. At an extremely low temperature (< -20 °C), hydrogels will freeze and lose their flexibility. The ionic conductivity will also decrease in the cold environment. At an extremely high temperature, the water in hydrogels evaporate quickly, and hydrogels will shrink and become stiff. Besides, the battery is also at risk of thermal shock. When suffering from strong deformations like local stress or twisting, hydrogels may break up, and batteries may fail.

3. Hydrogel electrolytes at low temperatures

Recently, researchers have proposed three different states of water in the hydrogel: non-bound water (NBW), weakly bound water (WBW), and strongly bound water (SBW).[82] The free water NBW, the main hydrogel component, has almost no interactions with hydrogel networks but interacts intimately with other free water molecules through hydrogen bonding. Regretfully, the formation of ice is due to the well-organized arrangement of free water molecules connected by hydrogen bonding.[83] On the other hand, WBW and SBW have slight and intense interactions with functional groups on hydrogel networks, respectively. As the freezing temperature of NBW is 0 °C and that of SBW is even close to -100 °C, it is suggested that the stronger interactions between water molecules and hydrogel networks could result in the lower freezing temperature of water in hydrogels.[84] This provides two strategies to depress the freezing temperature of hydrogel electrolytes: one is to break the intermolecular hydrogen bonding between free water molecules, e.g., by introducing hydrated ions like Zn^{2+} or polyol solvent like ethylene glycol (EG); the other one is to enhance the interactions between water molecules and hydrogel networks thus suppressing the existence of free water, e.g., by employing or grafting hydrophilic functional groups such as -COOH or $-CONH_2$.

For hydrogel electrolytes of zinc-based batteries, apart from maintaining their anti-freezing ability, it is also imperative to ensure the ionic conductivity at a satisfactory level. One of the keys to achieving hydrogel electrolytes with high ionic conductivity is to keep sufficient free water in the hydrogel networks, which greatly facilitates free ions movement.[17] However, too much free water molecules in the hydrogel may sacrifice the anti-freezing property. Luckily, researchers have made attempts and gained some inspiring results to achieve a balance between freezing tolerance and ionic conductivity or even improve both properties simultaneously. In the following parts, recent advances and various approaches for developing anti-freezing hydrogel and flexible zinc-based batteries are introduced (**Table 2**). Besides, several other anti-freezing strategies not yet been applied to flexible zinc-based batteries are also presented and discussed for inspiration.

Table 2. Anti-freezing methods for zinc-based batteries with hydrogel electrolytes.

Method	Hydrogel substrate	Freezing tolerance	Ionic conductivity	Battery Performance*	Ref.
Adding salt	PANa	-50 ℃	5.7 S m^{-1} @ -20 ℃	130 mAh g^{-1} 87%/10000 cycles @ -20 ℃	ZIB[44]
Adding salt	PAM	-20 ℃	10.4 S m^{-1} @ -20 ℃	105 mAh g^{-1} 98%/500 cycles @ -20 ℃	ZIB[85]
Adding salt	Xanthan Gum	-20 ℃	5.0 S m^{-1} @ -20 ℃	119 mAh g^{-1} 83%/450 cycles @ -20 ℃	ZIB[86]
Adding salt	PAMPS-K/MC	-20 ℃	18.1 S m^{-1} @ -20 ℃	754 mAh g^{-1} > 70 cycles (24h) @ -20 ℃	ZAB[50]
Adding polyol	PVA	-60 ℃	10.1 S m^{-1} @ -35 ℃	133.8 mAh g^{-1} 90%/2000 cycles @ -35 ℃	ZIB[87]
Adding polyol	PAM	-20 ℃	14.9 S m^{-1} @ -20 ℃	146.7 mAh g^{-1} 61%/1000 cycles @ -20 ℃	ZIB[88]
Adding polyol	PAM/PAA	-35 ℃	3.8 S m^{-1} @ -20 ℃	506.2 mAh g^{-1} > 100 cycles @ -20 ℃	ZAB[45]
Hydrogel modification	PAM	-20 ℃	14.6 S m^{-1} @ -20 ℃	226 mAh g^{-1} 75%/600 cycles @ -20 ℃	ZIB[48]
Hydrogel modification	PAA	-25 ℃	199 S m^{-1} @ -20 ℃	691 mAh g^{-1} @ -20 ℃ > 600 cycles @ 25 ℃	ZAB[89]

* Battery discharge capacity and cycling retention.

3.1 Introducing salt solutions

In our daily life, anti-freezing strategies have been widely employed. For example, salt is sprinkled on the roads to prevent them from freezing. Through introducing additives like salt, the hydrogen bonding between free water molecules is reduced, substituted by the interactions between water and hydrated ions from salt solutions, therefore suppress the ice crystallization and lower the freezing point. It is also noteworthy that the ionic conductivity could be improved by addition of suitble salt ions. Inspired by this, similar strategies have also been applied to developing anti-freezing hydrogel electrolytes for flexible zinc-based batteries.

For example, Huang and colleagues reported a concentrated hydrogel electrolyte sodium polyacrylate (PANa) to enable the operation of NiCo//Zn battery under -20 °C.[44] By absorbing high concentrated (6 M) KOH solution, the hydrogen bonding between water molecules is weakened by the concentrated ions (K^+, Zn^{2+}, and OH^-), and the freezing temperature decreases. In addition to the favorable mechanical properties of PANa hydrogel, it can be easily stretched by 1400% under -20 °C. Even at an extremely low temperature of -50 °C, this hydrogel electrolyte can still be extended by 900% (**Figure 2a**). Meanwhile, by virtue of the sufficient free-moving ions, the ionic conductivity of the electrolyte reaches 5.7 S m^{-1} under -20 °C, higher than that of many other polymer electrolytes. As a result, this concentrated hydrogel-based NiCo//Zn battery delivers a high capacity of 130 mAh g^{-1} and exceptional capacity retention of 87% after 10000 cycles. The use of concentrated hydrogel electrolyte on the flexible zinc-air battery (ZAB) was also reported by Zheng and colleagues.[50] In their work, a double-network hydrogel electrolyte (covalently crosslinked poly(2-acrylamide-2-methylpropanesulfonic acid potassium salt) (PAMPS-K) skeleton and interpenetrated methylcellulose (MC) chains, abbreviated as PAMPS-K/MC) in the presence of concentrated KOH solution (5 M) retainede favorable ionic conductivity of 18.1 mS cm^{-1} and satisfactory mechanical flexibility at -20 °C. Besides, through differential scanning calorimetry (DSC) measurement, it was found that the freezing temperature of the hydrogel could be decreased significantly from -0.2 to -30.5 °C as the KOH concentration was increased from 0 to 5 M. Moreover, the fabricated ZAB showed excellent tolerance against a cold environment (-20 °C) without an obvious decline in electrochemical performances and mechanical strength. Considering the feasibility of this strategy, Huang's previous study on PANa hydrogel also showed potential in functioning as electrolytes for anti-freezing flexible ZABs.[27]

Apart from the flexible alkaline zinc-based battery, similar methods are also employed by the zinc-ion battery (ZIB) with neutral or acid electrolyte to facilitate its operation in the cold environment. For example, Wang et al. took advantage of the high solubility of $ZnCl_2$ and the strong salt tolerance of xanthan gum to prepare high-concentration salt (12 M $ZnCl_2$) electrolyte (HCSE) for ZIBs.[86] By merit of the anti-freezing HCSE with high ionic conductivity of 13.8 mS cm^{-1} at 20 °C and 5 mS cm^{-1} at -20 °C, the fabricated ZIB delivered correspondingly high specific discharge capacity of 283 mAh g^{-1} and 119 mAh g^{-1}, as well as remarkable cycling stability of 90.3% and 83% capacity retention, respectively. Even under the bending condition, this HCSE ZIB still presented a capacity retention of 90.1% when bent at 90° for 10 cycles and 81.3% when bent at 180°

for another 20 cycles at -20 °C, showing reliable mechanical flexibility and favorable electrochemical performance in the subzero working condition. Apart from this work, a flexible anti-freezing Zn/LiFePO4 battery was also assembled by Zhu et al. using PAM concentrated of dual salts solution (2 M $ZnSO_4$ and 4 M LiCl, abbreviated as ZL-PAM), as shown in **Figure 2b**.[85] It is believed that the cooperation of the hydrated cations (Zn^{2+} and Li^{+}) not only lowers the freezing temperature of ZL-PAM but also improves the cycle reversibility of the zinc anode. Besides, Parkin and co-workers also verified that the cation Li^{+} could form $Li_2O/LiCO_3$ on the zinc surface, which effectively suppressed the zinc dendrite, while the anion Cl^{-} could facilitate ion transport.[90] As a result, the fabricated Zn/LiFePO4 battery delivered a superb rate performance upon cooling down to -20 °C from room temperature (**Figure 2c**), as well as a near 100% capacity retention after 500 cycles at -20 °C with a coulombic efficiency of more than 99.5% (**Figure 2d**). Besides, the mechanical property was perfectly maintained after storing the battery at -20 °C for 24 hours, enabling the potential application in wearable electronics among a wider temperature range (**Figure 2e**).

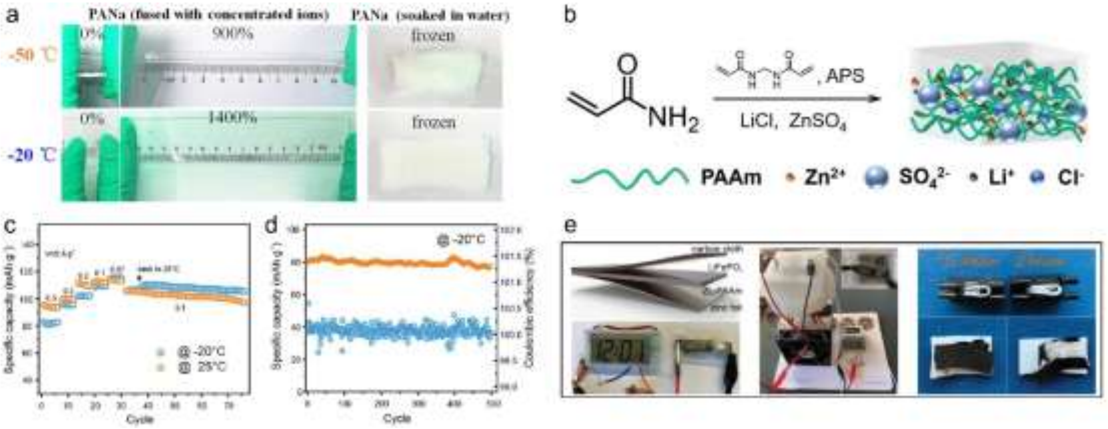


Figure 2. (a) Stretchability of the PANa hydrogel at different temperatures infused with

concentrated ions and deionized water, respectively.[44] Copyright 2019, American Chemical Society. (b) Schematic illustration of synthesis of the ZL-PAM hydrogel. (c) Rate performance and (d) cycling stability (0.5 A g^{-1}) of the Zn/$LiFePO_4$ battery at −20 °C. (e) Bending-state battery at −20 °C.[85] Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

3.2 Introducing polyol solvents

Antifreeze solution (normally polyol solvent) is widely utilized as an engine coolant to guarantee the operation of automobiles in winter. Similarly, without a proper cryoprotectant, a hydrogel-based battery can not operate in a subzero temperature environment. Glycerol and EG, two common polyol solvents, are often selected as cryoprotectants due to their free solubility with water. Their strong interaction with water molecules through hydrogen bonding severely impairs the interactions among water molecules, thus inhibiting the ice crystallization and lowering the freezing temperature.[83] Recently, strategies of introducing polyol solvents as cryoprotectants have aroused great interest of researchers to prepare anti-freezing hydrogel electrolytes for flexible zinc-based batteries.

For example, Chen and co-workers developed a flexible anti-freezing Zn-MnO_2 battery using a borax-crosslinked PVA/glycerol (PVA-B-G) hydrogel as an electrolyte.[87] A facile freeze/thaw method was applied to the PVA-B-G gelation in the precursor solution, a binary solvent of glycerol/salt solution (2 M $ZnSO_4$ and 0.2 M $MnSO_4$) with borax addition. Borate ions formed by borax hydrolyzation in water ($B(OH)_4^-$) could easily crosslink with PVA and glycerol via complexation. Besides, with abundant hydrogen bonds formed among PVA, glycerol, and water molecules, integrated 3D networks were constructed, further enhancing the mechanical strength of the PVA-B-G hydrogel and facilitating ion transportation (**Figure 3a**). On the other hand, with the effect of glycerol, the PVA-B-G hydrogels could be twisted, bent, and even stretched to 400-500% strain without mechanical property degradation in the extremely cold environment of -35 °C as shown in **Figure 3b**. As a result, the PVA-B-G hydrogel electrolyte displayed a high ionic conductivity of 10.1 mS cm^{-1} (**Figure 3c**), and the capacity retention of the assembled Zn-MnO_2 battery retained 90% after 2000 cycles at -35 °C (**Figure 3d**). Soon after, Chen et al. developed the Zn-MnO_2 battery based on a polyacrylamide/graphene oxide/ethylene glycol (PAM/GO/EG) hydrogel electrolyte using different materials but the same functionality.[88] The above-mentioned works show common strategy in electrolyte development. That is, the researchers construct the anti-freezing hydrogel electrolyte by synergistically combining the stable hydrogel substrate (PVA/PAM), mechanical property enhancing additives (borax/GO), polyol cryoprotectant (glycerol/EG), and salt solution ($ZnSO_4$ and $MnSO_4$), which may effectively guide the design of future anti-freezing hydrogel.

Another promising approach for improving the electrolyte is to modify the hydrogel through a solvent-displacement process, by substituting water in the hydrogel with polyol cryoprotectant. Representatively, Zhou et al. employed this method by immersing a water-based Ca-alginate/PAM hydrogel in cryoprotectant (glycerol, EG, sorbitol, or mixture of them) for minutes to several hours.[91] The wt% of the cryoprotectant within hydrogels was increased and the anti-freezing capacity of hydrogel was enhanced with increasing immersion time. For example, the fully immersed EG-based hydrogel could remain unfrozen and flexible even at -70 °C. This outstanding anti-freezing ability results from substitution of abundant free water in the hydrogel by the cryoprotectant, thus lowering the freezing point of the hydrogel. However, to the best of our knowledge, this strategy has never been applied in a zinc-based battery. Considering the favorable inter-solubility between cryoprotectant and standard salt solution for zinc-based batteries (i.e., KOH, $ZnCl_2$, and $ZnSO_4$), it is expected that the mixture of these two will supplant single cryoprotectant to further develop the anti-freezing hydrogel for zinc-based batteries in the future.

Very recently, researchers have found that the addition of polyols could also improve the zinc reversibility in aqueous electrolytes.[92] From the work of Pan and co-workers,[93] polyol molecules (e.g., EG) could form hydrogen bonding with water molecules, thus lowering the hydrogen evolution reaction (HER) activity and increasing the cycling coulombic efficiency (CE). Moreover, the addition of polyols significantly decreased the conductivity of Zn^{2+}, which suppressed the fast growth of zinc dendrites. Although these works are about aqueous electrolytes, similar results are expected for hydrogel electrolytes.

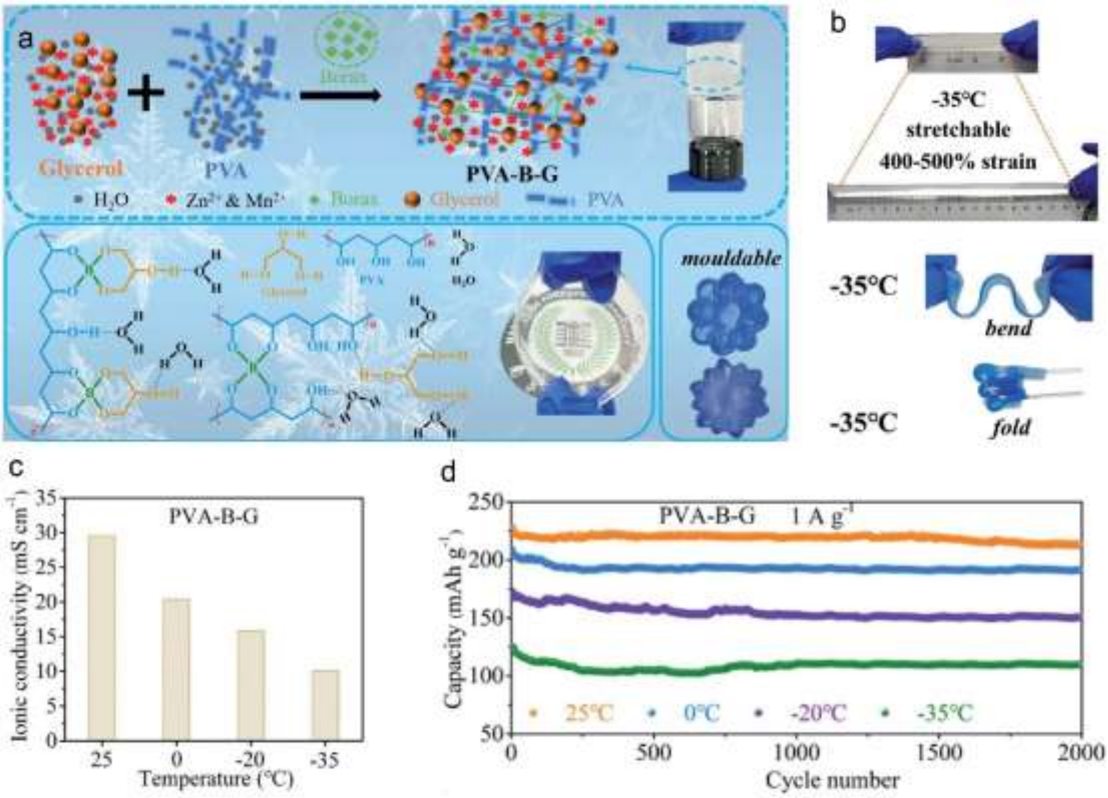


Figure 3. (a) The synthesis schematic and multi-complexation of the integrated 3D network within PVA-B-G. (b) Photographs of PVA-B-G under stretching, bending, and folding at -35 °C. (c) The ionic conductivity of PVA-B-G at different temperatures. (d) Cycling performances of the PVA-B-G battery at 1 A g^{-1} at different temperatures.[87] Copyright 2020, Royal Society of Chemistry.

3.3 Hydrogel network modification

Different kinds of hydrogels have various polymer chain structures and affiliated functional groups. Most groups in the hydrogel system are hydrophilic, which means water molecules will interact with these groups through strong hydrogen bonds (i.e., -NH_2, -OH, and -COOH) and form SBW. Researchers have also found that the formation of SBW will decrease the freezing temperature of hydrogel significantly.[84] However, the anti-freezing effect of hydrogels. Therefore, it is important to figure out the extent of interaction between water molecules and various hydrophilic groups. From the density functional theory (DFT) calculation results obtained by Chen and co-workers,[89] the interaction energy (E_{int}) between the PVA terminal hydroxyl group and neighboring water molecules is -6.11 kcal mol^{-1}. In comparison, a more polarized carboxyl group in PAA has a larger E_{int} value of -12.92 kcal mol^{-1}. When the carboxyl group is further alkalified (alkalified-PAA, denoted as A-PAA), its E_{int} with water molecules increases to -16.96 kcal mol^{-1} (**Figure 4a**). As a result, the freezing point of PVA with 10 wt% KOH solution is -13 °C, while the A-PAA containing 10 wt% KOH solution is -25 °C, indicating that the more polarized group further suppresses the freezing point of hydrogels. To further investigate its electrochemical application in the extremely cold temperature, Chen et al. filled this A-PAA with 30 wt% KOH solution as a hydrogel electrolyte for flexible ZAB. Under -20 °C, its ionic conductivity reached 199 mS cm^{-1} (**Figure 4b**), and the fabricated ZAB retained excellent electrochemical performances compared to room temperature (**Figure 4c**). Moreover, the A-PAA-based ZAB could be bent, folded, or twisted under -20 ℃, indicating its outstanding low-temperature adaptability (**Figure 4d**). This research demonstrates the significance of hydrophilic groups in depressing the freezing temperature and provides guidance for selecting proper hydrogel substrates to facilitate zinc-based batteries working in the cold environment.

In addition to exploiting the initial hydrophilic groups in the hydrogel network, Zhi et al. presented a novel EG based waterborne anionic polyurethane acrylate/PAM (EG-waPUA/PAM) hydrogel system by introducing a new hydrophilic group hydroxyl from EG and firmly anchoring it onto the hydrogel networks through covalent bond.[48] Under the synergistic effect of EG-waPUA and PAM, the E_{int} of EG-waPUA-PAM-water ranges from -16.53 to -17.49 kcal mol^{-1}, which is significantly higher than the E_{int} of EG-waPUA-water and PAM-water (-6.7 and -10.67 kcal mol^{-1}, respectively). The strong interaction between the hydrophilic groups and water molecules effectively prevents the ice crystallization within EG-waPUA/PAM. Consequently, even at -20 °C, this anti-freezing hydrogel (AF-gel) containing 2 M $ZnSO_4$ and 0.1 M $MnSO_4$ retained a good ionic conductivity of 14.6 mS cm^{-1} (only 10% lower than that at room temperature) and remarkable flexibility. Moreover, the AF-gel electrolyte based Zn-MnO_2 battery delivered a high discharge capacity of 226 mA h g^{-1} at -20 °C, while the counterpart PAM-based battery nearly failed. This hydrogel network modification strategy by introducing a new hydrophilic group (hydroxyl from EG) compensates the deficient interaction between the initial group (amino from PAM) with water molecules. Remarkably, the synergistic effect of these two functional groups plays a role of “1+1>2” in further depressing the freezing point of hydrogels.

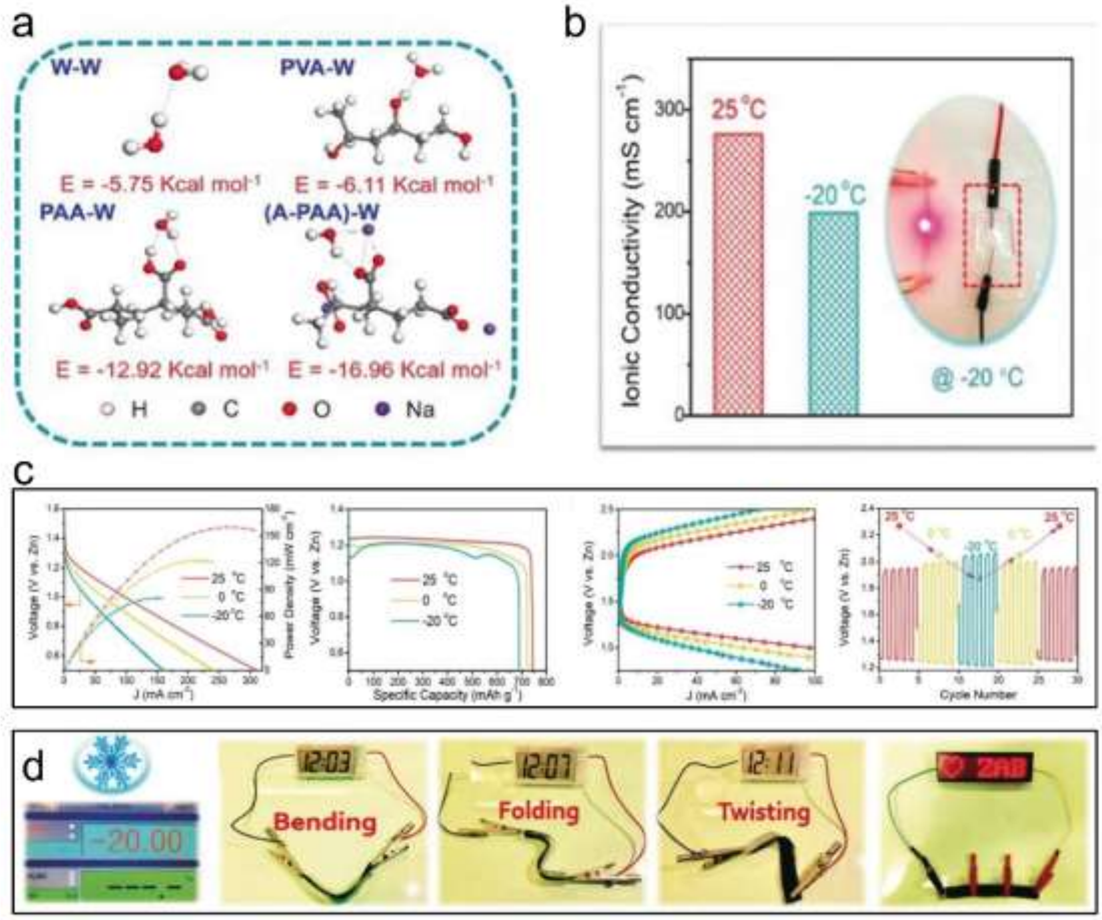


Figure 4. (a) Molecular models used to simulate interactions between water molecules and different terminal groups in polymers. (b) Ionic conductivity of KOH-filled A-PAA hydrogel at 25 and -20 °C. (c) Temperature-dependent performances of the flexible ZAB at different temperatures: polarization and power density; discharge capacity at 5 mA cm^{-2}; charge and discharge profiles; and cycle performance at 2 mA cm^{-2}. (d) Photographs of the flexible ZAB under different deformations at -20 °C.[89] Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

3.4 Other approaches

Apart from the three main strategies including introducing salt and polyol solvents, and hydrogel network modification, other methods can also be adopted to prepare anti-freezing hydrogels for zinc-based batteries. For example, Yan et al. designed and synthesized an anti-freezing PAM hydrogel based on a zwitterionic poly(ionic liquid) (PIL), which contained equal positively and negatively charged groups in one unit (**Figure 5a**).[94] The author believed that the water molecules strongly interacted with the zwitterionic groups through charge-dipole and dipole-dipole. Hence, the ice crystallization was inhibited and the freezing temperature was depressed to -26 °C (**Figure 5b and c**). As a result, this PIL hydrogel achieved an ionic conductivity of 1.1 S m^{-1} (with 10 wt% KCl solution) (**Figure 5d**) and a superb stretchability of 900% under -20 °C (**Figure 5e**). Besides, by virtue of the synergistic effect of the reversible ionic bonding and hydrogen bonding, the PIL hydrogel even exhibited a self-healing ability (**Figure 5f**).

Recently, Tao and co-workers employed DMSO as a cryoprotectant to develop an aqueous electrolyte with an extremely low freezing temperature of -130 °C.[95] DMSO has similar physicochemical properties like polyol cryoprotectant (glycerol/EG) that they can both mix with water in any ratio and regulate the freezing point. Furthermore, DMSO could effectively suppress the zinc dendrite as well, which has been confirmed by Wang et al.[96] Afterward, Jiang et al. took advantage of this DMSO/water binary solvent as a precursor solution to synthesize anti-freezing PVA hydrogel.[97] By adjusting the ratio of DMSO/water, the PVA hydrogel retained admirable flexibility even at -70 °C. Furthermore, the author noted that the dielectric constant of DMSO ($\varepsilon = 46.7$) was higher than that of other kinds of cryoprotectants like EG ($\varepsilon = 37.0$), which suggested improved ion dissociation and conductivity using DMSO as an anti-freezing agent. As a result, the ionic conductivity of this hydrogel can still reach 1.1 S m^{-1} under -70 °C. Very recently, He and co-workers found that the PVA with DMSO/water mixture solvent would polymerize faster than PVA with pure water or DMSO.[98] Moreover, they provided a novel strategy for scalable fabrication. Based on these findings, it is expected that the mixture of DMSO and Zn^{2+} salt solution will lead to a hydrogel electrolyte with higher ionic conductivity and further promote the electrochemical performance of flexible zinc-based batteries at the extremely low temperature.

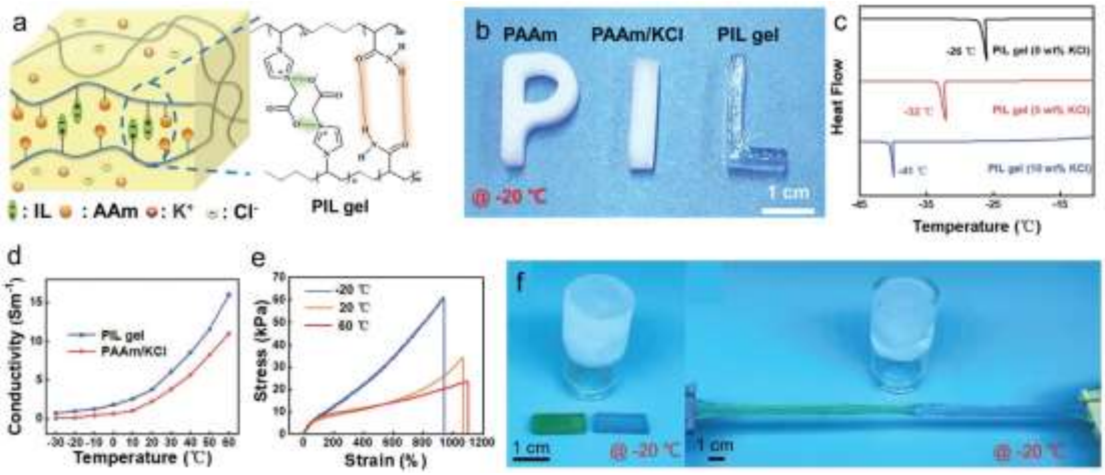


Figure 5. (a) Chemical structure and (b) photograph of the anti-freezing zwitterionic PIL gel. (c) DSC tests of the PIL gels with different KCl concentrations. (d) Ionic conductivity and (e) uniaxial tensile tests of the PIL gel under various temperatures. (f) Self-healing ability of the PIL gel at -20 °C.[94] Copyright 2020, Royal Society of Chemistry.

3.5 Current challenges

Although tremendous efforts have been made to improve the performances of hydrogel electrolytes and the corresponding zinc-based batteries at subzero temperature, challenges still exist in the current research as follows:

(1) The ionic conductivity of the hydrogel electrolyte inevitably deteriorates in a subzero temperature environment, which further leads to the degradation of the zinc-based batteries. Efforts should be devoted to raising the ionic conductivity as high as possible.

(2) Although introducing salt and polyol solvents has been proven effective for hydrogel anti-freezing, the salts may precipitate as the temperature declines, and the newly introduced polyol will dilute the salt concentration. Both of them can reduce the ionic conductivity of the hydrogel electrolytes. Additionally, the addition of flammables may bring extra safety issues. On the other hand, too much modification on the polymer chains will complicate the manufacturing process and raise costs.

(3) The hydrogel surface is more likely to freeze compared to its inner part.[99] The resulting poor ice/electrode interface of the battery will significantly increase the interfacial resistance and degrade the battery performance. Unfortunately, methods for designing anti-freezing hydrogel surfaces remain to be developed.

(4) The existing anti-freezing methods for hydrogel electrolytes are still limited and ineffective for practical applications. Other effective and cost-efficient ways are still waiting to be explored.

(5) Apart from the hydrogel electrolytes, the low-temperature performances of the electrodes are also crucial to zinc-based batteries. Generally, the electronic conductivity and ion diffusion rate of the electrode will decline at a lower temperature, which will

further decrease the battery rate performance.[100] It is urgent to find ways to activate the electrode materials in the low temperature and improve the electrode/electrolyte compatibility.

4. Hydrogel electrolytes at high temperatures

Preventing dehydration at high temperatures and thermal shock are one of the main challenges for zinc-based batteries with hydrogel electrolytes. In this section, practical strategies for resolving these issues are summarized and evaluated (**Table 3**). Meanwhile, the recent progress of zinc-based batteries employing these strategies is introduced. Other advanced methods for developing dehydration-tolerant hydrogel and thermal-stable energy storage devices are also reviewed to provide insight for zinc-based batteries at extremely high temperatures.

Table 3. Anti-dehydration methods for zinc-based batteries with hydrogel electrolytes.

Method	Hydrogel substrate	Water retention	Battery Performance*	Ref.
Adding salt	PAM	70% after 120 hours @ 10% RH, 25 ℃	--	--[101]
Adding polyol	PAM/PAA	19% after 48 hours @ 25 ℃	640.9 mAh g^{-1} > 30 cycles @ 70 ℃	ZAB[45]
Hydrogel modification	PANa	97% after 185 hours @ 25 ℃	ZAB 800 cycles ZIB 16000 cycles @ 25 ℃	ZAB/ZIB[27]
Adding inorganic particles	PVA	63% after 40 hours @ 25 ℃	> 144 cycles @ 25 ℃	ZAB[35]
Adding inorganic particles	PAA/PVA	90% after 12 hours @ 25 ℃	742 mAh g^{-1} > 200 hours cycling @ 25 ℃	ZAB[36]

Elastomer coating	PAM	92% after 24 hours @ 50% RH, 80 °C	260 mAh g^{-1} > 150 cycles @ 80 °C	ZIB[49]

* Battery discharge capacity and cycling performance.

4.1 Strategies for dehydration

4.1.1 Salt and polyol additives and hydrogel network modification

Free water NBW not only readily freeze at a subzero temperature but also suffer from dehydration in the ambient environment. Since both phenomenons obey the mechanism discussed in Section 2, strategies for anti-freezing hydrogels can also be applied to suppress dehydration in the hydrogel system. Bai et al. found that by introducing hydrated salts (i.e., LiCl, $MgCl_2$, and KAc), which interact intimately with water molecules, the water retention capacity of PAM hydrogel was strengthened significantly, as shown in **Figure 6a**.[101] Especially LiCl, which has been widely used as electrolyte additives for ZIBs, exhibited a more hydratable property than the other two.[85]

Among zinc-based batteries, ZABs are more susceptible to water loss due to the half-open system, which gradually leads to battery performance degradation. Therefore, It is urgent to minimize water evaporation, thus maintaining the battery performance for a long period. Apart from the salt introduction method, polyols can also enhance the water retention ability of hydrogels and have already been employed in flexible ZABs. Recently, Xu and co-workers successfully suppressed PAM/PAA hydrogel water loss by introducing different concentrations of glycerol (**Figure 6b**).[45] Moreover, after baking at 70 °C for 12 hours, the volume of the hydrogel was hardly changed, and the hydrogel still adhered tightly to both the zinc electrode and air electrode, indicating an intimate interfacial contact (**Figure 6c**). Also, the fabricated ZAB showed a high discharge capacity retention of 96.63% at 70 °C (compared to the room temperature, 640.92 mAh g^{-1}). Unfortunately, the water loss was alleviated but still inevitable. In the future, polyol and hydrated ions can combine and it is expected that their synergistic effect may further enhance the hydrogel water retention and battery life.

In Section 2.3, the positive effect of highly hydrophilic polymer chains in lowering freezing temperature is demonstrated. Recently, Huang et al. also found another use in suppressing water loss from hydrogels. The testing results showed that the PANa hydrogel held a stronger water retention capacity than PVA hydrogel, which could be explained by the higher E_{int} between the carboxyl groups and water molecules. Even after 185 hours, the water content of PANa hydrogel still remained 97.3% (the value of counterpart PVA hydrogel is 77.6%).[27] Besides, no salt precipitation was observed in the PANa hydrogel after being exposed to the ambient environment for 6 days. As a result, the PANa hydrogel electrolyte with superb water retention capacity elongated the cycle life of the fabricated ZAB and Zn//NiCo battery to unprecedented 800 cycles and 16000 cycles, respectively (**Figure 6d and e**). Apart from the comparison between PANa and PVA hydrogel, Zhao et al. also confirmed that the PANa hydrogel held a superior water retention capacity than the PAM hydrogel.[34] So far, it is obvious to conclude that the anti-freezing and anti-dehydration properties of hydrogels can be obtained simultaneously by the same strategies, which may further guide the future design and synthesis of hydrogel electrolytes for a long-life and wide-range zinc-based batteries.

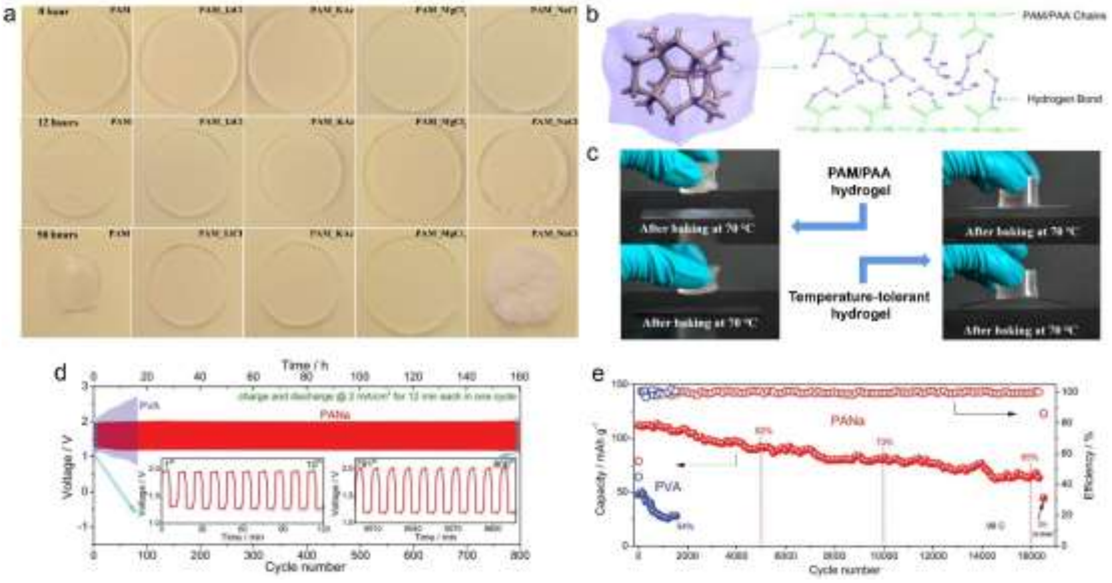


Figure 6. (a) Water retention capability of PAM hydrogels with various salts.[101] Copyright 2014, AIP Publishing. (b) Schematic illustration of the hydrogen bonding interactions taking place between glycerol, the PAM/PAA polymer chains, and water molecules. (c) Adhesion of the temperature-tolerant hydrogel after baking at 70 °C for 12 hours.[45] Copyright 2020, American Chemical Society. Long-term cycling performances of the (d) ZAB and (e) Zn//NiCo battery using the PANa hydrogel electrolyte.[27] Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

4.1.2 Inorganic particle additives

Doping is regarded as an effective approach for modifying hydrogel inner network structures. It is common to dope and disperse inorganic particles uniformly within the network to form hydrogel nanocomposites. They have exhibited great enhancement in hydrogel water retention capacity. Recently, Zhong et al. found that the addition of silica (SiO_2) can effectively alleviate the water loss in PVA hydrogels (**Figure 7a**).[35] By optimizing the weight ratio of SiO_2 (5 wt%), the aggregation (crystallinity) of the PVA matrix was reduced as substantiated by the decreased characteristic peak at 19.5°, as shown in **Figure 7b**. Therefore, more PVA chains were freed to interact with water molecules, leading to an enhanced water retention ability (**Figure 7c**). Also, the ionic conductivity of the PVA-5 wt% SiO_2 was increased due to the porous PVA matrix with a sufficient ion pathway (**Figure 7d**). As a result, the fabricated flexible ZAB successfully extended the discharge time to over two times of pure PVA-based ZAB (**Figure 7e**). However, it is noteworthy that excessive SiO_2 (9 wt%) fillers may damage the stable PVA inner structure and harm the overall performance. Apart from the nonmetallic ceramic oxides, metallic ceramic oxides like zirconium dioxide (ZrO_2), titanium oxide (TiO_2), and zinc oxide (ZnO) are also effective in enhancing thermal stability and water retention capacity of hydrogels.[102-104]

Most recently, Zhong et al. further incorporated graphene oxide (GO) with abundant hydrophilic groups (i.e., hydroxyl and carboxyl) into the PAA/PVA hydrogel matrix to form a new hydrogel system PVAA-GO.[36] It was believed that the strong interaction between GO and PAA/PVA chains established a more intact hydrogel network with sufficient interspace for water holding (**Figure 7f**). As a result, the PVAA-GO hydrogel could retain over 90 wt% water after 12 hours, whereas only 64.7 wt% water was held within the PVA hydrogel. Moreover, as shown in **Figure 7g**, the fabricated ZAB operated steadily for over 200 hours due to the successful water retarding of PVAA-GO, demonstrating great potential in the future commercial application. For other carbon-based hydrogel nanocomposites in water retention research, interested reader could refer to the review article.[105]

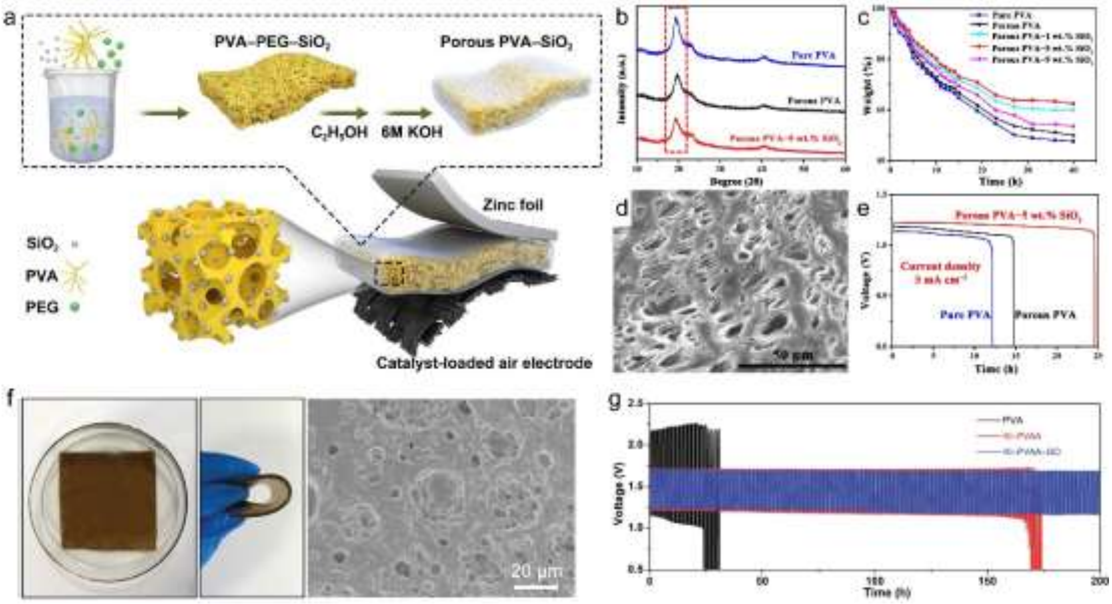


Figure 7. (a) Schematic diagram of the flexible ZAB and preparation process of the nanocomposite PVA hydrogel along with its inner structure. (b) XRD patterns and (c) water retention curves of the nanocomposite PVA hydrogels. (d) SEM image of the porous PVA-5 wt% SiO$_2$ hydrogel. (e) Discharge curves of ZABs using nanocomposite PVA hydrogels.[35] Copyright 2019, Elsevier. (f) Optical images and SEM image of the PVAA–GO hydrogel. (g) Cycling performance of the PVAA–GO based ZAB at 2 mA cm^{-2}.[36] Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

4.1.3 Other methods

A main reason for hydrogel dehydration is the completely exposed hydrogel surface, where water evaporates continuously to the ambient environment without any protection. From this perspective, coatings as protection layers on the hydrogel surface can avoid direct exposure of hydrogel surface to the outside, thus retarding the water loss physically. Recently, Zhao et al. successfully mitigated hydrogel dehydration by employing an Ecoflex elastomer as a coating on the PAM hydrogel.[106] The testing results showed that the water content of the protected hydrogel remained nearly unchanged after 2 days, while the uncoated hydrogel lost 85% water. Furthermore, since the elastomer coating and salt/polyol introducing strategies are not interfering with each other, these two strategies can work simultaneously to enhance the water retention capacity of hydrogels further and even endow their anti-freezing property (refer to the discussion in Section 2.1, 2.2, and 3.1.1). Unfortunately, most elastomers are electrically insulating. Even worse, when applied to the battery, the elastomer coating will block the direct contact between hydrogel electrolytes and electrodes, directly disabling the battery operation. To fully exploit the advantage in water retention but also overcome the insulating problem of the elastomer coating, most recently, Mo et al. integrated electrodes inside the PAM hydrogel electrolyte and then coated polydimethylsiloxan (PDMS) elastomer on the hydrogel surface to fabricate environmental adaptive Zn-MnO_2 batteries (EA batteries) (**Figure 8a**).[49] In this way, the PAM hydrogel electrolyte contacted intimately with electrodes and was protected from water evaporation at the same time. Moreover, the addition of EG and 2 M $ZnSO_4$ within the PAM hydrogel further enhances its water retention and anti-freezing capacity. By these improvements, the EA battery exhibited excellent performances under a wide temperature range from -20 °C to 80 °C (**Figure 8b and c**). **Figure 8d** showed that even placed in boiling water (100 °C), the coated EA battery could power an electronic watch successfully.

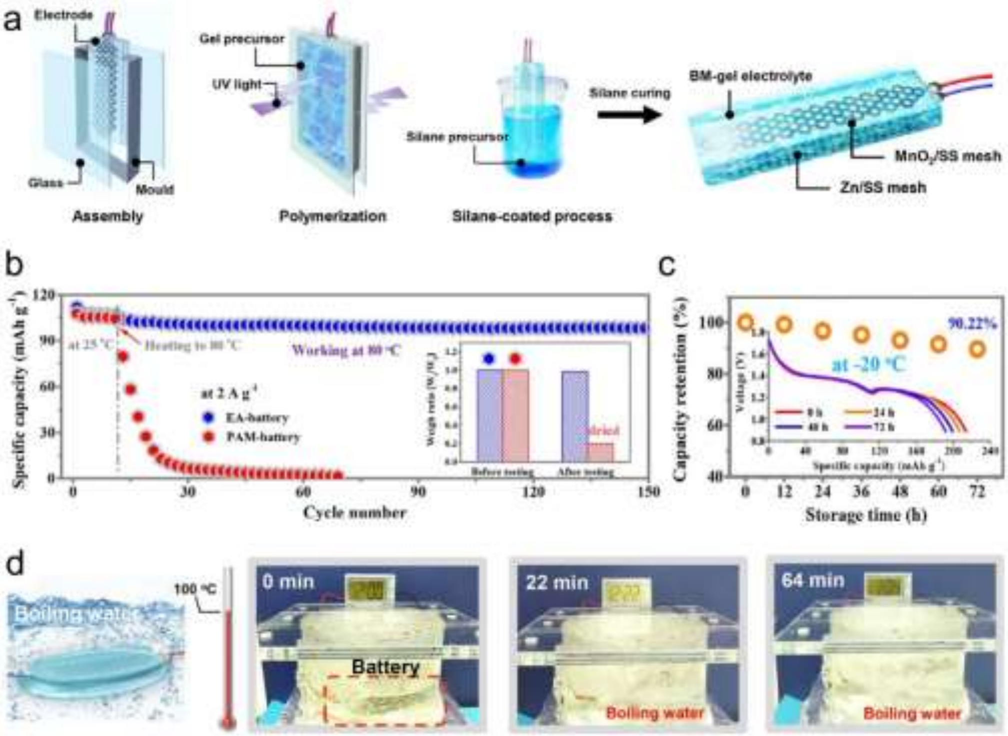


Figure 8. (a) Schematic illustration of the fabrication process of EA battery. (b) Lifetime comparisons of EA battery and PAM battery working at 80 °C. (c) Capacity retention of the ice-sealed EA battery at -20 °C. (d) Schematic illustration and anti-heating test of the EA battery when powering an electronic watch in boiling water.[49] Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

4.2 Strategies for safe flexible zinc-based batteries

4.2.1 Smart thermo-reversible hydrogels

Wearable energy storage devices inevitably interact with human beings intimately. Therefore, severe battery overheating should be completely suppressed for safety. Recently, a new kind of smart material, thermo-reversible hydrogel, has been employed within the flexible zinc-based battery to effectively prevent battery thermal shock.[107] The thermo-reversible hydrogel holds a unique sol-gel phase transition property. The hydrogel is liquid-state at a relatively low temperature (e.g., 20 °C) but gel-state at a high temperature (e.g., 70 °C), as shown in **Figure 9a**. For a detailed mechanism, interested readers can refer to the corresponding articles.[108, 109] The key is that the ion migration is prohibited when changing to gel-state. Consequently, the overheated battery is shut down automatically until operating again under proper temperature (**Figure 9b**). Considering the current research is still in its very early stage with limited reported works, herein some representative studies are discussed to provide design strategies and inspire readers.

Recently, Zhi et al. reported a smart thermo-reversible hydrogel electrolyte poly(N-isopropylacrylamide (NIPAM)-co-Acrylic acid (AA)) (PNA) and successfully applied this hydrogel electrolyte to a rechargeable Zn/MnO_2 battery.[110] When heating to 70 °C, the resistance of PAN electrolyte increased nearly 9 times to that of room temperature, thus severely limited the battery operation (**Figure 9c**). Consequently, the specific capacity of the fabricated Zn/MnO_2 battery decreased significantly from 145 to 50 mAh g^{-1} as the temperature was decreased from 20 to 70 °C, as shown in **Figure 9d**. After cooling to room temperature, the battery electrochemical performance could restore to its initial state, ensuring multiple uses (**Figure 9e**). It is also worth mentioning that the sol-gel transition temperature can be adjusted by changing the ratio of NIPAM/AA to meet different shutting down conditions. However, the authors also noted that the solubility of zinc ion in this PAN hydrogel (about 0.6 M) was lower than that in other normal electrolytes (generally above 2 M), which severely limited the rate performance and specific capacity of the battery. Unfortunately, this is a common problem in other thermo-reversible hydrogels (e.g., Pluronic) as well, and no effective solution has ever been reported.[29, 37] In the future, more hydrated zinc salt and hydrogel structure modification methods can be exploited to improve the compatibility with zinc ions.

Although the liquid-state thermo-reversible hydrogels guarantee free ion migration, the existence of hydrogel copolymers inevitably impairs the ionic conductivity to some extent compared to the zinc salt solution electrolyte. For this reason, Zhu et al. suggested employing thermo-reversible hydrogels as a coating on the battery separator rather than the electrolyte to minimize the negative effect on the ionic conductivity while maintaining the functionality of overheating self-protection.[78] The thermo-reversible hydrogel PNIPAM/AM was synthesized through an *in situ* free radical polymerization in water with NIPAM monomer and acrylamide (AM). Unlike the sol-gel transition hydrogel, the copolymer PNIPAM/AM was freestanding and only went through gel-gel transition, which was achieved by adjusting the concentration of NIPAM and the crosslinker N, N'-methylene-bisacrylamide (MBAA). As shown in **Figure 9f**, the PNIPAM/AM hydrogel exhibited a porous structure at room temperature (25 °C), which allowed the free migration of ions. Upon heating to 60 °C, the hydrogel contracted, and the porous structure disappeared, indicating the ion pathway had been inhibited successfully (**Figure 9g**). The researchers then immersed this hydrogel into 0.25 M $Zn(CF_3SO_3)_2$ solution and coated it onto the battery separator. By this approach, PNIPAM/AM hydrogel served as a thermal gate to switch the on/off of the ZIB. Meanwhile, the zinc salt solution could be exploited to ensure high ionic conductivity. As a result, the fabricated ZIB achieved a high specific capacity of 168.7 mAh g^{-1} at a current density of 0.1 A g^{-1}. Even at the high discharge rate of 5 A g^{-1}, the specific capacity still maintained 105.8 mAh g^{-1}. Moreover, the battery operation could be completely shut down at 60 °C and recover to the initial state after back to room temperature, exhibiting a favorable safety control and reversibility (**Figure 9h**).

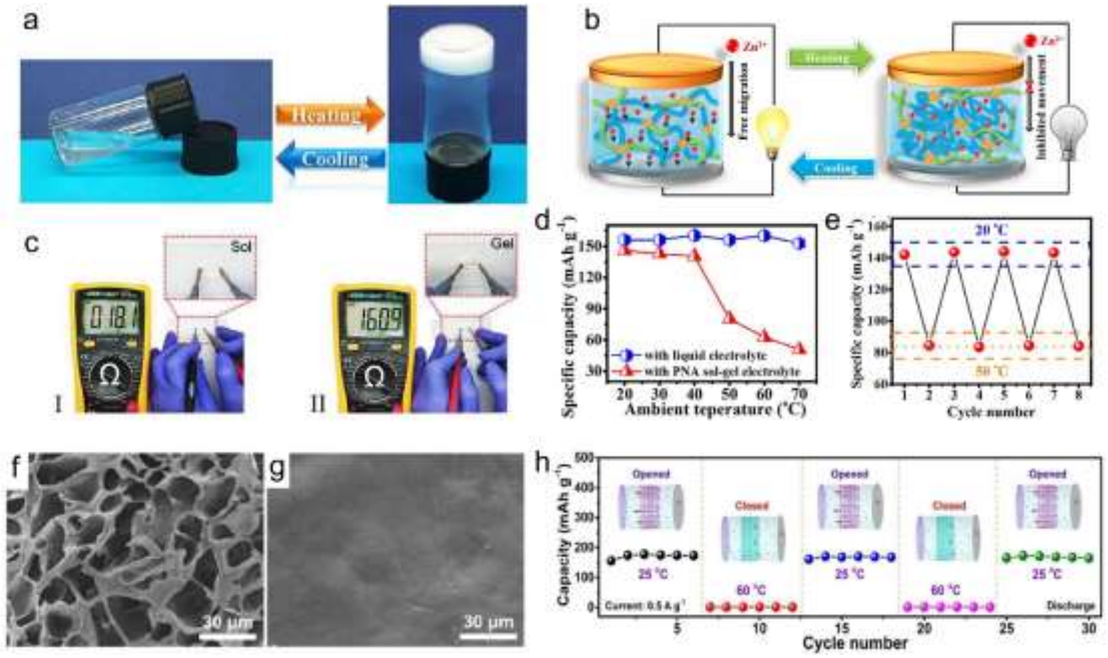


Figure 9. (a) Photographs of the reversible sol-gel transition process. (b) Design principle of smart safe ZIBs based on the thermo-reversible hydrogel electrolyte. (c) Resistance of PNA in the sol (I) and gel (II) states. (d) Self-protection capability and (e) reversible cycles of the PNA based battery.[110] Copyright 2018, Elsevier. SEM images of the PNIPAM/AM hydrogel at (f) 25 °C and (g) 60 °C. (h) Safety performance of the PNIPAM/AM based ZIB.[78] Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

4.2.2 Other methods

Different application forms of the thermo-reversible hydrogel PNIPAM in other smart devices can also be used to inspire zinc-based battery design. For example, Yu et al. took advantage of the heating-contraction property of PNIPAM hydrogel to develop a switcher.[71] As shown in **Figure 10**, when the switcher was heated, the contracted PNIPAM hydrogel lost contact with the electrode, thus cut off the circuit. After cooling down, the hydrogel recovered to its original state and contacted the electrode again. This same strategy could be adopted to construct hydrogel electrolytes with proper zinc salt components for zinc-based batteries. Nevertheless, the frequent stick-peel cycles may cause poor contact between electrode and electrolyte, which needs to be seriously considered.

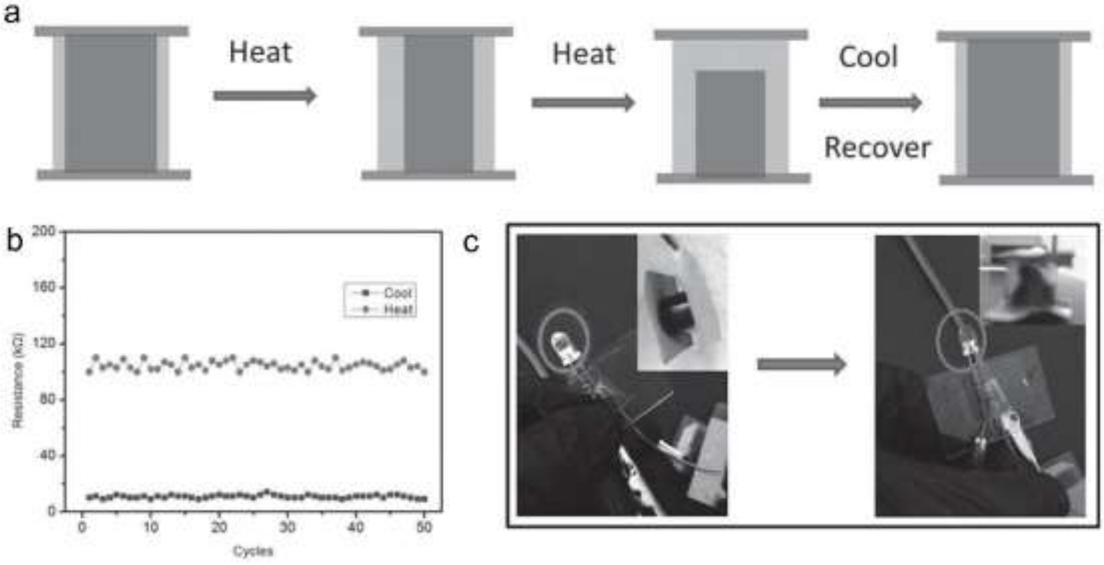


Figure 10. (a) Schematic of working mechanism of the switcher device based on the thermal-responsive PNIPAM hydrogel. (b) Cycling performance of the switcher device. (c) The switching behavior in a circuit.[71]. Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Apart from the use of thermo-responsive hydrogels, a brand new thermal self-protection approach for flexible Zn-MnO_2 batteries has been proposed by Fan and co-workers very recently (**Figure 11a**).[51] By adjusting the $ZnCl_2$ concentration of the PAM hydrogel, the inner moisture can be equivalent to the surrounding environment (25 °C and 70% RH), and the hydrogel could maintain its mass unchanged even after 10 days (**Figure 11b**). However, when the temperature went up, the moisture equilibrium was interrupted, and a large amount of water (about 40 wt%) inside PAM hydrogel evaporated quickly just like sweating (**Figure 11c**). As a result, heat was dissipated with the evaporated water, and the overheated battery was shut down automatically due to inactive ion migration (**Figure 11d**). After back to room temperature, the PAM hydrogel could reabsorb water to its initial weight again (**Figure 11c**). Subsequently, the degraded battery regained its high electrochemical performances as well. Besides, the dehydration and reabsorption of water within hydrogels exhibited high reversibility, ensuring the long-run safety of zinc-based batteries (**Figure 11e**). However, in the ambient environment of low RH, the effect of hydrogel reabsorption may at a discount. Moreover, too much time (nearly 9 hours) for reabsorption to the initial state can hinder the battery practical application. Further work should be conducted to facilitate the development of this fancy idea.

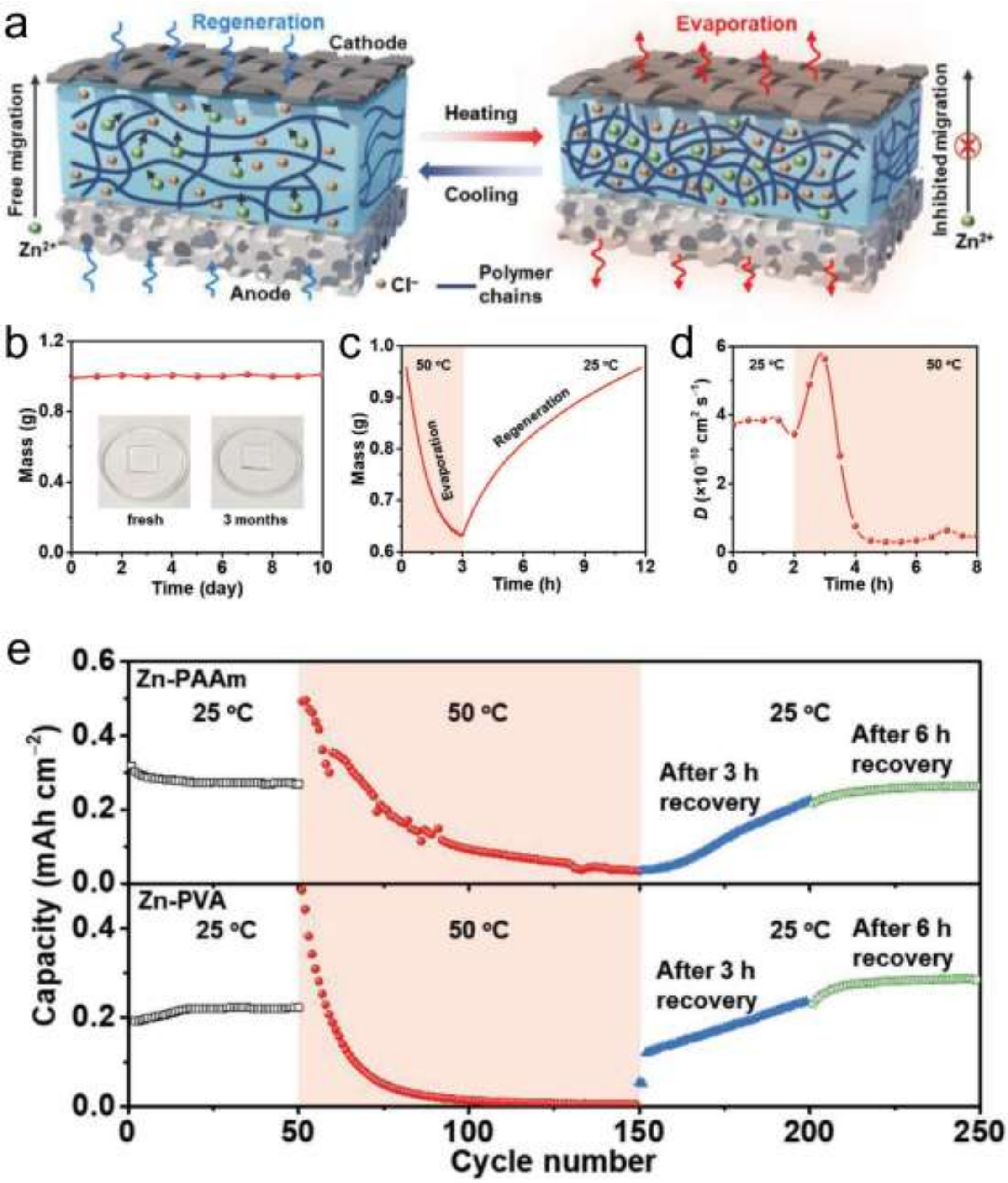


Figure 11. (a) Working principle of the thermal self-protective ZIBs based on hygroscopic hydrogel electrolyte. (b) Mass variation of the hydrogel when exposed in ambient environment. (c) Mass change of the hydrogel at 50 °C and subsequent mass recovery at 25 °C. (d) Ion diffusion coefficient of the hydrogel electrolyte from 25 °C to 50 °C. (e) Thermal-responsive reversibility of the Zn-MnO_2 batteries.[51] Copyright 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

4.3 Current challenges

From the previous discussion, researchers have proposed various approaches, including improving water retention and external protection to retard hydrogel dehydration at a high temperature. Besides, smart hydrogels have been applied to ensure battery safety. However, still many issues remain to be addressed at present:

(1) Regretfully, the water evaporation in the hydrogel electrolyte can only be alleviated but not avoided. Besides, the relative humidity (RH) should also be considered to evaluate the water retention capacity of hydrogel electrolytes. Since the salt will precipitate with water loss, the battery performances degrade distinctly, especially for batteries with high concentration hydrogel electrolytes.

(2) More research should focus on the electrode/electrolyte interface since the water loss usually starts from the hydrogel surface, which directly contacts the electrodes. The dried hydrogel surface will lose its wettability and adhesiveness, leading to increased battery resistance at the electrode/electrolyte interface.

(3) The encapsulation technologies for zinc-based batteries should be further improved to meet the practical application requirements. Besides, alternative additives should be evaluated considering the high cost of the current hydrogel fillers.

(4) At present, the strategies for safe operation of flexible zinc-based batteries are only limited to employing smart hydrogel materials. Besides, current strategies indeed lower the fire risk by shutting down the battery but unable to prevent or stop the fire immediately when the battery gets fire. More effective methods such as applying non-

flammable materials should be further explored.

5. Hydrogel electrolytes under deformations

Flexible zinc-based batteries inevitably undergo deformations like bending and stretching in practical applications. However, the mechanical properties of inner hydrogel electrolytes are still far below the requirement. In this section, potential methods for enhancing the hydrogel mechanical properties are introduced (**Table 4**). Moreover, self-healing strategies for more extreme conditions like hydrogel fracture are also taken into account.

Table 4. Mechanical properties of enhanced hydrogel electrolytes.

Method	Hydrogel Substrate	Mechanical Strength*	Elongation	Deformation tolerance	Ref.
Adding polyol	PAM/PAA	145 kPa	900%	Bending Stretching Compressing	ZAB[45]
Adding DMSO	PVA	3720 J m^{-2}	900%	Stretching knotting	--[111]
Adding salt	PVA	153.41 MJ m^{-3}	--	Stretching	--[112]
DN hydrogel	PANa/cellulose	550 kPa	1200%	Twisting knotting Bending	ZAB[52]
DN hydrogel	PAM/alginate	2022 J m^{-2}	500%	Hammering Cutting Twisting	ZIB[113]
DN hydrogel	PAM/cellulose	158 kPa	1400%	Bending	ZIB[79]
DN hydrogel	PVA/cellulose	950 kPa	440%	Bending Stretching	ZAB[114]
Adding inorganic particles	PVA	863 kPa	470%	Bending	ZAB[35]

* Tensile strength and fracture toughness.

5.1 Strategies for enhancing hydrogel mechanical properties

5.1.1 Polyol and inorganic particle additives

Polyol solvent not only plays an important role in anti-freezing and anti-dehydration hydrogels but also exhibits effectiveness in enhancing hydrogel mechanical properties. For example, Zhang et al. immersed the alginate/PVA hydrogel in various polyol solvents (EG, glycerol, and sorbitol) to displace the water partially.[115] As the solvent displacement time increased (0 to 4 hours), both the mechanical strength and elasticity improved until the displacement balance state was achieved (**Figure 12a**). Later, a quantitative study by Liu et al. further proved that increased the EG:water ratio would enhance the mechanical strength of PVA hydrogels (**Figure 12c**).[63] This is because the plentiful hydrogen bonding and crystalline domains enhanced the interaction among PVA chains. However, too much EG (i.e. EG:water of 4:1) will lead to high crystal density, which increases the hydrogel rigidity and decreases the elasticity. This phenomenon can also be explained by the SEM images shown in **Figure 12b** that porous hydrogel structure will transform to dense networks with the increase of polyol solvent. For battery application, Chen et al. fabricated a flexible ZAB with an optimized PAM/PAA hydrogel (50% glycerol).[45] The test results showed that under various deformation conditions (e.g., bending, hammering, and cutting), the mechanically enhanced ZAB could maintain good operation.

As demonstrated in section 4.1.2, nanocomposite hydrogels doping with inorganic particles such as SiO_2 and GO possess modified networks. In general, a small amount of particle doping can effectively improve the hydrogel mechanical properties, while excessive amount may harm.[35] Furthermore, Fu et al. found that the doping silica size is also crucial to the hydrogel microstructure.[61] Various types of polymer chains (e.g., PVA, PAA, and PAM) with different crosslinking degrees also show mechanical differences when accepting the same doping modification.[116] Therefore, it is significant to find mutual-matching doping and hydrogel materials to maximize the hydrogel mechanical properties. Relevant applications on zinc-based batteries have been illustrated in section 4.1.2, which will not be repeated here.

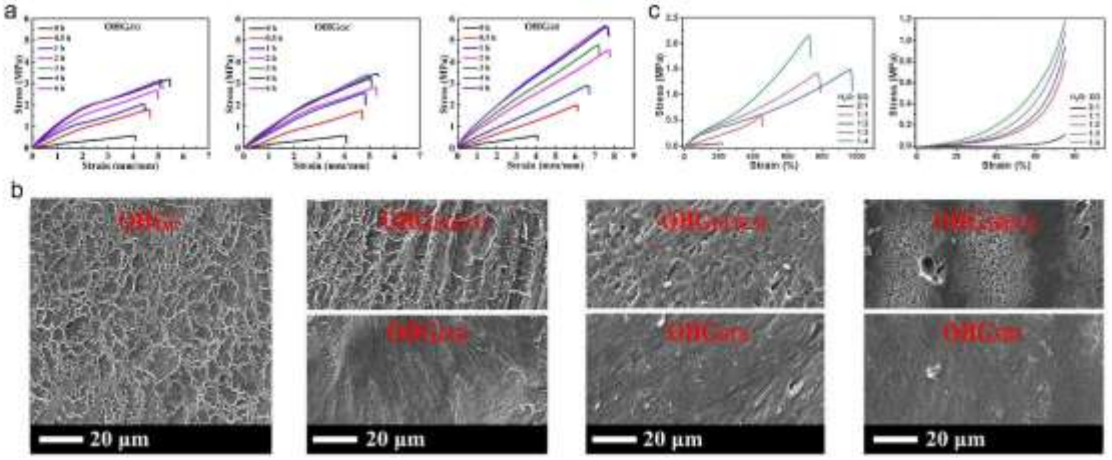


Figure 12. (a) Tensile stress-strain curves and (b) SEM images of the alginate/PVA hydrogel with different polyol solvents for different immersing times.[115] Copyright 2020, Frontiers Media S.A. (c) Tensile and compressive stress-strain curves of the PVA hydrogel with different EG:water ratios.[63] Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

5.1.2 Double-network (DN) hydrogels

DN hydrogels consist of two different polymer chains (networks). Generally, the first network is formed by highly covalent crosslinking long chains, making it tough and strong, while the second network is loosely and physically crosslinked by short chains, endowing its softness and elasticity.[117] The two networks further intimately entangle together to assemble tough and stretchable hydrogels. Even containing 90 wt% of water, the DN hydrogel can still maintain desirable mechanical properties, making it an ideal electrolyte for robust zinc-based batteries.[118] Recently, Liu et al. introduced a device-level tough and flexible Zn-MnO_2 battery based on a PAM/alginate DN hydrogel.[113] The covalently crosslinked PAM chains constructed basic hydrogel frameworks, which the second alginate network crosslinked by Zn^{2+} ionic bonding interpenetrated in (**Figure 13a**). When suffering from stress, the weak ionic bonding broke to dissipate mechanical energy, while the strong PAM network deformed but kept integrity (**Figure 13b**). After unloading, the PAM network went back to its original state, and the alginate network reconstructed by the reversibly reformed Zn^{2+} ionic bonding, ensuring its multiple-stretching stability (**Figure 13b**). As a result, This DN hydrogel exhibited a high fracture toughness of 2022.4 J m^{-2}, about 5 times that of pure PAM hydrogel (**Figure 13c**). Even being trodden for 2 days, the discharge capacity of the fabricated Zn-MnO_2 battery hardly changed (**Figure 13d**). It is worth mentioning that other metal ions (e.g., Ca^{2+} and Fe^{3+} ions) can also crosslink the second network by ionic bonding.[119]

Following the same design principle, Ma et al. developed a PANa (first network)/cellulose (second network) DN hydrogel, with slight difference in the hydrogen bonding crosslinked second network.[52] Besides, this DN hydrogel showed an impressive alkaline-tolerant property. After absorbing 6 M KOH solution, the DN hydrogel electrolyte could still be easily stretched to over 1000% strain, coupled with high ionic conductivity of 0.28 S cm^{-1}. The researchers then applied this DN hydrogel electrolyte to fiber-shape ZABs, which also exhibited an elongation of 500% (**Figure 13e**). Interestingly, the fabricated ZAB's electrochemical performances were enhanced slightly due to the enlarged electrode/electrolyte contact interface (**Figure 13f and g**). Similarly, Chen et al. reported a flexible ZAB equipped with a mechanically enhanced PVA/bacterial cellulose (BC) DN hydrogel electrolyte.[114] By merit of hydrogen bonding between BC and PVA chains, the PVA/BC hydrogel's mechanical strength was increased by about 9 times compared to the pure PVA hydrogel (0.1 MPa to 0.95 MPa). The fabricated flexible ZAB exhibited a super long discharge-charge cycle of 440 hours. Apart from deformations like stretching and bending, shear is also a critical yet long-ignored issue to flexible zinc-based batteries, which will lead to the facile electrode/electrolyte detachment. Hence, based on tough PAM/cellulose DN hydrogel, Wang et al. further suggested sewing the flexible Zn-MnO_2 battery to obtain shear resistance.[79] As shown in **Figure 13h**, the suture line fixed the electrodes and hydrogel electrolyte effectively and prevented them from sliding. Under a high shear force of 38 N, the unsewed battery's zinc anode completely detached from the hydrogel electrolyte, showing no discharge capacity. As a contrast, the sewed battery showed about 65% capacity retention (**Figure 13i**).

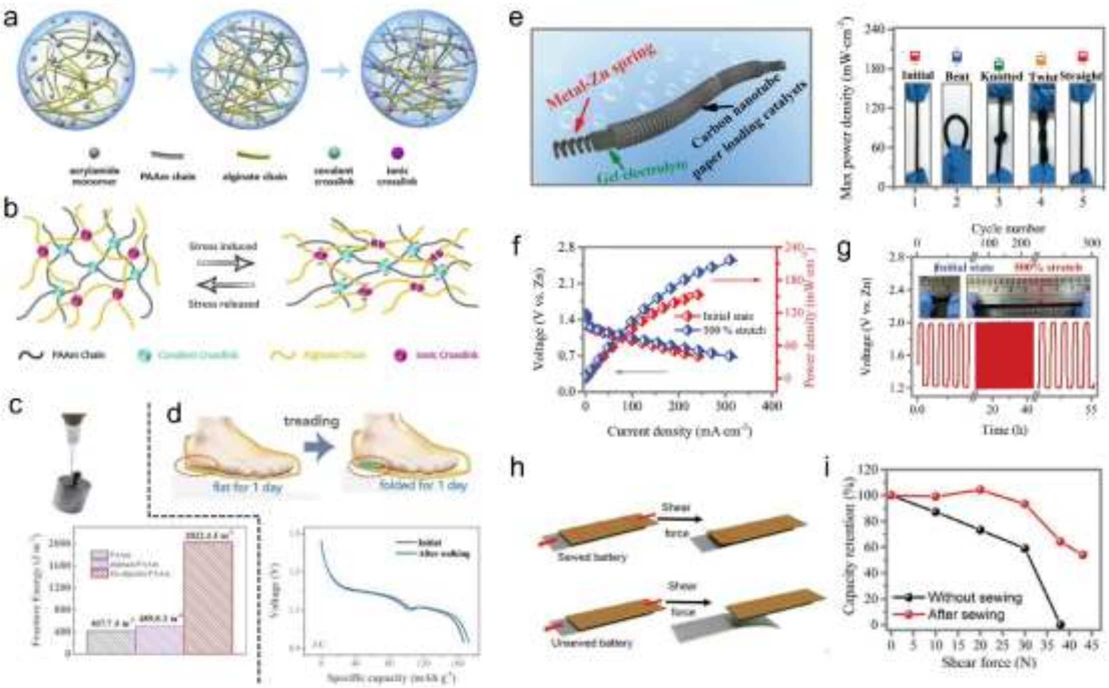


Figure 13. (a) Schematic of the evolution of the PAM/alginate DN hydrogel structure. (b) Energy dissipation mechanism of the PAM/alginate DN hydrogel. (c) Fracture toughness of different hydrogels. (d) Discharge curve of the battery after 2 days' treading.[113] Copyright 2019, Elsevier. (e) Schematic and max power density of fiber-shape ZABs under different deformation statuses. (f) Polarization and corresponding power density curves of the fiber-shape ZAB at initial and 500% stretching state. (g) Cycling test of the fiber-shape ZAB under 5 mA cm^{-2} and 500% strain.[52] Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (h) Schematic illustration of the process under shear force for sewed battery and unsewed battery. (i) Capacity retention of the sewed battery and unsewed battery under different shear force.[79] Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

5.1.3 Other approaches

Qiu and co-workers recently developed a novel solvent-exchange method for constructing robust and anti-swelling PVA hydrogels (Exogel).[111] Interestingly, different from the method introduced in section 5.1.1 to replace water with polyols, this strategy deployed water to replace another polar solvent DMSO. The researchers first dissolved PVA powders in the DMSO solvent to keep a non-aggregated and protracted state since the PVA chains were inclined to first interact with DMSO, a strong hydrogen bonding acceptor. Then, water (weak hydrogen bonding acceptor) replaced DMSO, and the PVA chains could reconnect intimately by hydrogen bonding. This way, Exogel could achieve a denser and more homogeneous crosslinking network than the conventional freezing-thawing made PVA (Cryogel). As mechanical enhancement verification, the Exogel showed high fracture energy of 3720 J m^{-2}, nearly 3 times that of the Cryogel. Moreover, the swelling ratio of Exogel remained no change after 100 hours. Theoretically, by substituting the water with salt solution, this robust hydrogel has great potential to serve as electrolytes for zinc-based batteries.

Apart from this, researchers found that the mechanical properties of hydrogels could be improved after soaking in salt solutions.[120, 121] Most recently, He and co-workers further investigated the effect of different ions on the hydrogel mechanical performances employing the Hofmeister effect and successfully altered the mechanical properties to a broad range.[112, 122] Using PVA as a model system, it was found that the strength and toughness of hydrogels with different anions and cations followed the order: $SO_4^{2-} > CO_3^{2-} > Ac^- > Cl^- > NO3^- > I^-$ and $K^+ > Na^+ \approx Cs^+ > Li^+ > Ca^{2+} \approx Mg^{2+}$, respectively (**Figure 14b**). This was because ions like SO_4^{2-} and CO_3^{2-} could facilitate the formation of hydrogen bondings between PVA chains while ions like Li^+ and Ca^{2+}

might break them (**Figure 14a**). Furthermore, from the SEM images shown in **Figure 14c**, the PVA-SO_4 had denser porous networks than the PVA-NO_3. As a result, the Na_2SO_4 treated PVA exhibited a strength, toughness, and modulus of 15.53 MPa, 153.41 MJ m^{-3}, and 2500 kPa, greatly higher than that of $CaCl_2$ treated PVA of 0.09 MPa, 2.48 MJ m^{-3}, and 34 kPa, respectively (**Figure 14d**). Towards flexible zinc-based batteries, this finding could provide salt choices for constructing high-strength hydrogel electrolytes. That is, using $ZnSO_4$, the hydrogel may obtain enhanced mechanical strength than using $ZnCl_2$. Moreover, although the addition of LiCl could improve the battery cycling performance, the mechanical properties of hydrogel electrolytes could be harmed.[85]

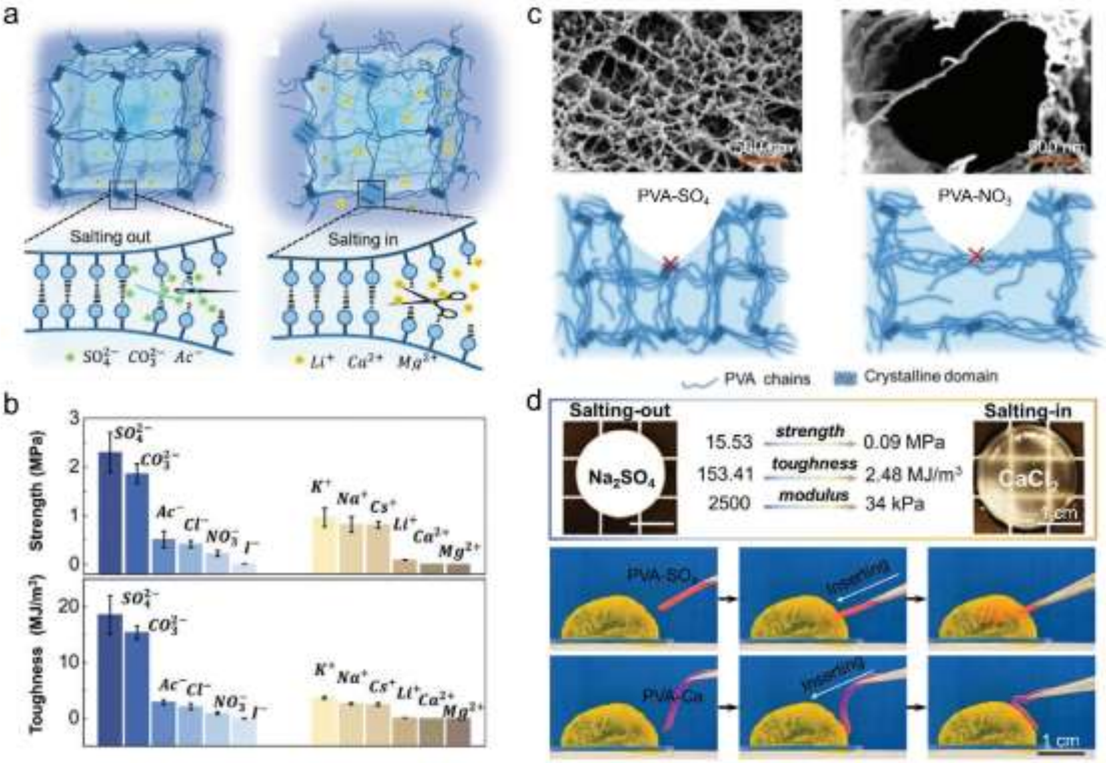


Figure 14. (a) Schematics of the formation and break of hydrogen bonding among PVA polymer chains induced by different ions. (b) Strengths and toughness of PVA

hydrogels tuned by various anions and cations. (c) SEM images and corresponding schematics of PVA–SO_4 and PVA–NO_3 networks. (d) Comparisons between mechanical properties of Na_2SO_4 and $CaCl_2$ treated PVA hydrogels: a stiff PVA hydrogel toughened by 1 M Na_2SO_4 could penetrate a soft brain-tissue-mimicking hydrogel while a soft PVA hydrogel treated with 1 M $CaCl_2$ could not.[112] Copyright 2021, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

5.2 Strategies for self-healing hydrogels

5.2.1 Dynamically reversible bonding among polymer chains

Take a step further, the hydrogel electrolyte may suffer from rupture during the daily use of flexible zinc-based batteries, leading to permanent battery failure. In this case, hydrogel electrolytes with self-healing properties can be a good choice to resolve this problem effectively. Generally, self-healable hydrogels are based on reversible dynamic bonding, for example, hydrogen bonding and ionic bonding. Niu et al. exploited the hydrogen bonding to construct self-healable PVA/zinc trifluoromethanesulfonate ($Zn(CF_3SO_3)_2$) hydrogel electrolytes for ZIBs.[80] These reversible hydrogen bonding formed dynamically among PVA chains. After hydrogel breaking, the fractured parts could reconnect to the original state through the rebuilt hydrogen bonding (**Figure 15a**). On the other hand, by virtue of the PVA synthesis process of switching liquid to hydrogel state, the battery electrodes could be integrated into the hydrogel framework to achieve all-in-one batteries (**Figure 15b**). Therefore, as shown in **Figure 15c**, both the hydrogel electrolyte and electrodes could reconnect together after fracturing.

Benefiting from these merits, the fabricated ZIB presented almost unchanged capacity retention of 81.4 mAh g^{-1} after 3 times cutting-healing cycles (**Figure 15d**). Analogically, Huang et al. synthesized a self-healable PANa hydrogel using Fe^{3+} ion as a crosslinker.[47] This ionic crosslinked PANa-Fe^{3+} hydrogel exhibited an alkaline-tolerant capability. After absorbing 6 M KOH solution, the PANa-Fe^{3+} hydrogel could still keep its shape and unique self-healing property. The researchers further fabricated an alkaline flexible Zn/NiCo battery, which displayed a high discharge capacity of 250 mAh g^{-1}. Moreover, the battery discharge capacity retained 87% after 4 times cutting-healing cycles. It is believed that this self-healable hydrogel electrolyte can also be applied to other alkaline zinc-based batteries like ZABs. Zhi and co-workers also reported a self-healable PAM hydrogel-based Zn-MnO_2 battery. Through adjusting the crystal structure of the MnO_2, the electrochemical performances can be further enhanced.[123]

In fact, in addition to reversibly physical bonding, covalent bonding can also achieve self-healable hydrogels.[124] However, the self-healing process using covalent bonding generally demands external stimuli, such as certain pH or light, limiting the application in energy storage devices. Interested readers may refer to these review articles.[125-127]

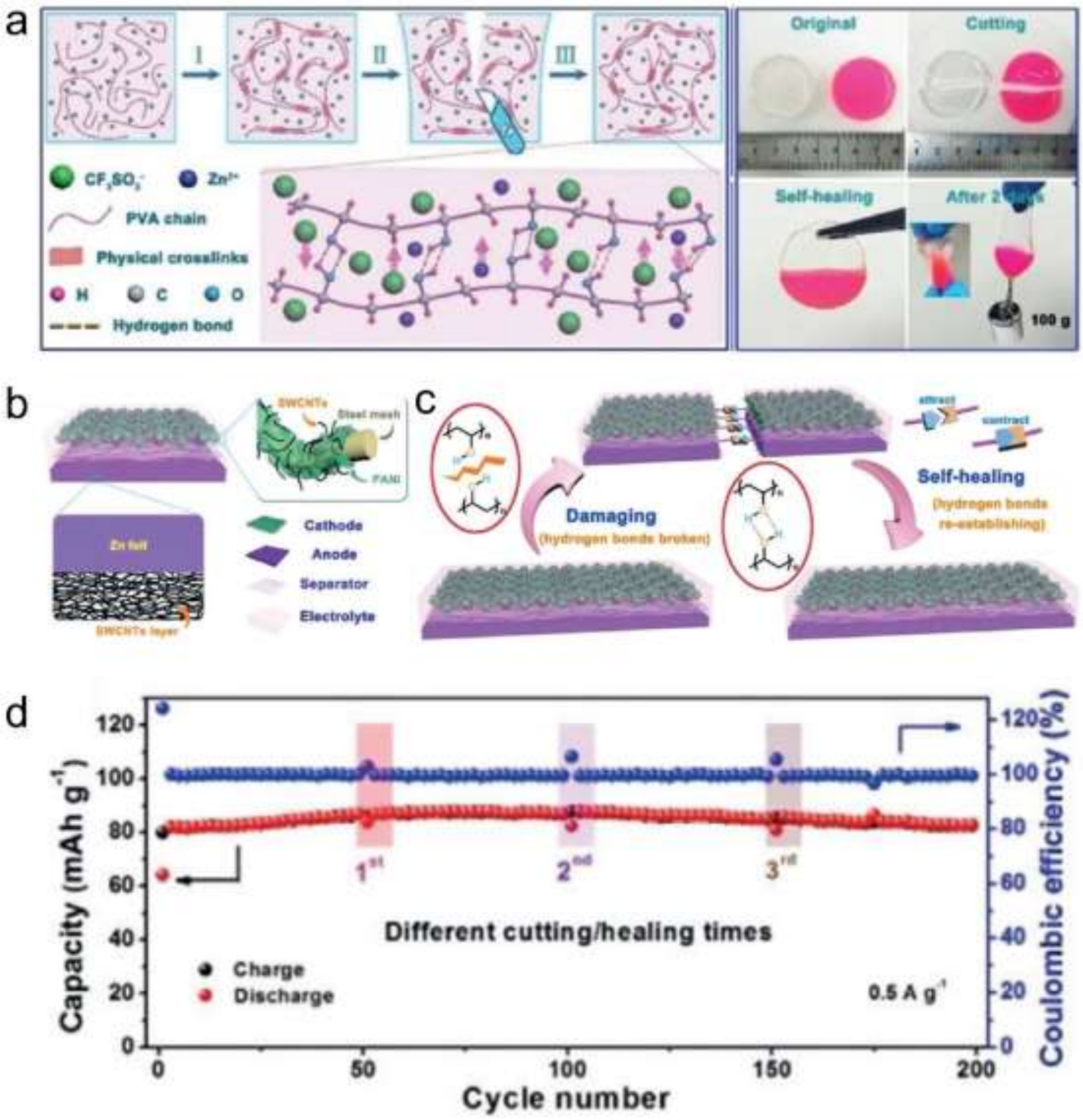


Figure 15. (a) Process of fabricating self-healing PVA hydrogel electrolyte and its self-healing behavior. (b) Schematic illustration of an integrated all-in-one ZIB's structure and (c) its self-healing process. (d) Cycle performance of the self-healable ZIB at original state and after multiple cutting/self-healing times.[80] Copyright 2019, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

5.2.2 Other methods

Apart from these conventional self-healing approaches, several novel strategies have recently emerged and been applied in zinc-based batteries. For example, Zhou et al. fabricated a Zn-Cu primary battery with a diode-type hydrogel electrolyte.[128] The hydrogel diode comprised of two oppositely charged hydrogels, the polycation hydrogel (PE^+) and polyanion hydrogel (PE^-), which adhered tightly through strong electrostatic interactions existing at the PE^+/PE^- interface (**Figure 16a**). Therefore, the hydrogel diode delivered a desirable peeling force of 63 N/m (**Figure 16b**), and the fabricated flexible Zn-Cu battery showed an ultra-stability over 2000 times stretching cycles (**Figure 16c**). Thanks to the repeatable adhesion of the PE^+ and PE^-, a particular separate-storage method could be applied to prevent the battery self-discharge and preserve the battery electrochemical performances. Even after 8 days, the separately stored battery power output hardly changed, whereas the counterpart (integrated battery) nullified completely (**Figure 16d**). It is believed that this strategy could be applied to other self-healable energy storage systems for performance preservation.

The thermo-reversible hydrogels discussed in section 4.2.1 could also be used as self-healable hydrogel electrolytes for zinc-based batteries. For example, Zhao and co-workers introduced a ZIB using a block copolymer PEO-PPO-PEO hydrogel electrolyte (PHE) with a unique cooling-recovery capability.[29] Possessing a different temperature range from PNIPAM, the PHE was in liquid-state at low temperature (-5 °C) but transferred to hydrogel-state after heating to room temperature (25 °C). Therefore, by a simple cooling-heating process, not only the damaged electrolyte layer could restore to its original state but also the electrode/electrolyte contact rebuilt intimately (**Figure 16e**). The fabricated ZIB exhibited a high capacity retention of 90% after 300 cycles, as shown in **Figure 16f**. More impressively, although the battery capacity decreased significantly after a strong folding (100 kPa), it could soon recover to 98% capacity retention by cooling-heating in just 5 minutes (**Figure 16g**). Most recently, Bae and colleagues reported an application of alkaline Pluronic solid-state electrolyte (APSE) in ZABs.[37] Besides the self-healing ability, the APSE also exhibited an unprecedented CO_2-tolerance property, which greatly elongated the battery lifetime in the ambient environment compared to the liquid KOH (**Figure 16h**). Furthermore, two series bent batteries could light up an LED, demonstrating its potential in wearable devices.

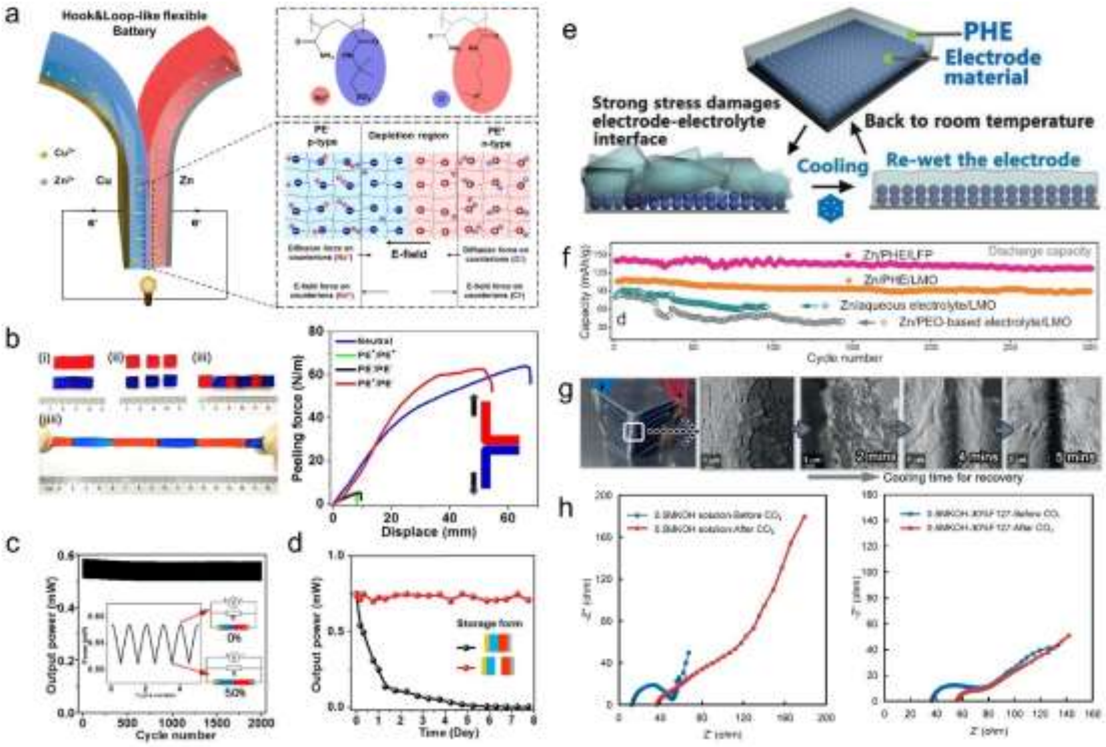


Figure 16. (a) Schematics of a flexible Zn-Cu battery with a diode-type hydrogel electrolyte. (b) Peeling force curves of two as-contacted hydrogels. (c) Power output variations of the Zn-Cu battery over 2000 stretching cycles. (d) Power output as a function of time for the Zn-Cu battery in different storage forms.[128] Copyright 2018,

Elsevier. (e) The cooling-recovery function of the thermo-reversible PHE. (f) Discharge capacity retention of various ZIBs. (g) SEM images of the broken PHE-electrode area after strong folding (100 kPa) and the recovered area after cooling at -5 °C.[29] Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (h) AC impedance spectra of the aqueous KOH and APSE based ZAB before and after CO_2 corrosion.[37] Copyright 2021, American Chemical Society.

5.3 Current challenges

Various methods have been applied successfully to improve the mechanical properties of hydrogel electrolytes. Extreme deformations such as bending, stretching, folding, and even cutting can be withstood by hydrogel electrolytes through careful design. However, tremendous efforts are needed to address the existing challenges.

(1) Despite the approaches above indeed improve the mechanical properties of hydrogels compared to their unmodified state somehow, it is still far from the market standard. Moreover, there is always a trade-off between ionic conductivity and mechanical strength of hydrogels.[57]

(2) Since the flexible zinc-based batteries inevitably undergo bending or stretching in the daily life, the fatigue of hydrogel electrolytes after multiple times deformations should be comprehensively studied and assessed.[129]

(3) It always takes a long duration to obtain a well-repaired hydrogel electrolyte after a fracture. Novel ultrafast self-healing technologies should be further explored.

(4) The stretchable and bendable electrodes compatible with hydrogel electrolytes

should also be well-designed to meet the assembled batteries' flexibility. Besides, evaluation standards of mechanical properties should be set not only for the hydrogel electrolytes but also the zinc-based batteries.

6. Constructing all-around hydrogel electrolytes for zinc-based batteries

In the former sections, targeted strategies have been introduced for endowing hydrogel electrolytes with different functions to face different extreme conditions. Some strategies, such as the DN hydrogel structure, only contribute to a single hydrogel function, while some can realize double functions simultaneously, like doping nanoparticles. However, regretfully, no individual strategy can satisfy all requirements for hydrogel electrolytes to work under all the extreme conditions at the same time. Therefore, appropriately combining various strategies becomes a promising way.

Figure 17 lists different hydrogel functionalities towards extreme conditions and their corresponding improving strategies. Each strategy from one column can cooperate freely with one from other columns to realize all-around hydrogel electrolytes. Nevertheless, there are many to be noted when making the combinations. For different strategies (each column), their effects vary substantially. For example, hydrogels with polyol solvents can keep unfrozen even at -70 ℃, while the effect of hydrogel network modification is relatively limited (-20 ℃). Besides, the same strategy shows different effects for various hydrogel functionalities, as can be reflected in the unsatisfactory increment in water retention ratio of hydrogel electrolytes by polyol solvents(from 9.6%

to 19.1% after 48 hours).[45] It is also noteworthy that the widely used hydrated salt LiCl for water retention may do harm to the hydrogel's mechanical strength.[112] When applied in zinc-based batteries, the ionic conductivity should be taken into consideration. The addition of polyol solvents will dilute the electrolyte concentration, thus leading to a decline in ionic conductivity. Luckily, from the existing reports, concentrated salt solvents are competent for most cold environments (down to -20 °C). Therefore, it is suggested that the polyol solvents are more suitable to be employed at the extremely cold temperature (below -20 °C). Moreover, by doping nanoparticles into hydrogels, not only the water retention and mechanical property but also the ionic conductivity can be further improved. On the other hand, the hydrogel electrolytes of ZIBs and ZABs hold a discrepant pH, which may affect the choice of combination. There must be a trade-off between the four functionalities and battery electrochemical performances. How to find a balance and meanwhile maximize the improvement become the priority.

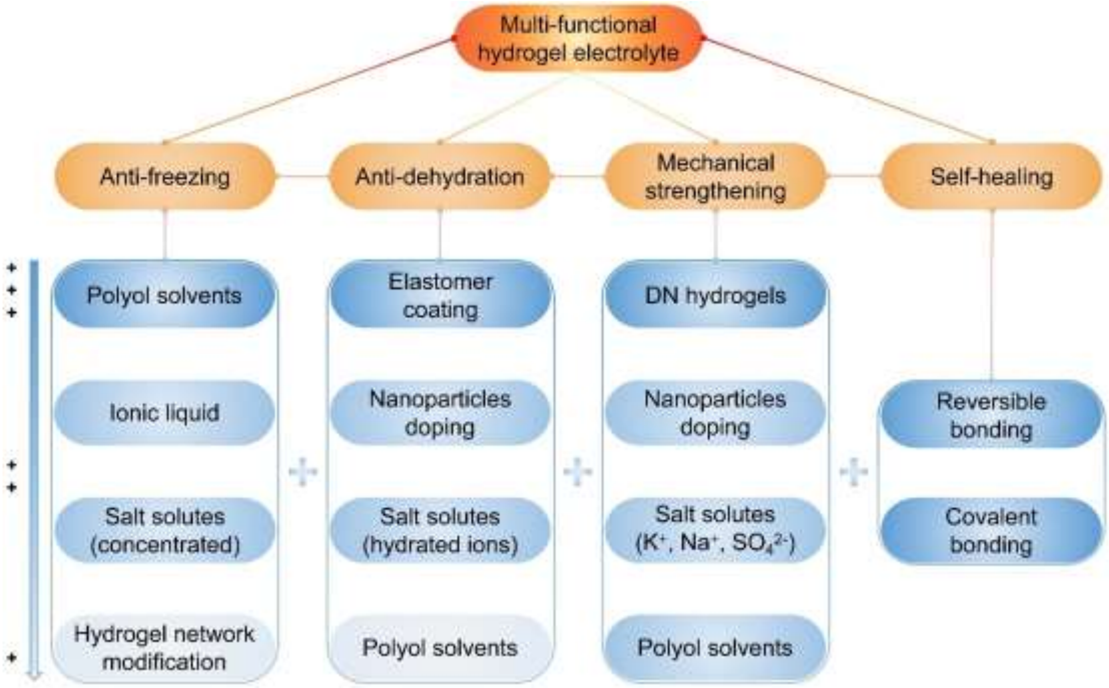


Figure 17. Summary of design strategies to construct multi-functional hydrogel electrolytes. The effect degree of each strategy from very effective, effective, and middle effective are represented as color from deep blue, blue, and light blue, respectively. Each strategy from one column can cooperate freely with one from other columns.

Recently, Wong and co-workers provided a pioneering example of designing all-around hydrogel electrolytes for Zn-MnO_2 batteries under extreme conditions.[130] Following the design strategies we summarized, cellulose with abundant hydroxyl groups was used as a hydrogel substrate, while glycerol served as an anti-freezing agent (**Figure 18a**). The crosslinker tetraethyl orthosilicate (TEOS) bound with cellulose and glycerol covalently to form a robust 3D structure, hence leading to admirable mechanical properties. Moreover, the hydroxyl groups provided sufficient reversible hydrogen bonding, which not only endowed the hydrogel with a self-healing ability but also interacted intimately with water molecules and thus retaining a high water retention capability. As a result, the optimized hydrogel (CT3G30) delivered an ultralow freezing point of -64.6 °C, a high tensile strength of 2.11 MPa at 846.5% elongation, and a self-healing efficiency of 82.6% (**Figure 18b and c**). By merit of the high ionic conductivity (19.4 mS cm^{-1}) at -40 °C, correspondingly, the fabricated Zn-MnO_2 battery exhibited a 76.4% specific capacity retention of 211.8 mAh g^{-1}, which could even on a par with other ZIBs at room temperature. Besides, 2000 cycles could be achieved at 60 °C, demonstrating its thermo-stability. Even being immersed in boiling water, the battery was still able to deliver electricity to electronics. Apart from the outstanding performances towards extreme environments, the CT3G30 hydrogel also exerted effectiveness on suppressing zinc dendrite and side reaction, as shown in **Figure 18d and e**. These phenomena can be explained as follows: 1) The negatively charged groups on the cellulose chains interact with Zn^{2+} and homogenize the zinc deposition 2) cellulose chains and glycerol trap the free water molecules through hydrogen bonding, so the water activity is reduced. It is exciting to see the successful application of the combination strategy in flexible ZIBs with excellent performance.

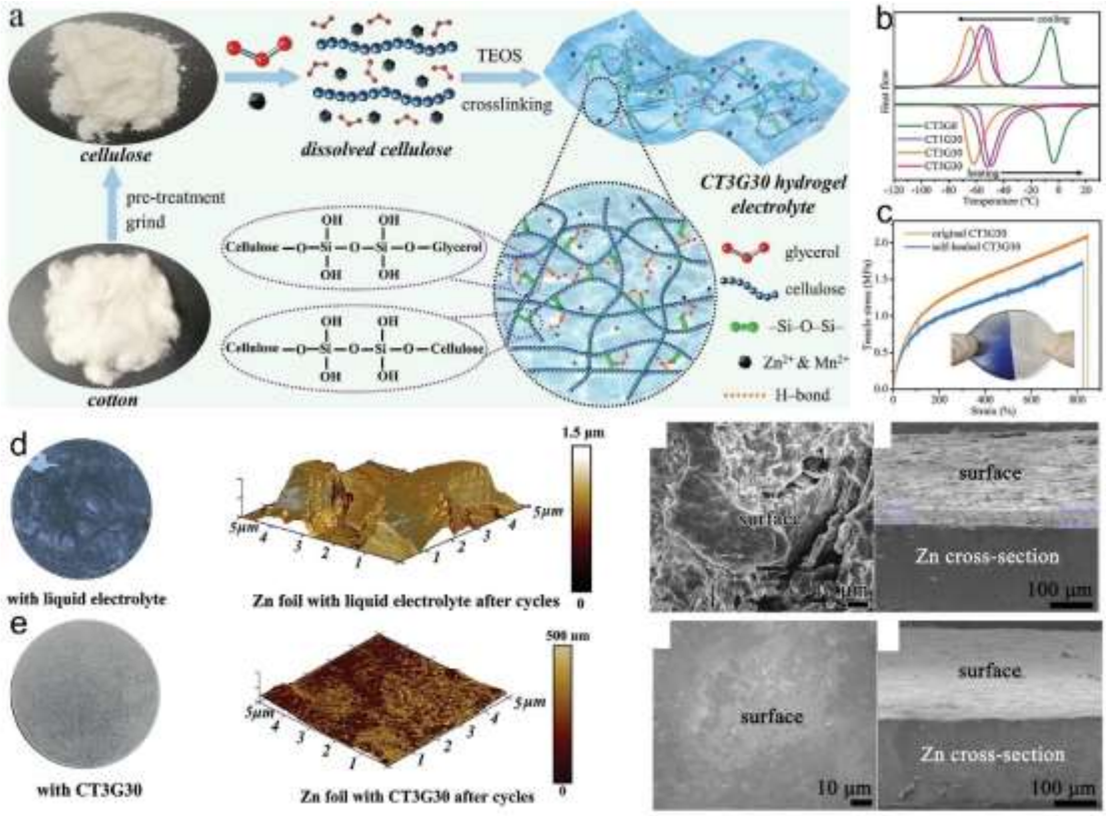


Figure 18. (a) Synthesis schematic of the CT3G30 hydrogel electrolyte. (b) DSC curves of the CT3G30 hydrogel electrolyte. (c) Tensile stress-strain curves of the original and self-healed CT3G30 hydrogel electrolyte. (d) Characterization of the zinc surface with liquid electrolyte. (e) Characterization of the zinc surface with CT3G30 hydrogel electrolyte.[130] Copyright 2021, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Besides, many other combinations follow the design strategies in **Figure 17** to construct all-around hydrogels. For example, Han et al. reported a carrageenan/PAM DN hydrogel (mechanical strengthening and hydrogen bonding for self-healing) with EG addition (anti-freezing and anti-dehydration).[131] Xue et al. developed a copolymerized hydrogel (acrylic acid-co-maleic acid) with the addition of ferric ions (self-healing), boron nitride nanosheet (anti-dehydration and mechanical strengthening), and glycerol (anti-freezing, anti-dehydration, and mechanical strengthening).[132] Mo et al. designed an alginate/PAM DN hydrogel (mechanical strengthening) with EG (anti-freezing and anti-dehydration) and elastomer coating (anti-dehydration).[49] Unfortunately, in this work, the battery did not show a self-healing performance since the elastomer did not show the self-healing ability. In the future, self-healable elastomers should be further developed.[133, 134]

Towards the methods mentioned above, the only drawback is that they are mainly for ZIBs with neutral or acid hydrogel electrolytes, where all-around alkaline ZIBs and ZABs are absent in the existing research. By combining the work from Ma,[52] Song,[36] and Huang[27] et al., it is promising to witness the birth of all-around alkaline zinc-based batteries by constructing PANa/cellulose DN hydrogel (mechanical strengthening) with 6 M KOH solution (anti-freezing), SiO_2/GO nanoparticles (anti-dehydration), and ferric ions (self-healing).

7. Summary and outlooks

Hydrogel electrolytes are the critical component in the flexible zinc-based battery since they serve as ion conductors and electrode separators. Albeit with satisfying performances in the normal environment, they inevitably suffer from degradation when working under extreme conditions. In this review, the impacts of extreme working conditions (i.e., low temperature, high temperature, and mechanical deformations) on the hydrogel electrolytes and the fabricated zinc-based batteries are systematically reviewed. Correspondingly, we also present multiple solutions and discuss their current challenges. It is exciting to witness the battery operating over a wide temperature range with a long duration without sacrificing too much electrochemical performance, which is crucial for practical application. Moreover, the flexibility and toughness have also greatly improved, as the hydrogel electrolytes can be readily stretched or twisted thousands of times without damage, even in the subzero temperature environment. However, extensive efforts are needed for further development of hydrogel electrolytes and the flexible zinc-based batteries. Based on the above discussion, the following potential future research directions are highlighted:

(1) Although the combination strategy has been proven successful in building all-around hydrogel electrolytes, research on the fraction of each additive is still absent. Considering insufficient and excessive additives are ineffective, balancing the additives and optimizing the combined strategies becomes a good solution. Meanwhile, with the rapid development of artificial intelligence (AI), deep learning will have great potential in selecting well-organized recipes to achieve low-cost, simple-fabrication, and all-around hydrogel electrolytes. Most importantly, the electrochemical performance of the optimized zinc-based batteries should be carefully evaluated and, in turn, further guide the design strategy.

(2) Due to the narrow electrochemical stable potential window (ESPW), the voltage of aqueous zinc-based batteries always remain at a low level (< 2 V). Recently, based on the “water-in-salt” design, a highly concentrated “water-in-gel” electrolyte successfully raised the operating voltage of ZIBs to 2.1 V, providing a new approach towards high-voltage aqueous batteries. Also, the high concentration of salt simultaneously improves the battery adaptation at extreme temperatures. Besides,

by pH decoupling, low concentration hydrogels can also significantly increase the voltage. However, the use of high concentration salt and ion exchange membrane for pH decoupling is costly. Novel inexpensive and effective strategies are encouraged for high-voltage flexible aqueous zinc-based batteries.

(3) The reaction mechanism between the electrode and hydrogel electrolyte has not been thoroughly investigated yet. From the perspective of polymer chains, they may interact with the zinc electrode to form solid electrolyte interface (SEI). From the perspective of solvent components, additives like DMSO can inactivate water molecules and suppress the HER side reaction. Considering the diversity of electrodes (Zn anode; Mn etc. oxides; Pt etc. catalysis; Carbon cloth etc. substrates), hydrogel electrolytes (cellulose, PVA, PAM, PAA, etc.), and electrolyte additives, more efforts should be devoted to gaining a comprehensive understanding about the electrode/electrolyte interface.

(4) Although flexible zinc-based batteries are still in the lab stage, the ultimate goal is commercialization. Regretfully, the zinc dendrite growth is a significant issue but their behavior under extreme conditions have not been investigated. On the other hand, the battery fabrication process is not simplified because of the complicated synthesis steps of electrodes and hydrogel electrolytes. Besides, the battery encapsulation technology has not obtained much attention yet. On the other hand, flexible micro zinc-based batteries are suitable power sources for implantable electronics by virtue of their safe and biocompatible nature. Advanced technologies like 3D printing are promising to fill in the research gap of all-in-one micro batteries

with different shapes.

(5) The large-scale application of various types of electronics not only brings a huge market demand for batteries but also creates a problem for battery recycling and secondary use. From the perspective of environmental sustainability, biomaterials and bio-degradable hydrogels are highly recommended. These materials can be completely degraded to CO_2 and H_2O by microorganisms or processed to powder for reuse. Moreover, reabsorbing aqueous solutions also showed potential in recovering hydrogel performances. Unfortunately, the electrodes are mainly made of inorganic materials, which require a separated (from organic hydrogels) and more complicated recycling prfocess. In the future, biomaterial-based electrodes compatible with the hydrogel electrolytes can be developed to construct more eco-friendly flexible batteries.

(6) In addition to the extreme conditions discussed in this review, consideration of other extreme conditions may also be needed. For example, in the high humidity environment, the hydrogel electrolytes with water uptake ability will absorb moisture in the air, leading to concentration dilution and ionic conductivity decline. In the underwater applications, the hydrogel electrolyte is expected to have an anti-swelling ability. As for the deep-sea environment, the high pressure and high salinity should also take into account. When alkaline zinc-based batteries work under a high CO_2 concentration environment, an anti-CO_2 hydrogel electrolyte is urgently needed, etc. Therefore, targeted/combined strategies towards various extreme conditions should be further investigated.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Reference

[1] P. Tan, B. Chen, H. Xu, H. Zhang, W. Cai, M. Ni, M. Liu, Z. Shao, *Energy Environ. Sci.* **2017**, *10*, 2056.

[2] Y. Zhao, J. Guo, *InfoMat* **2020**, *2*, 866.

[3] C. Zhao, Y. Lu, L. Chen, Y. S. Hu, *InfoMat* **2020**, *2*, 126.

[4] M. Liao, L. Ye, Y. Zhang, T. Chen, H. Peng, *Advanced Electronic Materials* **2019**, *5*, 1800456.

[5] Y. Miao, P. Hynan, A. Von Jouanne, A. Yokochi, *Energies* **2019**, *12*, 1074.

[6] N. Nitta, F. Wu, J. T. Lee, G. Yushin, *Mater. Today* **2015**, *18*, 252.

[7] X.-G. Yang, T. Liu, Y. Gao, S. Ge, Y. Leng, D. Wang, C.-Y. Wang, *Joule* **2019**, *3*, 3002.

[8] K. Xu, *Energy & Environmental Materials* **2019**, *2*, 229.

[9] H. Cha, J. Kim, Y. Lee, J. Cho, M. Park, *Small* **2018**, *14*, 1702989.

[10] Y. Wang, C. Chen, H. Xie, T. Gao, Y. Yao, G. Pastel, X. Han, Y. Li, J. Zhao, K. Fu, *Adv. Funct. Mater.* **2017**, *27*, 1703140.

[11] G. Qian, X. Liao, Y. Zhu, F. Pan, X. Chen, Y. Yang, *ACS Energy Letters* **2019**, *4*, 690.

[12] F. Wang, X. Wu, C. Li, Y. Zhu, L. Fu, Y. Wu, X. Liu, *Energy & Environmental Science* **2016**, *9*, 3570.

[13] H. Zhang, X. Liu, H. Li, I. Hasa, S. Passerini, *Angew. Chem. Int. Ed.* **2021**, *60*, 598.

[14] J. Song, K. Xu, N. Liu, D. Reed, X. Li, *Mater. Today* **2021**, DOI: 10.1016/j.mattod.2020.12.003.

[15] H. Li, L. Ma, C. Han, Z. Wang, Z. Liu, Z. Tang, C. Zhi, *Nano Energy* **2019**, *62*, 550.

[16] Y. Zuo, K. Wang, P. Pei, M. Wei, X. Liu, Y. Xiao, P. Zhang, *Materials Today Energy* **2021**, 100692.

[17] J. Liu, M. Hu, J. Wang, N. Nie, Y. Wang, Y. Wang, J. Zhang, Y. Huang, *Nano Energy* **2019**, *58*, 338.

[18] Y. Li, J. Fu, C. Zhong, T. Wu, Z. Chen, W. Hu, K. Amine, J. Lu, *Advanced Energy Materials* **2019**, *9*, 1802605.

[19] Y. Zhang, Y.-P. Deng, J. Wang, Y. Jiang, G. Cui, L. Shui, A. Yu, X. Wang, Z. Chen, *Energy Storage Materials* **2021**, *35*, 538.

[20] X. Gong, Q. Yang, C. Zhi, P. S. Lee, *Advanced Energy Materials* **2020**, DOI: 10.1002/aenm.2020033082003308.

[21] Z. Pan, J. Yang, J. Jiang, Y. Qiu, J. Wang, *Materials Today Energy* **2020**, *18*, 100523.

[22] T. Liu, J. Mou, Z. Wu, C. Lv, J. Huang, M. Liu, *Adv. Funct. Mater.* **2020**, *30*, 2003407.

[23] H. Jia, Z. Wang, B. Tawiah, Y. Wang, C.-Y. Chan, B. Fei, F. Pan, *Nano Energy* **2020**, *70*, 104523.

[24] Z. Wang, H. Li, Z. Tang, Z. Liu, Z. Ruan, L. Ma, Q. Yang, D. Wang, C. Zhi, *Adv. Funct. Mater.* **2018**, *28*, 1804560.

[25] Y. Wei, Y. Shi, Y. Chen, C. Xiao, S. Ding, *Journal of Materials Chemistry A* **2021**, *9*, 4415.

[26] Y. Guo, J. Bae, Z. Fang, P. Li, F. Zhao, G. Yu, *Chem. Rev.* **2020**, *120*, 7642.

[27] Y. Huang, Z. Li, Z. Pei, Z. Liu, H. Li, M. Zhu, J. Fan, Q. Dai, M. Zhang, L. Dai, C. Zhi, *Advanced Energy Materials* **2018**, *8*, 1802288.

[28] L. Ma, S. Chen, X. Li, A. Chen, B. Dong, C. Zhi, *Angew. Chem.* **2020**, *132*, 24044.

[29] J. Zhao, K. K. Sonigara, J. Li, J. Zhang, B. Chen, J. Zhang, S. S. Soni, X. Zhou, G. Cui, L. Chen, *Angew. Chem. Int. Ed.* **2017**, *56*, 7871.

[30] H. Li, Z. Tang, Z. Liu, C. Zhi, *Joule* **2019**, *3*, 613.

[31] H. Li, C. Han, Y. Huang, Y. Huang, M. Zhu, Z. Pei, Q. Xue, Z. Wang, Z. Liu, Z. Tang, *Energy & Environmental Science* **2018**, *11*, 941.

[32] Z. Cao, H. Hu, M. Wu, K. Tang, T. Jiang, *Journal of Materials Chemistry A* **2019**, *7*, 17581.

[33] H. Miao, B. Chen, S. Li, X. Wu, Q. Wang, C. Zhang, Z. Sun, H. Li, *J. Power Sources* **2020**, *450*, 227653.

[34] S. Zhao, K. Wang, S. Tang, X. Liu, K. Peng, Y. Xiao, Y. Chen, *Energy Technology* **2020**, *8*, 1901229.

[35] X. Fan, J. Liu, Z. Song, X. Han, Y. Deng, C. Zhong, W. Hu, *Nano Energy* **2019**, *56*, 454.

[36] Z. Song, J. Ding, B. Liu, X. Liu, X. Han, Y. Deng, W. Hu, C. Zhong, *Adv. Mater.* **2020**, *32*, e1908127.

[37] S. Zhao, D. Xia, M. Li, D. Cheng, K. Wang, Y. S. Meng, Z. Chen, J. Bae, *ACS applied materials & interfaces* **2021**.

[38] K. Wu, J. Huang, J. Yi, X. Liu, Y. Liu, Y. Wang, J. Zhang, Y. Xia, *Advanced Energy Materials* **2020**, *10*, 1903977.

[39] C. Y. Chan, Z. Wang, H. Jia, P. F. Ng, L. Chow, B. Fei, *Journal of Materials Chemistry A* **2021**, *9*, 2043.

[40] Y. Guo, J. Bae, F. Zhao, G. Yu, *Trends in Chemistry* **2019**, *1*, 335.

[41] X. Li, Y. Tang, H. Lv, W. Wang, F. Mo, G. Liang, C. Zhi, H. Li, *Nanoscale* **2019**, *11*, 17992.

[42] F. Liu, M. W. Urban, *Prog. Polym. Sci.* **2010**, *35*, 3.

[43] M. S. Jhon, J. D. Andrade, *Journal of biomedical materials research* **1973**, *7*, 509.

[44] H. Wang, J. Liu, J. Wang, M. Hu, Y. Feng, P. Wang, Y. Wang, N. Nie, J. Zhang, H. Chen, Q. Yuan, J. Wu, Y. Huang, *ACS applied materials & interfaces* **2019**, *11*, 49.

[45] R. Chen, X. Xu, S. Peng, J. Chen, D. Yu, C. Xiao, Y. Li, Y. Chen, X. Hu, M. Liu, H. Yang, I. Wyman, X. Wu, *ACS Sustainable Chemistry & Engineering* **2020**, *8*, 11501.

[46] Y. Shi, H. Ha, A. Al-Sudani, C. J. Ellison, G. Yu, *Adv. Mater.* **2016**, *28*, 7921.

[47] Y. Huang, J. Liu, J. Wang, M. Hu, F. Mo, G. Liang, C. Zhi, *Angew. Chem. Int. Ed. Engl.* **2018**, *57*, 9810.

[48] F. Mo, G. Liang, Q. Meng, Z. Liu, H. Li, J. Fan, C. Zhi, *Energy & Environmental Science* **2019**, *12*, 706.

[49] F. Mo, G. Liang, D. Wang, Z. Tang, H. Li, C. Zhi, *EcoMat* **2019**, *1*.

[50] N. Sun, F. Lu, Y. Yu, L. Su, X. Gao, L. Zheng, *ACS applied materials & interfaces* **2020**, *12*, 11778.

[51] P. Yang, C. Feng, Y. Liu, T. Cheng, X. Yang, H. Liu, K. Liu, H. J. Fan, *Advanced Energy Materials* **2020**, *10*, 2002898.

[52] L. Ma, S. Chen, D. Wang, Q. Yang, F. Mo, G. Liang, N. Li, H. Zhang, J. A. Zapien, C. Zhi, *Advanced Energy Materials* **2019**, *9*, 1803046.

[53] E. M. Ahmed, *Journal of advanced research* **2015**, *6*, 105.

[54] W. E. Hennink, C. F. van Nostrum, *Advanced drug delivery reviews* **2012**, *64*, 223.

[55] H. Li, C. Han, Y. Huang, Y. Huang, M. Zhu, Z. Pei, Q. Xue, Z. Wang, Z. Liu, Z. Tang, Y. Wang, F. Kang, B. Li, C. Zhi, *Energy & Environmental Science* **2018**, *11*, 941.

[56] J. Maitra, V. K. Shukla, *Am. J. Polym. Sci* **2014**, *4*, 25.

[57] Y. Wu, S. Joseph, N. Aluru, *The Journal of Physical Chemistry B* **2009**, *113*, 3512.

[58] B. A. Miller-Chou, J. L. Koenig, *Prog. Polym. Sci.* **2003**, *28*, 1223.

[59] Z. Zhang, C. Zuo, Z. Liu, Y. Yu, Y. Zuo, Y. Song, *J. Power Sources* **2014**, *251*, 470.

[60] Z. Wei, J. He, T. Liang, H. Oh, J. Athas, Z. Tong, C. Wang, Z. Nie, *Polymer Chemistry* **2013**, *4*, 4601.

[61] Q. Wang, R. Hou, Y. Cheng, J. Fu, *Soft Matter* **2012**, *8*, 6048.

[62] R. Liu, S. Liang, X.-Z. Tang, D. Yan, X. Li, Z.-Z. Yu, *J. Mater. Chem.* **2012**, *22*, 14160.

[63] Q. Rong, W. Lei, L. Chen, Y. Yin, J. Zhou, M. Liu, *Angew. Chem. Int. Ed. Engl.* **2017**, *56*, 14159.

[64] K. Lu, T. Jiang, H. Hu, M. Wu, *Frontiers in chemistry* **2020**, *8*.

[65] T. N. T. Tran, H.-J. Chung, D. G. Ivey, *Electrochim. Acta* **2019**, *327*, 135021.

[66] J. Park, M. Park, G. Nam, J. s. Lee, J. Cho, *Adv. Mater.* **2015**, *27*, 1396.

[67] P. Sun, J. Chen, Y. Huang, J.-H. Tian, S. Li, G. Wang, Q. Zhang, Z. Tian, L. Zhang, *Energy Storage Materials* **2021**, *34*, 427.

[68] Y. Lu, T. Zhu, N. Xu, K. Huang, *ACS Applied Energy Materials* **2019**, *2*, 6904.

[69] M. Chen, J. Chen, W. Zhou, X. Han, Y. Yao, C. P. Wong, *Adv. Mater.* **2021**, *33*, 2007559.

[70] K. K. Sonigara, J. Zhao, H. K. Machhi, G. Cui, S. S. Soni, *Advanced Energy Materials* **2020**, *10*, 2001997.

[71] Y. Shi, C. Ma, L. Peng, G. Yu, *Adv. Funct. Mater.* **2015**, *25*, 1219.

[72] F. Meng, H. Zhong, D. Bao, J. Yan, X. Zhang, *J. Am. Chem. Soc.* **2016**, *138*, 10226.

[73] J. Fu, D. U. Lee, F. M. Hassan, L. Yang, Z. Bai, M. G. Park, Z. Chen, *Adv. Mater.* **2015**, *27*, 5617.

[74] K. Braam, V. Subramanian, *Adv. Mater.* **2015**, *27*, 689.

[75] W. Ling, F. Mo, J. Wang, Q. Liu, Y. Liu, Q. Yang, Y. Qiu, Y. Huang, *Materials Today Physics* **2021**, 100458.

[76] H. Dong, J. Li, S. Zhao, Y. Jiao, J. Chen, Y. Tan, D. J. Brett, G. He, I. P. Parkin, *ACS applied materials & interfaces* **2020**.

[77] Y. Zhang, Y. Chen, X. Li, M. Alfred, D. Li, F. Huang, Q. Wei, *J. Power Sources* **2021**, *482*, 228963.

[78] J. Zhu, M. Yao, S. Huang, J. Tian, Z. Niu, *Angew. Chem. Int. Ed.* **2020**, *59*, 16480.

[79] D. Wang, H. Li, Z. Liu, Z. Tang, G. Liang, F. Mo, Q. Yang, L. Ma, C. Zhi, *Small* **2018**, *14*, e1803978.

[80] S. Huang, F. Wan, S. Bi, J. Zhu, Z. Niu, J. Chen, *Angew. Chem. Int. Ed. Engl.* **2019**, *58*, 4313.

[81] H. Gao, Z. Zhao, Y. Cai, J. Zhou, W. Hua, L. Chen, L. Wang, J. Zhang, D. Han, M. Liu, L. Jiang, *Nature communications* **2017**, *8*, 15911.

[82] Y. Jian, S. Handschuh-Wang, J. Zhang, W. Lu, X. Zhou, T. Chen, *Materials Horizons* **2021**, *8*, 351.

[83] Y. Zhao, Z. Chen, F. Mo, D. Wang, Y. Guo, Z. Liu, X. Li, Q. Li, G. Liang, C. Zhi, *Advanced science* **2020**, *8*, 2002590.

[84] V. M. Gun'ko, I. N. Savina, S. V. Mikhalovsky, *Gels* **2017**, *3*.

[85] M. Zhu, X. Wang, H. Tang, J. Wang, Q. Hao, L. Liu, Y. Li, K. Zhang, O. G. Schmidt, *Adv. Funct. Mater.* **2019**, *30*, 1907218.

[86] Y. Chen, J. Zhao, Y. Wang, *ACS Applied Energy Materials* **2020**, *3*, 9058.

[87] M. Chen, W. Zhou, A. Wang, A. Huang, J. Chen, J. Xu, C.-P. Wong, *Journal of Materials Chemistry A* **2020**, *8*, 6828.

[88] Y. Quan, M. Chen, W. Zhou, Q. Tian, J. Chen, *Frontiers in chemistry* **2020**, *8*, 603.

[89] Z. Pei, Z. Yuan, C. Wang, S. Zhao, J. Fei, L. Wei, J. Chen, C. Wang, R. Qi, Z. Liu, *Angew. Chem.* **2020**, *132*, 4823.

[90] X. Guo, Z. Zhang, J. Li, N. Luo, G.-L. Chai, T. S. Miller, F. Lai, P. Shearing, D. J. Brett, D. Han, *ACS Energy Letters* **2021**, *6*, 395.

[91] F. Chen, D. Zhou, J. Wang, T. Li, X. Zhou, T. Gan, S. Handschuh-Wang, X. Zhou, *Angew. Chem.* **2018**, *130*, 6678.

[92] J. Hao, L. Yuan, C. Ye, D. Chao, K. Davey, Z. Guo, S. Qiao, *Angew. Chem.*

[93] R. Qin, Y. Wang, M. Zhang, Y. Wang, S. Ding, A. Song, H. Yi, L. Yang, Y. Song, Y. Cui, *Nano Energy* **2021**, *80*, 105478.

[94] Z. Liu, Y. Wang, Y. Ren, G. Jin, C. Zhang, W. Chen, F. Yan, *Materials Horizons* **2020**, *7*, 919.

[95] Q. Nian, J. Wang, S. Liu, T. Sun, S. Zheng, Y. Zhang, Z. Tao, J. Chen, *Angew. Chem. Int. Ed.* **2019**, *58*, 16994.

[96] L. Cao, D. Li, E. Hu, J. Xu, T. Deng, L. Ma, Y. Wang, X.-Q. Yang, C. Wang, *J. Am. Chem. Soc.* **2020**.

[97] Y. Ye, Y. Zhang, Y. Chen, X. Han, F. Jiang, *Adv. Funct. Mater.* **2020**, *30*, 2003430.

[98] S. Wu, Y. Alsaid, B. Yao, Y. Yan, Y. Zhao, M. Hua, D. Wu, X. Zhu, X. He, *EcoMat* **2021**.

[99] Z. He, C. Wu, M. Hua, S. Wu, D. Wu, X. Zhu, J. Wang, X. He, *Matter* **2020**, *2*, 723.

[100] L. An, B. Huang, Y. Zhang, R. Wang, N. Zhang, T. Dai, P. Xi, C. H. Yan, *Angew. Chem. Int. Ed.* **2019**, *58*, 9459.

[101] Y. Bai, B. Chen, F. Xiang, J. Zhou, H. Wang, Z. Suo, *Appl. Phys. Lett.* **2014**, *105*, 151903.

[102] C.-C. Yang, *Materials Science and Engineering: B* **2006**, *131*, 256.

[103] J. Adebahr, N. Byrne, M. Forsyth, D. R. Macfarlane, P. Jacobsson, *Electrochim. Acta* **2003**, *48*, 2099.

[104] L. Fan, Z. Dang, G. Wei, C.-W. Nan, M. Li, *Materials Science and Engineering: B* **2003**, *99*, 340.

[105] A. Alam, Y. Zhang, H.-C. Kuan, S.-H. Lee, J. Ma, *Prog. Polym. Sci.* **2018**, *77*, 1.

[106] H. Yuk, T. Zhang, G. A. Parada, X. Liu, X. Zhao, *Nature communications* **2016**, *7*, 12028.

[107] B. Jeong, S. W. Kim, Y. H. Bae, *Advanced drug delivery reviews* **2012**, *64*, 154.

[108] S. S. Soni, K. B. Fadadu, A. Gibaud, *Langmuir* **2012**, *28*, 751.

[109] L. Li, L. H. Lim, Q. Wang, *Polymer* **2008**, *49*, 1952.

[110] F. Mo, H. Li, Z. Pei, G. Liang, L. Ma, Q. Yang, D. Wang, Y. Huang, C. Zhi, *Science Bulletin* **2018**, *63*, 1077.

[111] L. Xu, S. Gao, Q. Guo, C. Wang, Y. Qiao, D. Qiu, *Adv. Mater.* **2020**, *32*, e2004579.

[112] S. Wu, M. Hua, Y. Alsaid, Y. Du, Y. Ma, Y. Zhao, C. Y. Lo, C. Wang, D. Wu, B. Yao, J. Strzalka, H. Zhou, X. Zhu, X. He, *Adv. Mater.* **2021**, DOI: 10.1002/adma.202007829e2007829.

[113] Z. Liu, D. Wang, Z. Tang, G. Liang, Q. Yang, H. Li, L. Ma, F. Mo, C. Zhi, *Energy Storage Materials* **2019**, *23*, 636.

[114] N. Zhao, F. Wu, Y. Xing, W. Qu, N. Chen, Y. Shang, M. Yan, Y. Li, L. Li, R. Chen, *ACS applied materials & interfaces* **2019**, *11*, 15537.

[115] J. W. Zhang, D. D. Dong, X. Y. Guan, E. M. Zhang, Y. M. Chen, K. Yang, Y. X. Zhang, M. M. B. Khan, Y. Arfat, Y. Aziz, *Frontiers in chemistry* **2020**, *8*, 102.

[116] X. Tong, J. Zheng, Y. Lu, Z. Zhang, H. Cheng, *Mater. Lett.* **2007**, *61*, 1704.

[117] J. P. Gong, Y. Katsuyama, T. Kurokawa, Y. Osada, *Adv. Mater.* **2003**, *15*, 1155.

[118] J. Y. Sun, X. Zhao, W. R. Illeperuma, O. Chaudhuri, K. H. Oh, D. J. Mooney, J. J. Vlassak, Z. Suo, *Nature* **2012**, *489*, 133.

[119] C. H. Yang, M. X. Wang, H. Haider, J. H. Yang, J. Y. Sun, Y. M. Chen, J. Zhou, Z. Suo, *ACS applied materials & interfaces* **2013**, *5*, 10418.

[120] Y. Yang, X. Wang, F. Yang, H. Shen, D. Wu, *Adv. Mater.* **2016**, *28*, 7178.

[121] Q. He, Y. Huang, S. Wang, *Adv. Funct. Mater.* **2018**, *28*, 1705069.

[122] M. Hua, S. Wu, Y. Ma, Y. Zhao, Z. Chen, I. Frenkel, J. Strzalka, H. Zhou, X. Zhu, X. He, *Nature* **2021**, *590*, 594.

[123] D. Wang, L. Wang, G. Liang, H. Li, Z. Liu, Z. Tang, J. Liang, C. Zhi, *ACS nano* **2019**, *13*, 10643.

[124] Y. Amamoto, H. Otsuka, A. Takahara, K. Matyjaszewski, *Adv. Mater.* **2012**, *24*, 3975.

[125] Y. Yang, X. Ding, M. W. Urban, *Prog. Polym. Sci.* **2015**, *49*, 34.

[126] D. L. Taylor, M. In Het Panhuis, *Adv. Mater.* **2016**, *28*, 9060.

[127] W. Mai, Q. Yu, C. Han, F. Kang, B. Li, *Adv. Funct. Mater.* **2020**, *30*, 1909912.

[128] J. Duan, W. Xie, P. Yang, J. Li, G. Xue, Q. Chen, B. Yu, R. Liu, J. Zhou, *Nano Energy* **2018**, *48*, 569.

[129] W. Zhang, X. Liu, J. Wang, J. Tang, J. Hu, T. Lu, Z. Suo, *Engineering Fracture Mechanics* **2018**, *187*, 74.

[130] M. Chen, J. Chen, W. Zhou, X. Han, Y. Yao, C. P. Wong, *Adv. Mater.* **2021**, *33*, e2007559.

[131] S. Han, C. Liu, X. Lin, J. Zheng, J. Wu, C. Liu, *ACS Applied Polymer Materials* **2020**, *2*, 996.

[132] S. Xue, Y. Wu, M. Guo, Y. Xia, D. Liu, H. Zhou, W. Lei, *Soft Matter* **2019**, *15*, 3680.

[133] C.-H. Li, C. Wang, C. Keplinger, J.-L. Zuo, L. Jin, Y. Sun, P. Zheng, Y. Cao, F. Lissel, C. Linder, *Nature chemistry* **2016**, *8*, 618.

[134] J. Chen, F. Li, Y. Luo, Y. Shi, X. Ma, M. Zhang, D. Boukhvalov, Z. Luo, *Journal of Materials Chemistry A* **2019**, *7*, 15207.