batteries

Review

Recent Progress and Challenges of Flexible Zn-Based Batteries with Polymer Electrolyte

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Abstract: Zn-based batteries have been identified as promising candidates for flexible and wearable batteries because of their merits of intrinsic safety, eco-efficiency, high capacity and cost-effectiveness. Polymer electrolytes, which feature high solubility of zinc salts and softness, are especially advantageous for flexible Zn-based batteries. However, many technical issues still need to be addressed in Zn-based batteries with polymer electrolytes for their future application in wearable electronics. Recent progress in advanced flexible Zn-based batteries based on polymer electrolytes, including functional hydrogel electrolytes and solid polymer electrolytes, as well as the interfacial interactions between polymer electrolytes and electrodes in battery devices, is comprehensively reviewed and discussed with a focus on their fabrication, performance validation, and intriguing affiliated functions. Moreover, relevant challenges and some potential strategies are also summarized and analyzed to help inform the future direction of polymer-electrolyte-based flexible Zn-based batteries with high practicability.

Keywords: Zn-based battery; polymer electrolytes; wearable electronics; interfacial interactions

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1. Introduction

With the rapid development of portable and wearable electronics, such as wearable sensors for health monitoring, flexible batteries have attracted significant research interest due to their vast application potential [1–4]. An ideal flexible battery possesses the merits of small size, mechanical flexibility, electrochemical stability and adaptability to deformation in practical usage. At present, lithium-ion batteries (LIBs) dominate the mainstream market, ranging from smartphones to electric vehicles, due to their intrinsic high voltage and high energy density. Unfortunately, the severe safety issues associated with the flammable and toxic organic electrolytes used continue to seriously hinder the development of flexible LIBs for wearable applications [5–7]. Therefore, substantial efforts have been devoted to identifying suitable alternatives. In recent years, zinc-ion batteries (ZIBs) have attracted much attention by virtue of their inherent safety, high capacity, eco-efficiency and satisfactory energy density, and have been identified as promising substitutes for LIBs [8–12].

For aqueous ZIBs, metallic Zn can be directly utilized as the anode due to its intrinsic stable chemical properties, possessing a high theoretical capacity of 5854 mAh cm^{-3} (or 820 mAh g^{-1}) [13,14]. However, there are some challenges that occur in aqueous systems, which adversely affect the long-term stability of ZIBs. A key issue is that of zinc dendrites, which are normally caused by uneven Zn deposition. The irregular and rough morphology of the dendrites can easily lead to short-circuits [15,16]. Other key issues include side-reactions, which originate from the water splitting process of the aqueous electrolyte, including the hydrogen evolution reaction (HER) and corrosion. These unfavorable side-reactions result in the exhaustion of water and surface passivation of the Zn anode, leading to low battery efficiency [17,18]. Additionally, some cathode materials are slightly soluble in aqueous solution, resulting in gradual capacity deterioration. Fortunately, ion-conductive polymer electrolytes can effectively alleviate the above-mentioned issues. Due to the unique quasi-solid-state characteristics, the salt ions can be well dispersed and transmitted inside the gel matrix, offering the ion conductivity required for electrochemical reactions [19,20]. In addition, polymer electrolytes can serve as separators to avoid short-circuiting and can inhibit the dissolution of active materials relative to liquid electrolytes, while their intrinsic mechanical strength can, to some extent, suppress dendritic growth. Moreover, polymer electrolytes, which are soft and viscous, can form an intimate contact with the electrodes to decrease the interface impedance, and show a high level of compatibility with flexible ZIBs [21].

Therefore, substantial effort has been invested in research to develop polymer electrolytes for flexible Zn-based batteries. Fundamental polymer electrolytes for flexible batteries should possess the following advantages which act synergistically: (1) high ionic conductivity; (2) strong mechanical strength yet softness; (3) good interfacial compatibility; and (4) extreme temperature tolerance. Through precise design of the polymer chemistry, such as introducing additives, grafting functional groups, or regulating the hydrogel network, many novel polymer electrolytes with associated functionalities have been exploited. These enable ZIBs with high performance, high capacity, responsiveness to external stimuli, and extreme tolerance to deformation for wearable applications, creating increased opportunities for versatile energy storage [22]. In this review, state-of-the-art Zn-based batteries based on polymer electrolytes, including hydrogel electrolytes, solid polymer electrolytes, and hybrid electrolytes, are summarized, and battery configuration, the rational selection of materials, and polymer engineering technologies are examined. Furthermore, an overview of existing challenges and future opportunities is presented for the further development of flexible Zn-based batteries.

2. Fundamentals of Flexible Zn-Based Batteries

Flexible Zn-based batteries generally comprise flexible cathodes, ultra-thin zinc foil as the anode and ionic conductive polymer electrolytes [23]. The self-standing cathode normally contains flexible current collectors, such as carbon nanotube paper, carbon cloth and graphite paper, on the surface of which the cathode materials, binder and conductor are mixed and coated. The polymer electrolytes, which normally serve as both the electrolyte and separator, play a vital role in ion transport to ensure electrochemical performance. All the component layers need to interact closely and be interrelated to decrease interface impedance and to maintain device-level flexibility.

2.1. Aqueous Rechargeable Zn-Based Batteries

The electrochemical mechanism by which Zn-based batteries operate is related to both the cathode materials and anode. Considerable research effort has been devoted to developing high performance cathode materials for Zn-based batteries, such as (i) manganese (Mn)-based compounds; (ii) vanadium (V)-based compounds; (iii) nickel (Ni)- or cobalt (Co)-based compounds; (iv) Prussian blue analogs (PBAs); and (v) organic materials. The reaction mechanisms of Zn-based batteries remain controversial and are subject to debate. To date, several reaction electrochemistry mechanisms have been proposed, including chemical conversion reactions, Zn^{2+} intercalation/extraction, co-insertion, and hybrid mechanisms (Figure 1a) [24]. Due to their wide variety of atomic architectures, morphology, and phases, manganese oxides (i.e., MnO_2, Mn_2O_3) display various electrochemical properties. However, whatever the initial architecture, manganese oxides suffer from persistent issues of serious structural collapse and large volumetric change resulting from repeated insertion of large amounts of hydrated Zn^{2+} ions during charging and discharging processes, leading to rapid capacity deterioration. V-based compounds can deliver high specific capacity and broad variation range, but the low ion diffusion coefficient and poor conductivity cause their long-term cycling properties to seriously deteriorate. For Ni–Zn or Co-Zn batteries, severe zinc dendrite formation normally adversely affects the specific capacity and the Coulombic efficiency. PBA-based materials possess a 3D porous framework structure, which can achieve unique structural and electrochemical stability. However, they still suffer from relatively low specific capacity and low energy density. Organic materials have been considered as environmentally friendly cathode materials with low-toxicity and sustainability. Unfortunately, organic materials are associated with poor stability due to their inherent insolubility in aqueous electrolytes [25,26].

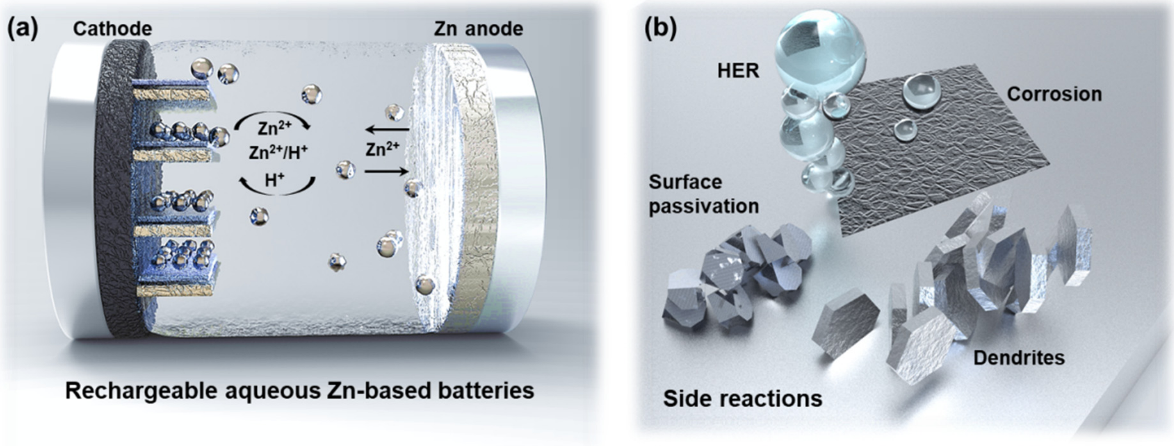


Figure 1. (**a**) Schematic illustration of working mechanism, and (**b**) side reactions of rechargeable Zn-based batteries in mild acid/neural electrolytes.

The working mechanism of a metallic Zn anode in a mild acid/neural electrolyte can be represented as the reversible deposition-dissolution of zinc ions ($Zn \leftrightarrow Zn^{2+} + 2e^-$). These reaction processes are carried out synchronously on both sides of the electrodes. Considering the intercalation/extraction mechanism as an example, the Zn dissolves from the anode side into the electrolyte during the discharging process; at the same time, the soluble Zn^{2+} is transported through the electrolyte to the cathode side and then inserts into the cathode materials. However, during the charging process, the Zn^{2+} ions are extracted from the cathode materials back into the electrolyte. Following this, if the dissolved Zn^{2+} ions collide and combine with electrons in the electrolyte, they are deposited onto the surface of the Zn anode [27]. These two reactions alternate during the cyclic charging-discharging process.

For rechargeable Zn-based batteries in aqueous electrolytes, there are some persistent challenges associated with the metallic Zn anode. One challenge concerns irregular and rough Zn dendrites that are easily formed under an electric field, which may cause short-circuiting. Other challenges include parasitic side-reactions that may occur in the aqueous electrolyte, such as interfacial HER of the Zn anode, corrosion and surface passivation, which can lead to deterioration in battery performance (Figure 1b) [28,29]. Apart from the Zn anode, some cathode materials dissolve slightly in aqueous electrolyte, resulting in a decline in capacity. Fortunately, these problems can, to some extent, be alleviated by use of polymer electrolytes. The unique quasi-solid characteristics of polymer electrolytes can not only inhibit the dissolution of active materials, but can also serve as a separator to prevent short-circuits and hinder Zn dendrite growth. Furthermore, the intrinsic features of mechanical flexibility, safety, eco-friendliness, and good interfacial compatibility make polymer electrolytes suitable for manufacturing flexible Zn-based batteries [30,31].

2.2. Polymer Electrolytes

Depending on their composition, polymer electrolytes for Zn-based batteries can be classified into three main categories: solid polymer electrolytes, hydrogel electrolytes, and hybrid polymer electrolytes. For solid polymer electrolytes, zinc salts can be directly dissolved by the polymer chains or with a small amount of organic solvent. Hydrogel electrolytes are generally swollen with abundant water in which zinc salts are dissolved. Hybrid polymer electrolytes are normally copolymerized or crosslinked together by several kinds of polymers. These intrinsic features endow polymer electrolytes with the dimensional stability of a flexible quasi-solid state, which, at the same time, can provide favorable ionic conductivity for electrochemical performance, making them especially advantageous for the fabrication of flexible batteries.

Some representative polymer electrolytes are summarized in Table 1, showing their molecular structures and general characteristics. As hydrogel electrolytes normally only serve as supporting frameworks swollen with abundant water containing dissolved zinc salts, they face the persistent challenge of a narrow electrochemical stable potential window. Thus, the voltage of Zn-based batteries equipped with hydrogel electrolytes always remains at a relatively low level of <2.0 V. Fortunately, the dissolved Zn ions in the water within the hydrogel matrix can transport between the electrodes without significant resistance; thus, some hydrogel electrolytes can exhibit higher comparative ionic conductivity relative to liquid-based electrolytes. Solid polymer electrolytes possess a much wider voltage window because they do not contain any water inside the gel matrix. However, their low ionic conductivity and poor interface compatibility with electrodes has seriously limited research into solid polymer electrolytes. Typically, poly(ethylene oxide) (PEO) has been applied as a solid polymer electrolyte in both lithium-ion and Zn-based batteries, whereby Zn^{2+} ions are transferred by segmental motion [32]; however, relatively low ionic conductivity remains a challenge. The most commonly used materials for hydrogel electrolytes are polyvinyl alcohol (PVA), polyacrylamide (PAM), and polyacrylic acid (PAA), which contain abundant hydrophilic groups on the side-chains and are, therefore, able to absorb large amounts of water [21]. Moreover, the hydroxyl and carbonyl groups within the gel matrix mean that hydrogel electrolytes show high affinity and adhesiveness to electrodes [33]. However, the mechanical properties of the physical crosslinking PVA and PAM materials require further improvement. In addition, sodium polyacrylate (PANa) can withstand a 6 M KOH solution post-absorption, demonstrating strong alkali resistance [34]. The synthesis process of PANa is relatively more complicated than that for PAA, and it is hard to store for a long period due to the occurrence of hydrolysis side-reactions in a strong alkali environment. Generally, xanthan gum and gelatin containing long chains of repeated monosaccharide/peptide units are used as thickening agents to produce the hydrogel state. Their synthesis processes are straightforward but the mechanical properties of the resultant hydrogels are normally unsatisfactory due to poor physical crosslinking. Recently, some functional polymer electrolytes with intriguing special properties, such as low-temperature tolerance, thermoresponsiveness and self-healing capacity, have been developed, suggesting high effectiveness for energy storage applications. These are discussed in-depth in the following sections.

Table 1. Some representative polymer electrolytes for Zn-based batteries.

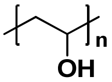
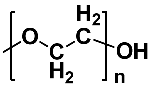
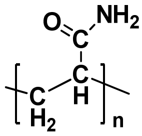
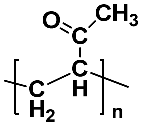
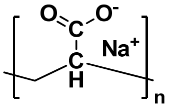
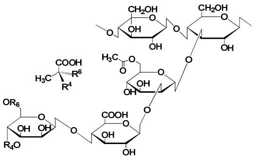
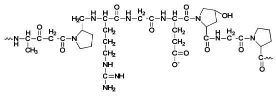
Names of Hydrogel	Molecular Structures	Functional Groups	Features	Ionic Conductivity (S cm^{-1})	Cathode Material	Mechanical Properties	Refs.
Polyvinyl alcohol (PVA)		Hydroxyl	Self-healable	0.05–12.6	Polyaniline nanorods 123 mAh g^{-1} 0.1 A g^{-1}	Physical crosslinking Stretchable	[35]

Table 1. *Cont.*

Names of Hydrogel	Molecular Structures	Functional Groups	Features	Ionic Conductivity (S cm^{-1})	Cathode Material	Mechanical Properties	Refs.
Poly(ethylene oxide) (PEO)		Hydroxyl	Reusable	1.09×10^{-6}–6.33×10^{-3}	MnO_2 140 mAh g^{-1} 0.5 mA cm^{-2}	Physical crosslinking Flexible	[36,37]
Polyacrylamide (PAM)		Amide	Reusable	2.15×10^{-3}	V_2O_5 271 mA h g^{-1} 2 C	Chemical crosslinking Stretchable	[38]
Polyacrylic acid (PAA)		Carboxyl	Self-healable	0.288	MnO_2 5.6 mAh cm^{-2} 0.5 mA cm^{-2}	Physical/chemical crosslinking Stretchable	[39,40]
Sodium polyacrylate (PANa)		Sodium carboxylate	Self-healable Alkali resistant	0.17	NiCo 259 mAh g^{-1} 5.8 C	Physical crosslinking Stretchable	[34]
Xanthan gum		Polysaccharide	Biodegradable	1.46×10^{-2}	MnO_2 260 mA h g^{-1} 1 C	Physical crosslinking Fragile	[41]
Gelatin		Peptides	Biodegradable	6.15×10^{-3}–2.0×10^{-2}	$LiMn_2O_4$ 110 mAh g^{-1} at 25 mA g^{-1}	Physical crosslinking Fragile	[42]

2.3. Configuration

The configurations of flexible batteries can be classified into three categories, as shown in Figure 2. Substantial research effort has been focused on planar batteries with a sandwich architecture, in which the three layers of a Zn anode, polymer electrolyte and a cathode are linked tightly together layer-by-layer [23]. 2D flexible micro in-plane batteries, consisting of two slotted electrolytes printed onto a flexible polyethylene terephthalate (PET) substrate, are especially suitable as power accessories for flexible electronic systems fabricated by various printing technologies [43]. Fiber-shaped batteries possess a 1D configuration with small size, which can achieve extreme flexibility that enables tunable amounts of fiber batteries to be utilized as cotton yarns that can be woven/knitted into energy textiles for wearable applications [44,45]. However, the manufacturing process for 1D fiber-shaped batteries is much more difficult than that for assembly into a 2D configuration.

With respect to potential for application, each cell architecture has its own advantages and disadvantages. Planar batteries with a sandwich structure can use stacked thick electrodes, which can be conducive to better battery performance, such as high energy density. However, additional electrode current collectors and diaphragm layers are required. Such a multi-layer structure and a thicker battery will increase the hardness of the battery and adversely affect the flexibility of the battery. The 2D in-plane battery which has interdigital anode and cathode integrated in one plane, can effectively reduce the thickness of the battery and thus achieve improved flexibility. The ion transmission distance between the two electrodes will be greatly reduced, which is conducive to the realization of high power density. However, due to limitations in the electrode active materials, the energy density needs to be further improved. Similar to the planar plug-in battery, linear fiber-shaped batteries with a one-dimensional structure possess great advantages for the integration of practical devices due to their exceptional flexibility and deformability. However, their electrochemical performance, especially of the thick electrode (corresponding to high energy density), as well as the complicated industrial manufacturing technologies involved, require further development for optimization.

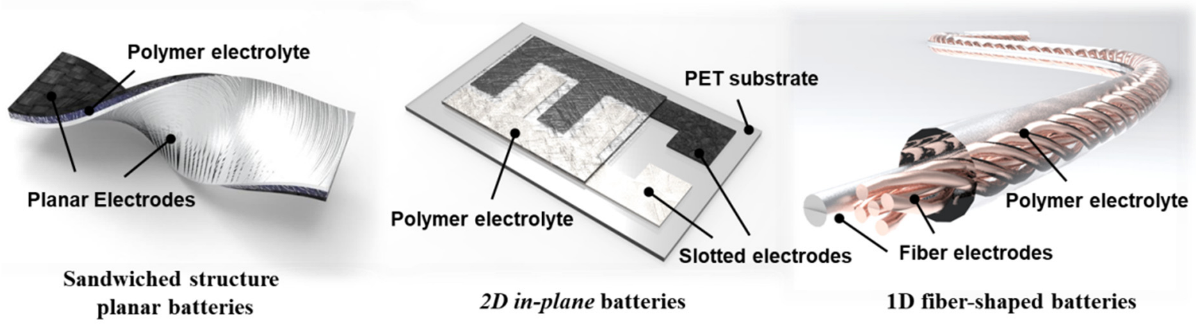


Figure 2. Diverse configurations of flexible batteries.

3. Advanced Flexible Zn-Based Batteries with Functional Polymer Electrolytes

In recent years, intensive efforts have been devoted to the development of advanced flexible Zn-based batteries with diverse functionalities to satisfy the requirements of different practical scenarios, such as extreme temperature tolerance, durability, and thermal protection. In the research undertaken, the functional batteries not only achieve superior electrochemical performance, but can also endure or respond to various external stimuli, demonstrating their excellent versatility for complicated working environments. To realize these smart functionalities, the most common strategy is to design elaborate advanced polymer electrolyte materials and to integrate them into battery devices. These approaches are comprehensively summarized in the following sections.

3.1. Low-Temperature Tolerant Zn-Based Batteries

When working at sub-zero temperatures, the water in hydrogel electrolytes inevitably freezes, decreasing the ionic conductivity and leading to performance deterioration of Zn-based batteries [46]. Extensive efforts have been devoted to developing low-temperature tolerant Zn-based batteries, which can maintain both mechanical flexibility and high ionic conductivity in extremely cold conditions. One common strategy to suppress the freezing of hydrogel electrolytes is to introduce additives, such as hydrated salts or polyol solvent, into the polymer matrix to inhibit the intermolecular hydrogen bonding between free water molecules. For instance, Wang et al. synthesized a concentrated PANa hydrogel electrolyte containing a 6 M KOH solution, which enabled the assembled NiCo//Zn battery to work stably even at −20 °C (Figure 3a) [47]. More impressively, this concentrated hydrogel electrolyte could be stretched by 1400% with high ionic conductivity of 5.7 S m^{-1} under −20 °C. The resultant flexible NiCo//Zn battery with the concentrated hydrogel exhibited a high capacity of over 130 mAh g^{-1} with exceptional retention of 87% after 10,000 cycles. As well as providing hydrated ions, introducing polyol solvents, such as glycerol and ethylene glycol (EG), as cryoprotectants can also improve the freezing tolerance of hydrogel electrolytes. For example, Chen et al. reported an anti-freezing flexible Zn-MnO_2 battery equipped with a borax-crosslinked PVA/glycerol (PVA−B−G) hydrogel [48]. In this study, the PVA−B−G hydrogel was synthesized by crosslinking PVA and glycerol with borate ions, constructing integrated 3D networks (Figure 3b). Even at the extremely cold temperature of −35 °C, the PVA−B−G hydrogel still exhibited excellent mechanical properties that could easily be stretched to 400–500% strain. This anti-freezing hydrogel electrolyte also delivered a high ionic conductivity of 10.1 mS cm^{-1}, which enabled the prepared Zn-MnO_2 battery to show high capacity retention of 90% after 2000 cycles under −35 °C. The combination of the synergistic effects of hydrated ions and polyol solvents as additives is expected to further improve the low-temperature tolerance of hydrogel electrolytes.

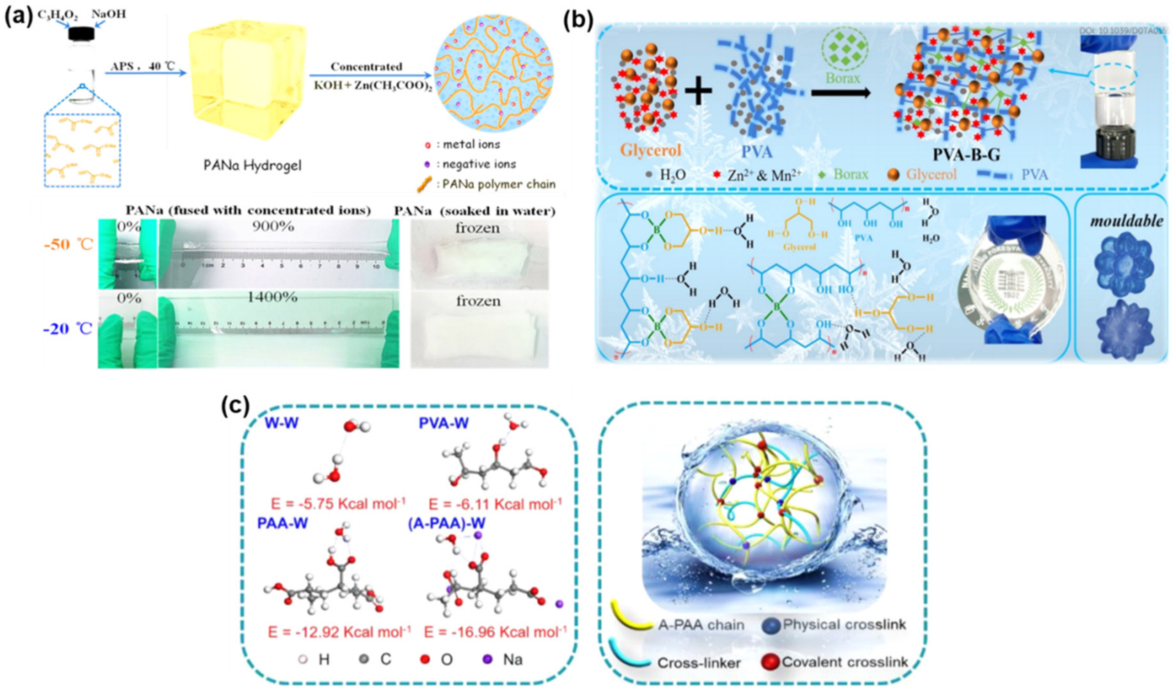


Figure 3. (**a**) The molecular structure and stretchability of the anti-freezing concentrated PANa hydrogel electrolyte. Reproduced with permission from [47]. (**b**) Schematic fabrication of PVA−B−G hydrogel. Reproduced with permission from [48]. (**c**) Molecular models and simulated interactions between terminal groups and water molecules in different hydrogels. Reproduced with permission from [49].

The other common strategy to suppress the freezing of water in the hydrogel is to conduct hydrogel network modification, such as by introducing hydrophilic groups (i.e., –OH, $-NH_2$, –COOH) into the hydrogel network to interact with the free water molecules. For instance, Pei et al. exploited an alkalified PAA hydrogel filled with 30 wt% KOH solution, which exhibited a high ionic conductivity of 199 mS cm^{-1} at −20 °C (Figure 3c) [49]. The interaction energy of the carboxyl group with water molecules in the PAA matrix obtained by density functional theory calculation was −12.92 kcal mol^{-1} in its initial state, which increased to −16.96 kcal mol^{-1} after the alkalified treatment, thus realizing better freezing tolerance. A flexible ZAB was fabricated which could retain both good electrochemical performance and mechanical stability and which sustained bending, twisting, and folding deformations at −20 °C, indicating outstanding low-temperature adaptability.

3.2. Thermoresponsive Zn-Based Batteries

Thermo-reversible hydrogel is a new kind of smart material, which can display unique sol-gel phase transition behavior. Thermoresponsive hydrogel materials normally adopt a liquid-state at relatively low temperature, but can automatically transform into a gel-state upon heating to a high temperature. This process can be reversed when cooling back to a low temperature. The unique thermo-reversible property of this material makes it suitable for thermal shock prevention in high-power batteries. For instance, Chen et al. developed a thermoresponsive and hygroscopic hydrogel electrolyte based on a poly(N-isopropylacrylamide (NIPAM) monomer for supercapacitors [50]. By controlling the ion migration inside the gel matrix through sol-gel transition, this thermoresponsive hydrogel electrolyte could deteriorate the electrochemical performance at high temperature and restore it to the initial state after cooling to room temperature, manifesting a self-protection effect. However, the limited solubility of zinc salt in this thermoresponsive hydrogel electrolyte adversely affected the specific capacity of the assembled battery. To improve the ionic conductivity of these thermoresponsive hydrogel materials, Zhu et al.

suggested employing this material as a thin separator coating instead of an electrolyte to minimize the adverse effect on ion migration [51]. The hydrogel was synthesized using the thermoresponsive NIPAM monomer and coated onto a separator. At room temperature, the surface of this hydrogel showed a porous structure, indicating abundant ion pathways. Upon heating to 60 °C, the porous structure disappeared, thus inhibiting ion migration (Figure 4a). The fabricated ZIB showed a high specific capacity of 168.7 mAh g^{-1} at 0.1 A g^{-1}, which could be shut down upon heating to 60 °C, displaying favorable battery performance and the functionality of self-protection (Figure 4b).

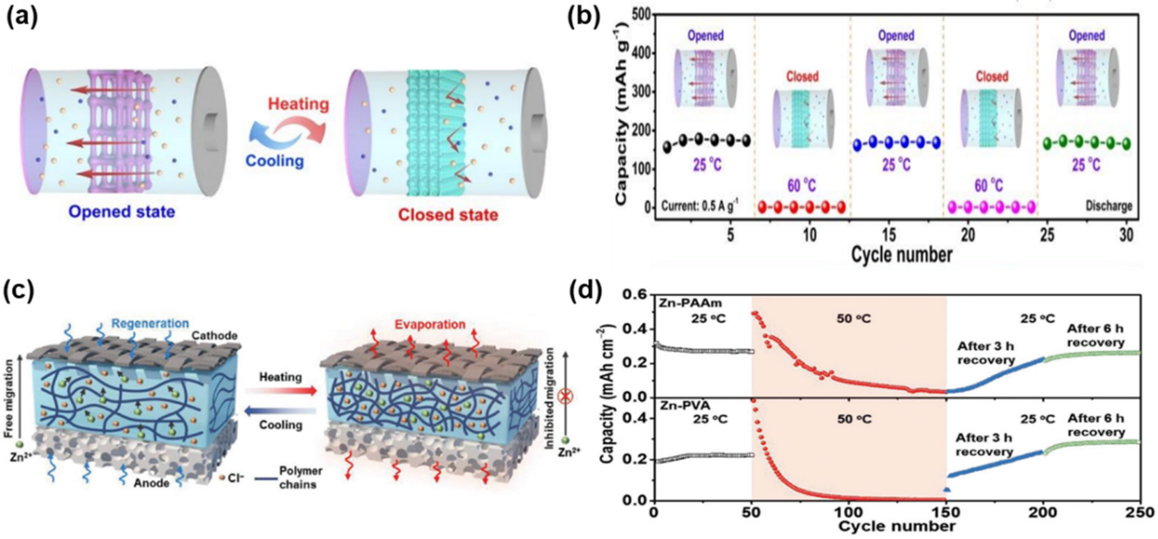


Figure 4. (**a**) Schematic illustration of thermal self-protective ZIBs with PNIPAM/AM electrolytes. (**b**) Safety performance of the self-protective ZIB. Reproduced with permission from [51]. (**c**) Working principle of the self-protective ZIBs with hygroscopic hydrogel electrolyte. (**d**) The reversibility performance of the thermoresponsive ZIBs. Reproduced with permission from [52].

Apart from sol-gel transition, a new thermal self-protection strategy for improving the practicability and durability of Zn-MnO_2 batteries through thermo-reversible property has been proposed [52]. In this research, the inner moisture of the synthesized PAM hydrogel electrolyte was controlled by adjusting the $ZnCl_2$ concentration so that it could keep balance with the surrounding environment (25 °C and 70% relative humidity (RH)), enabling the hydrogel to maintain its whole mass even after 10 days (Figure 4c). However, upon heating to high temperatures, a large amount of moisture (~40 wt%) evaporated from the PAM hydrogel matrix, akin to sweating, thus dissipating the heat and automatically shutting down the over-heated battery. After cooling back to room temperature, the PAM hydrogel electrolyte was able to reabsorb moisture form the ambient environment and the battery performance was restored to its initial state. The whole process of dehydration and reabsorption of moisture as the temperature changed evidenced high reversibility, guaranteeing the long-run safety of Zn-MnO_2 batteries (Figure 4d).

3.3. Self-Healing Zn-Based Batteries

In practical use, the flexible and wearable Zn-based batteries inevitably suffer from rupture and damage, especially under extreme deformations. In this case, hydrogel electrolytes with an intriguing self-healing property represent a good choice to tackle this issue. In general, self-healing ability is achieved by reversible dynamic bonding, such as hydrogen bonding, π–π conjugation, metal ionic bonding, or ester bonding [49]. For example, Niu et al. developed a self-healable hydrogel electrolyte based on PVA/zinc trifluoromethanesulfonate ($Zn(CF_3SO_3)_2$), in which abundant hydrogen bonding could dynamically form among PVA chains to realize the self-healing effect (Figure 5a) [35]. While connecting two fractured parts of the hydrogel electrolytes together, the separated halves healed sufficiently such that the crack disappeared and electrochemical performance was restored (Figure 5b). The resultant ZIB displayed a high capacity for retention of over 81.0 mAh g^{-1} after three breaking-healing cycles.

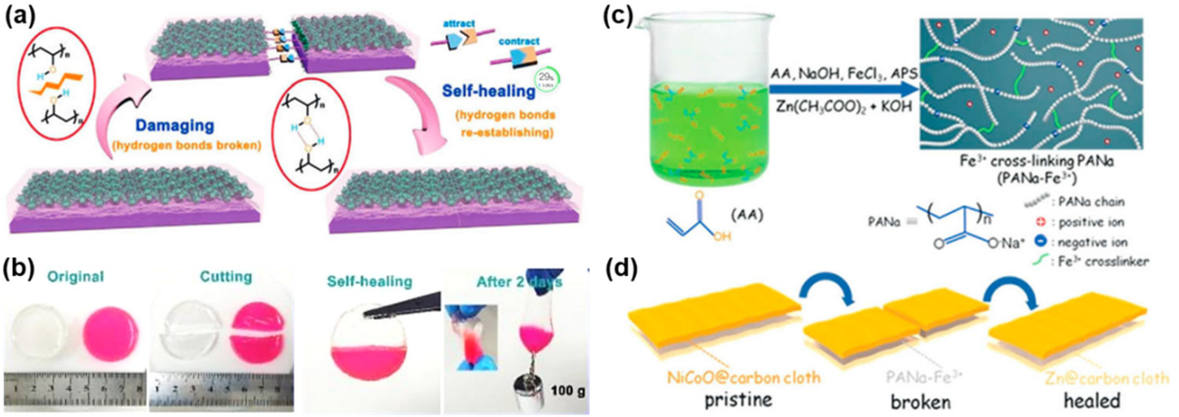


Figure 5. (**a**) Working mechanism of the self-healing PVA/$Zn(CF_3SO_3)_2$ hydrogel electrolyte. (**b**) The self-healing behaviors of the self-healable hydrogel electrolyte. Reproduced with permission from [35]. (**c**) Fabrication of the self-healable ionic-crosslinked hydrogel electrolyte. (**d**) Schematic illustration of the self-healing ZIBs. Reproduced with permission from [53].

In addition, Huang et al. exploited a self-healable hydrogel triggered by ferric ions crosslinking [53]. In this research, the Fe^{3+} ionic crosslinking formed among PANa chains bestowed the hydrogel electrolyte with an alkaline-tolerant capability and unique self-healing property (Figure 5c). The assembled flexible Zn/NiCo battery exhibited a high discharging capacity of 250 mAh g^{-1} with a high retention of 87% after four cutting-healing cycles (Figure 5d). Compared to the reversible physical bonding, the covalent bonding enabled higher self-healing efficiency due to its more stable bonding force [54]. However, self-healing effects based on covalent bonding are generally triggered by external stimuli, such as light, moisture or pH, hindering their application in batteries.

3.4. All-Solid-State Zn-Based Batteries

Zn-based batteries are normally fabricated in an aqueous system for flexible batteries. However, the issue of water evaporation and side-reactions caused by water seriously hinder the development of flexible aqueous batteries. Therefore, the construction of liquid-free all-solid-state electrolytes with high ionic conductivity, long-term stability and a wide electrochemical window has great potential for the development of flexible Zn-based batteries, although this is still in its infancy. Poly(vinylidene fluoride hexafluoropropylene) (PVHF)/poly(ethylene oxide) filled with zinc salts or ionic liquid has been widely utilized as a solid polymer electrolyte, showing good flexibility and modulus [55,56]. Considering the general incompatibility of solid–solid electrochemical interfaces arising from the stronger electrostatic bonding from divalent Zn^{2+}, introducing inorganic fillers with a large surface area and rich surface chemistry represents a promising strategy to facilitate the dissociation and transport of Zn ions in solid polymer electrolytes [57,58]. Chen et al. developed a solid polymer electrolyte fabricated by MXenes well-dispersed PVHF grafted with poly(methyl acrylate) (PVHF/MXene-g-PMA) [59]. The abundant functional groups on the surface of MXene facilitated in-plane ion migration and compatibility between MXene and the polymeric matrix, which enabled the PVHF/MXene-g-PMA to deliver high ionic conductivity of 2.69×10^{-4} S cm^{-1} at room temperature (Figure 6a). Benefitting from the solvent-free characteristics and compatible interface, the assembled all-solid state ZIB exhibited stable electrochemical performance that could operate in a wide temperature range from −35 °C to 100 °C without HER. No obvious capacity loss was observed after being stored at low or high temperatures.

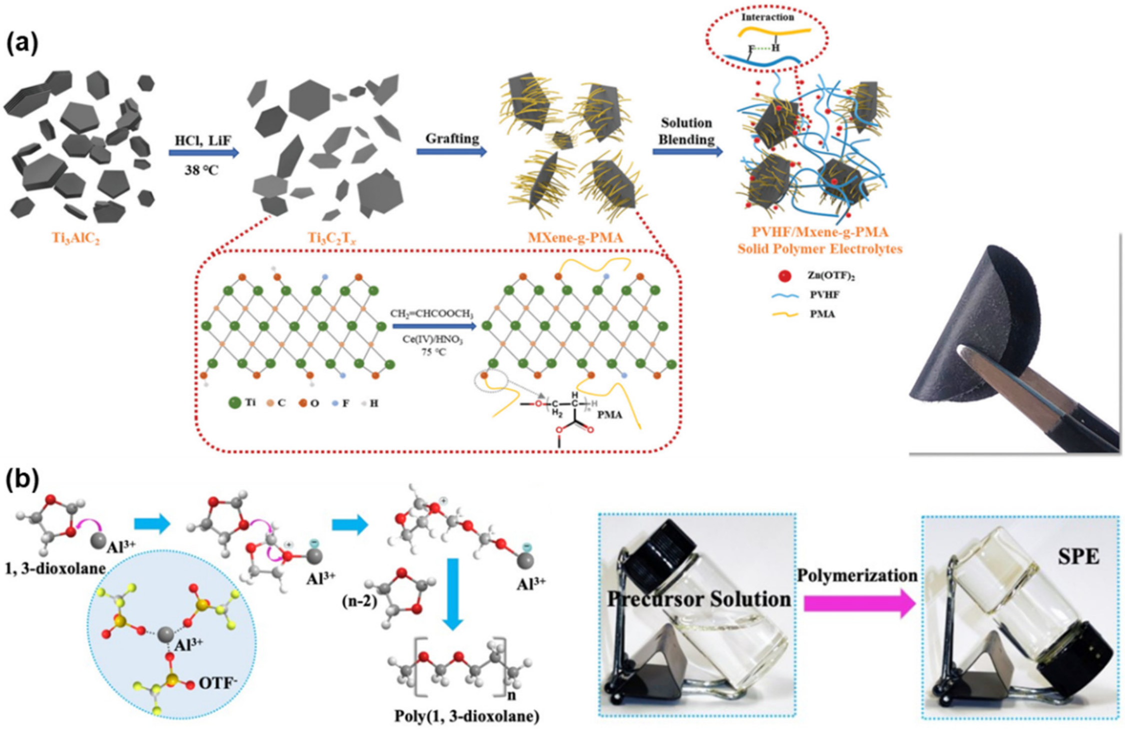


Figure 6. (**a**) Schematic fabrication of the solid state MXene-*g*-PMA electrolyte. Reproduced with permission from [59]. (**b**) The reaction mechanism of the 1,3-dioxolane based solid polymer electrolytes. Reproduced with permission from [60].

The in situ construction method for solid-state batteries can effectively reduce interfacial impedance and voltage polarization of flexible/wearable batteries, leading to higher Coulombic efficiency. For instance, Ma et al. fabricated an amorphous poly(1,3-dioxolane)-based solid electrolyte through in situ polymerization, which was able to deliver an ultra-high ionic conductivity of 19.6 mS cm^{-1} at room temperature, as shown in Figure 6b [60]. The resultant zinc symmetric battery could reversibly charge/discharge over 1800 h cycles without dendrite growth. The assembled ZIBs based on the in-situ-formed polymer electrolytes could work stably with high capacity retention of 98% after 2000 bending cycles. The evolution of quasi-solid-state ZIBs to liquid-free all-solid-state batteries may provide a promising solution to the occurrence of zinc dendrites and side-reactions to achieve reliable flexible batteries.

4. Interaction between Electrodes and Polymer Electrolytes

Due to its intrinsic electrochemical stability, metallic Zn can be used directly as the anode for Zn-based batteries. However, during the charging process, rough and irregular zinc dendrites are easily formed, which may cause short-circuiting. Moreover, some side-reactions which originate from aqueous solution, including hydrogen evolution reactions (HERs), corrosion, and surface passivation, can seriously affect the stability of the Zn anode. For the cathode of Zn-based batteries, the dissolution of some active materials and the formed electronically insulating electrode-electrolyte interface layers, which are normally referred to the SEI layers, affects the battery performance of Zn-based batteries with respect to capacity, rate capability, cyclic life, and so on [61,62]. In the following section, research into the effects of the interaction between electrodes and polymer electrolytes will be briefly discussed, with a view to providing new perspectives for improving the performance stability of Zn-based batteries.

4.1. Stabilization of Zn Anodes for Aqueous Zn-Based Batteries

For electrode stabilization, an ideal SEI layer would not only protect the cathode materials from exfoliation but would also contribute to the suppression of corrosion and dendrite growth at the Zn anode, which are important factors for the improvement of battery performance [63]. Huang et al. proposed a quasi-solid electrolyte interface (quasi-SEI) based on a PANa hydrogel electrolyte that could significantly facilitate the electrochemical stability of flexible Zn-NiCo and Zn-air batteries [34]. In their study, the homogeneous quasi-SEI was shown to be able to effectively eliminate the Zn dendrites and enhance ion transport. The acrylate groups grafted on the PANa electrolyte chain exhibited strong electrostatic interaction with Zn ions, leading to uniform Zn ion deposition without local nucleation of Zn (Figure 7a). Analogously, Ling et al. developed a self-healable hydrogel electrolyte with rigid-flexible backbones based on carboxymethyl cellulose, which showed a high ionic conductivity of 23.1 mS cm^{-1} due to the improvement in the interfacial compatibility by hydrophilic groups [64]. The synergistic effects of self-healing property, good interfacial compatibility and strong mechanical strength of the self-healable hydrogel electrolyte prompted more disciplined Zn plating/stripping (Figure 7b).

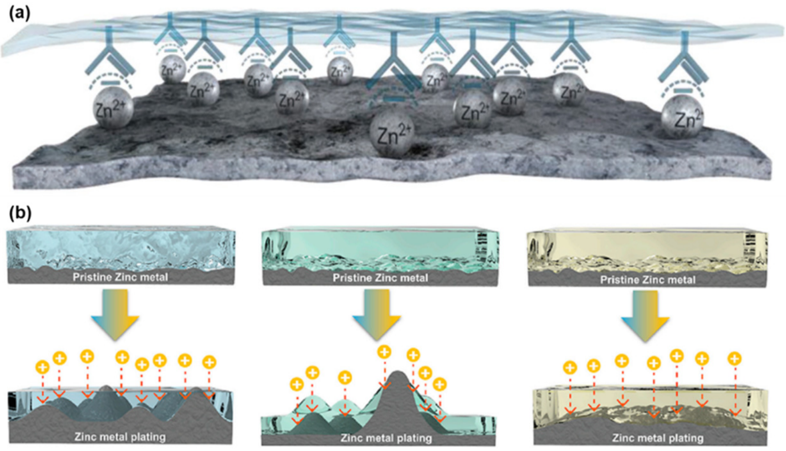


Figure 7. (**a**) Schematic illustration of the formation of quasi-SEI between PANa electrolyte and Zn anode. Reproduced with permission from [34]. (**b**) Schematic illustration of morphology evolution for Zn foils with liquid electrolyte, pure PAM and self-healable hydrogel electrolyte. Reproduced with permission from [64].

In addition, it is also important to stabilize the Zn anode through suppression of parasitic HER. For example, Zhu et al. reported that introducing Li^+ ions as an additive in a PAM-based hydrogel electrolyte could inhibit HER by suppressing the zinc hydrate [65]. Without adding Li salts, the Zn anode normally displayed a rough surface due to the presence of dendrites. After adding Li salts, the deposited Zn adopted a hexagonal rod conformation. This could be explained in terms of facilitation of Zn nuclei by the Li ions, leading to the growth of hexagonal Zn. When Zn^{2+} and Li^+ ions were coordinately attracted to the Zn anode, a new SEI was obtained. During this process, Li ions replaced zinc ions as the hydrated cations, thus avoiding Zn^{2+} hydration and suppressing HER [66].

4.2. Improvement of Electrochemical Peformance of Cathodes

Compared to the SEI layers formed on the anode, the cathode-electrolyte interface (CEI) layer is relatively more stable. Analogously to SEI, the interfacial compatibility between the cathode and the polymer electrolyte remains a challenging issue. There is the prospect of introducing an artificial CEI which can not only enhance ion transport between the polymer electrolyte and the cathode, but can also prevent the exfoliation of cathode active materials. For instance, Zhao et al. constructed an artificial CEI based on [EMIM]PF_6-PEDOT:PSS with a 3D porous architecture, which was coated on a Bi_2S_3-based cathode (Figure 8a) [67]. During the charging/discharging process, the active Bi_2S_3 caused volumetric expansion and pulverization. The artificial CEI layer could not only effectively accommodate the mechanical stress, thus inhibiting the pulverization of cathode materials, but could also form abundant ion transport channels to enhance the high ion conductivity of the electrode (Figure 8b).

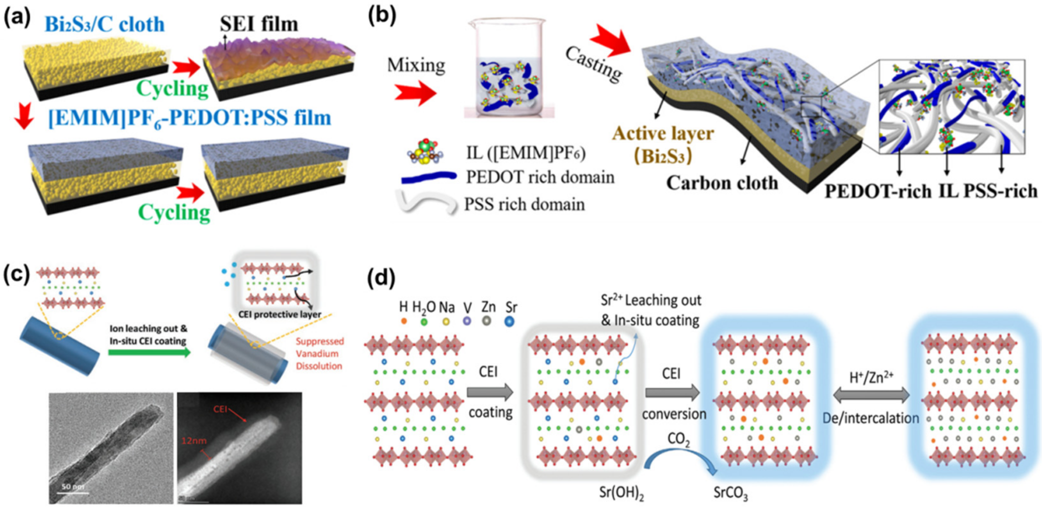


Figure 8. (**a**) Schematic illustration and (**b**) fabrication process of the [EMIM]PF_6-PEDOT:PSS films. Reproduced with permission from [67]. (**c**) Schematic design principle and (**d**) working mechanism of the in situ CEI layer. Reproduced with permission from [68].

Analogously, Zhang et al. developed an in situ artificial CEI that could kinetically suppress the dissolution of vanadium-based active materials in the aqueous electrolyte (Figure 8c) [68]. In this research, the strontium ion was introduced into the vanadium oxide layers to serve as a sacrificial guest. After a conversion step, a $SrCO_3$-based CEI coating layer could be formed. Following this, sodium ions were introduced into the vanadium oxide layers as a pillar guest, which was able to effectively stabilize the layer structure after strontium was leached out. The resultant CEI coating could not only prevent the dissolution of vanadium into the aqueous electrolyte, but could also alleviate self-discharge during open-circuit voltage resting. Therefore, this in situ cathode CEI strategy could enable better battery cyclability (Figure 8d).

5. Summary and Perspective

In this review, recent progress in the development of flexible Zn-based batteries with polymer electrolytes has been summarized and discussed. Compared to liquid electrolytes, polymer electrolytes can not only effectively prevent leakage and relieve the dissolution of active materials but can also alleviate dendrite growth and side-reactions to some extent, offering stable electrochemical performance. Due to the mechanical flexibility and good compatibility of the interfacial contact, polymer electrolytes are advantageous for flexible Zn-based batteries. However, there are still some issues that hinder the commercialization of polymer electrolytes for ZIBs which are highlighted in the following sections.

(1) It is noteworthy that, with the increase in demand for flexible batteries, the demand for solid-state and quasi-solid-state batteries is also increasing. In particular, zinc metal anodes are often used directly in zinc-based batteries, but it is difficult to solve the problem of dendrite growth associated with the use of a liquid electrolyte which may cause short-circuiting. Using polymer electrolytes with enhanced mechanical properties is an effective solution for the alleviation of dendritic growth and side-reactions, such as HER and corrosion. In general, the use of polymer electrolytes does not change the intrinsic electrochemical reactions of the battery electrodes. However, relatively larger thickness polymer electrolytes may degrade the battery performance,

especially by reducing the energy density, which is a specific problem that needs to be solved through future research.

(2) The mechanical properties of a battery include its intrinsic flexibility, layer cohesion (self-strength), interlayer adhesion, etc. Its flexibility is determined by the Young's modulus of the battery. When polymer electrolytes are used for the fabrication of battery devices, the Young's modulus of the electrolyte will largely determine the Young's modulus of the battery. It should be noted that the electrode materials and the current collectors also need to be considered. The softness of polymer electrolytes (such as the comfort of wearable applications of flexible batteries) and their mechanical strength (tensile limit and impact resistance) represent a trade-off. Therefore, numerous researchers have focused on the design of advanced materials and electrolyte configurations to enhance their mechanical strength. For example, a double network structure can be used to enhance mechanical strength, such as in terms of tensile and compressive properties. The flexibility of a physical/chemical crosslinked single network is also satisfactory, but, at present, attention is focused on the whole device (especially the collector). Li et al. have discussed the softness from a device-level perspective [69]. Yang et al. also discussed the softness of the entire Zn-based battery, in which the softness of the electrolyte is often ignored [70]. These concerns indicate that the softness of the electrolyte needs to be considered further. In addition, for polymer-based flexible battery devices, the adhesion between the electrolyte and the layers should be considered to ensure the structural integrity of devices by increasing the adhesion between layers.

(3) When working at extremely cold temperatures, the performance of the electrode materials, especially the electrochemical activity and the ion diffusion rate, will inevitably deteriorate, but, to date, this has not received much attention compared to hydrogel electrolytes. Moreover, due to the water splitting that may occur under an electric field, most aqueous Zn-based batteries containing a mild electrolyte only exhibited a narrow voltage window of <2.0 V. Recently developed "water-in-salt" electrolytes could significantly increase the voltage window of aqueous ZIBs to 2.1 V. However, the high cost is hindering implementation at scale. Therefore, the development of hydrogel electrolytes with a wider electrochemical potential window is to be encouraged for high-voltage aqueous flexible batteries.

(4) The ultimate purpose of the development of flexible Zn-based batteries is commercialization. However, the persistent issues of zinc dendrite formation and side-reactions, such as HER and corrosion, continue to adversely affect the stability of the Zn anode. In addition, due to the complicated synthesis of electrode materials and the involved chemical modification of hydrogel electrolytes, the fabrication and assembly processes of flexible batteries are not sufficiently simplified with production efficiency needing improvement. Advanced manufacturing technologies, such as 3D printing and screen printing can be integrated and applied into the fabrication of high-performance batteries for enhanced efficiency.

(5) During daily use as a portable power accessory for wearable electronics, flexible batteries inevitably undergo frequent extreme deformations. The mechanical stability of polymer electrolytes is thus of great significance for the long-term usability of flexible batteries. However, most hydrogel electrolytes are insufficiently durable to endure frequent deformations and external impacts. New technologies for the synthesis of super-tough or fast self-healing polymer electrolytes should be further explored and disseminated. Moreover, due to unavoidable direct contact of wearable batteries with the human body in realistic use, guaranteeing the biocompatibility of polymer electrolytes is also critical for wearable applications.

(6) A well-formed SEI can not only improve the compatibility between electrodes and electrolyte to facilitate the rate of ion flow, but can also prevent the cathodes from pulverization and inhibit side-reactions. Additionally, building an artificial SEI with larger specific active surface area could effectively alleviate concentration polarization,

which is instrumental in increasing the electronic conductivity and suppression of Zn dendrites. However, the fundamental mechanism of interfacial reaction between the polymer electrolytes and electrodes is still insufficient. Furthermore, the SEI is usually affected and destroyed by the surface topography changes of the Zn anode due to dendrite growth. Further research efforts should be dedicated to the stabilization of the SEI.

(7) Multifunctional polymer electrolytes can effectively broaden the application range of flexible Zn-based batteries to satisfy diverse application requirements. Some intriguing functionalities, such as extreme temperature tolerance, thermoresponsive properties, and self-healing ability have been summarized in the preceding sections. Many other potential functionalities, including photodetection, electrochromism, and shape memory are also worthy of exploration for the development of advanced flexible batteries. In addition, the integration of flexible Zn-based batteries with other wearable device systems, such as sensors, self-powering generators, and energy conversion devices has been identified as a promising direction for next-generation wearable electronics.

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References

1. Li, Y.; Fu, J.; Zhong, C.; Wu, T.; Chen, Z.; Hu, W.; Amine, K.; Lu, J. Recent Advances in Flexible Zinc-Based Rechargeable Batteries. *Adv. Energy Mater.* **2019**, *9*, 1802605. [CrossRef]
2. Yu, P.; Zeng, Y.; Zhang, H.; Yu, M.; Tong, Y.; Lu, X. Flexible Zn-Ion Batteries: Recent Progresses and Challenges. *Small* **2019**, *15*, 1804760. [CrossRef] [PubMed]
3. Zhao, Y.; Guo, J. Development of Flexible Li-Ion Batteries for Flexible Electronics. *InfoMat* **2020**, *2*, 866–878. [CrossRef]
4. Qian, G.; Liao, X.; Zhu, Y.; Pan, F.; Chen, X.; Yang, Y. Designing Flexible Lithium-Ion Batteries by Structural Engineering. *ACS Energy Lett.* **2019**, *4*, 690–701. [CrossRef]
5. Kim, T.; Song, W.; Son, D.-Y.; Ono, L.K.; Qi, Y. Lithium-Ion Batteries: Outlook on Present, Future, and Hybridized Technologies. *J. Mater. Chem. A* **2019**, *7*, 2942–2964. [CrossRef]
6. Xiong, R.; Pan, Y.; Shen, W.; Li, H.; Sun, F. Lithium-Ion Battery Aging Mechanisms and Diagnosis Method for Automotive Applications: Recent Advances and Perspectives. *Renew. Sustain. Energy Rev.* **2020**, *131*, 110048. [CrossRef]
7. Han, X.; Lu, L.; Zheng, Y.; Feng, X.; Li, Z.; Li, J.; Ouyang, M. A Review on the Key Issues of the Lithium Ion Battery Degradation among the Whole Life Cycle. *ETransportation* **2019**, *1*, 100005. [CrossRef]
8. Tang, B.; Shan, L.; Liang, S.; Zhou, J. Issues and Opportunities Facing Aqueous Zinc-Ion Batteries. *Energy Environ. Sci.* **2019**, *12*, 3288–3304. [CrossRef]
9. Fang, G.; Zhou, J.; Pan, A.; Liang, S. Recent Advances in Aqueous Zinc-Ion Batteries. *ACS Energy Lett.* **2018**, *3*, 2480–2501. [CrossRef]
10. Blanc, L.E.; Kundu, D.; Nazar, L.F. Scientific Challenges for the Implementation of Zn-Ion Batteries. *Joule* **2020**, *4*, 771–799. [CrossRef]
11. Zhang, N.; Chen, X.; Yu, M.; Niu, Z.; Cheng, F.; Chen, J. Materials Chemistry for Rechargeable Zinc-Ion Batteries. *Chem. Soc. Rev.* **2020**, *49*, 4203–4219. [CrossRef] [PubMed]
12. Shin, J.; Lee, J.; Park, Y.; Choi, J.W. Aqueous Zinc Ion Batteries: Focus on Zinc Metal Anodes. *Chem. Sci.* **2020**, *11*, 2028–2044. [CrossRef] [PubMed]

13. Wang, T.; Li, C.; Xie, X.; Lu, B.; He, Z.; Liang, S.; Zhou, J. Anode Materials for Aqueous Zinc Ion Batteries: Mechanisms, Properties, and Perspectives. *Acs Nano* **2020**, *14*, 16321–16347. [CrossRef] [PubMed]
14. Du, W.; Ang, E.H.; Yang, Y.; Zhang, Y.; Ye, M.; Li, C.C. Challenges in the Material and Structural Design of Zinc Anode Towards High-Performance Aqueous Zinc-Ion Batteries. *Energy Environ. Sci.* **2020**, *13*, 3330–3360. [CrossRef]
15. Yang, Q.; Li, Q.; Liu, Z.; Wang, D.; Guo, Y.; Li, X.; Tang, Y.; Li, H.; Dong, B.; Zhi, C. Dendrites in Zn-Based Batteries. *Adv. Mater.* **2020**, *32*, 2001854. [CrossRef] [PubMed]
16. Li, S.; Fu, J.; Miao, G.; Wang, S.; Zhao, W.; Wu, Z.; Zhang, Y.; Yang, X. Toward Planar and Dendrite-Free Zn Electrodepositions by Regulating Sn-Crystal Textured Surface. *Adv. Mater.* **2021**, *33*, 2008424. [CrossRef] [PubMed]
17. Yi, Z.; Chen, G.; Hou, F.; Wang, L.; Liang, J. Strategies for the Stabilization of Zn Metal Anodes for Zn-Ion Batteries. *Adv. Energy Mater.* **2021**, *11*, 2003065. [CrossRef]
18. Xie, C.; Li, Y.; Wang, Q.; Sun, D.; Tang, Y.; Wang, H. Issues and Solutions toward Zinc Anode in Aqueous Zinc-Ion Batteries: A Mini Review. *Carbon Energy.* **2020**, *2*, 540–560. [CrossRef]
19. Aziz, S.B.; Woo, T.J.; Kadir, M.; Ahmed, H.M. A Conceptual Review on Polymer Electrolytes and Ion Transport Models. *J. Sci Adv. Mater. Dev.* **2018**, *3*, 1–17. [CrossRef]
20. Bocharova, V.; Sokolov, A.P. Perspectives for Polymer Electrolytes: A View from Fundamentals of Ionic Conductivity. *Macromolecules* **2020**, *53*, 4141–4157. [CrossRef]
21. Wu, K.; Huang, J.; Yi, J.; Liu, X.; Liu, Y.; Wang, Y.; Zhang, J.; Xia, Y. Recent Advances in Polymer Electrolytes for Zinc Ion Batteries: Mechanisms, Properties, and Perspectives. *Adv. Energy Mater.* **2020**, *10*, 1903977. [CrossRef]
22. Wang, Z.; Li, H.; Tang, Z.; Liu, Z.; Ruan, Z.; Ma, L.; Yang, Q.; Wang, D.; Zhi, C. Hydrogel Electrolytes for Flexible Aqueous Energy Storage Devices. *Adv. Funct Mater.* **2018**, *28*, 1804560. [CrossRef]
23. Pan, Z.; Yang, J.; Jiang, J.; Qiu, Y.; Wang, J. Flexible Quasi-Solid-State Aqueous Zn-Based Batteries: Rational Electrode Designs for High-Performance and Mechanical Flexibility. *Mater. Today Energy* **2020**, *18*, 100523. [CrossRef]
24. Li, H.; Ma, L.; Han, C.; Wang, Z.; Liu, Z.; Tang, Z.; Zhi, C. Advanced Rechargeable Zinc-Based Batteries: Recent Progress and Future Perspectives. *Nano Energy* **2019**, *62*, 550–587. [CrossRef]
25. Selvakumaran, D.; Pan, A.; Liang, S.; Cao, G. A Review on Recent Developments and Challenges of Cathode Materials for Rechargeable Aqueous Zn-Ion Batteries. *J. Mater. Chem. A* **2019**, *7*, 18209–18236. [CrossRef]
26. Deng, Y.-P.; Liang, R.; Jiang, G.; Jiang, Y.; Yu, A.; Chen, Z. The Current State of Aqueous Zn-Based Rechargeable Batteries. *ACS Energy Lett.* **2020**, *5*, 1665–1675. [CrossRef]
27. Shi, Y.; Chen, Y.; Shi, L.; Wang, K.; Wang, B.; Li, L.; Ma, Y.; Li, Y.; Sun, Z.; Ali, W. An Overview and Future Perspectives of Rechargeable Zinc Batteries. *Small* **2020**, *16*, 2000730. [CrossRef]
28. Naveed, A.; Yang, H.; Shao, Y.; Yang, J.; Yanna, N.; Liu, J.; Shi, S.; Zhang, L.; Ye, A.; He, B. A Highly Reversible Zn Anode with Intrinsically Safe Organic Electrolyte for Long-Cycle-Life Batteries. *Adv. Mater.* **2019**, *31*, 1900668. [CrossRef]
29. Naveed, A.; Yang, H.; Yang, J.; Nuli, Y.; Wang, J. Highly Reversible and Rechargeable Safe Zn Batteries Based on a Triethyl Phosphate Electrolyte. *Angew. Chem. Int. Ed.* **2019**, *58*, 2760–2764. [CrossRef]
30. Shi, B.; Li, Z.; Fan, Y. Implantable Energy-Harvesting Devices. *Adv. Mater.* **2018**, *30*, 1801511. [CrossRef]
31. Liu, Y.; Pharr, M.; Salvatore, G.A. Lab-on-Skin: A Review of Flexible and Stretchable Electronics for Wearable Health Monitoring. *ACS Nano* **2017**, *11*, 9614–9635. [CrossRef] [PubMed]
32. Yi, J.; Guo, S.; He, P.; Zhou, H. Status and Prospects of Polymer Electrolytes for Solid-State Li–O 2 (Air) Batteries. *Energy Environ. Sci.* **2017**, *10*, 860–884. [CrossRef]
33. Jost, K.; Durkin, D.P.; Haverhals, L.M.; Brown, E.K.; Langenstein, M.; De Long, H.C.; Trulove, P.C.; Gogotsi, Y.; Dion, G. Natural Fiber Welded Electrode Yarns for Knittable Textile Supercapacitors. *Adv. Energy Mater.* **2015**, *5*, 1401286. [CrossRef]
34. Huang, Y.; Li, Z.; Pei, Z.; Liu, Z.; Li, H.; Zhu, M.; Fan, J.; Dai, Q.; Zhang, M.; Dai, L. Solid-State Rechargeable Zn//Nico and Zn–Air Batteries with Ultralong Lifetime and High Capacity: The Role of a Sodium Polyacrylate Hydrogel Electrolyte. *Adv. Energy Mater.* **2018**, *8*, 1802288. [CrossRef]
35. Huang, S.; Wan, F.; Bi, S.; Zhu, J.; Niu, Z.; Chen, J. A Self-Healing Integrated All-in-One Zinc-Ion Battery. *Angew. Chem.* **2019**, *131*, 4357–4361. [CrossRef]
36. Karan, S.; Sahu, T.B.; Sahu, M.; Mahipal, Y.; Agrawal, R. Characterization of Ion Transport Property in Hot-Press Cast Solid Polymer Electrolyte (Spe) Films: [Peo: Zn (Cf3so3) 2]. *Ionics* **2017**, *23*, 2721–2726. [CrossRef]
37. Hiralal, P.; Imaizumi, S.; Unalan, H.E.; Matsumoto, H.; Minagawa, M.; Rouvala, M.; Tanioka, A.; Amaratunga, G.A. Nanomaterial-Enhanced All-Solid Flexible Zinc− Carbon Batteries. *ACS Nano* **2010**, *4*, 2730–2734. [CrossRef]
38. Chan, C.Y.; Wang, Z.; Li, Y.; Yu, H.; Fei, B.; Xin, J.H. Single-Ion Conducting Double-Network Hydrogel Electrolytes for Long Cycling Zinc-Ion Batteries. *ACS Appl. Mat. Interfaces* **2021**, *13*, 30594–30602. [CrossRef]
39. Zhu, X.; Yang, H.; Cao, Y.; Ai, X. Preparation and Electrochemical Characterization of the Alkaline Polymer Gel Electrolyte Polymerized from Acrylic Acid and Koh Solution. *Electtrochim. Acta* **2004**, *49*, 2533–2539. [CrossRef]
40. Gaikwad, A.M.; Whiting, G.L.; Steingart, D.A.; Arias, A.C. Highly Flexible, Printed Alkaline Batteries Based on Mesh-Embedded Electrodes. *Adv. Mater.* **2011**, *23*, 3251–3255. [CrossRef]
41. Zhang, S.; Yu, N.; Zeng, S.; Zhou, S.; Chen, M.; Di, J.; Li, Q. An Adaptive and Stable Bio-Electrolyte for Rechargeable Zn-Ion Batteries. *J. Mater. Chem. A* **2018**, *6*, 12237–12243. [CrossRef]

42. Han, Q.; Chi, X.; Zhang, S.; Liu, Y.; Zhou, B.; Yang, J.; Liu, Y. Durable, Flexible Self-Standing Hydrogel Electrolytes Enabling High-Safety Rechargeable Solid-State Zinc Metal Batteries. *J. Mater. Chem. A* **2018**, *6*, 23046–23054. [CrossRef]
43. Gaikwad, A.M.; Arias, A.C.; Steingart, D.A. Recent Progress on Printed Flexible Batteries: Mechanical Challenges, Printing Technologies, and Future Prospects. *Energy Technol.* **2015**, *3*, 305–328. [CrossRef]
44. Sun, C.-F.; Zhu, H.; Baker III, E.B.; Okada, M.; Wan, J.; Ghemes, A.; Inoue, Y.; Hu, L.; Wang, Y. Weavable High-Capacity Electrodes. *Nano Energy* **2013**, *2*, 987–994. [CrossRef]
45. Zhang, Y.; Zhao, Y.; Ren, J.; Weng, W.; Peng, H. Advances in Wearable Fiber-Shaped Lithium-Ion Batteries. *Adv. Mater.* **2016**, *28*, 4524–4531. [CrossRef]
46. Pei, Z.; Ding, L.; Wang, C.; Meng, Q.; Yuan, Z.; Zhou, Z.; Zhao, S.; Chen, Y. Make It Stereoscopic: Interfacial Design for Full-Temperature Adaptive Flexible Zinc–Air Batteries. *Energy Environ. Sci.* **2021**, *14*, 4926–4935. [CrossRef]
47. Wang, H.; Liu, J.; Wang, J.; Hu, M.; Feng, Y.; Wang, P.; Wang, Y.; Nie, N.; Zhang, J.; Chen, H. Concentrated Hydrogel Electrolyte-Enabled Aqueous Rechargeable Nico//Zn Battery Working from −20 to 50 °C. *ACS Appl. Mat. Interfaces* **2018**, *11*, 49–55. [CrossRef]
48. Chen, M.; Zhou, W.; Wang, A.; Huang, A.; Chen, J.; Xu, J.; Wong, C.-P. Anti-Freezing Flexible Aqueous Zn–Mno 2 Batteries Working at −35 °C Enabled by a Borax-Crosslinked Polyvinyl Alcohol/Glycerol Gel Electrolyte. *J. Mater. Chem. A* **2020**, *8*, 6828–6841. [CrossRef]
49. Pei, Z.; Yuan, Z.; Wang, C.; Zhao, S.; Fei, J.; Wei, L.; Chen, J.; Wang, C.; Qi, R.; Liu, Z. A Flexible Rechargeable Zinc–Air Battery with Excellent Low-Temperature Adaptability. *Angew. Chem. Int. Ed.* **2020**, *59*, 4793–4799. [CrossRef]
50. Yang, H.; Liu, Z.; Chandran, B.K.; Deng, J.; Yu, J.; Qi, D.; Li, W.; Tang, Y.; Zhang, C.; Chen, X. Self-Protection of Electrochemical Storage Devices Via a Thermal Reversible Sol–Gel Transition. *Adv. Mater.* **2015**, *27*, 5593–5598. [CrossRef]
51. Zhu, J.; Yao, M.; Huang, S.; Tian, J.; Niu, Z. Thermal-Gated Polymer Electrolytes for Smart Zinc-Ion Batteries. *Angew. Chem. Int. Ed.* **2020**, *59*, 16480–16484. [CrossRef] [PubMed]
52. Yang, P.; Feng, C.; Liu, Y.; Cheng, T.; Yang, X.; Liu, H.; Liu, K.; Fan, H.J. Thermal Self-Protection of Zinc-Ion Batteries Enabled by Smart Hygroscopic Hydrogel Electrolytes. *Adv. Energy Mater.* **2020**, *10*, 2002898. [CrossRef]
53. Huang, Y.; Liu, J.; Wang, J.; Hu, M.; Mo, F.; Liang, G.; Zhi, C. An Intrinsically Self-Healing Nico | | Zn Rechargeable Battery with a Self-Healable Ferric-Ion-Crosslinking Sodium Polyacrylate Hydrogel Electrolyte. *Angew. Chem. Int. Ed.* **2018**, *57*, 9810–9813. [CrossRef]
54. Amamoto, Y.; Otsuka, H.; Takahara, A.; Matyjaszewski, K. Self-Healing of Covalently Cross-Linked Polymers by Reshuffling Thiuram Disulfide Moieties in Air under Visible Light. *Adv. Mater.* **2012**, *24*, 3975–3980. [CrossRef] [PubMed]
55. Ma, L.; Chen, S.; Li, N.; Liu, Z.; Tang, Z.; Zapien, J.A.; Chen, S.; Fan, J.; Zhi, C. Hydrogen-Free and Dendrite-Free All-Solid-State Zn-Ion Batteries. *Adv. Mater.* **2020**, *32*, 1908121. [CrossRef] [PubMed]
56. Liu, Z.; Luo, X.; Qin, L.; Fang, G.; Liang, S. Progress and Prospect of Low-Temperature Zinc Metal Batteries. *Adv. Powder Mater.* **2022**, *1*, 100011. [CrossRef]
57. Liu, W.; Liu, N.; Sun, J.; Hsu, P.-C.; Li, Y.; Lee, H.-W.; Cui, Y. Ionic Conductivity Enhancement of Polymer Electrolytes with Ceramic Nanowire Fillers. *Nano Lett.* **2015**, *15*, 2740–2745. [CrossRef]
58. Zhai, H.; Xu, P.; Ning, M.; Cheng, Q.; Mandal, J.; Yang, Y. A Flexible Solid Composite Electrolyte with Vertically Aligned and Connected Ion-Conducting Nanoparticles for Lithium Batteries. *Nano Lett.* **2017**, *17*, 3182–3187. [CrossRef]
59. Chen, Z.; Li, X.; Wang, D.; Yang, Q.; Ma, L.; Huang, Z.; Liang, G.; Chen, A.; Guo, Y.; Dong, B. Grafted Mxene/Polymer Electrolyte for High Performance Solid Zinc Batteries with Enhanced Shelf Life at Low/High Temperatures. *Energy Environ. Sci.* **2021**, *14*, 3492–3501. [CrossRef]
60. Ma, L.; Chen, S.; Li, X.; Chen, A.; Dong, B.; Zhi, C. Liquid-Free All-Solid-State Zinc Batteries and Encapsulation-Free Flexible Batteries Enabled by in Situ Constructed Polymer Electrolyte. *Angew. Chem.* **2020**, *132*, 24044–24052. [CrossRef]
61. Bommier, C.; Ji, X. Electrolytes, Sei Formation, and Binders: A Review of Nonelectrode Factors for Sodium-Ion Battery Anodes. *Small* **2018**, *14*, 1703576. [CrossRef] [PubMed]
62. An, S.J.; Li, J.; Daniel, C.; Mohanty, D.; Nagpure, S.; Wood III, D.L. The State of Understanding of the Lithium-Ion-Battery Graphite Solid Electrolyte Interphase (Sei) and Its Relationship to Formation Cycling. *Carbon* **2016**, *105*, 52–76. [CrossRef]
63. Tripathi, A.M.; Su, W.-N.; Hwang, B.J. In Situ Analytical Techniques for Battery Interface Analysis. *Chem. Soc. Rev.* **2018**, *47*, 736–851. [CrossRef] [PubMed]
64. Ling, W.; Mo, F.; Wang, J.; Liu, Q.; Liu, Y.; Yang, Q.; Qiu, Y.; Huang, Y. Self-Healable Hydrogel Electrolyte for Dendrite-Free and Self-Healable Zinc-Based Aqueous Batteries. *Mater. Today Phys.* **2021**, *20*, 100458. [CrossRef]
65. Zhu, M.; Wang, X.; Tang, H.; Wang, J.; Hao, Q.; Liu, L.; Li, Y.; Zhang, K.; Schmidt, O.G. Antifreezing Hydrogel with High Zinc Reversibility for Flexible and Durable Aqueous Batteries by Cooperative Hydrated Cations. *Adv. Funct. Mater.* **2020**, *30*, 1907218. [CrossRef]
66. Yan, X.; Chen, Z.; Wang, Y.; Li, H.; Zhang, J. In-Situ Growth of Zno Nanoplates on Graphene for the Application of High Rate Flexible Quasi-Solid-State Ni-Zn Secondary Battery. *J. Power Source* **2018**, *407*, 137–146. [CrossRef]
67. Zhao, Y.; Ma, L.; Zhu, Y.; Qin, P.; Li, H.; Mo, F.; Wang, D.; Liang, G.; Yang, Q.; Liu, W. Inhibiting Grain Pulverization and Sulfur Dissolution of Bismuth Sulfide by Ionic Liquid Enhanced Poly (3, 4-Ethylenedioxythiophene): Poly (Styrenesulfonate) for High-Performance Zinc-Ion Batteries. *ACS Nano* **2019**, *13*, 7270–7280. [CrossRef] [PubMed]

68. Zhang, L.; Zhang, B.; Hu, J.; Liu, J.; Miao, L.; Jiang, J. An in Situ Artificial Cathode Electrolyte Interphase Strategy for Suppressing Cathode Dissolution in Aqueous Zinc Ion Batteries. *Small Meth.* **2021**, *5*, 2100094. [CrossRef]
69. Li, H.; Tang, Z.; Liu, Z.; Zhi, C. Evaluating Flexibility and Wearability of Flexible Energy Storage Devices. *Joule* **2019**, *3*, 613–619. [CrossRef]
70. Yang, Q.; Chen, A.; Li, C.; Zou, G.; Li, H.; Zhi, C. Categorizing Wearable Batteries: Unidirectional and Omnidirectional Deformable Batteries. *Matter* **2021**, *4*, 3146–3160. [CrossRef]