Journal of Semiconductors
(2021) 42, 101603
doi: 10.1088/1674-4926/42/10/101603

REVIEWS

Recently advances in flexible zinc ion batteries

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Abstract: Flexible batteries are key component of wearable electronic devices. Based on the requirements of medical and primary safety of wearable energy storage devices, rechargeable aqueous zinc ion batteries (ZIBs) are promising portable candidates in virtue of its intrinsic safety, abundant storage and low cost. However, many inherent challenges have greatly hindered the development in flexible Zn-based energy storage devices, such as rigid current collector and/or metal anode, easily detached cathode materials and a relatively narrow voltage window of flexible electrolyte. Thus, overcoming these challenges and further developing flexible ZIBs are inevitable and imperative. This review summarizes the most advanced progress in designs and discusses of flexible electrode, electrolyte and the practical application of flexible ZIBs in different environments. We also exhibit the heart of the matter that current flexible ZIBs faces. Finally, some prospective approaches are proposed to address these key issues and point out the direction for the future development of flexible ZIBs.

Key words: flexible electrodes; flexible electrolytes; wearable zinc batteries

Citation: C Li, P Li, S Yang, and C Y Zhi, Recently advances in flexible zinc ion batteries[J]. *J. Semicond.*, 2021, 42(10), 101603. http://doi.org/10.1088/1674-4926/42/10/101603

1. Introduction

The flexible electronic devices such as artificial electronic skins[1], implantable medical devices[2] and consumer electronics[3] show the fast development in recent years due to the boom in wearable/flexible energy-storage devices[4–9]. Meanwhile, they also request high-performance power sources with corresponding flexibility and ultrathin and safe properties. However, current energy storage devices exhibit characteristics of too thickness and heavy hardness. To overcome these drawbacks, the development of flexibility of energy-storage devices is inevitable and urgent. In addition, although lithium-ion batteries (LIBs) possess higher voltage and energy density, the insecurity of organic electrolyte hinders its wearable application. The aqueous zinc ion batteries (ZIBs) exhibit high safety and abundant reserves[10–13], low standard redox potential of Zn/Zn^{2+} of –0.76 V[14] *vs.* the standard hydrogen electrode (SHE), and high theoretical volume capacity of metal Zn anode of 5855 mA·h/cm^3[5]. Thus, advanced flexible aqueous ZIBs are a promising way to provide an alternative to apply in many aspects.

In this review, we consider different design strategies aiming at preparing flexible ZIBs with the outstanding performances based on proposed literatures. Meanwhile, the developments of flexible current collectors, electrode materials and electrolytes are stated. We then discuss various practical application scenarios of flexible ZIBs in recent reports. Furthermore, the performance comparison of various flexible ZIBs is summarized to clearly state the promising directions, facing challenges and improved alternatives. Finally, key scientific problems limiting the further development of flexible ZIBs are clarified and the corresponding solutions are also proposed.

2. Schematic designs of flexible ZIBs

Flexible ZIBs were normally equipped with the property of the resistance to external deformation. What it means was that under external forces from all directions, the electrochemical performance of flexible ZIBs was not affected or very weak. For this purpose, every component of flexible ZIBs including anode, cathode and electrolyte need to exhibit the property of softness. However, parts of traditional batteries generally were constructed employing rigid/fragile materials. Therefore, from electrodes to electrolytes, they were all necessary to design and prepare in reasonable way. In addition, the overall structure of the flexible ZIBs also need to be taken into consideration.

2.1. Flexible electrodes for flexible ZIBs

As for anode of flexible ZIBs, there were two approaches to reach this target. Firstly, thin Zn foil and Zn wire were directly used to be anode of flexible ZIBs[15, 16]. However, the deformability of Zn metal was limited due to the performance of shape memory. Under the continuous bending and torsion, metal Zn anode was easily damaged and thus cannot be used in many situations[17]. Secondly, applying flexible current collectors coated or electroplated Zn powder was an effectual method, such as electrically depositing onto the surface of the carbon cloth as SEM image exhibited in Fig. 1(a)[18].

With respect to cathode of flexible ZIBs, similar to anode bonding with flexible substrates, loading cathode materials on flexible current collectors was a common way to acquire flexible cathodes. In general, conductive (such as carbon black, acetylene black and carbon nano tube) and binding additives (such as carboxymethyl cellulose, polyvinylidene fluoride and polytetrafluoroethylene) were applied to mix with cath-

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Received 30 JUNE 2021; Revised 30 JULY 2021.

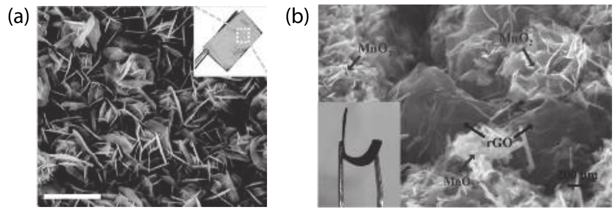

Fig. 1. (a) SEM image of the zinc anode by electrically depositing onto a carbon cloth. Adopted with permission from Ref. [18], Copyright 2019, Royal Society of Chemistry. (b) SEM image and the photographs (the inset) of the MnO_2/rGO sample on carbon cloth. Adopted with permission from Ref. [19], Copyright 2018, Nature Publishing Group.

ode materials. Then, the mixed slurry was coated on the surface of conductive substrates (such as carbon cloth, carbon paper and metal wires) with flexibility. Finally, flexible electrode plate after drying was obtained. Nevertheless, this approach existed some drawbacks. For example, the transport of electrons and ions would be limited due to the existence of conducting additives and binders. Apart from that, under external forces, cathode materials fell off flexible substrates as a result of limited contact area among them. Based on these, many researchers paid attention on *in situ* growing method. In other words, active materials were *in situ* formed on the corresponded flexible substrates through hydrothermal method, electrodeposition and so on. Fig. 1(b) displayed the SEM image of the MnO_2/rGO sample on carbon cloth by *in-situ* growing method, revealing excellent flexibility of cathode part[19].

Recently, researchers tended to use flexible current collectors as flexible basis and then the active materials were integrated on their faces to prepare flexible electrodes. With regard to flexible substrates, there were two choices. The one was metal-based current collectors such as titanium or stainless-steel wires. The other was carbon-based substrates such as carbon cloth, carbon nanotube (CNT) fiber or CNT paper.

2.2. Flexible electrolytes for flexible ZIBs

As a general rule, flexible ZIBs employed hydrogel electrolytes incorporating into different salt solution such as $ZnSO_4$, $ZnCl_2$, $Zn(ClO_4)_2$, $Zn(NO_3)_2$ and $Zn(CF_3SO_3)_2$. The hydrogel electrolyte could be classified into two categories: i) natural polymers. ii) synthetic polymers.

2.2.1. Natural polymer hydrogel electrolytes

Natural polymers, e.g., gelatin, cellulose and sodium alginate, had excellent physicochemical properties that afforded fabrication of advanced hydrogel electrolytes for flexible electronic devices: non-toxicity, hydrophilicity, thermodynamic stability, the high capacity for swelling for high ion conductivity and simple craft. Therefore, abundant natural gel electrolytes had been reported to assemble flexible ZIBs. Zhi *et al.* adopted a gelatin-based natural polymer hydrogel electrolyte to fabricate flexible ZIBs that had excellent resistance to deformation, namely, after cutting 4 times, bending 800 times, hammering 5 times and other deformations, flexible ZIBs still kept excellent electrochemical performance[20]. Meanwhile, they also explored a sewable Zn-MnO_2 battery based on a nanofibrillated cellulose/ployacrylamide hydrogel electrolyte, leading to withstand a large shearing force of 43 N[21]. For sodium alginate (SA) natural polymer (Fig. 2(a)), it was usually selected to be as flexible electrolyte because of its superb mechanical performance and simple processing of fabricating. Zhou *et al.* adopted SA-based hydrogel electrolyte to assemble flexible ZIBs that exhibited excellent mechanical property of bearing a high weight and a high ionic conductivity of 1.83×10^{-2} S/cm[22].

2.2.2. Synthetic polymer hydrogel electrolytes

In fact, most flexible gel electrolytes were chemically synthesized polymer hydrogels. This was ascribed to be able to carry on the structure design reasonably so that flexible hydrogel electrolytes were applied to a variety of scenarios. In addition, chemically synthesized polymer hydrogels could be divided into two categories: i) chemically cross-linked hydrogels; ii) physically cross-linked hydrogels. In general, the use of chemically crosslinked hydrogel electrolytes in flexible ZIBs was a mainstream trend such as common polyacrylamide (PAM)-based hydrogel. On the basis of superior interface compatibility and highly water content, PAM-based polymer electrolytes had been widely used in ZIBs. Numerous amide groups (-$CONH_2$) and network structure were beneficial for ion mobility. Zhi *et al.* reported a quasi-solid-state washable and tailorable elastic yarn ZIBs on the basis of PAM polymer electrolyte (Fig. 2(b)) with ion conductivity of 17.3×10^{-3} S/cm at room temperature[23]. Meanwhile, a high specific capacity of 302.1 mA·h/g and volumetric energy density of 53.8 mW·h/cm as well as excellent cycling stability of 98.5% capacity retention after 500 cycles were obtained by the yarn ZIBs[23].

Although chemically crosslinked hydrogel electrolytes had met most application scenarios, physically crosslinked hydrogel electrolytes had unique advantages for flexible ZIBs under certain circumstances. Just as its name implies, physically crosslinked hydrogels were synthesized through physical interaction including van der Waals' force, hydrogen bonding and electrostatic interactions. The most common example was poly(vinyl alcohol) (PVA)-based hydrogel. Fig. 2(c) delivered a self-healing PVA hydrogel electrolyte with high ion conductivity for flexible ZIBs. After multiple cutting/self-healing cycles, the flexible ZIBs still exhibited stable specific capacity of 81.4 mA·h/g[24].

2.3. All-in-one flexible ZIBs

Apart from pursing flexible electrodes and electrolytes, the flexible ZIBs could be fabricated using all-in-one strategy of structural designing. Niu *et al.* reported a scalable assembly strategy to prepare flexible ultrathin ZIBs *via* all-in-one integrated architecture. The acquired flexible ultrathin ZIBs could be controllably tailored and edited into desired shapes and structures, and the tailored miniature flexible ZIBs still exhibited great electrochemical performance[25]. Fig. 3(a) showed schematic process of flexible ultrathin ZIBs. A scalable assembly strategy was employed to fabricate flexible ultrathin ZIBs with all-in-one integrated architecture by combining blade coating with rolling assembly technologies[25]. The ultrathin all-in-one flexible ZIBs could maintain a highly capacity retention of 97.3%, and high discharge capacity of 132.1 mA·h/g after 1000 cycles (Fig. 3(b))[25]. In addition, Zhi *et al.* proposed another approach to prepare all-in-one flexible ZIBs. They fabricated all-solid-state ZIBs enabled by *in situ* constructed polymer electrolyte (Fig. 3(c)). After 20 000 cycles at 0.5 A/g, the capacity of flexible ZIB remained

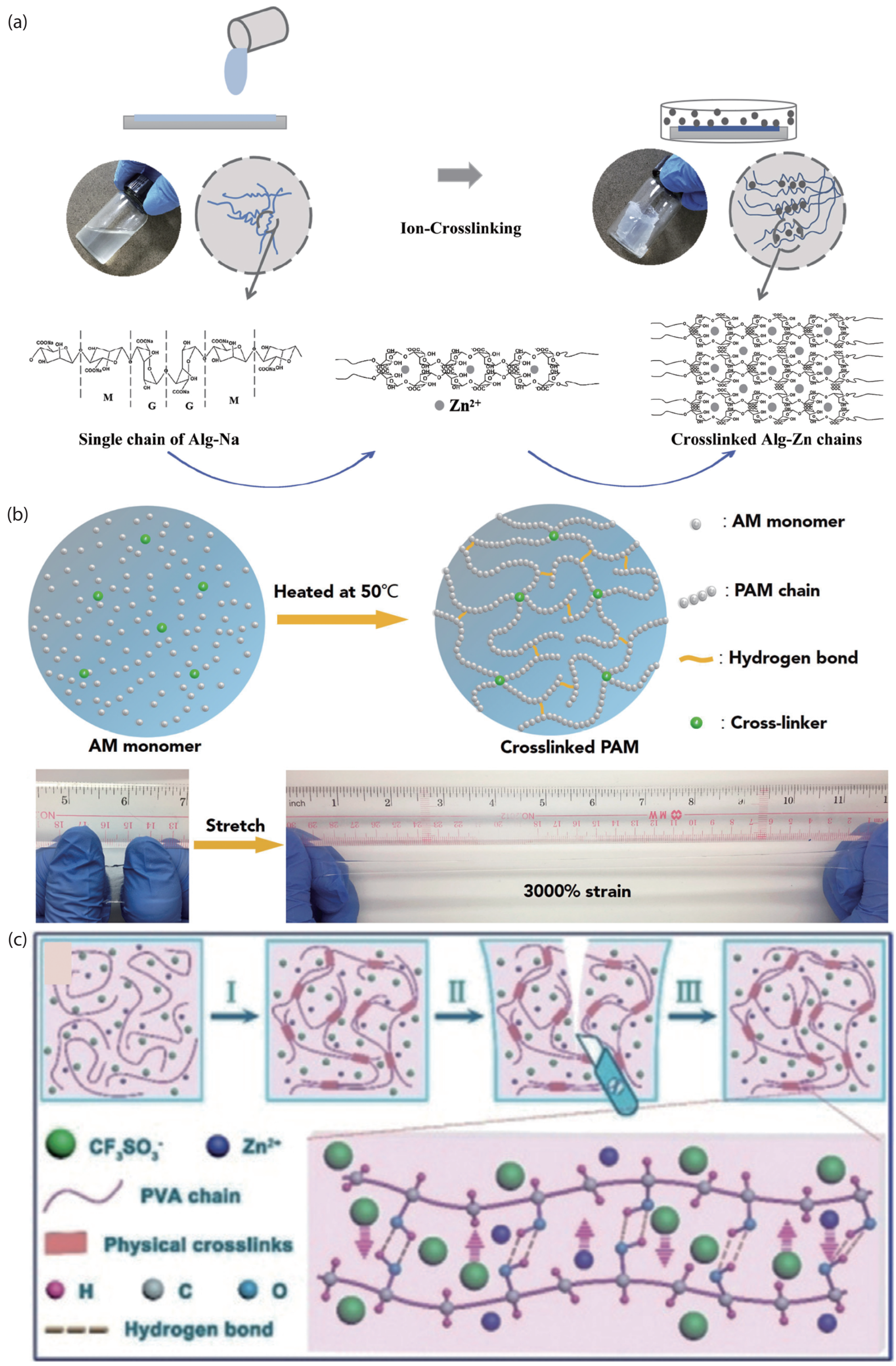

Fig. 2. (Color online) (a) The process diagram of SA-based hydrogel electrolyte. Adopted with permission from Ref. [22], Copyright 2020, Elsevier. (b) The schematic diagram of PAM-based hydrogel. Adopted with permission from Ref. [23], Copyright 2018, American Chemical Society. (c) The structure diagram of fabricating PVA-based self-healing electrolyte. Adopted with permission from Ref. [24], Copyright 2019, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

105.8 mA/g and the coulombic efficiency maintained more than 99.75 % (Fig. 3(d))[26].

3. Functional application of flexible ZIBs

Flexible ZIBs had been reported into applying in many situations including mechanical practicability (stretching, compressing, bending and folding), self-healing, low temperature, smart transformation and others. In these categories, there were many interesting findings found by researchers. The details would be introduced below.

3.1. Mechanical performance

The mechanical practicality was the most basic requirement of flexible ZIBs and researches were widely focused on the mechanical properties in the past few years. Zhi *et al.* firstly reported good compressive performance of PAM-based hydrogel electrolyte[27], and then modified the PAM hydro-

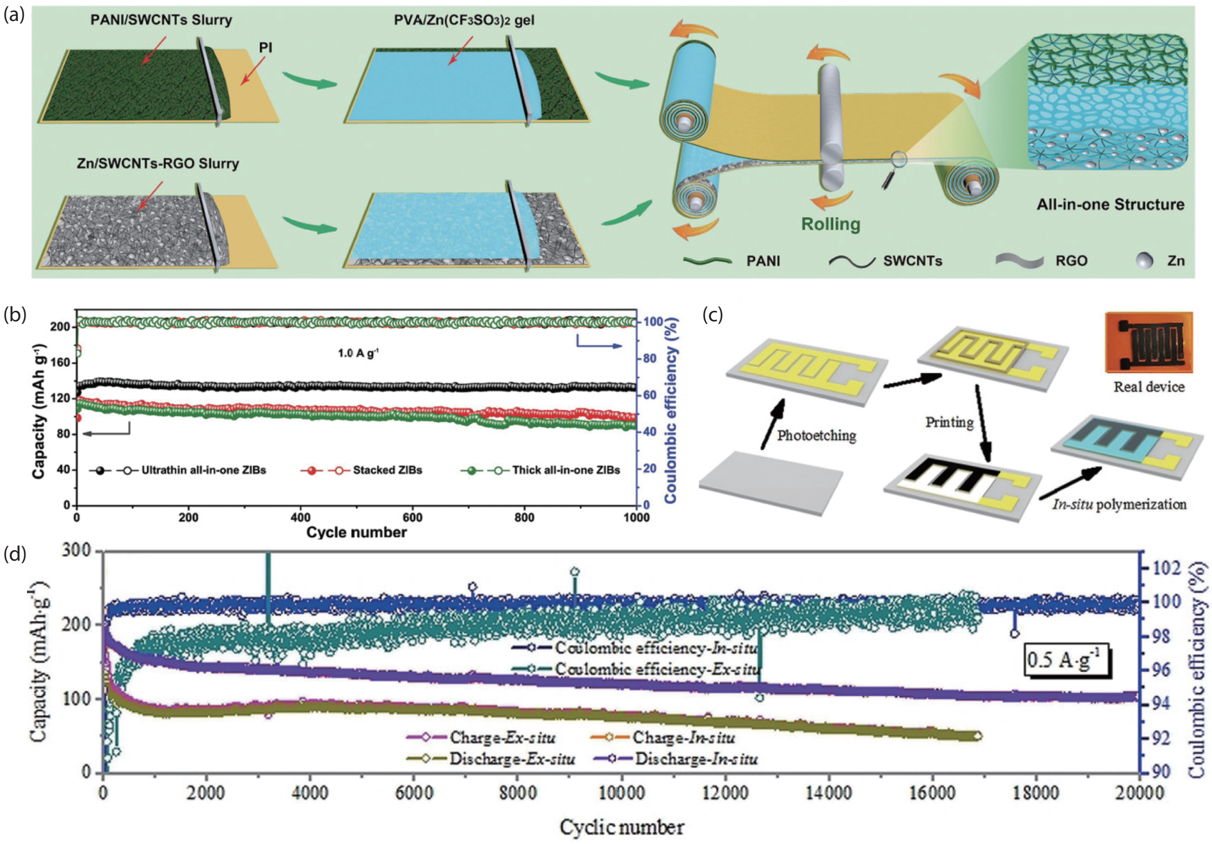

Fig. 3. (Color online) (a) The schematic process of design and (b) the cycle performance of ultrathin all-in-one ZIBs. Adopted with permission from Ref. [25], Copyright 2021, John Wiley & Sons. (c) Schematic illustration of fabrication procedures and (d) cycle performance of in-plane batteries. Adopted with permission from Ref. [26], Copyright 2020, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

gel by bringing in natural polymer SA[28]. Fig. 4(a) exhibited a demonstration of mechanically durable and device-level tough Zn-MnO_2 battery with high flexibility. After walking and car run-over, the discharge capacities of flexible ZIBs were still high similar to initial state. Whereafter, Huang *et al.* also reported the hydrogel electrolytes on the basis of PAM and SA to assemble flexible ZIB (Fig. 4(d))[29]. Fig. 4(e) delivered the tensile strength of 674.28 kPa and compressive strength of 16.29 MPa of Zn-reinforced SA-PAM SE due to the strengthening mechanism of Zn^{2+} cross-linked SA. And the capacity loss per cycle of the flexible ZIB was the lowest after 10 000 cycles (Fig. 4(f))[29]. In addition, integrated all-in-one ZIBs still revealed great electrochemical performance even when they are bent to nearly 360°, reaching a stable capacity of 137 mA·h/g (Figs. 4(g)–4(i))[30]. With regard to flexible ZIB with lightweight MnO_2/graphene membrane, it also showed capacity stability under external forces such as folding as shown in Figs. 4(j) and 4(k)[31].

3.2. Self-healing performance

Conventional batteries lost electrochemical performance when damaged. Thus, automatic repair of damaged batteries without affecting the performance of the battery itself was extremely important. Especially for flexible batteries, they were easily damaged when using in many fields. Herein, self-healing performances of various flexible ZIBs were summarized. Zhi *et al.* employed self-healing carboxylated-polyurethane as the substrate for electrodes to assemble flexible self-healing Zn-MnO_2 battery[32]. Figs. 5(a) and 5(b) showed after self-healing, flexible Zn-MnO_2 battery still displayed high capacity and powered an electric watch. Meanwhile, they explored the self-healing performance of flexible ZIBs in an alkaline environment. Figs. 5(c)–5(e) displayed excellent self-healing performance of flexible NiCo-Zn battery by using a self-healable hydrogel electrolyte comprising sodium polyacrylate cross-linked by ferric ions (Fe^{3+})[33]. Apart from healing hydrogel electrolyte, a self-healing flexible ZIB was also studied by using all-in-one self-healing electrodes. Fig. 5(f) exhibited flexible ZIBs assembled by all-in-one cathode by VS_2 nanosheets growing on carbon cloth, anode by electrochemically deposited Zn nanowires and a self-healing hydrogel electrolyte. After cutting the ZIB, repaired hydrogel electrolyte and electrodes all restored their original state and thus flexible ZIBs remained excellent electrochemical performance[34].

3.3. Low temperature performance

Due to the freezing, low ion conductivity and slow dynamics of aqueous electrolyte at low temperature, the aqueous metal ion batteries occurred the loss of capacity and power with the drop of temperature. Improving low temperature performance of aqueous batteries including flexible ZIBs had attracted the attention of scientists. Zhi *et al.* synthesized ethylene glycol-based waterborne anionic polyurethane acrylates (EG-waPUA) and then copolymerized EG-waPUA precursor and AM monomers to fabricate an EG-waPUA/PAM based dual crosslinked hydrogel. Next, the antifreezing Zn-MnO_2 batteries (AF-battery) on the basis of the hydrogel were assembled and delivered a high specific capacity of 226 mA·h/g at 0.2 A/g at –20 °C[18]. Fig. 6(a) exhibited the demonstration of AF-battery powered a series of electronic devices. Chen

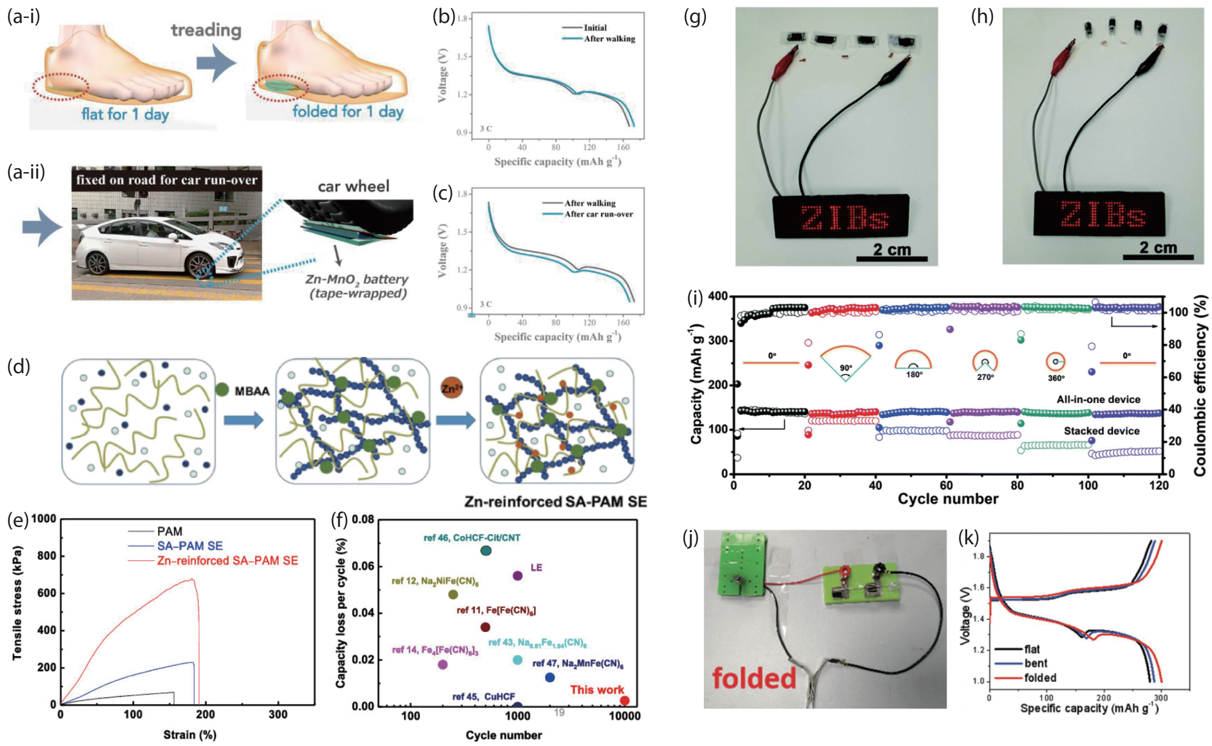

Fig. 4. (Color online) (a) Illustrations of the Zn-MnO$_2$ battery i) being placed under foot and ii) going through car run-over. (b) Discharge curve of the battery after 2 days' everyday treading. (c) Discharge curve of the battery after 20 times of random run-over by cars on road. All the discharge curves were recorded at 0.924 A/g (3C rate). Adopted with permission from Ref. [28], Copyright 2019, Elsevier. (d) Schematics of the evolution of the Zn-reinforced SA-PAM SE hydrogel structure. (e) Tensile strength of the Zn-reinforced SA-PAM SE. (f) Capacity loss per cycle of all kinds of flexible ZIBs. Adopted with permission from Ref. [29], Copyright 2020, American Chemical Society. Optical images of a "ZIBs" LED powered by four all-in-one ZIBs in series (g) without bending and (h) under bending. (i) Cycling performance of the all-in-one and stacked ZIBs at 0.5 A/g under flat and different bending states. Adopted with permission from Ref. [30], Copyright 2019, Royal Society of Chemistry. (j) The flexible ZIB is subjected to fold deformation. (k) Galvanostatic charge/discharge curves of the ZIB cell under different mechanical deformations. Adopted with permission from Ref. [31], Copyright 2021, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

et al. also revealed great low-temperature performance of flexible Zn-MnO$_2$ battery based on PAM/EG gel electrolyte (Fig. 6(b))[35]. Whereafter, Zhu *et al.* researched high zinc reversibility for flexible ZIBs employing PAAm hydrogel consisting of 2 mol/L ZnSO$_4$ and 4 mol/L LiCl (ZL-PAAm) at low temperature. Fig. 6(c) showed the voltage-time curves of Zn plating-stripping in ZL-PAAm under different temperatures, indicating excellent zinc reversibility of Zn//Zn symmetric cells with the ZL-PAAm. Meanwhile, the assembled flexible Zn-LiFePO$_4$ full cell shows a great cycle performance of 500 cycles at −20 °C, further confirming the excellent zinc reversibility benefiting from the ZL-PAAm[36].

3.4. Others

Apart from mechanical practicality, self-healing performance and working at low temperature, a series of flexible ZIBs particularly designed for special situations were studied and recorded. This expanded the application range of flexible ZIBs. Zhi *et al.* firstly reported a smart safe rechargeable flexible ZIBs based on sol-gel transition electrolytes. With the help of thermal-stimulus responsive polymer of poly(N-isopropylacrylamide) (PNIPAM), the synthesized hydrogel delivered a smart reaction of flexible ZIBs, namely, over a critical temperature, the polymer chains precipitated out of solution, resulting in stopping work of flexible ZIBs. Fig. 7(a) exhibited the process of the transformation. When the temperature was lower than the critical temperature, the battery restored its original state and worked again without any changing[37]. Therewith, Niu *et al.* further confirmed the feasibility of smart flexible ZIBs (Fig. 7(b)). They employed a smart thermal-gated PNIPAM/AM-5@GF hydrogel electrolyte to achieve evolution of the pore from an open to closed structure. Meanwhile, it displayed the phenomenon of a surface wettability transition from hydrophilic to hydrophobic states. The assembled flexible ZIBs showed thermal-responsive ability and self-protection behavior at high temperature[38]. Under extreme circumstances, flexible ZIBs remained excellent electrochemical performance. Wang *et al.* fabricated the hydrogel with high ionic conductivity (28.8 mS/cm) that cotton cellulose nanofiber grafted by xanthan gum-polyacrylamide (XG-PAM/CNF). Fig. 7(c) showed the practical submarine-use of flexible ZIBs, indicating use of possibility of flexible ZIBs in extreme environments[39]. Additionally, regulating electrochemical performance was achieved by reasonable design for flexible gel electrolytes. Fig. 7(d) revealed that particularly designed zwitterionic sulfobetaine/cellulose semi-interpenetrating networks gel (ZSC-gel) provided high ion conductivity (24.6 mS/cm) for flexible ZIBs. And then flexible Zn-MnO$_2$ assembled with ZSC-gel showed great cycling performance of 10 000 cycles[40]. Finally, the performance comparison of flexible ZIBs using in different situations was summarized in Table 1. Notably, flexible ZIBs were used in many fields and revealed great electrochemical performance. However, production in a large scale re-

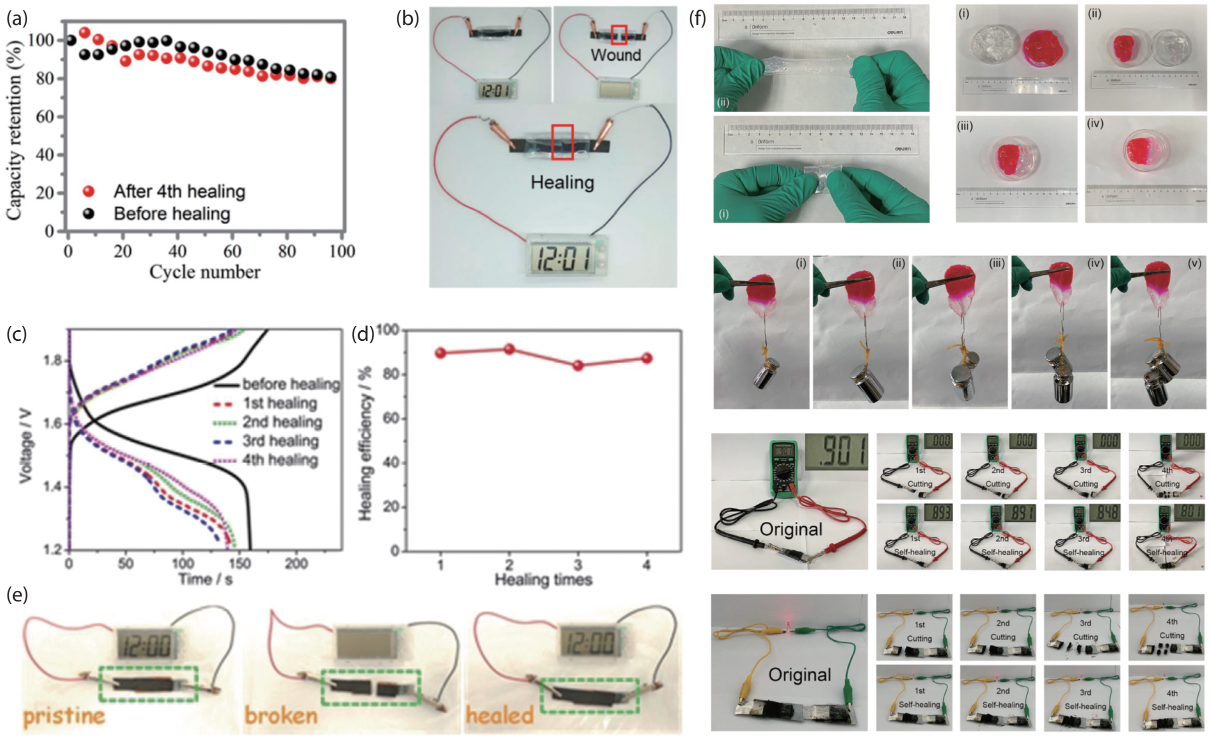

Fig. 5. (Color online) (a) Cycling performance of the obtained flexible Zn-MnO_2 battery before healing and after fourth healing. (b) Demonstration of a self-healing flexible Zn-MnO_2 battery powering an electric watch before and after cutting and after healing. Adopted with permission from Ref. [32], Copyright 2019, American Chemical Society. (c) Charging and discharging profiles of alkaline flexible NiCo-Zn batteries before and after multiple cutting/healing cycles. (d) Healing efficiency calculated from (c). (e) Demonstration of a self-healing flexible NiCo-Zn battery powering an electric watch before and after cutting and after healing. Adopted with permission from Ref. [33], Copyright 2018, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. (f) Demonstration of hydrogel electrolytes and the battery using all-in-one electrodes after each time of the self-healing process. Adopted with permission from Ref. [34], Copyright 2021, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

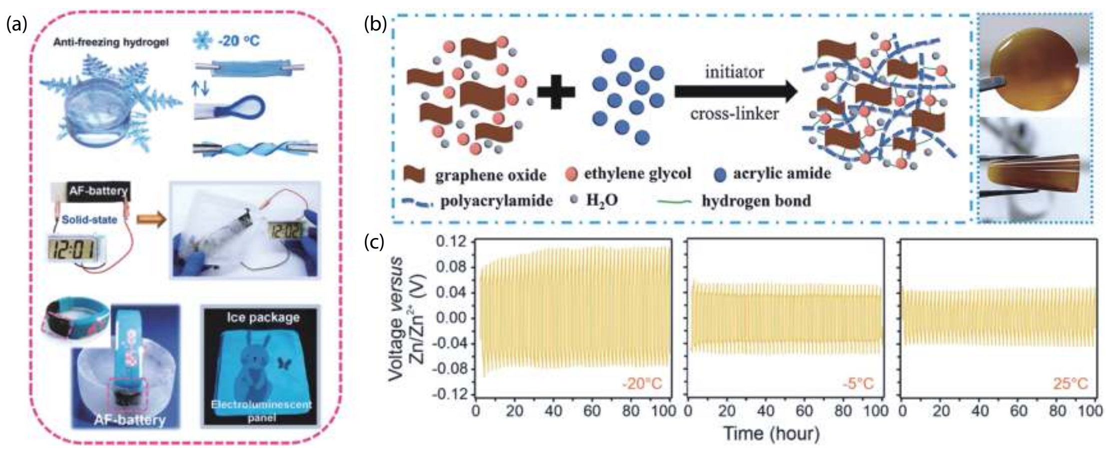

Fig. 6. (Color online) (a) The demonstration of AF-battery powered a series of electronic devices. Adopted with permission from Ref. [18], Copyright 2019, Royal Society of Chemistry. (b) The schematic diagram of anti-freezing gel electrolyte based on PAM/EG gel electrolyte. Adopted with permission from Ref. [35], Copyright 2020, Frontiers Media S.A. (c) The voltage curves of Zn plating-stripping in ZL-PAAm under different temperatures. Adopted with permission from Ref. [36], Copyright 2020, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

mained a challenge and it was also necessary to develop flexible ZIBs for more application scenarios.

4. Challenges and perspectives

From above review, reported flexible ZIBs exhibit superior flexibility, self-repairability, multiple environmental adaptation, intelligence and ideal electrochemical performance including specific capacity and cyclic stability. This lays a solid foundation for practical application of flexible ZIBs in the future. However, the practical application of flexible ZIBs is not yet commercialized owing to several challenges and issues discussed below. In order to develop practical flexible ZIBs that can be fabricated in a large scale, overcoming or alleviating the following difficulties would be especially vital.

(1) High-performing flexible current collectors and electrodes. At present, widespread-usage flexible current collect-

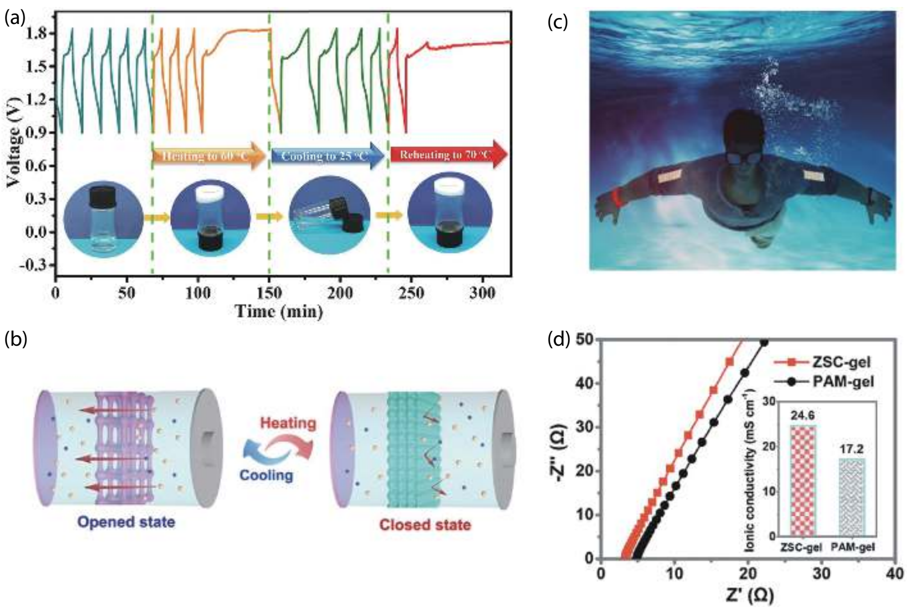

Fig. 7. (Color online) (a) The process of the smart reaction of flexible ZIBs when temperature changes. Adopted with permission from Ref. [37], Copyright 2018, Science China Press. (b) The schematic diagram of smart rection. Adopted with permission from Ref. [38], Copyright 2020, John Wiley & Sons. (c) The demonstration of practical submarine-use of flexible ZIBs assembled by XG-PAM/CNF hydrogel electrolyte. Adopted with permission from Ref. [39], Copyright 2020, American Chemical Society. (d) Ion conductivity of zwitterionic sulfobetaine/cellulose semi-interpenetrating networks gel (ZSC-gel). Adopted with permission from Ref. [40], Copyright 2020, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Table 1. The performance comparison of flexible ZIBs using in different situations.

Function		Cathode material	Flexible electrolyte	Plateau (V)	Capacity (mA·h/g)	Cycle	Ref.
Mechanical properties		α-MnO_2	PAAm	1.35/1.15	94 (4 C)	1000	[27]
		α-MnO_2	Zn-alginate/PAAm	1.35/1.15	144.5 (0.88 A/g)	500	[28]
		$Na_{0.5}FeFe(CN)_6$	Zn-alginate/PAAm	1.1/1.0	50 (20 C)	10 000	[29]
		rGO/PANI	Cellulose nanofiber	1.0	~ 100 (1 A/g)	500	[30]
		MnO_2/graphene	–	1.35/1.15	~ 125 (2 A/g)	2000	[31]
Self-repairability		δ-MnO_2	CPU	1.35/1.15	106 (20 C)	10 000	[32]
		NiCo	PANa-Fe^{3+}	1.55	225 (24 C)	–	[33]
		VS_2	PVA	0.7/0.6	~ 135 (0.2 A/g)	40	[34]
Low temperature resistance		α-MnO_2	EG-waPUA/PAM	1.35/1.15	~ 75 (2.4 A/g, –20 °C)	600	[18]
		α-MnO_2	PAM/GO/EG	1.35/1.15	~ 90 (1 A/g, –20 °C)	1000	[35]
		$LiFePO_4$	ZL-PAAm	1.13	~ 40 (0.5 A/g, –20 °C)	500	[36]
Others	Smart reaction	α-MnO_2	PNA	1.35/1.15	104 (0.5 A/g)	550	[37]
		PANI	PNIPAM/AM	1.0 (25°)	~ 125 (1 A/g)	1000	[38]
	Submarine-use	α-MnO_2	XG–PAM/CNF	1.35/1.15	~ 147 (4 C)	1000	[39]
	Ion-conductivity	α-MnO_2	ZSC-gel	1.35/1.15	74 (30 C)	10 000	[40]

ors are metal foil and mesh including titanium and stainless-steel wires or carbon-based materials including carbon paper and cloth. Nevertheless, because of memory effect of metal materials and finite elongation of carbon materials, the metal- and carbon-based current collectors do not fully meet demand in some situations. Therefore, other flexible current collectors are also researched and developed. Although some flexible conductors such as indium tin oxide (ITO) have been developed[41, 42], high cost and brittleness restrict its large-scale applications in flexible wearable devices in a large scale. In this regard, the related research needs to be explored deeply. A relatively common flexible electrodes are conductive polymers such as polypyrrole (PPy)[43, 44], polyaniline (PANI)[45, 46] and polyethylene dioxythiophene (PEDOT)[47, 48]. However, these electrodes are only employed to assemble supercapacitor due to lacking to high electroconductibility. Thus, developing conductive polymers with higher electrical conductivity is key issue to obtain fit flexible electrodes for flexible ZIBs.

(2) Flexible hydrogel electrolyte with wide operation potential window. The battery discharging plateau of aqueous ZIBs is confined because of the narrow electrochemically operation potential window of aqueous electrolyte. Therefore, in order to prepare flexible ZIBs with high discharging voltage, the hydrogel electrolyte with wide operation voltage window is inevitable. Up to now, the hydrogel with high concentrated salts contained provides a potential candidate for achieving high voltage[49–52]. However, in view of cost and craft process, high concentrated salt based the hydrogel is not a good choice for flexible ZIBs. The "water-in-gel" electrolyte achieving wide operation potential window[53] guides a new and valuable direction for high-voltage flexible ZIBs. Meanwhile, the cost and process of fabricating are reduced

and simplified. In the future, researchers need to deeply and more detailedly do research in this direction.

5. Conclusion

In summary, flexible ZIBs have been fabulously fashionable and generally researched since 2015. The development of flexible ZIBs is still in its infancy even if there are some evolutions to some extent. On the one hand, flexible current collectors or flexible electrodes need to be further developed to make flexible ZIBs suitable for more practical scenarios. On the other hand, flexible hydrogel electrolytes with wide operation potential window are extremely significant to assemble high-voltage flexible battery. Therefore, it is necessary to overcome and battle these key issues. Only if these two challenges are solved, can we carry flexible ZIBs forward further. In this review, we have implemented a brief discussion on the challenges and perspectives existed in the development of flexible ZIBs. We also propose a direction that need to be further researched in the future so that flexible ZIBs can make a step closer to commercial application.

Acknowledgements

This research was supported by the National Key R&D Program of China under Project 2019YFA0705104.

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