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Recent Advances in Flexible Zinc-based Rechargeable Batteries

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Flexible Zn-based batteries are regarded as the promising alternatives to flexible lithium-ion batteries for the wearable electronics owing to the naturally advantages of zinc, such as environmental-friendly and low cost. In the past of few years, flexible Zn-based batteries have been studied intensively and exciting achievements have been obtained in this field. However, the development of flexible Zn-based batteries is still at an early stage. In this article, challenges of developing flexible lithium-ion batteries are firstly present. Then, this paper presents a brief overview of recent progress in flexible zinc secondary batteries from the perspective of advanced materials and some issues that remain to be addressed.

1. Introduction

Flexible batteries refer to primary or secondary batteries with special mechanical properties which can be rolled, bent, twisted, or folded. Such batteries are freed from the constraints of rigidity and weight that characterize current portable batteries.[1] Application areas impacted by flexible batteries include smart electronics (e.g., wearables), medical (e.g., Patient tracking and location), communications (e.g., internet of things tags), and others. To provide a power source for these applications, flexible batteries delivering a high volumetric energy density are particularly desirable because there is often a limited volume for integrating the batteries into these applications.[2] To date, there have been commercial efforts to manufacture lithium thin film batteries (< 1 mm in thickness) being flexible and suitable for use in card-type and wearable devices.[3] However, these thin and flexible lithium-ion batteries have typically exhibited far less volumetric energy densities (<200 Wh/L) than those of conventional lithium-ion batteries (<650 Wh/L).[4] This performance roll-off is largely due to the fact that high barrier encapsulation of air and moisture sensitive lithium battery materials can severely impact the effective volumetric efficiency as the batteries are miniaturized. Therefore, high volumetric energy density lithium batteries with thickness < 1 mm will be critical to enabling flexible electronics.[5] To this end, notable advancements have been made in the design of flexible lithium-sulfur and lithium-air batteries – those cathode chemistries enable high theoretical energy densities of 2800 and 6940 Wh/L, respectively – yet there remains substantial room for improvement.[6-8]

The potential to yield high volumetric capacities by using less environmentally sensitive materials in the batteries sees zinc as an attractive anode alternative to lithium. In addition to the stability, zinc is likely to experience less cost pressure on raw material availability compared to lithium. In all cases, zinc secondary batteries represent a highly promising area of technology for their potential deployment in an increasing number of highly functional flexible and low-cost electronics. Existing technologies such as Zn-MnO_2 and Zn-air batteries have emerged

from renewed interests in making them rechargeable.[9-15] Companies working in rechargeable, polymer Zn-MnO_2 batteries have demonstrated that this new zinc secondary battery chemistry is well suited to a broad range of features for flexible electronics at reduced cost.[5] Recent developments in flexible Zn-air and other metal-air batteries have also showed great promise with high volumetric energy density merits, despite of their limitations in power performance.[7] Nevertheless, we could expect further progress in zinc-based technologies towards improved battery performance and flexibility as compatible, reversible cathode chemistries are developed.

In this Research News, a progression of flexible lithium-ion battery approaches and challenges is outlined, followed by a brief review of recent progress in flexible zinc secondary batteries from the perspective of advanced material approaches and some issues that remain to be addressed. This leads to the conclusion that using intrinsically stable and cost-effective zinc battery chemistries could have the highest potential to be the future of energy storage for flexible electronics.

2. Challenges of Flexible Lithium-ion Batteries

Lithium-ion batteries have been investigated as a power source for feature-driven applications in flexible electronics, owing to their relatively high energy and power densities and decent cycling life.[16] Traditional lithium-ion batteries employ a liquid electrolyte and are typically in non-flexible constructions such as of button cell,[17] cylindrical cell,[18] and pouch cell[19]. To improve the flexible robustness of the batteries, the current rigid battery components and metal casing should be either substituted with intrinsically flexible materials or made into flexible forms by integrating soft supports. To date, there have been many academic and industrial efforts at developing flexible lithium thin film batteries that are based on either solid polymer or inorganic electrolytes.[20] With thin lithium polymer batteries, the liquid electrolyte is replaced by solid polymer electrolyte films that offer a better form factor and flexibility. The polymer electrolytes contain lithium salts within a variety of polymer hosts such as

polyvinylidene fluoride and can have ionic conductivities of 10^{-4} S/cm at ambient temperature.[21] In this configuration, however, safety concern is still raised due to the low flammability of the polymer electrolytes.[5] The use of non-flammable ceramic electrolytes such as lithium phosphorous oxynitride (LiPON) makes them possible to alleviate this issue but pay for the price of their relatively poor conductivity (10^{-5}–10^{-7} S/cm). In addition, these ceramic electrolytes, in general, are very fragile to the internal stresses of flexing.[22]

Furthermore, there are limitations of lithium-ion batteries to maintain their high energy density when downsized to thinner fashion (< 1mm) in order to meet thin-film design flexibility. Using lithium technologies require high barrier packaging (e.g., metal foil laminates in hundreds of microns) to seal off the highly reactive lithium in the battery from the environment. Aside from lacking mechanical flexibility, this packaging also adversely affects thickness and volumetric energy density from an overall cell design perspective. Standard bulk lithium polymer batteries generally have good volumetric energy densities in the range of 400 Wh/L and beyond with the cell thickness greater than 1 mm.[5] However, their volumetric energy densities significantly drop to less than 200 Wh/L for cells thinner than 1 mm. For an example, a 40 mAh, 0.55 mm thin, flexible lithium-ion battery (CG-063555) developed by Panasonic has a calculated volumetric energy density of approximately 143 Wh/L. Recently, a more compact monolithic cell structure based on the LiPON systems was developed by the Oak Ridge National Laboratory. In general, this approach showed the ability to reduce the cell thickness to only 0.2 mm with good bonding between the cell layers for flexibility, but with limited volumetric energy densities well below 100 Wh/L and at higher cost associated with vacuum deposition processes.[23]

As we look forward to flexible and miniaturized electronics, the use of environmentally sensitive lithium battery chemistries needs to be reconsidered. This together with packaging complexity cause significant drop-offs of the volumetric energy density. To defend against this

limitation, it will need innovations both in the battery component materials and in improved cell and packaging structures.

3. Flexible Zn-based Rechargeable Battery

As an electrode material, zinc has many advantages over lithium, such as low cost (≈ 0.9 $/Ib), superior abundance in the earth crust (almost 300 times higher than that of lithium) and low redox equilibrium potential (Zn/Zn^{2+}).[24-25] More remarkably, using environmentally insensitive zinc enables easier and cheaper fabrication and packaging of Zn-based batteries than those of lithium-based countparts. As a consequence, conventional Zn-based batteries, such as Zn-MnO_2, Zn-Ni, and Zn-air, have been commercialized for a long time but are mainly produced in rigid forms for low-drain, non-flexible electronic gadgets. These batteries possess a similar configuration, which consists of a zinc anode, an aqueous alkaline electrolyte solution and a cathode (i.e., MnO_2, $Ni(OH)_2$, air electrode). **Figure** 1 shows the discharge reaction mechanisms of Zn-MnO_2, Zn-Ni, and Zn-air batteries. Among them, both Zn-MnO_2 and Zn-Ni batteries are closed systems, with the MnO_2 and NiOOH cathodes taking active roles in the redox reaction, while Zn-air batteries are half-open system where the air cathode is just charge-transfer media and the reactant (i.e., oxygen) is delivered from outside the cell. Owing to the irreversibility of discharge products, these batteries are mainly primary batteries or only exhibit limited rechargeability and couldn't meet the requirement of economical and enviroment-friendly.[8, 26]

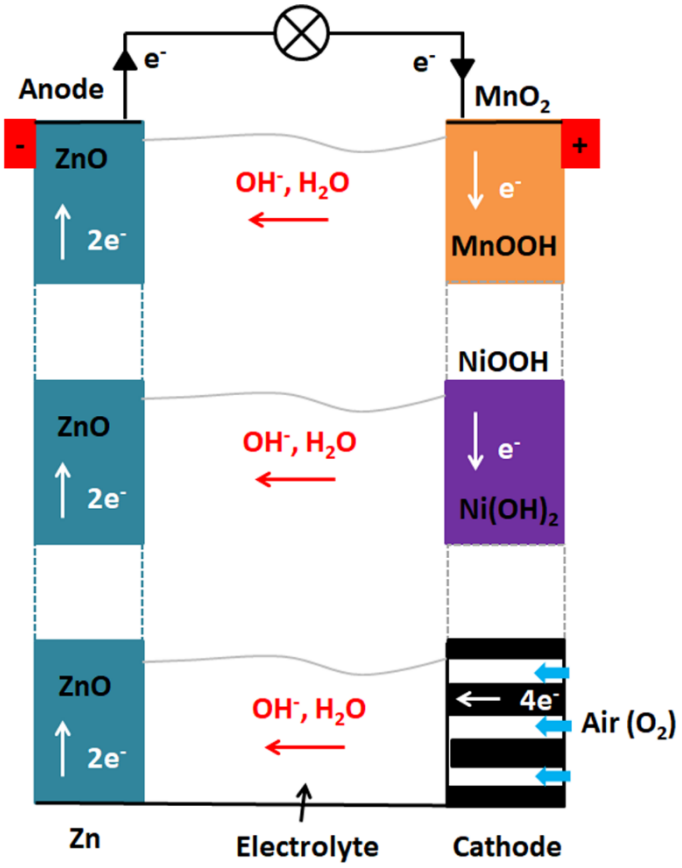

Figure 1. Schematics showing three discharge mechanisms of Zn-MnO_2, Zn-Ni, and Zn-air batteries.

The recent development of nanomaterials and nanotechnology have strongly propelled the emergence of Zn-based batteries with excellent rechargeability through optimizing structure, composite, and morphology of their components, etc. Accordingly, their application in flexible batteries is particularly interesting as zinc has a relatively high specific capacity of 820 mAh/g, especially a high volumetric capacity of 5854.8 mAh/cm^3.[27] For example, flexible ultrathin film Zn-MnO_2 battery, namely ZincPoly battery, has been successfully commercialized by Imprint Energy based on a high conductivity (10^{-3} S/cm) polymer electrolyte and printing technology.[5] As shown in **Figure 1**, the ZincPoly battery with thickness of less than 0.5 mm can output energy density up to 300 Wh/L, which is superior than that of flexilbe lithium-ion battery with same thickness. Additionally, the security coupled with outstanding economic cost not only in rare materials but also in productoin engineering make ZincPoly battery much more

conspicuous. Therefore, flexible rechargeable Zn-based batteries will most likely be utilized as a cost-effective, high durable flexible energy storage technology, which would boost the further development of wearable electronics. To this end, continuous improvements are required for the performance of flexible Zn-based batteries.

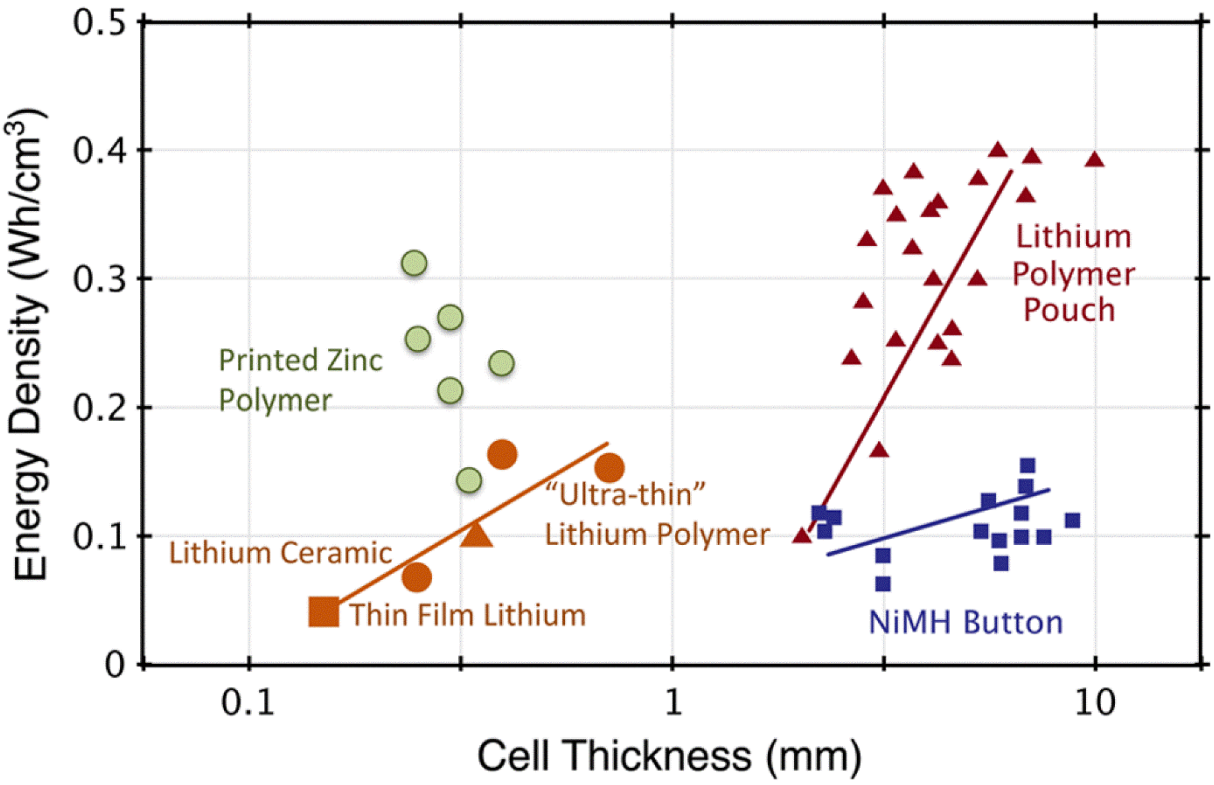

Figure 2. The energy density of different batteries with various thickness. Reproduced with permission.[5] Copyright 2015, Institute of Electrical and Electronics Engineers.

3.1. Energy Density

Energy density is one of the key evaluation standards for flexible Zn-based batteries. Different from the intercalation/deintercalation mechanism of Li-ion batteries, Zn-based batteries are relied on conversion chemistry between anode and cathode. Such conversion mechanism suggests their specific energy density partly depends on the choice of cathode materials. Based on the volume of discharge products, the specific energy density of Zn-MnO_2, Zn-Ni, Zn-Ag and Zn-air battery can be calculated to be 1344 Wh/L, 1542 Wh/L, 2351 Wh/L and 6070 Wh/L, respectively. With no doubt, Zn-air battery is the most promising system in

terms of specific energy density. However, its half-open structure that ensured oxygen from atomsphere continuously diffuse into the system could potentially bring lethal moisture loss of the electrolyte and destroy the battery within few days once being put to use.[28] Thus, seeking for a novel cathode material with high capacity as well as low density to construct a Zn-based battery whose energy density could rival the Zn-air battery but less suffers from the half-open structure will be likely a future direction. For instance, flexible Zn-Co_3O_4 battery with specific energy density of 2807 Wh/L (equals to 470 Wh/kg based on the weight of discharge products) has been developed.[24]

However, the practical speicific energy density of Zn-based batteries is far below their theoretical speicific energy density. For example, the conventional Zn-Ni battery and Zn-Co_3O_4 battery only exhibit practical energy density of 70 Wh/kg and 241 Wh/kg, respectively.[24] It is significantly less than their theoretical energy density based on the weight of discharge products, which is 345 Wh/kg and 470 Wh/kg, respectively. Similarly, the practical energy density of the reported Zn-air battery is also lower than its theoretical energy density (520 Wh/kg_{ZnO} versus 1086 Wh/kg_{ZnO}).[15] The poor depth dischargeability of Zn (always less than 30%) is considered to be the main reason to this appearance as the discharge product of $Zn(OH)_4^{2-}$ would easily convert to insoluble and nonconductive ZnO.[29-30] It could overlap the zinc anode and separate it from electrolyte and then impede the discharge process. Therefore, increasing the Zn depth of discharge will sharply enhance the energy density of Zn-based batteries. Methods such as adding electrolyte additives[31-32] to prevent dehydration of $Zn(OH)_4^{2-}$ has been demonstrated with the ability of partly tackel this problem, but couldn't radically resolve the low practical energy density of Zn-based batteries. Consequently, other more innovative strategies have been under exploration. The novel configuration of zinc anode may offer a potentially effective approach to tackel this challenge. For instance, a three-dimensional (3D) monolithic, porous, aperiodic sponge zinc anode shown in **Figure 2** with function of strongly increasing the Zn depth of discharge up to 90% has been successfully manufactured and be utilized in Zn-air and

Zn-Ni batteries.[29-30, 33] As compared to Li-ion battery with the same energy output of 24 kWh, the prototype of 3D Zn-Ni battery could save 35 wt% of weight (100 kg, corresponding to 14000 L of zinc anode).[29] More interestingly, the 3D Zn-Ni battery exhibits superior cycling ability up to 54000 cycles with no significant decrease of discharge-charge voltage. Meanwhile, the 3D sponge zinc anode was also employed to fabricate a rechargeable Zn-Ag battery, which exhibits excellent cycling ability within 34 cycles without no capacity loss.[30] Although the reported Zn-air, Zn-Ni and Zn-Ag batteries based on 3D sponge zinc anode are not a flexible one, it could provide a promising solution and promote the advance of flexible Zn-based battery with high energy density.

Alternatively, increasing the loading of cathode active materials could boost the energy density of Zn-based batteries as well. Whereas, it is noteworthy that the accumulation of active materials to a certain extent could bring down the overall flexibility of the cathode. Additionally, it could reduce the conductivity of the cathode as the oxide or hydroxide nature of cathode materials. Indeed, integrating active materials with current collector via in-situ technique could decrease the interfacial contact resistance, but it is still a great challenge to increase the loading of integrated electrode. Therefore, in order to further address the low practical energy density of Zn-based battery, rational design of cathode architecture beyond integrated electrode should be considered.

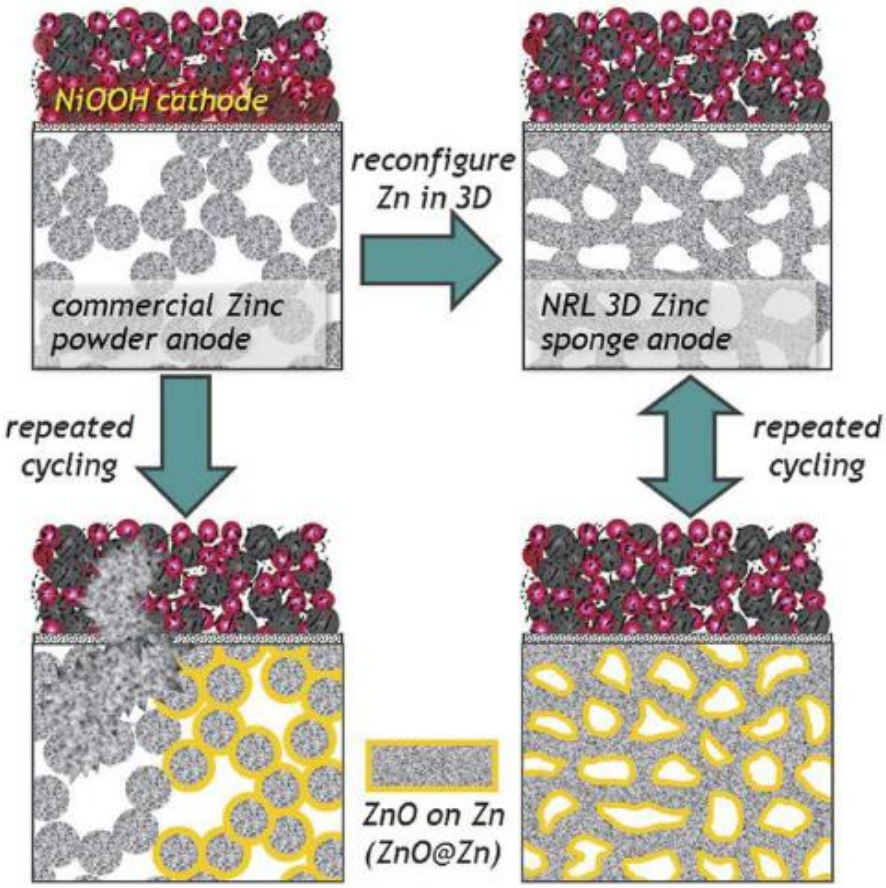

Figure 3. The schematic comparison of recharging Zn/Ni battery with different zinc anode (conventional powder zinc anode versus 3D sponge zinc anode). Reproduced with permission.[29] Copyright 2017, AAAS

3.2. Rechargeability

Similar to lithium metal anode, using pure zinc as the anode of Zn-based batteries could also result in the formation of zinc dendrite and then distinctly decrease the cycling durability of zinc anode, as well as the safety of the overall system. This is considered to be another crticial factor in developing Zn-based batteries with superior rechargeability that could compared to that of conventional lithium-ion batteries.[8, 29, 34] While, as compared to large volume of flexible Zn-based batteries literature that focused on cathode materials or electrolyte system, research papers that conentrated on the mechanism of zinc dendritic growth are surprisingly rare. This suggests a sluggish progresses in developing high performance zinc anode with superior stability. The research progress made in lithium dendrite growth revealed that soft substrate is helpful in mitigating the lithium dendrite during the electroplating process because of stress

relaxation.[35] However, whether the dendritic zinc growth process is suppressed or facilitated in flexible Zn-based batteries under different stress states caused by enternal force is still not clear. In addition, similar reports about zinc dendrite growth under stress have not been published until very recently. Therefore, with the aim of further develop flexible Zn-based batteries with high stability, it is paramount important to investigate the dendrite growth mechanism, especially under the influence of external force, through in-situ characterization technique (i.e., in-situ cryo-TEM[36]), simulating computation, or other advanced techniques. This could eventually lead to effective approaches to increase the stability of zinc anode.

Following the logic of the invention of lithium-ion battery, another strategy to strongly improve the rechargeability of Zn-based batteries is transforming them to "zinc-ion"-based battery. For instance, a highly reversible aqueous Zn-MnO_2 battery, which is based on zinc anode, modified $ZnSO_4$/$MnSO_4$ electrolyte and α-MnO_2 nanofiber cathode, was successfully demonstrated very recently.[37] This battery shows outstanding long cycle stability with only 8% capacity reduction after 5000 cycles at a rate of 5C, which results from its unique battery chemistry with H^+ and Zn^{2+} coinsertion. This work opens a revolutionary opportunity for the development of flexible Zn-MnO_2 batteries with superior cycling ability. Indeed, after that, several two dimensional (2D) film structure flexible Zn-MnO_2 batteries based on the similar electrolyte system (i.e., PVA/$ZnCl_2$/$MnSO_4$) have been reported.[9, 38] For example, the prototype of as-prepared flexible Zn-MnO_2 battery could cycle up to 300 cycles with capacity retention of 83.7 %.[9]

As compared to the other Zn-based batteries, rechargeable Zn-air battery is a special one as its cathode materials are the oxygen from ambient atmosphere. During the discharge-charge process of rechargeable Zn-air batteries, the reactions of $O_2+2H_2O+4e^- \overset{redox}{\longleftrightarrow} 4OH^-$ that occurred at the air cathode are a kinetically sluggish process which need high performance bi-functional catalysts to effectively facilitate oxygen reduction reaction (ORR) and oxygen

evolution reaction (OER).[39-40] This revealed that the rechargeability of Zn-air batteries is largely depends on the employment of bi-functional catalysts, excluding the rechargeability of zinc anode. Accordingly, tremendous efforts have been devoted to develop high-activity, high-stability and cost-effecitive bi-functional catalysts for rechargeable flexible Zn-air battery. Fortunately, great achievements have been obtained in this area. For example, Co_3O_4 with different morphology (i.e., ultrathin layers[41], hollow nanospheres[42], nanoparticles[43], etc.) coupled with carbon materials have been reported for rechargeable flexible Zn-air batteries. Furthermore, defected carbon-based materials fabricated by doping[44] or etching[45] also demonstrates promising application in rechargeable flexible Zn-air batteries.

3.3. Flexible Electrolyte

As another essential part of battery system, electrolyte has to be flexible beyond conventinoal functions in terms of fabricating a flexible Zn-based battery. Therefore, conventional aqueous electrolyte couldn't meet the requirements of flexible Zn-based batteries as its intrinsic character of good fluidity, which could't maintain a steady form and effectively segregate the electrodes to prevent short circuit. Accordingly, gel electrolyte that is consisted of polymer gelata and corresponding aqueous electrolyte, has been explored and been widely employed in flexible Zn-based batteries,[46] thanks to their relatively good mechanical property orginated from the frame and functional groups provided by polymer gelata.[47] Generally speaking, the performance of gel electrolyte strongly depends on the choice of gelata and the proportion of each element. Polyvinyl alcohol (PVA) with many function groups of hydroxyl could be dissolved in aqueous electrolyte via the assistant of relatively high temperature (~90°C) and is regarded as a perfect gelata. For example, PVA/$ZnCl_2$/$MnSO_4$[9, 38], PVA/KOH/ZnO[48-49] and PVA/KOH[50-51] gel electrolyte have been utilized as the electrolyte of flexible Zn-MnO_2, Zn-Ni, and Zn-air batteries, respectively. Beyond PVA, other gelata such as gelatin[52], PEO[53], PAA[54] could also be used to construct gel electrolyte.

Gel electrolyte could, indeed, provide the requirement of flexiblity and avoid the leakage of liquid electrolyte together with its advantages of easy handle during the the process of fabrication. However, its relatively low ionic conductivity (10^{-3} S/cm) as compared to aqueous electrolyte (10^{-1} S/cm) would decrease the power density of flexible Zn-based batteries.[55] In this regard, Zhi et al. devoted their efforts to modify the zincate-based gel electrolyte and synthesized a novel hierarchical polymer electrolyte (HPE) comprised of gelatin and polyacrylamide (PAM),[56] leading to a successful demonstration of a wearable solid-state rechargeable Zn-MnO_2 battery based on HPE and α-MnO_2 nanorod/carbon nanotube (CNT) cathode. Benefit from the much improved ionic conductivity (1.76×10^{-2} S/cm) of the HPE, the as-fabricated flexible battery with thickness of 0.11 mm could deliver high energy density (6.18 mWh/cm^2) and high areal power density (148.2 mW/cm^2) at a rate of 2.772 A/g. As can be seen in **Figure 3**, this flexible battery could also sustain 1000 discharge/charge cycles with outstanding capacity retention of 97%. More interesting, remarkable safety and flexibility are also achieved for the flexible batteries, indicating the preeminent compliance and remarkable mechanical strength of the HPE. Such flexible Zn-MnO_2 battery could still survive under a number of severe deformations, such as being bent, punctured, and even being roasted or washed.

Although gel electrolyte could guarantee flexible Zn-based batteries with a certain degree of deformation, the fast loss of water similar to that of aqueous-based electrolyte still severely limits its practical application. Moreover, it is highly likely that the water loss would be accerlated once the gel electrolyte is subjected to severe deformation. This could be a vital problem for flexible Zn-based batteries, not even mention flexible Zn-air batteries with the inherent characteristics of half-open structure which is very sensitive to environment.[2, 28] Consequently, developing high performance electrolyte system with ionic conductivity comparable to that of aqueous solution (10^{-1} S/cm), environmental insensitive and excellent mechanical properties could be potentially very useful for the next generation flexible Zn-based

batteries. Borrowing the electrolyte system of solid lithium-ion battery, solid state electrolyte could be a choice given that its low ionic conductivity (10^{-5}–10^{-7} S/cm) can be significantly improved.[22] Additionally, exploring a gel electrolyte with the ability of self-healing, such as thermoreversible polymer hydrogel electrolyte[57], may also help to remarkably improve the tolerance of flexible Zn-based batteries to the damage caused by external force.

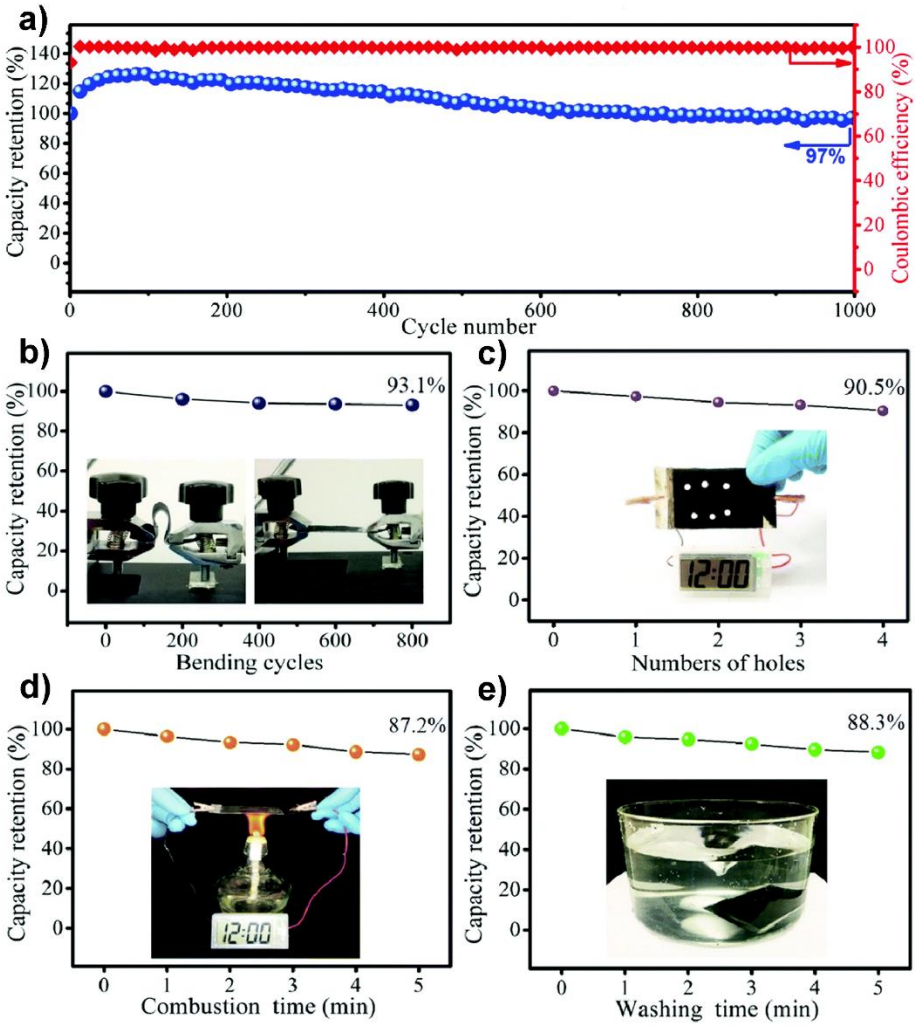

Figure 4. a) Long-term cycling performance and the corresponding coulombic efficiency of flexible rechargeable Zn/MnO_2 battery at 2.722 A/g. Electrochemical performance of flexible rechargeable Zn/MnO_2 battery under different deformation b) bending, c) puncturing, d) roasting, e) washing. Reproduced with permission.[56] Copyright 2017, Royal Society of Chemistry

3.4. Flexible Configuration and Category

The configuration of flexible Zn-based batteries is another technical challenge. Based on the literatures review, flexible Zn-based batteries featuring 2D film architecture almost takes up to 70% as the merits of 2D film construction, such as low requirements to electrodes and easy to assemble. In such 2D flexible Zn-based batteries, materials with characteristic of thin, toughness and conductivity (i.e., metal foil, carbon cloth) are ususally employed as the flexible electrodes or flexible substrate to carry active electrode materials via spraying, coating or in-situ depositing. Obviously, these materials are easy to obtain and could be easily laminated together to form a 2D film structure.

However, as compared to 2D film structure, 1D wire-shaped construction flexible batteries, which could provide flexibility of all direction (i.e., be tied, be twisted, etc.) and can be knitted in to fabrics, exhibit superior advantages and could be a promising solution towards wearable energy storage system.[15, 58] Whereas, since it is hard to assemble different components of battery together, especially coating an appropriate film electrolyte around electrodes to keep them isolated, fabricating a 1D fiber-shaped flexible Zn-based batteries is still a challenge both in academic and industry communities. Moreover, more requirements are demanded by 1D wire-shaped electrode, including but not limited to sufficient length and strength.[58] Therefore, up to today, only limited 1D flexible Zn-based batteries have been reported, not even mention real fiber-shaped Zn-based batteries that could be knitted or weave to form a certain pattern. In these reported 1D flexible Zn-based batteries, metal zinc wire is always employed both as active material and current collector. Whereas, the really consumed zinc only takes up extreme minority, suggesting great energy density loss because majority of zinc is inaccessible and acted as current collector. Consequently, coating a proper zinc film on a highly conductive substrate with efficient mechanical strength and light weight, such as conductive polymer materials, could be an effective alternative method to aviod the

unnecessary energy density loss . However unfortunately, to realize their application in flexible Zn-based batteries, their low conductivity should be intensively improved.

Beyond configuration, the category of flexible Zn-based batteries should be well considered and explored. Absolutely, flexible Zn-based batteries that could be bent, rolled, folded or twisted are successfully demonstrated by many academical communities. However, flexible Zn-based batteries, featuring stretchable or compressible that is also desired by wearable electronics, have been rarely reported as their critical requirements toward active materials and current collector. In spite of some stretchable Zn-based batteries have been successfully prepared through innovatively design of battery configuration, stretchable Zn-based batteries based on natrually stretchable electrodes are still regarded as a bottleneck for this technology.[59] Recently, a highly stretchable Zn-Ag_2O battery rooted from printing technology and a hyperelastic binder (polystyrene-block-polyisoprene-block-polystyrene) could provide some reference for the development of stretchable Zn-based batteries.[60]

3.5. Others

There is no doubt that tremendous evolutions have been achieved in flexible Zn-batteries, and all the as-prepared batteries demonstrate excellent stability after several numbers of deformations. However unfortunately, the dynamic impacts of mechanical deformation on the electrochemical behaviors of flexible Zn-based batteries are rarely discussed. There has been little systematic characterization/understanding for battery performance under dynamic bending related to the needs of practical flexible electronics. Apparently, the external force could result in different stress state along the flexible Zn-based batteries. For example, bending a 2D film structure cathode will cause tensile stress state on the top surface of the cathode accompanied with pressure stress state on the bottom surface of the electrode. This will further result in the fall off of active materials and crack generated on the cathode, and this phenomenon will turn to be more serious if it is occurred in the discharge/charge process. To probe the

influence of external forces on the performance of flexible Zn-based batteries, more efforts and advanced characterization technique also need to devote to this area.

As mentioned above, printing technology has been used to commercialize film Zn-MnO_2 battery since it is a promising method in terms of fabricating 2D structure flexible Zn-based batteries.[5] While, effective fabrication processes for 1D flexible batteries haven't been reported until recently, despite it is a prominent structure with many advantages. Therefore, future efforts should also be paid to develop novel fabrication process that can support large-scale, low cost production. In addition, as a new born area, the testing criteria of flexible Zn-based batteries haven't been established. For example, in order to obtain a meaningful conclusion about the recent advances of flexible Zn-based batteries, the comparison of energy density of them have been made and listed in Table 1. As can be seen, different groups calculated energy density based on different parameters, including but not limited to the weight of electrode active materials , the area or the volume of the flexible device. Apparently, it is hard for readers to compare them and obtain a deep impression. Additionally, volumetric energy density (Wh/L) is more important than gravimetric energy density (Wh/kg) for flexible Zn-based batteries due to its application in wearable electronic. Whereas, the latter is more common to see in the flexible Zn-based battery literatures. Consequently, similarly to Li-ion battery, the uniform assessment systems of flexible Zn-based batteries should be built up.

Table 1. Summary of energy density of flexible rechargeable Zn-based batteries based on the experimental results in literatures. [a)]

Battery Type	Shape	Electrode Materials	Volumetric (or area) Energy Density	Gravimetric Energy Density	Ref.
Zn-Ni	1D	Zn//Ni-NiO@CF	0.67 Wh/L $_{device}$	N/A	[48]
	2D	ZnO@CC// NiO@CC	7.76 Wh/L $_{cathode}$	323.3 Wh/kg $_{cathode}$	[49]

	2D	Zn@CC//MnO_2/ PEDOT@CC	33.95 Wh/L $_{device}$	504.9 Wh/kg $_{cathode}$	[9]
Zn-MnO_2	2D	Zn//MnO_2/CNT	6.18 mWh/cm^2 $_{device}$	N/A	[56]
	2D	Zn@CC//MnO_2@ CC	N/A	440 Wh/kg $_{cathode}$	[38]
Zn-Co_3O_4	2D	Zn@CF//Co_3O_4@ Ni foam	N/A	N/A	[24]
Zn-Ag	2D	Zn//Ag_2O	3.25 mWh/cm^2 $_{device}$	N/A	[60]
	2D	Zn//Co_3O_4@CC	N/A	546 Wh/kg $_{Zn}$	[41]
	2D	Zn//Nanoporous CF film	N/A	378 Wh/kg $_{Zn}$	[51]
	1D	Zn//Fe/N/C@CC	3.6 Wh/L $_{device}$	N/A	[52]
Zn-air	2D	Zn//RuO_2/CNT sheet	5.7 Wh/L $_{device}$	N/A	[53]
	2D	Zn//$LaNiO_3$/ NCNT@CC	2905 Wh/L $_{Zn}$	581 Wh/kg $_{Zn}$	[11]
	2D	Zn//Co_3O_4@SS mesh	N/A	874.6 Wh/kg $_{Zn}$	[12]
	1D	Zn//Co_3O_4/NrGO @ CF	36.1 Wh/L $_{device}$	649 Wh/kg $_{Zn}$	[15]

[a)]CF denoted as carbon fiber, CC denoted as carbon cloth, NCNT denoted as nitrogen doped CNT, SS denoted as stain-less steel, NrGO denoted as nitrogen doped reduced graphene oxide,. N/A denoted as Not applicable.

In general, the requriements of packaging materials for flexible Zn-based batteries are much lower than that of flexible Li-ion batteries, which is derived from the enviromental insensitive of zinc chemistries. Therefore, thinner and softer packaging materials can be used in common flexible Zn-based batteries. However, as a special Zn-based battery, flexible Zn-air battery with inherent feature of half-open structure to allow oxygen from the ambinet air diffuse in and out is critically to its packing materials. It has to be porous to ensure gas through but also need to be waterproof to avoid moisture loss of electrolyte. Obviously, it is a great challenge to develop this particular packaging materials because there has no benchmark for it, but is very desired for flexible Zn-air battery.

4. Conclusion

With the increasing demanding of wearable electronics, flexible Zn-based batteries have been incredibly popular and have attracted much attention since 2015. Although significant improvements have been achieved, the development of flexible Zn-base batteries is still at an

early stage. Taking commercial Li-ion battery as reference, which can deliver up to 650 Wh/L of energy density and can endure 1500 cycles of depth discharge/charge process, the practical energy density and the long-term durability of flexible Zn-based batteries are still poor and can't meet the demands of flexible electronic applications. However, the advantages of Zn-based batteries aforementioned strongly suggest it could be a promising substitution of Li-ion battery for using in flexible electronics, in terms of lower cost, more safety and higher volumetric energy density. To match the pace of flexible electronics, many novel strategies should be explored in order to further develop flexible Zn-based batteries with improved practical energy density and cycle life approximate to or superior than current Li-ion battery. Therefore, in this article, we have carried out a brief discussion on the challenges and points that existed in the development of flexible Zn-based batteries. We also examined issues that have been overlooked by some researchers, which should be well considered in the future flexible Zn-based batteries development.

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Flexible rechargeable Zn-based batteries are promising power sources for wearable electronics. This article will brief discuss the recent progress of flexible Zn-based batteries and outline some issues need to be addressed in the further develop flexible Zn-based batteries to meet the requirements of wearable electronics.

Keyword
Flexible; Zinc; Rechargeable; Batteries.

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Recent Advances in Flexible Zinc-based Rechargeable Batteries