

Materials Science

Zinc micro-energy storage devices powering microsystems

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Abstract: The increasing popularity of the Internet of Things and the growing microelectronics market have led to a heightened demand for microscale energy storage devices, such as microbatteries and microsupercapacitors. Although lithium microbatteries have dominated the market, safety concerns arising from incidents like self-ignition and explosions have prompted a shift towards new microscale energy storage devices prioritizing high safety. Zinc-based micro-energy storage devices (ZMSDs), known for their high safety, low cost, and favorable electrochemical performance, are emerging as promising alternatives to lithium microbatteries. However, challenges persist in the fabrication of microelectrodes, electrolyte infusion, device packaging, and integration with microelectronics. Despite these challenges, significant progress has been made over the last decade. This review focuses on the challenges and recent advancements in zinc-based micro-energy storage, offering unique insights into their applications and paving the way for the commercial deployment of high-performance ZMSDs.

Keywords: energy storage device, microbattery, microsupercapacitor, microsystem

INTRODUCTION

The burgeoning field of microscale electronic systems has catalyzed a parallel evolution in the realm of micro-energy storage devices. These devices, the linchpins of self-powered electronic systems, are vital in an array of applications—from the Internet of Things, wireless power systems, and tracking locators to micro-electromechanical systems, micro-robots, and implantable medical devices [1–4]. As critical elements in integrated systems, they facilitate seamless functionality across diverse sectors including environmental monitoring, entertainment, healthcare, industry, and defense. The true prowess of these systems lies in their ability to ingeniously merge microscale power sources with microelectronic devices, offering tailor-made solutions for a spectrum of challenges. Moreover, micro-energy storage systems play a pivotal role in harnessing the potential of renewable energy sources. They effectively bridge the gap between the erratic nature of renewable energy generation and the need for consistent power supply, thereby harmonizing the generation and storage of energy [5–8]. At present, microbatteries and microsupercapacitors stand as the twin foundations of micro-energy storage systems. These systems will embody an amalgamation of enhanced safety, robust stability, streamlined miniaturization, cost-effectiveness, superior power density, and remarkable energy density, setting the stage for a new era in micro-energy storage technology [9–11].

Lithium-based microbatteries featuring superior cycling performance and extended cycle life are now at

the forefront of the microbattery market [12]. To date, these batteries have found extensive applications in a range of fields including wearable devices, wireless power systems, trackers, and micro-electromechanical systems. Despite these advancements, the miniaturization of batteries presents a challenge: the reduction in the amount of active material relative to the overall battery composition. As battery sizes diminish, the volume portion of the electrodes significantly decreases, while the proportion of current collectors and packaging materials increases, leading to a reduced energy density of the batteries. In addition, the inherent complexity of their structural design escalates the difficulty in the manufacturing process. These factors collectively constitute key challenges in the design and fabrication of microelectrodes [13]. This change results in a significant decrease in both the energy density and areal capacity of the devices. A case in point is the energy density in common coin-cell lithium-ion batteries, which at 200 Wh L^{-1} , is less than half of that in batteries used in electric vehicles, typically around 600 Wh L^{-1} [14,15].

While lithium-based microbatteries are well-established for their superior performance and widespread market adoption, they are not without drawbacks. These include stringent production requirements and concerns about safety, particularly in terms of thermal stability and chemical reactivity. Given these challenges, there is a pressing need to develop new types of micro-energy storage systems. These systems should not only offer high performance but also prioritize safety and environmental sustainability, effectively compensating for the shortcomings inherent in current lithium microbattery technology [16–19]. Alternatively, micro-energy storage devices utilizing aqueous electrolytes stand out owing to their safety, cost-efficiency, and environmental sustainability. Among these, ZMSDs emerge as viable alternatives to their lithium-based counterparts. Zinc is plentiful in the Earth's crust, lending these devices an edge in terms of availability. They are characterized by impressive theoretical capacities, robust safety profiles, high energy densities, and environmental friendliness [20–23]. Distinctly, zinc anodes are compatible with aqueous electrolytes, facilitating a specific capacity of 820 mA h g^{-1} due to dual-electron transfer. This feature, alongside the enhanced ion diffusion rates and faster charging and discharging offered by aqueous electrolytes presents advantages that current lithium microbatteries have yet to achieve [24–26].

ZMSDs, mainly zinc-based microbatteries (ZMBs) and zinc-based microsupercapacitors (ZMSCs), have undergone extensive research in recent years [5]. Traditional storage devices consist of anode, cathode, electrolyte, separator, and casing. The anode in zinc batteries is primarily metallic zinc, supplemented by a few zinc-ion intercalation/deintercalation materials. A diverse array of cathode materials has been explored, including vanadium-based, manganese-based, Prussian blue analogs, spinel analogs, layered sulfides, and organic variants. Furthermore, halogens like chlorine, bromine, and iodine can form halogen batteries with zinc [27–31]. Zinc-based alkaline batteries, using silver oxide, nickel hydroxide, or air as counter electrodes to zinc, also exist [32]. Electrochemical zinc-ion capacitors, with their high safety, low cost, and assembly ease, are gaining popularity as potential low-cost future energy storage devices. The capacitors are divided into two primary types based on their energy storage mechanisms: one featuring a capacitive cathode and a battery-type zinc metal anode, the other comprising a battery-type cathode and a capacitive anode, each demonstrating enhanced performance over traditional double-layer capacitors [33–37]. In the realm of ZMSDs, the choice of electrode materials is pivotal and should be tailored to the specific microelectrode architecture to optimize energy density. The prevalent approach among researchers involves an initial fabrication of microelectrodes. These are subsequently infused with a quasi-solid-state electrolyte. The final step entails encapsulating the assembly to ensure isolation from the ambient air, culminating in the creation of

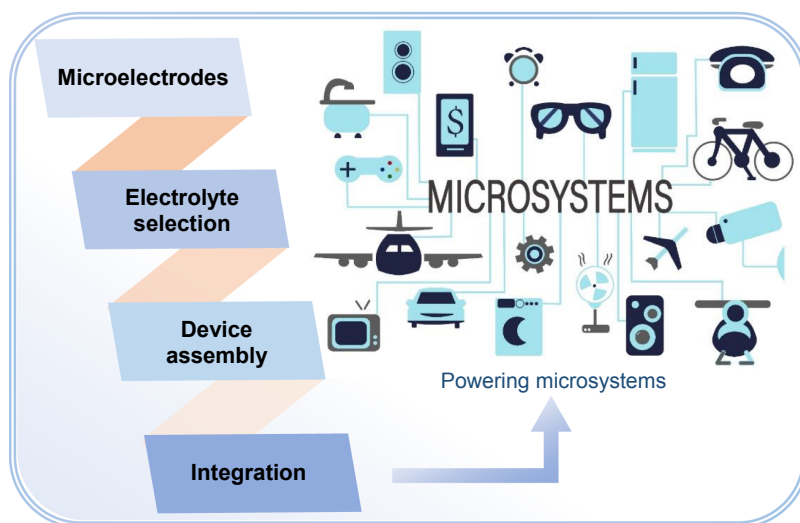


Figure 1 Overview of advancements in the miniaturized Zn micro-energy storage systems.

a quasi-solid-state ZMSDs. This approach underscores the intimate interplay between material selection and microscale engineering in advancing the efficacy of these energy storage systems.

In recent years, the field of ZMSDs has seen notable progress, albeit still in its nascent stages with much room for development. Unlike conventional energy storage systems, these miniaturized devices must balance the dual requirements of scalability in production and compatibility with small-scale applications. This review aims to provide an overview of the research advancements in these miniaturized systems and their integrated applications (Figure 1). We begin by introducing manufacturing technologies for ZMSDs, including the fabrication of high-performance microelectrodes and the assembly of miniaturized energy devices. A summary of the performance characteristics of some devices is provided. Subsequently, we analyze theoretical simulation techniques used for device performance testing. Finally, we summarize the integrated systems that have been successfully incorporated with ZMSDs. We hope this review garners further attention in this field and lays a solid foundation for the large-scale application of miniaturized devices.

FABRICATION OF Zn-BASED MICROELECTRODES

Developing ZMSDs with high theoretical capacity and safety is essential, particularly for meeting diverse requirements through tailor-made structural designs. The design of electrode structures is a critical aspect in ensuring the efficient and stable operation of Zn-based micro-devices. A key solution to this challenge lies in designing appropriate electrode structures that exhibit superior electrochemical performance. For instance, transitioning from traditional battery structures to a 2D interdigitated microelectrode architecture represents an effective optimization strategy [7,38]. Such microstructures, devoid of a separator between the anode and cathode, permit multidirectional ion diffusion. By minimizing the width or gap between the interdigitated electrodes and increasing their thickness within a planar, interlaced battery structure, the areal energy density can also be improved [39]. This is achievable as the interwoven anode and cathode design ensures uniform ion diffusion pathways. In simple terms, the planar interdigitated structure of the battery can be effectively

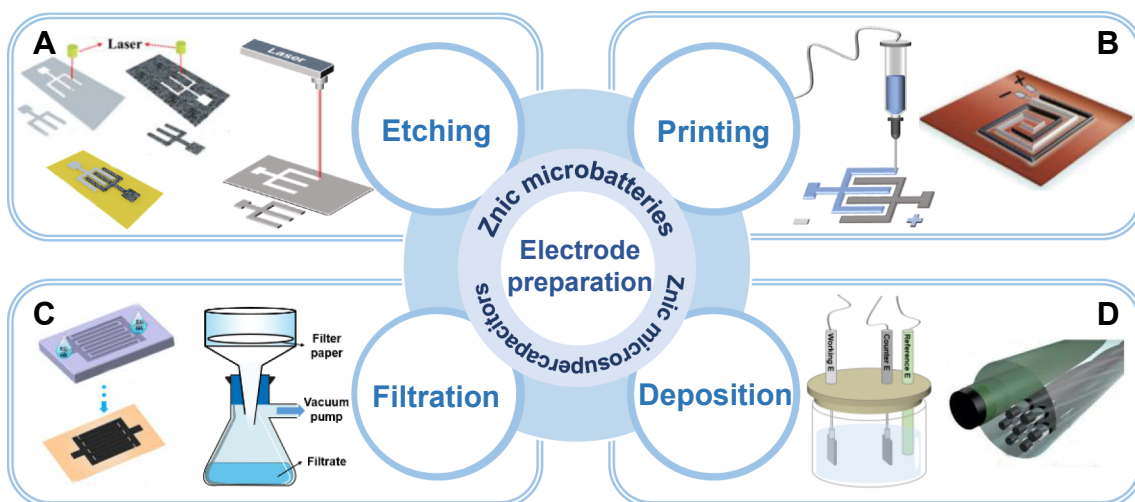


Figure 2 Several major fabrication techniques for Zn microelectrodes. (A) Etching, (B) printing, (C) filtration, (D) deposition.

leveraged to decouple the areal energy density and power density of micro-devices [9,40]. In addition to the interdigitated microelectrodes, there are traditional sandwich-type, compact Swiss roll-type with minimal footprint, and highly flexible fibrous-type microelectrodes designed to meet market demands. Every microelectrode should be developed towards miniaturization, enhanced safety, and mass production capabilities.

The preparation of microelectrodes should simultaneously meet the criteria of high precision and efficiency, requiring a balance between high-performance electrode manufacturing and mass production. Current research primarily focuses on techniques such as etching (including laser etching, photolithography, chemical etching), printing (such as inkjet printing, template printing, photopolymerization printing), vacuum filtration, and deposition (electrodeposition, vapor deposition, laser pulse deposition). These technologies enable the efficient fabrication of ZMSDs (Figure 2). The following is a systematic review of the fabrication of high-performance microelectrodes.

Etching technique

The miniaturization of energy storage devices poses a significant challenge due to the small size of their electrodes. Among various etching techniques, laser etching has gained widespread use, while a smaller number of researchers have opted for photolithography and chemical etching processes. The principle of etching technology involves selectively etching or stripping the target material. For example, laser etching works by high-energy lasers to burn, melt, or vaporize the target material, achieving patterned effects. In practical applications, researchers typically convert the electrode pattern to be etched into digital signals using a computer. These signals are inputted into a control card, which processes and converts them into electrical signals. This, in turn, controls the laser beam for etching purposes. Some microelectrodes require the inclusion of current collectors to facilitate electron transport [41,42]. Etching methods can be employed to construct microelectrodes with various morphologies incorporating current collectors, including coplanar interdigitated and Swiss-roll types.

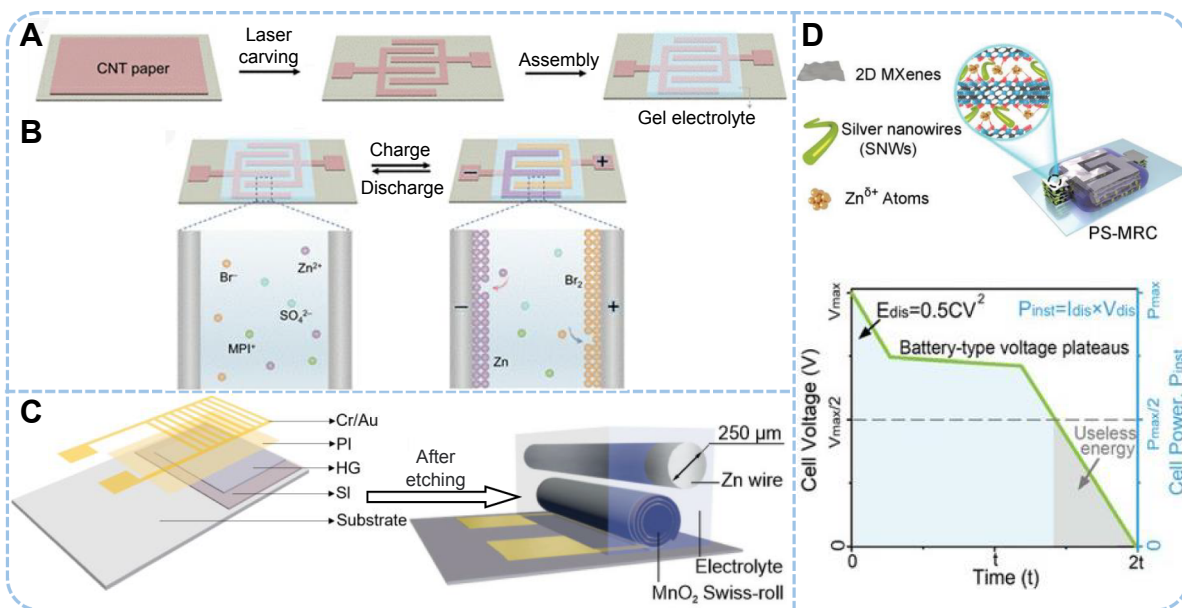


Figure 3 Microelectrodes fabricated by etching techniques. (A) The fabrication process of the Zn-Br₂ microbatteries and (B) *in situ* construction of Br₂ cathode and Zn anode during the charging process [43]. (C) Schematically illustration of the fabrication of the MnO₂ Swiss-roll microelectrode and MnO₂ Swiss-roll-based microbattery [50]. (D) Schematic diagram of a ZMSC after interlayer Zn²⁺ atomic injection and the incorporation of battery-type voltage plateau [60]. Reproduced with permission.

Given the limited assembly space in ZMBs, maximizing the energy density within this constrained volume is crucial. This can be achieved fully utilizing the active sites in the electrodes, thereby effectively enhancing the energy density of ZMBs. During the battery charging/discharging process, directly depositing/stripping ions from the electrolyte onto the current collector maximizes the utilization rate of the reactive active sites in the electrodes. Dai *et al.* [43] utilized laser etching to cut carbon nanotube paper into interdigitated shapes for use as anode and cathode current collectors (Figure 3A and B). By employing an electrolyte containing Zn²⁺ and Br⁻, energy storage was achieved through the deposition of Zn and Br₂ on the two carbon nanotube collectors during the charging process. Similarly, hydrophilic carbon nanotube paper rich in oxygen functional groups, obtained through laser etching, was used to create interdigitated cathode current collectors for Zn/I₂ microbatteries [44]. In another example, Liu *et al.* [45] grew Ni three-dimensional (3D) nanocones on interdigitated Au conductive layers obtained through laser etching to prepare Au-Ni current collectors. Subsequent deposition of MnO₂ and Zn as anode and cathode active materials significantly increased the contact area between the electrode and electrolyte, greatly enhancing the electrochemical performance of the device. Similar alloy interdigitated current collectors have also been used in the fabrication of ZMBs [46]. Moreover, hydroxide nanosheet arrays grown on carbon cloth or nickel-plated fibers, transformed into interdigitated microelectrodes through laser etching, allowed for full utilization of the reactive active sites within the electrodes. The fabrication of microelectrodes can also be achieved using solely laser technology [47–49].

Also, Qu *et al.* [50] have proposed a Swiss-roll battery fabrication technique (Figure 3C). They initially used photolithography on a substrate to construct a sacrificial layer, an expandable hydrogel layer, a non-expandable polyimide layer, and a current collector. By chemically etching away the sacrificial layer, a certain stress release is induced, causing the electrodes to curl into a cylinder resembling a Swiss roll.

Subsequently, Polyimide-MnO₂ is filled into the gaps of the Swiss roll, resulting in Swiss-roll-shaped microelectrodes. This fabrication method significantly reduces the footprint of micro-energy storage devices under microscale conditions and shows promising prospects in the field of micro-energy storage device fabrication. Similarly, this method can be adapted to construct coiled-core current collectors for ZMB fabrication [51].

Some ZMBs employ electrodes composed of active materials and highly conductive nanomaterials, eliminating the need for an internal current collector to assist in electrical conduction. Wu *et al.* [52] have fabricated interdigitated microelectrodes by laser etching a composite film of MnO₂, Ag, and CNTs, all at the nanoscale. The electrodes possess an intrinsic electronic transmission network and can be directly used in ZMB assembly. The presence of MnO₂ and Ag provides ZMBs with two discharge plateaus. Additionally, MXene materials, known for their excellent electrochemical performance and unique structure, confer high conductivity and a certain energy storage capacity [53,54]. By combining them with battery materials to create interdigitated electrodes, exceptional electrochemical performance is achieved without the need for an external current collector. For instance, Feng *et al.* [55] used laser etching on MXene-Zn and MXene-VS₂ mixed films to create cathode and anode interdigitated electrodes, showing excellent ion transport and electron diffusion rates. In another example, Zhao *et al.* [56] fabricated interdigitated electrodes from laser-etched MXene-TiS₂ films for use as anodes. The unique intercalation/extraction storage mechanism of zinc ions in the anode avoids the detrimental effects of zinc deposition on the metal zinc anode surface on battery performance.

In recent years, ZMSCs have gained widespread attention due to their low cost, environmental friendliness, and ease of manufacture. The low-cost advantage of carbon materials has led to their extensive use in capacitor manufacturing [57]. While conventional graphite electrodes have limited capacitance, Zhao *et al.* [58] enhanced the capacity of graphene-based MSCs by introducing graphene quantum dots on the surface of graphite paper. These graphene quantum dots, once added to the surface of graphite paper, facilitate the creation of interdigitated microelectrodes through laser etching. The incorporation of graphene quantum dots significantly enhances the energy density of ZMSDs. Besides carbon materials, highly conductive MXene is also suitable for the fabrication of ZMSCs [59]. For instance, silver nanowires are inserted between MXene nanosheets to prevent their stacking. Microelectrodes fabricated using laser etching on this material base exhibit excellent ion and electron transport efficiency. The presence of silver nanowires not only prevents the stacking of MXene nanosheets but also facilitates the redox reaction of Ag/AgCl (Figure 3D). This synergistic effect enhances the areal energy density of the device [60]. Similarly, BC@PPY (bacterial cellulose@polypyrrole) can be inserted between MXene layers, or bacterial cellulose and silver nanowires can be integrated into MXene layers to optimize their electrochemical properties [61,62]. Besides preventing the stacking of MXene nanosheets to enhance their electrochemical performance, microelectrodes constructed from ZnCl₂-modified MXene material can significantly improve the specific capacitance of ZMSCs [63]. Additionally, interdigitated MXene-based microelectrodes fabricated using laser etching technology, when annealed in an argon atmosphere, demonstrate a substantially extended lifespan [64].

Compared to film electrodes, 3D porous foam interdigitated electrodes offer a larger specific surface area, better facilitating their electrochemical performance. However, traditional 3D porous electrodes often sacrifice mass density in pursuit of high porosity, making it difficult to meet energy storage needs in confined spaces. To address this issue, Zhang *et al.* [65] used a hydrazine vapor-induced reduction method to simply

adjust the content of oxygen functional groups in MXene/GO films. Based on this, laser etching technology can be used to construct scalable, multifunctional ZMSCs. Additionally, laser-engraved graphene oxide-aramid nanofiber foam can be employed in the manufacture of ZMSCs [66].

Although etching techniques such as photolithography, laser etching, and chemical etching have been widely applied in ZMSDs, each method has its limitations. In photolithography, the high cost of lithography equipment is a bottleneck impeding further development. Compared to photolithography, laser engraving equipment offers more variety and is more cost-effective. However, in the process of microelectrode fabrication, if the laser power is too low or the target material too thick, it can result in unsuccessful microelectrode formation, thus limiting energy density. Moreover, chemical etching has a relatively narrow range of applicability. In the future, we should fully leverage the advantages of each etching technique to fabricate high-performance microelectrodes.

Printing technique

Due to its high controllability, flexibility, and production efficiency, printing has been widely used in the fabrication of micro-devices. Ink writing 3D printing (IW3P), template printing, and photopolymerization 3D printing are three common techniques. In the manufacturing of ZMSDs, printing processes are expected to become an integral part.

To successfully utilize IW3P for electrode fabrication, a thorough understanding of the impact of active materials, binders, solvents, and dispersants on ink rheology is essential. Additionally, two aspects must be considered: First, the printing ink must have high viscosity and plasticity. Without sufficient plasticity, successful electrode printing cannot be achieved. Second, measures must be taken to prevent the electrodes from deforming or cracking after drying. In this regard, Liu *et al.* [67] fabricated a zinc-air microbattery with an ultra-high areal energy density using IW3P. This storage mechanism differs from the traditional cathode intercalation/deintercalation in ZMBs. During charging, oxygen is catalyzed by the cathode electrode material and reacts with water in the electrolyte to produce OH⁻. This reacts with zinc powder to form Zn(OH)₄²⁻ thereby achieving energy storage. This printed zinc-air microbattery achieves an areal capacity of up to 71.1 mA h cm⁻². Similarly, Ren *et al.* [68] also created CNT@MnO₂//Zn microbatteries with a more complex pattern, and the battery exhibited good flexibility. With IW3P, CaVO//Zn [69] and V₂O₅//Zn microbatteries [70] have been constructed and demonstrated. However, electrodes prepared using IW3P often face the issue of cracking upon drying, making integration with complex-shaped electronic devices challenging. To address this, Ahn *et al.* [71] proposed a non-planar 3D printing technique based on IW3P (Figure 4A and B). They adjusted the viscosity and plasticity of electrode ink to enable printing on any curved substrate to create specific microelectrodes. Based on these electrodes, ZMBs can be seamlessly integrated with complex 3D objects. These ZMBs exhibit a high fill factor, avoiding unnecessary space waste and ensuring high energy density of the batteries.

Template printing, due to its simple equipment structure and low cost, is widely used in the field of ZMSDs. Screen printing is the most representative of these techniques. It involves pouring pre-mixed battery electrode ink into a screen with a pre-designed electrode pattern. A squeegee is then used to apply force to the ink on the screen and move it to the other end, pressing the ink through the patterned area onto the substrate. Wu's group [72] was the first to propose the fabrication of planar ZMBs using screen printing (Figure 4C).

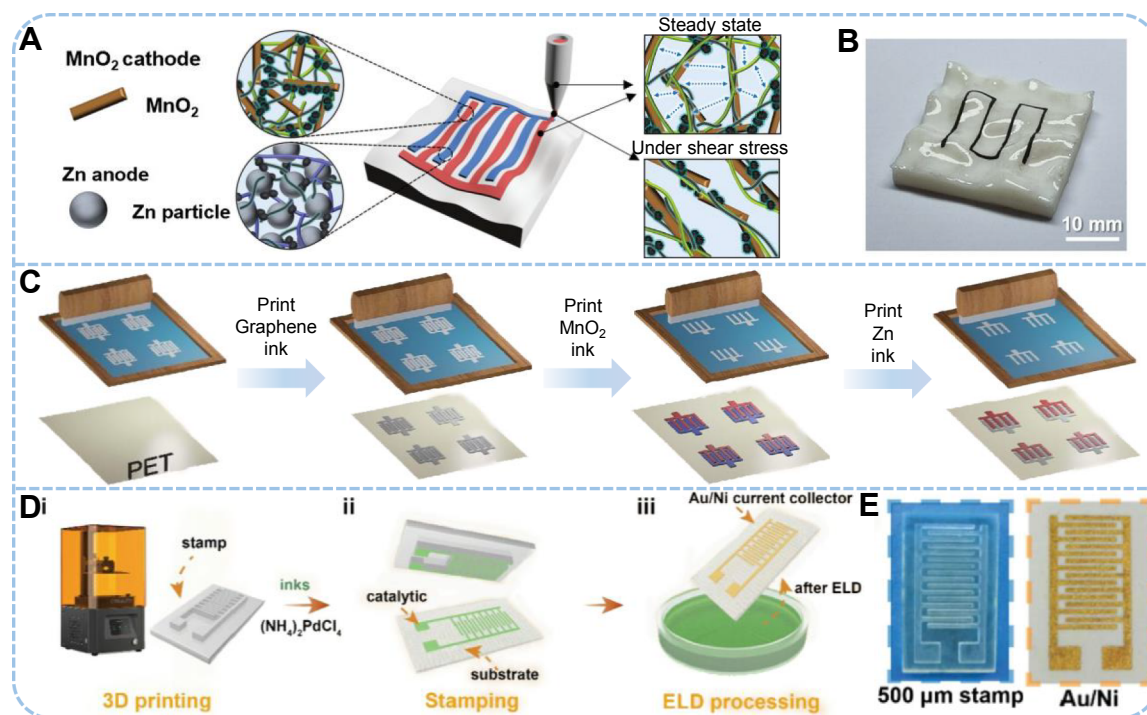


Figure 4 Microelectrodes fabricated by printing techniques. (A) Schematic illustration of the nonplanar 3D-printed electrode and (B) photographs of the nonplanar 3D-printed cathodes on 3D substrates [71]. (C) Schematic of screen-printing fabrication of printed Zn//MnO₂ microbatteries [72]. (D) Fabrication process of 2D metal patterns transformed from 3D printed stamp and (E) images of 500 μm stamp, Ni patterns on paper, and Au/Ni patterns on paper [78]. Reproduced with permission.

Zinc ink and manganese dioxide ink were used as anode and cathode materials, respectively, to create interdigitated electrodes through screen printing. The highly conductive graphene in the ink replaces traditional metal current collectors, providing high electron transfer efficiency in the electrodes. In addition, by introducing an affinity interlayer to enhance interface bonding, microelectrodes with ultra-high mass loading of Ce-MnO₂ (24.12 mg cm⁻²) and good mechanical stability can be fabricated [73]. The affinity interlayer composed of hydrophilic CNT-OH and hydrophobic carbon black can adjust the adhesion between the polyethylene terephthalate (PET) substrate and the active material layer, thus enabling the printing of high-loading electrodes.

Apart from screen printing, other printing methods have also been used in microelectrode preparation. Jiang *et al.* [74] used the Silhouette Cameo technique to create self-adhesive paper stencils for fabricating Zn//MnS MBs. They carved interdigitated electrode patterns on self-adhesive paper and adhered this paper onto a PET substrate as a stencil. The conductive silver paste was then spread over the PET substrate through the stencil to serve as the current collector, with MnS and Zn coated on top as the anode and cathode active materials, respectively. This fabrication method is highly flexible, allowing for the design of ZMBs of any shape and on various substrates, providing a practical approach to the design of ZMSDs. In addition, MXenes materials are widely used in the fabrication of ZMSCs using stencil printing technology. For instance, to fabricate Zn//V₃CrC₃T_x supercapacitors [75], (NH₄)₂PDCl₄ ink was spread through a stencil to create interdigitated electrode patterns, followed by chemical deposition to form Au and Ni current collectors. Subsequently, active materials were loaded onto the collectors and covered with a gel electrolyte. Moreover,

inserting certain molecules between the layers of MXene can effectively enhance the electrochemical performance of printed ZMSCs [76,77].

Photopolymerization printing can be used to create auxiliary units for the fabrication of microelectrodes. Wang *et al.* [78] proposed a method combining photopolymerization printing with imprinting to achieve high-precision microelectrodes with a minimum inter-electrode distance of 300 μm . Initially, a mold of the interdigitated electrode shape, made using a photopolymerization printer, was used to imprint ink containing $(\text{NH}_4)_2\text{PdCl}_4$ onto a flexible substrate. Chemical deposition was then employed to obtain Au/Ni current collectors, and finally, anode and cathode materials were deposited onto the collectors (Figure 4D and E). This fabrication process is characterized by its simplicity, speed, low cost, and excellent performance. Through mold transfer techniques, conductive substrates were prepared utilizing photopolymerization printing. Subsequent deposition of anode and cathode active materials on these conductive substrates enabled the fabrication of microelectrodes [79].

Printing technology is characterized by its versatility in patterns, flexible choice of electrode materials, capability to fabricate thick electrodes, ease of scaling up, and high precision. However, it also has certain drawbacks. For IW3P and template printing, both methods have stringent requirements for ink quality. In large-scale production, ink must be meticulously formulated to ensure printability. If the ink specifications do not meet the standards, it can result in significant material waste. Additionally, in terms of photopolymerization printing, most existing electrode fabrication methods are suitable only for laboratory-scale production and are still far from industrialization.

Filtration technique

Vacuum filtration involves placing a solid-liquid mixture into a funnel, which is separated from a beaker by filter paper. The liquid is forced into the beaker by the negative pressure created between the external atmospheric pressure and a vacuum pump, achieving solid-liquid separation. Microelectrodes prepared using vacuum filtration technology generally have a thin thickness, thus exhibiting high flexibility.

2D nanosheet materials are prone to aggregation during drying. Using vacuum filtration technology to directly form microelectrodes from their dispersions effectively avoids this issue. Heterostructures of V_2O_5 grown on graphene nanosheets have been adopted to fabricate ZMBs with vacuum filtration. The ZMBs exhibit a high capacity of up to 20 mA h cm^{-3} at 1 mA cm^{-2} [80]. Similarly, interdigitated electrodes consisting of inserted CNTs between the layers of V_2O_5 nanoribbons have been prepared using vacuum filtration (Figure 5A and B) [81]. Additionally, nanosheets grown with mesoporous polyaniline on graphene, characterized by high surface area, high conductivity, and abundant active sites, can also be employed in the fabrication of ZMBs using vacuum filtration [82]. Vacuum filtration is particularly interesting for making capacitor electrodes, which are mainly composed of carbon materials [83]. By vacuum filtration, symmetric interdigitated electrodes based on graphene can be obtained (Figure 5C–E) [84]. Introducing a high concentration of hydrated salt electrolyte ($15 \text{ mol L}^{-1} \text{ ZnCl}_2 + 1 \text{ mol L}^{-1} \text{ ZnI}_2$) to assemble with the microelectrodes resulted in a zinc-ion micro-supercapacitor. Unlike traditional capacitors, the electrolyte provides two redox pairs (I^-/I_2 and Zn/Zn^{2+}), thereby endowing the device with higher energy density.

Vacuum filtration is quite simple and cost-effective, but it suffers from several constraints. First, there is a significant reduction in the choice of electrode materials. Second, the overall preparation process is relatively

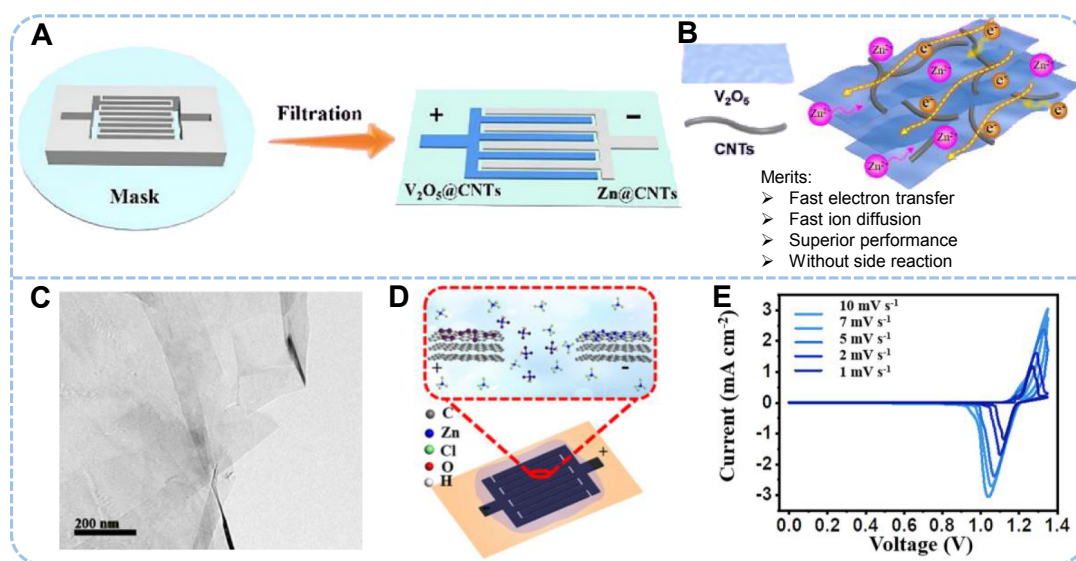


Figure 5 Microelectrodes fabricated by filtration techniques. (A) The illustration for preparation process of ZMBs and (B) schematic illustration of Zn^{2+} and electron fast transfer [81]. (C) Transmission electron microscopy (TEM) image of EG microelectrodes and (D) schematic of ZMSCs with hydrogel electrolyte, (E) CV curves from 1 to 10 $mV s^{-1}$ of ZMSCs [84]. Reproduced with permission.

cumbersome, which is not conducive to industrial application. These limitations hinder the broad implementation of vacuum filtration in large-scale manufacturing, particularly in sectors where diverse material requirements and rapid, streamlined production are critical.

Deposition technique

Currently, deposition techniques such as electrodeposition, chemical vapor deposition (CVD), and laser pulse deposition have been employed in the fabrication of microelectrodes.

Electrodeposition directly onto conductive substrates to grow active materials is a technique used in the fabrication of microelectrodes. When constructing microelectrodes using electrodeposition, the conductive substrate must have sufficient specific surface area to ensure ample active sites, thereby achieving high areal specific capacity and efficient electron/ion transfer rates. As shown in Figure 6A–C, Yang *et al.* [85] first electrodeposited a 3D porous conductive nickel base, then loaded active materials using the same technique. The 3D porous structure provided numerous attachment points for the active material, facilitating high areal loading of PEDOT-MnO₂. The resulting ZMBs exhibited an areal capacity of 0.78 $mA h cm^{-2}$. Similarly, in alkaline rechargeable Ni//Zn microbatteries [86], interconnected nanoporous nickel obtained through electrodeposition effectively enhanced the electrode's reaction sites. Additionally, the introduction of inactive Zn(OH)₂ greatly alleviated structural deformation during proton intercalation/extraction processes, endowing the Ni//Zn microbatteries with ultra-long cycle life. Electrodeposition can also be applied to the fabrication of highly flexible fiber-type microelectrodes. Zhai *et al.* [87] used this technique to deposit Zn on carbon fibers as the anode and PANI on polymer substrates as the cathode. The fiber-shaped anodes and cathodes exhibited ultra-high flexibility. Additionally, they introduced a carbon layer on the Zn anode surface, which suppressed the formation of zinc dendrites by homogenizing the anode surface electric field and providing abundant nucleation sites (Figure 6D). Similarly, MnO₂ or PANI can be electrodeposited on conductive fibers for the

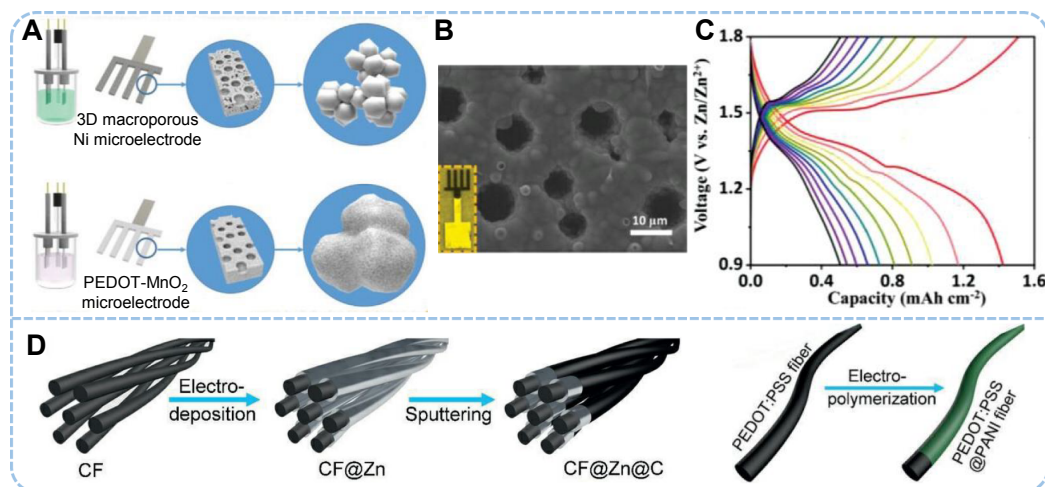


Figure 6 Microelectrodes fabricated by deposition techniques. (A) Schematic illustration of the fabrication processes of 3D macroporous Ni microelectrodes and PEDOT-MnO₂ microelectrodes. (B) Scanning electron microscopy (SEM) image of 3D macroporous Ni frame microelectrode. (C) Electrochemical performance of PEDOT-MnO₂ microelectrodes [85]. (D) Schematic illustration of the fabrication process of various fibers [87]. Reproduced with permission.

fabrication of fiber-type ZMBs [88,89]. Furthermore, Lv *et al.* [90] have utilized electrodeposition to assist in fabricating sandwich-type Ni//Zn microbatteries.

CVD is also a promising technology applied in the fabrication of microelectrodes. Wang *et al.* [91] have combined CVD with electrodeposition to create fibrous microelectrodes. Initially, carbon nanotube fibers are prepared using the CVD method, followed by the growth of nickel-cobalt bimetallic phosphide on the CNT fibers through electrodeposition. This structure features multi-level microcracks at the macro scale and a nanoflower morphology at the microscale, enhancing electrolyte permeation and providing abundant active sites. Additionally, vertically aligned graphene films produced via CVD exhibit a large specific surface area [92], strengthening the adhesion between the cathodic active material and the current collector, and facilitating uniform zinc deposition/stripping on the anode. In sandwich-type ZMBs, deposition techniques are extensively utilized. For instance, Trócoli *et al.* [93] have employed laser pulse deposition technology to fabricate thin-film electrodes.

Although ZMSCs, assembled with MXene cathodes and Zn anodes, have demonstrated excellent performance, there is still considerable room for improvement. Huang *et al.* [94] developed a ZMSC with a broad voltage window (1.60 V) using V₂CT_x as the cathode and Ti₃C₂T_x as the anode. They deposited V₂CT_x or Ti₃C₂T_x active materials on graphite-based interdigitated current collectors. Thanks to the unique structure of MXene, the ZMSC achieved rapid ion and electron transfer kinetics, displaying superior rate capability compared to the MXene/Zn system. Furthermore, ZMSCs fabricated by pairing battery-type cathode materials with MXene anode materials have demonstrated outstanding electrochemical performance. V₂O₅ and MXene materials were electrodeposited separately on graphite-based interdigitated current collectors. The ZMSC constructed on these electrode materials exhibited a stable operating voltage window of up to 1.65 V [95].

Although these deposition techniques have been applied in electrode fabrication, they all exhibit certain deficiencies. The commonly applied electrochemical deposition method is hampered by the complexity of the equipment, the necessity for multiple electrode assistance, and its dependency on the electrolyte and the

structure of the deposition material. The CVD method, while effective, struggles with issues like slow growth rates, uncontrollable environmental factors, and severe environmental pollution, making it less favorable for industrial applications. The major shortcoming of the laser pulse deposition technique lies in the non-uniform thickness of the resultant films.

The main advantages and disadvantages of the four techniques can be briefly outlined as follows. The printing technology is promising for electrode fabrication, offering material flexibility and reducing waste. In particular, 3D printing excels in microbattery production, enabling the creation of custom-designed batteries. However, printing is still on the way to the market because of cost and availability. Therefore, the development of cost-effective and commercially available 3D printing equipment would be crucial for advancing the production of microbatteries. In the realm of etching technologies, laser engraving, a key player in etching technologies, shows significant commercial promise, offering high precision crucial for microbattery manufacturing, despite a narrower material range than printing technologies. Its versatility extends beyond microelectrode preparation to cutting and other battery assembly processes. Nonetheless, access to etching facilities such as a laser is not always possible. On the other hand, the filtration technique, compared to printing and engraving, faces notable disadvantages in complex equipment and lower production efficiency. Its move towards commercial application is challenged by the need for high-efficiency production and the difficulty in constructing large-scale equipment. Finally, the deposition technology faces high costs and lower efficiency, making it less suitable for mass production and impacting product consistency, which are significant barriers to its commercialization. Addressing these challenges is essential to enhance its practical application competitiveness.

THEORETICAL SIMULATION ON Zn-BASED MICROELECTRODES

The primary objective for zinc-based micro-devices is to facilitate their versatile integration into daily life. Yet, the pursuit of outstanding mechanical stability, coupled with high energy density and electrochemical stability, presents a formidable challenge. While theoretical frameworks can guide the structural design of these devices, there often exists a substantial discrepancy between expected and actual performance, underscoring the importance of narrowing this gap. Experimentation to validate design results is typically resource-intensive, consuming significant amounts of time and effort. Consequently, the application of theoretical simulations emerges as a highly efficient strategy to optimize resource use [96,97].

For over fifty years, finite element analysis (FEA) has served as a versatile analysis and simulation tool. Its multi-scale modeling approach has accurately depicted a range of mechanical challenges encountered by devices under the influence of multi-field interactions. In the realm of micro-devices, finite element simulations enable the analysis of the device and its adaptability in terms of flexibility, including capabilities like bending, stretching, extending, and wrapping. Drawing inspiration from human joints, a lithium-based energy storage device was devised with a novel structure that emulates the joint surfaces and ligaments of the human body, conferring significant flexibility to the battery. Using FEA, the plastic deformation capabilities of the device were analyzed. The findings revealed that the maximum stress experienced by these areas under both bending and twisting deformations was less than their yield stress. This suggests that the structure of the micro-device maintains excellent flexibility and durability, avoiding plastic deformation under diverse forms

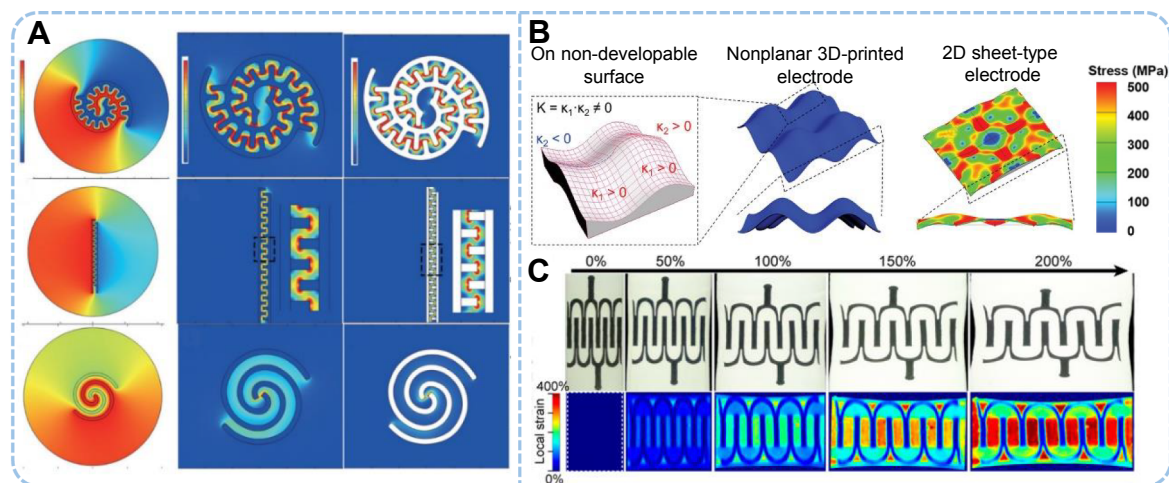


Figure 7 Theoretical simulation on Zn microelectrodes. (A) The simulations of potential, electric field distribution, and energy distribution of (top) concentric circle structured, (middle) straight interdigital, and (down) circular Zn-PANI microbatteries [79]. (B) FEA of a nonplanar 3D-printed electrode and a conventional 2D sheet-type electrode on non-developable surfaces. The left scheme depicts the non-developable surface with non-zero Gaussian curvature [71]. (C) Optical images (up) and corresponding strain maps in the stretching direction (down) of an interdigitated current collector under different global tensile strains. The contour of the current collector at 0% strain is shown in the dashed line [101]. Reproduced with permission.

of deformation [98]. Therefore, employing this simulation yields reliable experimental data, resulting in considerable cost savings.

Energy distribution

Simulations enable insights into the interplay between microelectrode structures and energy distribution within batteries, a crucial determinant of electrochemical performance. In a typical case, Li *et al.* [79] have innovated a concentric circle structure for ZMBs and conducted theoretical analyses of this structure with COMSOL (Figure 7A). The results illustrated a more homogeneous potential distribution within the concentric circle structure, in contrast to two-dimensional interdigitated and annular structures. Their simulations of energy distribution, where a color gradient from blue to red denotes increasing energy density, revealed that the concentric circle structure encompasses a larger high-energy region, implying a greater abundance of reactive active sites. Likewise, through simulation computations, Wang *et al.* [48] have determined the distribution of current density and electric potential in the electrolyte. The findings highlight the merits of the proposed structure, which proficiently suppresses the formation of zinc dendrites and promotes more uniform energy distribution within the cell. Also, Liu *et al.* [77] conducted an analysis of a ZMSC using the Ansys software. Their observations of uniform energy distribution and effective charge transfer phenomena underscore the superior electrochemical performance of designed devices.

Mechanical properties

Simulations focused on the mechanical attributes of devices offer a valuable understanding of their mechanical performance. Conventional ZMSDs, characterized by significant rigidity, face challenges in

aligning with intricately shaped electronic devices. Ahn *et al.* [71] utilized FEA to examine the stress distribution when electrodes are matched with substrates. In their curved surface model (Figure 7B), “ K ” denotes Gaussian curvature, with K_1 and K_2 representing two orthogonal principal curvatures, essential for ascertaining the smoothness of a three-dimensional surface. The finite element simulation indicated that curved printed electrodes endured almost negligible stress. Conversely, the alignment of two-dimensional planar electrodes with curved bases resulted in high stress at certain points, nearing 500 MPa, potentially leading to irreversible damage to the electrodes in practical scenarios. To cater to the flexibility demands of wearable electronics, Cheng *et al.* [61] developed a stretchable “island-bridge” structured device, facilitating the serial connection of three ZMBs. Employing the ABAQUS software, they examined the stress distribution of the device at 200% and 400% extension. The design proved effective in stress dissipation. During a 200% extension, the primary strain localized in the interconnect bridges devoid of ZMBs ($\epsilon_{\max} = 187\%$), with a minimal strain impact on the ZMB-inclusive segments ($\epsilon_{\max} = 19.9\%$), thereby preserving mechanical stability of the ZMB under device stretching.

Verification of simulation results

To verify the validity of the simulation result, a digital image correlation (DIC) technology has been developed in recent years [99,100]. This is a non-contact optical testing technique, allowing for the measurement of morphology, displacement, vibration, and deformation of any material without direct contact. The core principle of this method is to match the positions of identical pixel points in the speckle images of an object before and after its deformation. By determining the pixel displacement vector, this process can assess the total displacement of the object after deformation. DIC can perform various strain tests like stretching, twisting, and bending in micro-energy devices, and can be juxtaposed with results from FEA for experimental verification. For instance, Bai *et al.* [101] employed DIC to obtain strain images of stretchable ZMBs (Figure 7C). The investigation elucidated the strain behavior under stretching conditions. A sequence of optical images showcased the extent of deformation of a cross collector subjected to various levels of uniaxial stretching. The system exhibited stability at a strain of 200%, with local strain in the interdigitated electrodes demonstrating effective containment. Under a global strain of 200%, the strain in the interdigitated areas was limited to 47%. This phenomenon is attributed to the stretching load being predominantly absorbed by the expansion of the substrate at interspersed gaps.

ELECTROLYTE SELECTION AND DEVICE ASSEMBLY

Electrolyte selection and infiltration are equally pivotal in ZMSDs. Micro-devices composed of liquid electrolytes and microelectrodes frequently encounter challenges like electrolyte evaporation and leakage, impeding their practical use. Solid electrolytes, while remedying these issues, suffer from inferior conductivity and a current lack of comprehensive research on zinc-ion solid electrolytes globally, affecting their viability. Quasi-solid-state electrolytes have become extensively applied in ZMSDs, marrying the ionic conductivity akin to liquid electrolytes with the structural stability of solid-state versions. This ensures their compatibility with micro-energy storage devices, facilitating stable operation and superior electrochemical

performance. Moreover, traditional electrolytes mainly offer a basic physical framework for ion transport, making the exploration of functional electrolytes in ZMSDs of paramount scientific and applied importance [102,103].

Integrating quasi-solid-state electrolytes into ZMSCs primarily faces challenges due to their high viscosity and poor adhesion to microelectrodes. Design and fabrication must consider the electrolyte's wettability and adhesive properties with electrodes. The chemical compatibility of gel electrolytes with electrode materials is crucial to prevent side reactions that affect battery performance. Additionally, the viscosity and surface tension of the gel require careful adjustment to ensure effective wetting and penetration into the porous electrode [104]. The composition of gel electrolytes, consisting mainly of polymers, salts, and solvents, is crucial as variations in their ratios significantly affect wettability on electrode surfaces. Maintaining the right balance is essential for structural integrity and efficient ionic conduction. External factors like temperature and atmospheric pressure also influence wettability, with increased temperature reducing viscosity for better electrode wetting. In general, the porous and organized electrode structure enhances gel penetration, thus improving ion transport and battery performance [105].

At present, a range of polymers are employed for quasi-solid-state electrolytes, including polyvinyl alcohol [106], polyacrylamide [107], cellulose [108], xanthan gum [109], gelatin [110], guar gum [74], and carrageenan [111]. These polymers are first dissolved in liquid electrolytes and then treated to foster cross-linking between molecules, leading to the creation of an electrolyte highly compatible with the majority of microelectrodes. In certain conditions, gel electrolytes necessitate specific treatments to be utilized effectively. For example, for printing quasi-solid-state electrolytes on curved surfaces, gel electrolytes must demonstrate high pliability for successful application on non-level areas. Ahn *et al.* [71] have employed SiO₂ nanoparticles to modulate the rheological properties of gel electrolyte inks, thus facilitating the printing of these composite inks on curved bases. Moreover, some unconventional electrolytes have been developed for ZMSDs. One such example is the immersion of graphene oxide (GO) thin films into a 30 M zinc chloride salt-pack water-electrolyte, enabling activated carbon capacitors to function reliably in an expanded voltage range [112].

Encapsulation materials serving as protective coatings for ZMSDs are crucial for isolating internal sensitive components from the atmosphere, thereby averting the drying of quasi-solid-state electrolytes and potential side reactions. Polymer materials, lauded for their robust mechanical and chemical stability, as well as electrical insulation, find widespread application in these devices. Notable examples include polydimethylsiloxane (PDMS) [113], polyimide (PI) [114], polyurethane (PU) [115], PET [116], and silica gel (SiO₂) [117]. The process of assembling microelectrodes and electrolytes, coupled with the selection of appropriate encapsulation materials for device packaging, culminates in ZMSDs exhibiting diverse performance attributes. Table 1 [9,43,44,52,71–73,79–81,90,118–122] and Table 2 [60–62,64,65,75,94,95,123–126] present the performance features of selected ZMBs and ZMSCs, respectively.

APPLICATIONS AND INTEGRATION

Applications in microsystems

ZMSDs are apt for powering small-scale electronic gadgets. Utilizing non-planar 3D printing technology,

Table 1 Electrochemical performance of various microbatteries

Electrode	Electrolyte	Capacity (mAh cm ⁻²)	Energy density (mWh cm ⁻²)	Powder density (mW cm ⁻²)	Refs.
CNT//CNT	ZnSO ₄ + MPIBr/PAM	2.22	3.65	26.2	[43]
V ₂ O ₅ //Zn	Zn(CF ₃ SO ₃) ₂ /PVA	0.163	0.113	0.193	[81]
MnO ₂ -Ag//Zn	ZnCl ₂ + NH ₄ Cl/PAM	0.809	0.896	1.95	[52]
PANI//Zn	ZnCl ₂ /PVA	0.253	0.25	0.99	[79]
Ni//Zn	KOH + ZnO/PAM	0.723	1.3	328.3	[90]
MnO ₂ //Zn	LiCl+ZnCl ₂ + MnSO ₄ /PVA	7.21	8.43	21.62	[73]
CNT//Zn	ZnSO ₄ + MPPI/PAM	1.93	2.34	7.87 W cm ⁻³	[44]
LFP//LTO	PVDF-HFP/Al ₂ O ₃	1.62	–	–	[118]
LFP//LTO	LiPF ₆ /ETPTA	1.46	–	–	[119]
LNMO//LTO	LiTFSI/MA-PEG500	2.5	6.27	–	[120]
V ₂ O ₅ //Li	LiTFSI/PEO	0.15	–	75.5	[121]
NCA//Si	LiTFSI/PEO+TG	1.8	5.2	–	[9]
Li ₂ S//Li	LIPON	0.02	–	–	[122]
MnO ₂ //Zn	ZnSO ₄ + MnSO ₄ /PAM	36.1 mAh cm ⁻³	50.5 mWh cm ⁻³	–	[71]
MnO ₂ //Zn	ZnSO ₄ + MnSO ₄ /H ₂ O	19.3 mAh cm ⁻³	17.3 mWh cm ⁻³	150 mW cm ⁻³	[72]
V ₂ O ₅ //Zn	ZnSO ₄ /H ₂ O	20 mAh cm ⁻³	21 mWh cm ⁻³	526 mW cm ⁻³	[80]

Table 2 Electrochemical performance of various microsupercapacitors

Electrodes	Electrolyte	Capacitance (mF cm ⁻²)	Energy density (mWh cm ⁻²)	Power density (mW cm ⁻²)	Refs.
MnO ₂ //Ti ₃ C ₂ T _x	Zn(CF ₃ SO ₃) ₂ + MnSO ₄ /PAM	388	0.145	0.36	[61]
Ti ₃ C ₂ T _x //Zn	ZnCl ₂ /PVA	72.0	0.02	0.50	[64]
Ti ₃ C ₂ T _x /Ag/Zn//Ti ₃ C ₂ T _x /Ag	ZnCl ₂ /PAM	–	0.117	0.160	[60]
Ti ₃ C ₂ T _x //V ₂ O ₅	ZnSO ₄ /PAM	129	0.0489	0.673	[95]
V ₂ CT _x //Ti ₃ C ₂ T _x	ZnSO ₄ /PAM	200	0.0716	0.401	[94]
Ti ₃ C ₂ T _x /Ag//Zn	ZnCl ₂ + NH ₄ Cl/PAM	909	0.227	1.41	[62]
Ti ₃ C ₂ T _x /rGO//Zn-Ti ₃ C ₂ T _x /rGO	ZnSO ₄ /gelatin	83.96	0.0213	0.675	[65]
Ti ₃ Al ₂ T _x //V ₂ O ₅ -PANI	ZnSO ₄ + VOSO ₄ /gelatin	584	0.263	2.87	[123]
V ₃ CrC ₃ T _x //Zn	ZnSO ₄ /PVA	492.5	0.0511	5.75	[75]
CoMoO ₄ //AC	LiPF ₆	135.4	0.301	–	[124]
Mn/Mo//Mn/Mo	LiTFSI/PMMA	7.5	0.004	1	[125]
MnO ₂ //VN	LiTFSI/SiO ₂	16.1	0.009	–	[126]

Ahn *et al.* [71] have fabricated ZMBs that conform to the irregular contours of a human ear, demonstrating remarkable spatial efficiency (Figure 8A–C). In series, they can achieve an output voltage of around 3.6 V, enough to illuminate an LED, thereby confirming their suitability for powering devices like hearing aids. Furthermore, embedding ZMBs into textile fabrics allows them to energize wearable electronics. For instance, a trio of serially connected ZMBs can produce a substantial output voltage of 3.589 V [127], ample to power smartwatches, miniature LED displays, and smartphones (Figure 8D). Similarly, other micro-devices can directly power small electronic devices [69,112,128]. Furthermore, aiming to advance the usability of eco-friendly, safe, implantable devices for internal body monitoring, Chen *et al.* [129] have developed the Zn//AC microsupercapacitors. This capacitor, fitting into a standard-sized capsule, is ingestible by humans or animals. Its composition is benign to the body, with certain elements even acting as nutrients to foster growth and enhance tissue metabolism. Such innovation carves a niche for powering devices dedicated to in-body health assessment.

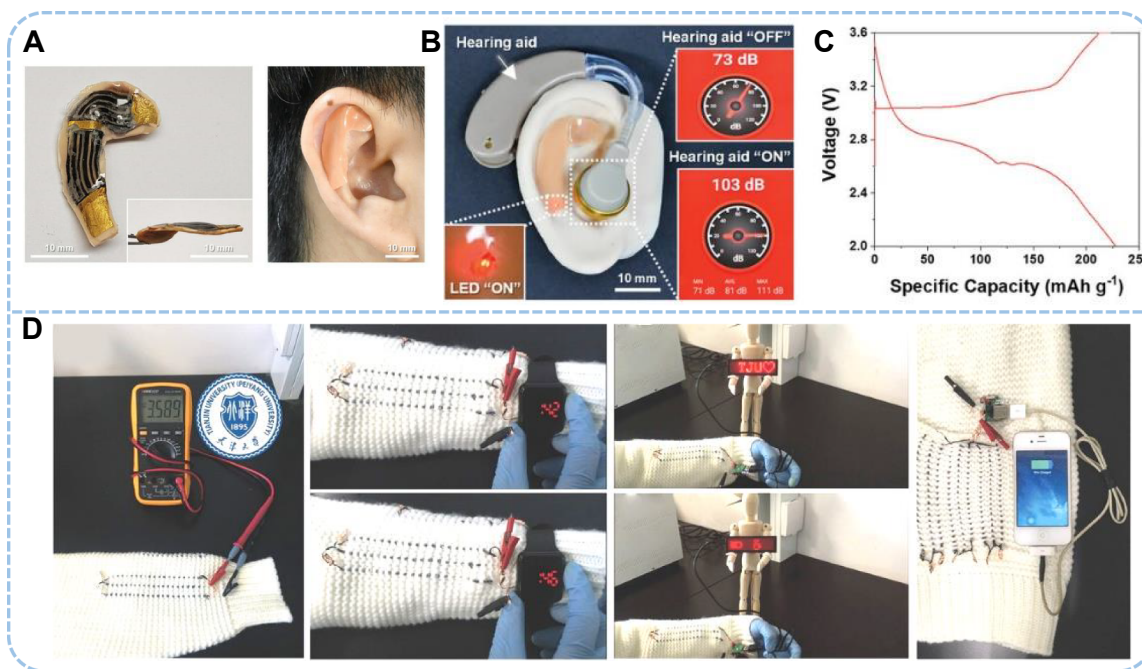


Figure 8 Applications of ZMSDs. (A) Photographs of the ear-shaped conformal ZMBs (left) that were seamlessly unitized with a human ear after being coated with a skin-safe silicone elastomer (right). (B) Photograph of the ear-shaped conformal ZMBs connected to a hearing aid equipped with an LED. Insets show the successful operation of the hearing aid by the conformal ZMBs, which were verified by the activated LED (left) and amplified sound (right). (C) Charge/discharge profiles of the ear-shaped conformal ZMBs (consisting of two unit cells connected in series) [71]. (D) Open-circuit voltage demonstration of a cloth knitted with three ZMBs (15 cm in length) in series, photographs of an LED watch, LED screen, and iPhone 4s powered by the ZMBs [127]. Reproduced with permission.

Integration for microsystems

The rapid development of intelligent microsystems and the Internet of Things is impressive, but micro-energy devices for compatibility with these systems represent a major bottleneck in their advancement. Most micro-systems currently rely on external power, failing to satisfy the demands of highly self-integrated systems. The creation of efficient self-integrated modules is thus a crucial solution. The intermittent nature of natural energy sources poses a significant constraint on their utilization. However, by integrating ZMSDs with energy transducers such as solar cells and nanogenerators, efficient harvesting of natural energy becomes feasible. For example, Bi *et al.* [130] have integrated quasi-solid-state Zn//MnO₂ microbatteries with flexible perovskite solar cells (FPSCs) (Figure 9A–C). Given that the open-circuit voltage of a single FPSC is 1.07 V, they serially connected two FPSCs to achieve the charging voltage required for the ZMBs. Owing to the high energy conversion efficiency of FPSCs, this entire integrated system is capable of completing its charging process within 30 s using solar energy. In addition to solar energy, wind energy represents a pivotal renewable resource. Li *et al.* [131] have developed an integrated system featuring flexible Zn//Ag₂O microbatteries and a wind turbine, effectively transforming wind energy into electrical energy for both collection and storage purposes. This system requires roughly 800 s to reach a charge of 1.8 V and can sustain a power output for about 2500 s under a 0.1 mA discharge current. Moreover, the integration of nanogenerators with ZMBs offers promising possibilities. A device comprising Zn//MnO₂ microbatteries and a triboelectric nanogenerator can store electrical energy generated through friction [132]. They are interconnected via a

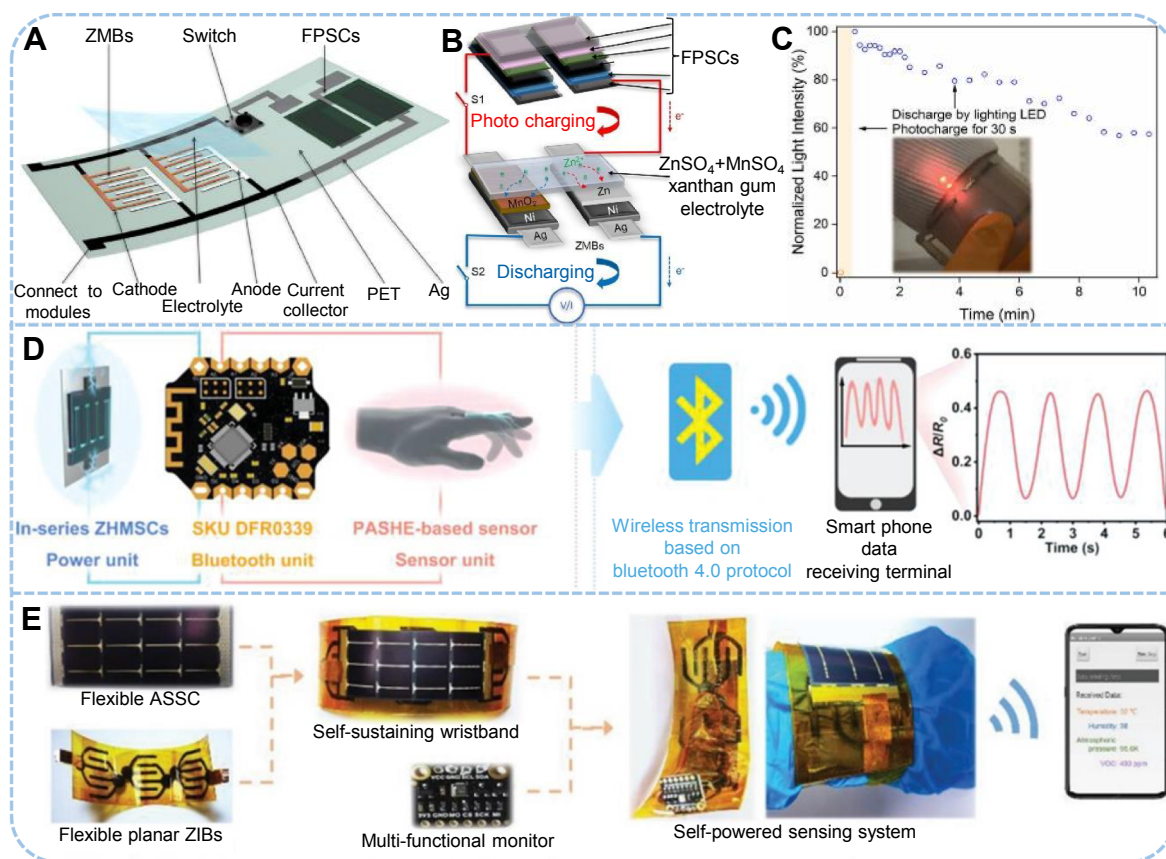


Figure 9 Integration of ZMSDs into microsystems. Schematics of the (A) device configuration and (B) working principle of the integrated flexible photo-rechargeable system. (C) The normalized light intensity of an LED bulb from the integrated flexible wristband powered by 2 series-connected photo-rechargeable devices. 30 s of photocharge followed by 10 min of continuous lighting. The inset shows the photograph of the wristband [130]. (D) The schematic microcircuit and related resistance changes of hydrogel-based sensor [83]. (E) Digital photographs demonstrating the integration process of the self-powered wearable sensing system [73]. Reproduced with permission.

rectifier, enabling the device to charge from finger-induced contact-separation motion on the nanogenerator. Such an integrated device can charge from 0.93 to 1.28 V within 29.65 min, delivering a discharge capacity of 10.9 $\mu\text{A h}$ at a 4 μA current.

Also, devices that combine ZMSDs with electronic components negate the need for external power circuits. For instance, such devices can be integrated with sensors to track health metrics, including finger rehabilitation movements, heart rate, and blood glucose levels. Zhang *et al.* [83] have developed a self-powered integrated system by combining a ZMSC, a Bluetooth module, and a sensor based on a poly-ampholyte synthetic hydrogel (Figure 9D). The strong adhesion of hydrogel enables it to attach to a finger, where finger movements change its resistance, transforming this into wireless electromagnetic signals. The information can then be wirelessly sent to a smartphone via Bluetooth. In a similar vein, Zhao *et al.* [123] have integrated ZMBs with sensors to monitor human health, utilizing images captured by the integrated device to determine arterial stiffness and cardiac health. Furthermore, Zn// MnO_2 ZMBs can be integrated with sensors for tracking human heart rate changes and pulse variations [133]. For blood glucose level detection, Jiang *et al.* [134] have combined a ZMB with a glucose sensor, facilitating swift monitoring of glucose levels. This integrated setup boasts a sensitivity of $464.2 \mu\text{A mM}^{-1} \text{cm}^{-2}$ ($1 \text{ M} = 1 \text{ mol L}^{-1}$), capable

of detecting glucose concentrations in the range of 0.5 to 6.0 mM. Requiring no external support devices for operation, the system only needs a current amplifier in the circuit to display glucose concentrations in a rapid response time of 1.6 s.

Furthermore, by integrating ZMSDs with energy conversion devices and electronic components, a unified system for both energy harvesting and supply is achieved. This system is capable of collecting natural energy, storing it, and transferring it to electronic modules as required. A fabricated integrated system encompasses three primary components: a ZMB, an amorphous silicon solar cell, and a sensor (Figure 9E) [73]. The solar cell harvests solar energy in both outdoor and indoor environments and the energy captured is stored within the ZMB module, which subsequently powers the sensor. This autonomous power-sensing system is capable of monitoring temperature, humidity, atmospheric pressure, and volatile organic compounds in diverse environments. Additionally, the information obtained by the sensors can be sent in real-time to a smartphone via Bluetooth.

SUMMARY AND PERSPECTIVE

In this review, we recapitulate the recent developments in the assembly and applications of ZMSDs. Starting with microelectrode fabrication processes, we explored the construction of high-performance microelectrodes and their basic performance aspects, including etching techniques, printing methods, vacuum filtration, and deposition processes. The summary extends to quasi-solid-state electrolytes and encapsulating materials used for assembling micro-energy devices, alongside enumerating the electrochemical performance of some exemplary micro-devices. Furthermore, we highlighted zinc-based micro-energy devices that have successfully powered devices. Conclusively, we described three types of integrated systems: first, systems combining power generation devices with ZMSDs; second, systems integrating ZMSDs with microelectronic devices; third, systems that incorporate power generation devices, ZMSDs, and microelectronic devices. While ZMSDs are vital as microscale energy storage or power components, substantial challenges still loom in realizing their commercial viability. Here we would like to offer some insights into their further development, as outlined in Figure 10.

Up-scalable production of microelectrodes. Advancing high-performance microelectrode fabrication technologies that are efficient, scalable, and cost-effective is pivotal for propelling zinc-based micro-devices toward commercialization. Choosing high-performance electrode materials for these devices is crucial, alongside implementing strategies to alleviate side reactions. Also, integrating electrodes with properties such as softness, elasticity, or stretchability is key to improving the mechanical properties of devices. In this regard, streamlining the electrode production process is essential for easing industrial manufacturing. Direct application of commercial materials in the construction of ZMSDs presents an effective strategy, greatly reducing the developmental timeline for industrial production lines. In addition, industrial-scale production techniques are necessary. Laser engraving technology, with its high precision and efficiency in microelectrode fabrication, offers substantial commercial potential. Using materials amenable to laser engraving can result in the production of thousands of microelectrodes per minute, achieving micrometer-scale device fabrication [135]. Similarly, inkjet-style 3D printing technology can produce microelectrodes with high precision and is capable of mass production, thus holding promising commercial applicability [136].

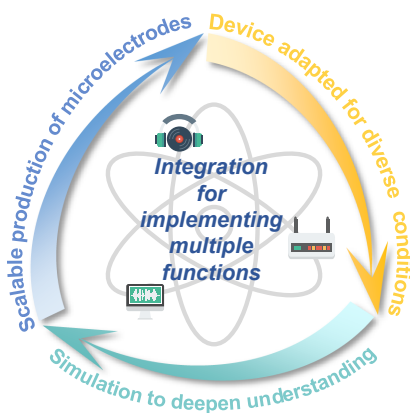


Figure 10 Future research directions for zinc-based energy storage microsystems.

Moreover, the distinct benefits of other fabrication techniques should be fully exploited to meet the diverse needs of microelectrode production.

Devices adapted for diverse environmental conditions. ZMSDs must function reliably under diverse environmental conditions in the future, where electrolytes and encapsulation materials are key. Implementing functional quasi-solid-state electrolytes that enable these devices to operate under extreme temperatures, bending, and other challenging conditions is necessary. Adding solvents like acetonitrile, ethylene glycol, and glycerol to electrolytes can significantly reduce their freezing points, facilitating operation in cold climates. Electrolytes with 1,5-pentanediol can also be used at high temperatures, up to 100°C [137]. Beyond broadening the temperature range with additives, infusing gel electrolytes with zinc trifluoroborate or perchlorate zinc can yield similar benefits [138,139]. Integrating self-healing zinc-ion gel electrolytes in these devices helps address potential electrolyte damage. Moreover, the stability of encapsulation materials is crucial for battery functionality. These materials must not react with battery components and should maintain their integrity without decomposing or altering in various operational environments, effectively isolating the sensitive internals of devices from the external atmosphere.

Theoretical simulation to deepen understanding. FEA is increasingly energetic in the study of micro-scale devices. In specialized microelectrode structures, it complements practical experimentation, which often requires substantial costs, including human and material resources, and presents considerable experimental challenges and low feasibility. FEA provides insights into the effects of changes in electrode structures on their electrochemical performance and mechanical stability. Despite its relative simplicity, there is still a discernible disparity between simulation outcomes and actual results. The advent of sophisticated testing equipment has enabled the testing of certain practical performances. Comparing these test results with simulation data substantially improves the accuracy of the information and conclusions. Thus, the optimal integration of FEA with advanced characterization tools creates a pathway to understanding the interplay between electrode structure and performance, significantly aiding in the design of high-performance microelectrodes.

Integration for implementing multiple functions. The development of high-performance integrated systems containing ZMSDs can significantly broaden the commercial scope of microsystems, enhancing their competitiveness in the market. Although lithium microbatteries have been introduced to the market,

their application is limited in environments that require high safety. The safer, environmentally friendly ZMSDs present wide-ranging new applications, including in the Internet of Things, healthcare, artificial intelligence, and sensor microelectronics. Due to the intermittent nature of renewable energy, its full potential remains untapped. Integrating ZMSDs with energy conversion units allows efficient harvesting of natural energy for daily convenience. For microelectronic devices that still rely on external power, integration with ZMSDs can eliminate the need for external wiring, vastly improving the ease of use of microelectronics. Integrated systems comprising energy converters, ZMSDs, and microelectronics can effectively harness renewable energy, achieving an efficient cycle of energy collection, storage, and usage, especially valuable in settings without external power sources.

ZMSDs offer higher safety and simpler manufacturing processes, and therefore, their further development is of great significance. Additionally, it is important to assemble zinc-based devices with good mechanical stability to enhance their practical lifespan and lay the foundation for their industrial application. While the industrial-scale production of high-performance ZMSDs remains a significant challenge at present, these devices are expected to present numerous commercial opportunities in the coming decades.

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Author contributions

J.N. and L.L. initiated and supervised the project. J.Z., W.H., J.N. and L.L. wrote the manuscript and designed the figures.

Conflict of interest

The authors declare no conflict of interest.

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