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High performance, environmentally benign and integratable Zn//MnO₂ microbatteries

Wenhui Lai,^a Yang Wang,^a Zhanwu Lei,^a Ronghe Wang,^a Ziyin Lin,^b Ching-Ping Wong,^b Feiyu Kang^{a, c} and Cheng Yang*^a

With the explosive development of wearable electronics and Internet of Things (IoT), it is highly desirable to develop miniaturized power sources possessing high performance, low-cost, environmentally benign and integratable characteristics. Rechargeable microbatteries (MBs) can be used as the main power source of the future miniaturized wearable electronics, which have aroused broad attentions recently. However, ever-reported MBs, such as micro-lithium batteries, have intrinsic safety hazards and environmental threats, and are not fully compatible with the green initiative of IoT. Here, we report the aqueous Zn//MnO₂ MBs, with the merits of green, low cost and sustainability. By using a simple and scalable fabrication strategy, Zn//MnO₂ MBs constructed with three-dimensional (3D) MnO₂@nickel nanocone arrays (NCAs) cathode, Zn@NCAs anode, and a mild aqueous electrolyte containing ZnSO4 and MnSO4, can be prepared in large scale. The as-prepared $Zn//MnO_2$ MB reveals a superior capacity of 53.5 μ Ah cm⁻² μ m⁻¹ at 1 C rate and a working voltage of 1.4 V. Moreover, it achieves a superior volumetric energy density of 71.3 μ Wh cm⁻² μ m⁻¹, together with a peak power density of 1621.4 µW cm⁻² µm⁻¹, substantially higher than the reported lithium-ion MBs. Such an ultrathin (74 µm in thickness), lightweight (30 mg per unit) and flexible Zn//MnO₂ MB component can power three pieces of LEDs. Last but not least, the fabrication strategy of our Zn//MnO₂ MBs is fully compatible with the flexible electronics processes. For instance, we demonstrated that these Zn//MnO₂ MBs could share the same fabrication process platform with radio frequency identification (RFID) tags. We envisage that our current technology would accelerate the use of miniaturized power inspire development of intelligent manufacturing technology. sources for IoT applications. and

Introduction

With the rapid development of wearable electronics and Internet of Things (IoT), high performance, environmentally benign, low-cost and integratable micro-power sources are urgently needed.¹⁻⁶ Currently, micro- power sources including microsupercapacitors (MSCs) and microbatteries (MBs) have attracted remarkable attention for their potential applications in the future intelligent bracelets,⁷ environmental monitoring equipment,^{8, 9} miniaturized medical implants devices,¹⁰ radio frequency identification (RFID) tags,¹¹ and skin induction electronic equipment,¹² and so forth. As a component for filtering, bypassing, coupling and fast charging and discharging applications, MSCs have been developed with significant advancements.^{13, 14} However, despite MBs can function as the main power of microsystem due to the high energy density and stable working voltage platform, yet the commercialization of MBs is far from success. On the other hand, with the initiative of

green and sustainable developments, it's critically important to develop scalable, highly safe and environmentally benign MB technologies, so as to cater to the ever-rising IoT market.

To above ends, MBs, which are designed to be integrated into micro-systems, such as micro- lithium-ion batteries have been intensively studied, functioning as the main power sources. $^{\rm 15\text{-}17}$ In order to shorten the transport length and further exploit the active materials, electrodes with well-defined three-dimensional (3D) nanostructure have been proposed; fabrication techniques such as photolithography, 3D printing, magnetron sputtering, electrodeposition etc., have been demonstrated effective in fabricating advanced electrodes with high performances.¹⁻⁴ For instance, Hailong Ning et al. fabricated 3D mesostructured lithium ion MBs based on LiMnO₂ cathodes and NiSn anodes, combining 3D holographic and conventional photolithographies to design and precisely control the architecture of microelectrodes, which showed high energy (6.5 μ Wh cm⁻² μ m⁻¹) and power (3.6 mW cm⁻² μ m⁻¹) densities.³ Even though it shows a theoretically high energy density for lithium ion MBs, there are still rooms to improve their energy density levels, and the ever reported fabrication processes are still complicated and involving hazardous chemicals, which significantly hinder their practical application.^{18, 19} In order to tackle these challenges, it is imperative to develop novel MB technologies, which can enable high energy density, full compatibility with flexible electronic fabrication processes, and eco-friendliness.

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Recently, aqueous rechargeable batteries with neutral pH value have attracted more attentions. Owing to the high ionic conductivity and the intrinsic non-flammability, these batteries may address some critical challenges such as high power and green characteristics, which show great promise in the future MB technology.²⁰⁻²⁵ For instance, Xu et al. reported the basic mechanism of the rechargeable zinc ion aqueous battery.²⁰ Pan et al. demonstrated a highly reversible Zn//MnO2 battery, which is composed of an $\alpha\text{-MnO}_2$ cathode, a zinc anode, and a mild aqueous electrolyte of $ZnSO_4$ and $MnSO_4$.²² In addition, $Zn//MnO_2$ battery based on the earth abundant MnO_2 cathode and Zn anode, has higher theoretical capacity than lithium ion battery.²⁶ Due to the eco-friendliness nature, it can be an excellent motif for the future IoT application. However, most prior studies on Zn//MnO₂ batteries were investigated at coin-cell level, and have rarely been discussed at MB level for micro-system applications.

Recent boom of planar interdigital electrode structure and advanced encapsulation technology gives us inspirations to develop high performance and integratable Zn//MnO₂ MBs.²⁷⁻³⁵ Xie *et al.* employed stencil printing and laser-processing techniques to prepare interdigited graphene based MSC components for flexible printed circuit (FPC) integrations, which not only prevented the risk of leakage, but also showed excellent mechanical flexibility, foldability and shape tailorability.⁷ Pikul *et al.* reported lithium-ion MBs based on interdigitated 3D bicontinuous nanoporous electrodes, showing excellent electrochemical performance.¹

Herein, we report an aqueous rechargeable Zn//MnO₂ battery technology involving microfabrication techniques, featured with superior volumetric energy performance, small form factor, low cost, integratability and high safety characteristics. MnO₂ nanofibers and Zn nanosheets were conformally deposited onto the nickel nanocone arrays (NCAs) current collector as cathode (MnO₂@NCAs) and anode (Zn@NCAs) respectively to assemble interdigital Zn//MnO₂ MBs. Benefit to the highly conductive nature of the 3D current collector and the intimate contact of the nanostructured electrode materials, these Zn//MnO₂ MBs exhibit outstanding electrochemical performance with a maximum volumetric energy density of 71.3 µWh cm⁻² µm⁻¹, a maximum power density of 1621.4 μ W cm⁻² μ m⁻¹ and excellent cycling stability, which are superior to most reported MBs, MSCs and even commercial products. In addition, the well-packaged Zn//MnO₂ MB component is ultrathin (74 µm), lightweight (0.03 g), and shows excellent mechanical stability. For demonstration, a single piece of such MB can drive three pieces of light emitting diodes (LEDs). On the other hand, the fabrication process of our Zn//MnO₂ MBs is compatible with that of many flexible electronics, such as radio frequency identification (RFID) antennas. In all, the rechargeable, high performance, environmentally benign and integratable Zn//MnO₂ MBs can potentially and excellently meet the future demand of wearable electronic products featured with green, low cost, highly integrated and safe characteristics. We envisage that this technology would boost the development of miniature power sources for IoT, and inspire the system level integration technology.

Experimental

Fabrication of NCAs and construction of interdigital architecture

A commercial conductive carbon paste (CH-8), serving as a conducting layer, was uniformly screen-printed onto a flexible thin PET substrate to achieve 10 μ m thickness and 12.4 Ω/\Box square resistance. A thin layer of NCAs were directly electrodeposited on the carbon ink layer.^{29, 30} The electrodeposition process was performed in a two-electrode system at a current density of 10 mA cm⁻² for 10 min, while the carbon ink and nickel foam were employed as cathode and anode, respectively. The electrodeposition solution was composed of nickel salt (NiCl₂-6H₂O, 200 g L⁻¹), crystal modifier (NH₄Cl, 40 g L⁻¹) and buffer agent (H₃BO₃, 100 g L⁻¹), where the pH value was adjusted to 4.0 using 10% HCl and 10% NH₃·H₂O solutions at 60 °C. After deposition, the samples were thoroughly rinsed with DI water to remove the impurities and dried at 120 °C for 30 min.

In order to obtain the interdigital structure, the NCAs coated films were laser-scribed using a commercial laser marking machine with a wavelength of 355 nm (Han's Laser EP-15-DW, maximum power: 5 W). During laser scribing process, only the nickel and carbon ink layers were ablated, forming an interdigital architecture, which can prevent short circuit between the two adjacent microelectrodes. Combining with digital computerized control system, we can conveniently regulate and control the width, interspace and the whole area of the integrated electrodes, implementing production in batches. Herein, the width and interspace of microelectrode were 300 μ m and 150 μ m, respectively, and the whole area of a single unit was controlled to be 0.48 $\rm cm^2$.

Electrodeposition of electrode materials

The Zn anode and MnO₂ cathode materials were sequentially electrodeposited conformally on each side of interdigital electrode. For MnO₂ cathode, the deposition process was carried out in a 0.05 M Mn(Ac)₂ aqueous solution for 90 s with titanium plate as the counter electrode, which employed a DC power system at 3.0 V voltage. And then the as-prepared sample was rinsed with deionized water for several times and dried in an oven at 120 °C for 30 min. Zn as the anode material was subsequently electrodeposited onto the other side of the microelectrodes in aqueous solution containing 25 mM Zn(Ac)₂ and 25 mM KCl at a constant current density of 1 mA cm⁻² for 90 s. After the deposition process, the full MB arrays were thoroughly washed with deionized water and dried in a vacuum oven at 90 °C for 2 h. In addition, MnO_2 was electrodeposited onto NCAs (MNC) with an area of 1×2 cm² as a single electrode. Under the same condition, MnO₂ deposited on a nickel plate (MNP), a carbon ink layer (MCI), a nickel foam (MNF) were used as the control samples.

MB Packaging

The as-prepared Zn//MnO₂ MBs were packaged by a simple stencil printing technique with polyurethane-based hot-melt glue as the cofferdams.^{7, 32} A mild aqueous solution containing 2 M ZnSO₄ and 0.2 M MnSO₄ was injected in the cell as the electrolyte. Polyurethane (Henkel Loctite 3542) was printed on the thin polyethylene terephthalate (PET) film to form regular cofferdams. And then the PET film was carefully hot-laminated on the MBs at a temperature of 60 °C by a heat-transfer machine for 10 minutes,

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ensuring a strong adhesion as well as adequate electrolyte in the cells.

Materials characterization and electrochemical measurements

The morphological and microstructural characteristics of the samples were studied by scanning electron microscopy (SEM, ZEISS SUPRA 55, Germany) and high-resolution transmission electron microscopy (HR-TEM, FEI G2 spirit, USA). In addition, X-ray diffraction (XRD, RINT2000 V/PC, Bruker DS, Germany) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, USA) were used to investigate the crystallographic information and chemical states of electrode materials.

Cyclic voltammetry (CV), galvanostatic charging/discharging (GCD) and electrochemical impedance spectroscopy (EIS) of the single electrodes and the full Zn//MnO₂ MBs with 2 M ZnSO₄ and 0.2 M MnSO₄ based electrolyte were investigated on an electrochemical station (VMP3, Bio-Logic, France). CV and GCD measurements of the MNC single electrode were carried out in the voltage range between 0 V and 0.8 V (vs. saturated calomel electrode (SCE)) in a three-electrode configuration, while the performance of Zn//MnO₂ MB was tested at a voltage window of 1 V to 1.9 V (vs. Zn/Zn²⁺) in a two-electrode configuration. The EIS tests were conducted in the frequency range between 100 kHz and 0.01 Hz with an amplitude of 5 mV at an open-circuit potential.³⁶

Results and discussion

The Zn//MnO₂ MBs based on 3D MnO₂@NCAs cathode and Zn@NCAs anode were prepared in a series of fabrication processes, as shown in Fig. 1. Conductive carbon ink as a low-cost and environmentally-friendly material was printed onto the flexible PET film, forming a uniform conductive surface. By using electrodeposition technique, NCAs with improved conductivity (square resistance: 0.04 Ω/\Box) were directly grown on the carbon layer, which can improve the contact with the active materials, release stress, and be compatible with roll-to-roll large-scale production.³⁰ Moreover, the NCAs could not be peeled off from the carbon layer very easily, showing excellent mechanical stability. After that, laser ablation technique was utilized to fabricate interdigital microelectrode arrays. Owing to the high efficiency and ultrahigh resolution (beam size as small as 10 µm), a batch of microelectrode arrays with precise dimension control could be obtained within several minutes. MnO₂ and Zn were separately chosen as the cathode and anode of interdigital electrodes, due to the characteristics of low cost, earth abundance and high theoretical capacities (1230 mAh g⁻¹ and 820 mAh g⁻¹, respectively). By involving electrodeposition technique, the electrode materials were sequentially deposited onto the nanostructured interdigital microelectrodes. Due to the 3D configuration of NCAs, the electrode materials can have excellent contact with the NCAs, as well as shortened ion diffusion length between anode and cathode, which can improve the power density of the Zn//MnO₂ MBs. Finally, we employed polyurethane-based hot-melt glue as cofferdams and an ultrathin PET film as cover layer to package Zn//MnO₂ MBs, maintaining excellent mechanical strength and flexibility of each MB unit.

The morphologies and microstructures of MnO₂ and Zn deposited



Fig. 1 Schematic illustrations of Zn//MnO₂ MBs. (a) PET substrate is printed with a layer of carbon ink and electrodeposited NCAs layer. The inset is an SEM image of NCAs, showing a height of approximately 1 μ m. (b) Laser-scribing fabrication of interdigital microelectrode arrays. The inset is a photographic image of an MB current collector unit, where the width and interspace of microelectrode are 300 μ m and 150 μ m, respectively. (c) Electrodeposited electrode materials. The insets are the SEM images of MnO₂@NCAs cathode and Zn@NCAs anode, respectively. (d) Packaged Zn//MnO₂ MBs. A thin PET film with polyurethane-based hot-melt glue as the cofferdam was coated on the Zn//MnO₂ MBs, which could prevent leakage of electrolyte. (e) A single piece of encapsulated Zn//MnO₂ MB unit.

onto the NCAs were examined by SEM and TEM, as shown in Fig. 2 and Fig. S2. The as-prepared MnO₂ electrode has a highly porous nanostructure with an average height of 1.5 µm, which is composed of interconnected nanofibers (Fig. 2a). And the length of MnO_2 fibers is typically less than 10 nm. Due to the porous nanostructured MnO₂, there are abundant contact interfaces and short ion diffusion distance between the electrode and electrolyte, which can indeed accelerate the electrochemical reaction. Zn anode with the nanosheet-like structure was also obtained by electrodeposition method, forming excellent contact with the NCAs (Fig. 2c). The height of the Zn nanosheets was controlled to be approximately 1.5 µm. The Zn anode with nanosheets structure possesses a high specific surface area, which can shorten ion diffusion length and facilitate electron transport. Notably, combining the Zn nanosheets with the 3D NCAs, an excellent cycling stability of Zn//MnO₂ MB can be obtained because the intermediate products generated from charging/discharging cycles can directly fall into the spaces of NCAs, without interfering the electrochemical reactions on the Zn anode.³⁷

In addition, the TEM images in Fig. S2 demonstrate that the electrodeposited MnO_2 exhibits a crystalline structure, while the Zn nanosheets display a hexagonal structure and high crystallinity. The measured lattice fringes of 0.21 nm are in agreement with the (101)

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Fig. 2 (a) Cross-sectional SEM image of MnO_2 deposited on the NCAs. (b) Magnified overview of MnO_2 cathode. (c) Cross-sectional SEM image of Zn electrodeposited onto the NCAs. (d) Magnified overview of Zn anode.

plane of Zn, corresponding to JCPDS NO.: 87-0713. Besides, the nanostructured electrode materials have both direct electrical interconnection and strong adhesion with the Ni scaffold, enabling a rapid electron transport property and mechanical stability, which is conducive to improve its electrochemical performance. Utilizing electrodeposition technique, nanostructured MnO_2 and Zn can be effectively and uniformly coated on the NCAs, which can also be confirmed from optical photographs (Fig. S3).

In order to investigate the detailed structural information of the electrode materials, XRD and XPS spectra of the as-prepared MnO₂@NCAs and Zn@NCAs are shown in Fig. S4 and Fig. S5. The three diffraction peaks of the as-synthesized NCAs are corresponding to the phase information of Ni (JCPDS NO.: 04-0850) (Fig. S4).³⁰ XRD pattern indicates the hexagonal structure and high crystallinity of the Zn nanosheets, which is in good agreement with the TEM results (JCPDS NO.: 87-0713).²⁴ On the other hand, the electrodeposited MnO₂ displays a low crystallinity from XRD, which is consistent with TEM observations. Fig. S5a shows the XPS full spectrum containing the feature peaks of Mn 2p, Mn 3s and O 1s. The high-resolution Mn 2p spectrum in Fig. S5b indicates that the binding energy separation between $Mn2p_{2/3}$ and $Mn 2p_{1/2}$ is about 11.8 eV, where the pecks of $Mn2p_{2/3}$ and $Mn 2p_{1/2}$ are centered at 642.0 eV and 653.8 eV, respectively, indicating the existence of Mn^{4+38} In addition, the O 1s spectrum further demonstrates the formation of MnO₂ (Fig. S5c). Additionally, a typical peak of Zn 2p at 1021.6 eV suggests that the Zn anode was deposited onto the NCAs scaffold successfully.39

In order to evaluate the electrochemical performance of the MNC positive electrode, a series of electrochemical characterizations were carried out in the $ZnSO_4$ and $MnSO_4$ based electrolyte with the working potential window from 0 V to 0.8 V (vs. SCE). As shown in Fig. 3a, the MNC electrode shows stable CV curves in the initial two cycles at 0.1 mV s⁻¹, there are two pairs of redox peaks in each cycle, which correspond to the ion-insertion reaction of both H⁺ and Zn^{2+,23} The two oxidation peaks are located at 0.52 V and 0.56 V, respectively, corresponding to the two voltage plateaus resulting from different ion insertion. The first voltage plateau is ascribed to the H⁺ insertion process, while the second

voltage plateau is mainly attributed to the Zn²⁺ insertion.²³ With the scan rate increasing from 0.1 mV s^{-1} to 1 mV s^{-1} , there are no significant differences in the shape of the curves except for the stacking of oxidation peaks, which is due to the gradually decline of Zn^{2+} insertion reaction (Fig. 3b). According to the reaction kinetics, the much larger size of Zn²⁺ than H⁺ may result in a greater charge transfer and diffusion resistance, which make the voltage and capacity in the second voltage plateau significantly drop. As a consequence, the \boldsymbol{H}^{*} insertion process dominates the reaction at high scan rates. The GCD tests are performed with different current densities ranging from 0.03 A cm⁻³ to 0.7 A cm⁻³, as shown in Fig. 3c. It is found that the two discharge plateaus in each GCD curve can match well with redox peaks of CV curves. Additionally, the highest volumetric capacitance of the MNC electrode can reach 28.3 mAh cm^{-3} (corresponding to 423.8 mAh g^{-1}) at 0.03 A cm^{-3} , which is superior than those of MCI, MNP and MNF electrodes (Fig. S6b, c). Besides, 70.3% of initial volumetric capacitance can be maintained when the current density is increased by approximately 23 times, showing excellent rate performance (Fig. 3d). The cycling stability of MNC positive electrode is shown in Fig. 3e, which suggests that 81.5% of the initial capacity can be preserved after 1000 cycles, making it a promising cathode for Zn//MnO₂ MBs. Furthermore, the EIS performance of MNC electrode can be evaluated by comparing the Nyquist curves in Fig. 3f and Fig. S6d. An equivalent circuit model used for fitting EIS data is shown in Fig. S7. Compared to MCI, MNP and MNF electrodes, MNC electrode demonstrates a small equivalent series resistance (6.9 Ω) and charge transfer resistance (3.1 Ω), which can be attributed to the excellent interfacial contact between MnO2 and NCAs architecture. On the other hand, a larger porous surface of MNC nanostructure can provide a shorter transport channel and diffusion path for electrons and ions.^{22, 40}

In order to investigate the potential MB application, we constructed rechargeable aqueous $Zn//MnO_2$ MB full cells. The electrochemical properties of the full $Zn//MnO_2$ MB are shown in Fig. 4 and Fig. S8. There are two pairs of redox peaks in the CV curves, which are consistent with the two discharge plateaus in the GCD curves at about 1.47 V and 1.28 V, respectively (Fig. 4a, b). The excellent electrochemical properties of $Zn//MnO_2$ MB can be ascribed to the insertion/extraction process of H⁺ and Zn²⁺, which is formulated as follows:²³

Cathode:	$MnO_2 + H^+ + e^- \leftrightarrow MnOOH$	(1)
	$\text{Zn}^{2+} + 2\text{MnO}_2 + 2e^- \leftrightarrow \text{ZnMn}_2\text{O}_4$	(2)
Anode:	$Zn \leftrightarrow Zn^{2+} + 2e^{-}$	(3)

Moreover, Zn anode with the nanosheet-like structure on the NCAs scaffold can prevent the enormous volume changes and the concomitant huge stresses, which is beneficial to the cycling stability of battery.³⁷

Based on the nanostructured feature and their intimate interfacial contact to the NCAs scaffold, the highly porous MnO₂ nanofibers and Zn nanosheets can enable excellent ion transport during electrochemical reactions. Besides, NCAs are employed as the 3D current collector to support the active materials, which exhibits unique characteristics as follows: i) due to the high aspect ratio of NCAs, the mass loading can be increased and thus improving the energy density of MBs; ii) the uniform NCA surface structure maintains an excellent electrical connection with the

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Fig. 3 Electrochemical characterizations of MNC electrode in $ZnSO_4$ (2 M) and $MnSO_4$ (0.2 M) based electrolyte. (a) CV curves of MNC in the initial two cycles at 0.1 mV s⁻¹. (b) CV curves under different scan rates ranging from 0.1 mV s⁻¹ to 1.0 mV s⁻¹. (c) GCD curves of MNC electrode at the scan rates between 0.03 A cm⁻³ to 0.7 A cm⁻³. (d) Volumetric capacitances of the MNC electrode with different current densities. (e) Cycling test of the MNC electrode. (f) Nyquist curves comparison of the MNC and MNP electrode, inset is a magnification of the high-frequency region.

electrode materials, which shortens the diffusion distance of ions and facilitates electron collection and transport, rendering superior power density; iii) the porous structure of the electrodes can help to accommodate drastic volume changes and alleviate the concomitant huge stresses, thereby improving the cycle life of the battery. $^{\rm 37,\ 41}$ As a consequence, the $Zn//MnO_2$ MB presents an average operating voltage of 1.4 V and a reversible capacity of 53.5 μ Ah cm⁻² μ m⁻¹ at 1 C rate (based on the active materials), which is superior to other reported MBs (Fig. S8b and Table S1), even including lithium ion MBs. Fig. 4b demonstrates the first chargedischarge curve of the Zn//MnO₂ MB at different working rates. At 6 C rate, the charge capacity of the $Zn//MnO_2$ MB is 30.29 μ Ah cm⁻² μ m⁻¹, while the charge capacity reaches 19.6 μ Ah cm⁻² μ m⁻¹, with a Coulombic efficiency of 65%, which is ascribed to the activation process. With the increase of C rate, the Coulombic efficiency rises gradually, and the MB still maintains a high discharge capacity. The capacity of the cell at a very high working rate (814 C) submits 1.365 μ Ah cm⁻² μ m⁻¹ level after 8 GCD cycles, showing excellent electrochemical stability and rate capability (Fig. 4b, c). Owing to a consequent H⁺ and Zn²⁺ insertion/extraction process, this aqueous Zn//MnO₂ MB presents a promising long-term cycling stability, with a capacity retention of 91.6 after 15 cycles and 60.2% after 100 cycles at a low rate of 1 C, as shown in Fig. 4c and d. The decay of capacitance can be ascribed to the slow dissolution and disruption of the MnO₂ cathode, as well as the volumetric changes and the concomitant stresses on account of the irreversible reaction. If the ions concentration in the electrolyte is improved to restrain the collapse of MnO₂ cathode and the irreversible reactions, the cycling performance could be further enhanced.²³ Finally, by optimizing the

electrode structures, the electrodes show both the low equivalent series resistance and charge transfer resistance (Fig. S8c).

In order to further evaluate the overall performance of our MBs, we compared the energy and power densities of the as-obtained MBs with state-of-the-art miniaturized energy-storage devices, as shown in Fig. 5. To the best of our knowledge, this is the first demonstration of MB based on the rechargeable Zn//MnO₂ system,



Fig. 4 Electrochemical properties of the aqueous $Zn//MnO_2$ MBs. (a) CV and (b) GCD curves of $Zn//MnO_2$ MBs at different scan rates and C rates. (c) Rate performance of the full cells at different C rates after 15 GCD cycles. (d) Cycling test of the full cells at 1 C rate after 100 GCD cycles.

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Fig. 5 Ragone plot displaying volumetric energy and power densities of our Zn//MnO₂ MBs and some recently reported micro- power sources (based on the volume of the unencapsulated MB or MSC). MB1: LiMnO₂-NiSn MBs;¹ MB2: LiMnO₂-NiSn MBs;³ MB3: PPYDBS-C MBs.²⁷

showing superior volumetric energy performance, low cost, and high safety characteristics. The Zn//MnO2 MB fabricated by and commercially-available laser-scribing technique electrodeposition technique, can exhibit a maximum energy density of 71.3 μ Wh cm⁻² μ m⁻¹ at a power density of 69.5 μ W cm⁻² μ m⁻¹ in mild aqueous electrolyte (based on the full cell). The maximum power density can reach 1621.4 μ W cm⁻² μ m⁻¹ at a very high working rate (814 C), whose capacity is 4.914 μ Ah cm⁻² μ m⁻¹. Compared with conventional MB fabrication technologies, our technology reported here can not only manifest the merits of green, low-cost, and scalable characteristics, but also deliver a peak energy density of 5 times higher than that of reported MBs, 45 times higher than that of reported MSCs, and possess supercapacitor-like power characteristic, as shown in Fig. 5 and Table S1.

Here we involved industry-adoptable techniques e.g. stencil printing and hot-lamination processes for packaging these Zn//MnO₂ MBs. A polyurethane based resin was used as cofferdams and a polyethylene terephthalate (PET) film (21 µm in thickness) was used as the cover layer, which can not only isolate each cell unit, but also effectively prevent the leakage of electrolyte during bending conditions. This packaging technology can also cater to the excellent rate capability and cycling stability of the MBs. Besides, the Zn//MnO₂ MB arrays demonstrate excellent mechanical flexibility, which can be rolled up easily (Fig. S9). The packaged $Zn//MnO_2$ MB exhibits a total thickness of 74 μ m and a weight of 30 mg. With such a small size, the Zn//MnO₂ MB could power light emitting diodes (LEDs), delivering a dazzling light, as shown in Fig. S10. Furthermore, the fabrication process of these MBs are compatible to the industrial processes for many other flexible electronic components; for instance, the fabrication of radio frequency identification (RFID) tags, as a representative application for IoT, can share the same fabrication process with our Zn//MnO₂ MBs, showing potential for green, low-cost and advanced applications. For demonstration, the RFID tag sample prepared

together with our Zn//MnO₂ MBs can be identified by a commercial ultra-high frequency (UHF) RFID reader (Fig. S11). Besides, a single unit of the Zn//MnO₂ MB can be charged by a commercial wireless charging device, showing potential for powering active RFID tags. In all, our Zn//MnO₂ MBs reveal lightweight, ultrathin, small-size, rechargeable, low cost and environmental-benign characteristics, which can excellently meet the growing demand of the IoT market.

Conclusions

In summary, we have successfully developed a Zn//MnO₂ MB technology, which shows a series of advantages, such as compatibility with flexible electronics fabrication process, small form factor, ultrathin geometry, high energy density and green characteristics. The rechargeable Zn//MnO2 MBs can deliver a remarkable capacity of 53.5 μ Ah cm⁻² μ m⁻¹ at 1 C rate. The cell is able to deliver a high volumetric energy density of 71.3 μ Wh cm⁻² μ m⁻¹ and a peak power density of 1621.4 μ W $cm^{-2} \mu m^{-1}$, as well as excellent cycling stability. As far as we know, the energy density level of our Zn//MnO2 MBs is superior than most reported MBs, MSCs and even commercial products, which can be ascribed to the unique nanostructured electrodes and superior electron and ion transport ability. Additionally, the ultrathin (74 μ m) and lightweight (30 mg) Zn//MnO₂ MB components exhibit outstanding mechanical flexibility, and can even endure severe bending. This technology would inspire the development of advanced MBs and boost the development of flexible and wearable electronics for IoT applications.

Conflicts of interest

There are no conflicts to declare.

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Graphical abstract



A Zn//MnO₂ micro-battery cell can power a light-emitting diode (LED) and share the same fabrication platform with many flexible electronic devices.

Keywords: Zn//MnO₂ micro-battery; microfabrication; low-cost; environmentally benign; electrochemistry

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