Journal of Materials Science and Chemical Engineering, 2019, 7, 19-28
https://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

Flexible Zinc-Manganese Dioxide Alkaline Batteries Based on Kelp Electrolytes

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How to cite this paper: Wang, S.Y. and Fan, X.Y. (2019) Flexible Zinc-Manganese Dioxide Alkaline Batteries Based on Kelp Electrolytes. *Journal of Materials Science and Chemical Engineering*, **7**, 19-28.
https://doi.org/10.4236/msce.2019.712003

Received: November 12, 2019
Accepted: December 9, 2019
Published: December 12, 2019

Abstract

Flexible energy-storage devices play a critical role in the development of portable, flexible and wearable electronics. In addition, biological materials including plants or plant-based materials are known for their safety, biodegradability, biocompatibility, environmental benignancy, and low cost. With respect to these advances, a flexible alkaline zinc-manganese dioxide (Zn-MnO_2) battery is fabricated with a kelp-based electrolyte in this study. To the best of our knowledge, pure kelp is utilized as a semi-solid electrolyte for flexible Zn-MnO_2 alkaline batteries for the first time, with which the as-assembled battery exhibited a specific capacity of 60 mA·h and could discharge for 120 h. Furthermore, the as-assembled Zn-MnO_2 battery can be bent into a ring-shape and power a light-emitting diode screen, showing promising potential for the practical application in the future flexible, portable and biodegradable electronic devices.

Keywords

Zinc-Manganese Dioxide Battery, Flexible Battery, Kelp-Based Electrolyte

1. Introduction

Recent progress in the development of portable, flexible and wearable electronics including wearable personal multiplayer, roll-up displays and smart clothes, is creating a brand new era to accelerate revolutionary changes in our lifestyles [1]-[6]. To meet the requirement of these versatile ubiquitous flexible and wearable devices, energy storage devices with high power-efficiency and excellent versatility to maintain their functionality are of great importance [7]-[13]. Among a variety of power supplies, zinc-manganese dioxide (Zn-MnO_2) alkaline batteries have triggered great academic and technological interest in the field of flexible batteries because of the stable output voltage platform, high specific capacity, high battery safety, non-toxicity, low cost (<\$90 kWh^{-1}, compared with ~\$200 kWh^{-1} for Li-ion batteries), and eco-friendliness [14] [15].

Traditional liquid-electrolyte-based Zn-MnO_2 alkaline batteries are usually fabricated with rigid and bulky configuration which cannot meet the flexible and portable requirements. Currently, quasi-solid-state polymer electrolytes play an important role in the development of flexible and portable Zn-MnO_2 alkaline batteries which are capable of maintaining battery performance as well as withstanding various deformations. For example, Gaikwad *et al.* [16] reported a stretchable Zn-MnO_2 battery based on an off-the-shelf compliant silver fabric substrate and a polyacrylic acid-KOH-ZnO gel polymer electrolyte. Wang *et al.* [17] fabricated a flexible Zn-MnO_2 battery with a copolymer electrolyte film made from polyvinyl alcohol, polyacrylic acid and KOH. In addition, Zeng *et al.* [18] and Su *et al.* [19] assembled flexible Zn-MnO_2 batteries using polyvinyl alcohol and cellulose-based polymer electrolytes respectively. Despite of the achievements so far, disposable electronic products (e.g., electronic wrinkle-free eye sticks) require a high frequency of battery replacement resulting in a large number of discarded batteries which are difficult to recycle and easy to burden the environment. Therefore, the aforementioned polymer materials-based electrolytes face the challenges of biodegradability to solve the accumulation problem of waste batteries.

In this respect, biological materials including plants or plant-based materials show promising potential owing to their high safety, environmental friendliness, low cost and biocompatibility. Among various biomaterials, kelp which is a kind of large seaweed (algae) has been widely used as food product and source for industrial production of soda, glass, and hydrocolloids [20]. However, few studies have investigated the kelp-based electrolytes for flexible Zn-MnO_2 batteries as well as the corresponding battery performances. Herein, to the best of our knowledge, pure kelp is utilized as a semi-solid electrolyte for flexible Zn-MnO_2 alkaline batteries for the first time. The structure and morphology of the pure kelp were characterized by X-Ray Diffraction (XRD) and scanning electron microscope (SEM) measurements. In addition, the cathode is fabricated by mixing MnO_2, carbon powders, polyvinylidene fluoride (PVDF) (dissolved in Methyl-2-pyrrolidinone (NMP) in a ratio of 3:10) on a flexible copper film. The XRD, SEM and mapping characterizations were also proceeded to demonstrate the successful fabrication of the MnO_2-based electrode. Furthermore, a layer-structured Zn-MnO_2 battery is obtained by laminating a pure kelp-based electrolyte between a zinc film anode and a same-sized MnO_2-based cathode. Excitingly, the resultant Zn-MnO_2 battery can be bent into a ring-shape and power a light-emitting diode (LED) screen simultaneously, exhibiting promising potential for the practical application in flexible and portable electronic devices. This study aims to take the first step to investigate a pure biomaterial (*i.e.* kelps) as an electrolyte with non-toxicity, biodegradability, high safety, low-cost and eco-friendliness for the application of flexible Zn-MnO_2 batteries.

2. Experimental Part

2.1. Materials and Preparation of Pure Kelp-Based Electrolyte Film

The pure kelp-based electrolyte film was prepared with the dried kelps from the market. The dried kelps were first washed carefully to remove the small grains at surface and soaked in the deionized water. After a day of soaking, the dried kelps were swollen into wet kelps with a certain thickness. Then the wet kelp was soaked into a potassium hydroxide solution (KOH) with a concentration of 6 mol/L to absorb the alkaline solutions. With this method, the pure kelp-based electrolyte film was fabricated.

2.2. Materials and Preparation of MnO_2 Cathode

MnO_2 cathode was prepared with a coating method. First, the MnO_2-based electrode paste was prepared by mixing MnO_2 powders, carbon powders (XC-72), polyvinylidene fluoride (PVDF) (dissolved in Methyl-2-pyrrolidinone (NMP) in a ratio of 3:10) by a corundum grinding bowl for 30 min. Then the as-prepared cathode paste was coated on a copper film by using a height adjustable applicator with thickness of 500 μm. The MnO_2-based paste coated copper film was then transferred into an oven for 12 h under 70˚C. Finally, the MnO_2 cathode was obtained.

2.3. Materials Characterization

In order to investigate the structure of the pure kelp-based electrolyte film and MnO_2 cathode, X-Ray Diffraction (XRD) measurement was carried out with a Bruker/D8 X-ray diffractometer with Cu K_α radiation in the range of $2\theta = 10˚$ to 90˚ and $2\theta = 10˚$ to 60˚ respectively. In addition, in order to investigate the morphology and composition information of the pure kelp-based electrolyte film and MnO_2 cathode, scanning electron microscopy (SEM) measurement was carried out with a S4800 which equipped with an energy-dispersive X-ray (EDX) analysis and elemental mapping. Due to the low electronic conductivity of the pure kelp, the freeze-dried kelp was sprayed with gold for 50 s before SEM characterization.

2.4. Battery Electrochemical Measurements

Flexible Zn-MnO_2 battery was assembled in a layered structure by laminating the kelp-KOH electrolyte between a zinc film anode (0.3 mm, 30 × 30 mm^2) and the as-prepared MnO_2-based cathode (30 × 30 mm^2). A plastic film was used to enhance the integrity of the obtained sandwich-like Zn-MnO_2 battery which was also used as the packing material. The galvanostatic discharge performance was conducted employing a multi-channel battery testing system (LAND CT2001A). The current densities used in this study were normalized to the active materials

(0.5 mA, 0.0782 g) or electrode area (0.5 mA, 30 × 30 mm^2).

3. Results and Discussion

As mentioned, biological materials including plants or plant-based materials are advantageous because of their high safety, environmental friendliness, low-cost, biodegradability and biocompatibility. In addition, biodegradable biomass is a promising material for the application of disposable electronic products. Among plenty of biomaterials, kelp is a kind of large seaweed (algae) which can be used in the field of food product and source for industrial production of soda, glass, and hydrocolloids [20]. **Figure 1** shows the photographs of the dried kelp bought from the market and the wet kelp after soaking in the deionized water for a day. Before soaking into 6 mol/L KOH electrolyte solution, the pure kelp was freeze-dried with a freeze dryer and its structure information was identified by XRD measurement. As shown in **Figure 2**, XRD pattern of the dried kelp exhibits a main peak at 29.4˚ and several small peaks at 23.1˚, 35.9˚, 39.4˚, 43.2˚, 47.1˚, and 47.5˚. These peaks correspond to (104), (012), (110), ($11\overline{3}$), (202), (024), and (018) planes of the $CaCO_3$ (JCPD #47-1743), indicating the existence of element Ca in the kelp which is carbonized in air. The existence of Ca is in agreement with the fact that kelps accumulate many minerals from the seawater over their lifetime, providing a rich source of calcium, sodium, magnesium, potassium, and other rare elements [21] [22]. To further investigate the ingredient and morphology information of the kelp, **Figure 3** shows SEM image, EDX analysis, and elemental mapping images of C, O of the dried pure kelp. Due to the low electronic conductivity of the pure kelp, the freeze-dried kelp was sprayed with gold for 50 s before SEM characterization. As biomass, the kelp consists of many cells which are bubble-like bumps in the case of freeze-drying as shown in **Figure 3(a)**. The EDX result suggests the existence of carbon (49.99 wt%), oxygen (43.45 wt%), calcium (2.49 wt%), magnesium (1.44 wt%), and potassium (0.83 wt%), sodium (0.36 wt%). Owing to the low concentration of sodium, magnesium, and potassium as well as the amorphous phase of the biological skeleton, the only carbonate ($CaCO_3$) is detected by the XRD measurement (**Figure 2**). Moreover, the elemental mapping results in **Figures 3(c)-(e)** show the even distribution element carbon and oxygen of the dried pure kelp, confirming its biological skeleton.

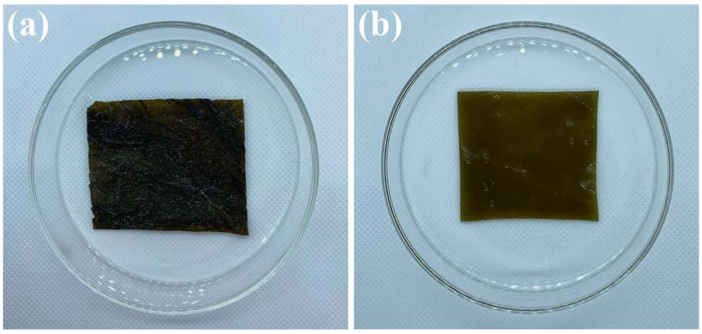

Figure 1. Photographs of (a) the dried kelp bought from the market, and (b) the wet kelp after soaking in the deionized water for a day.

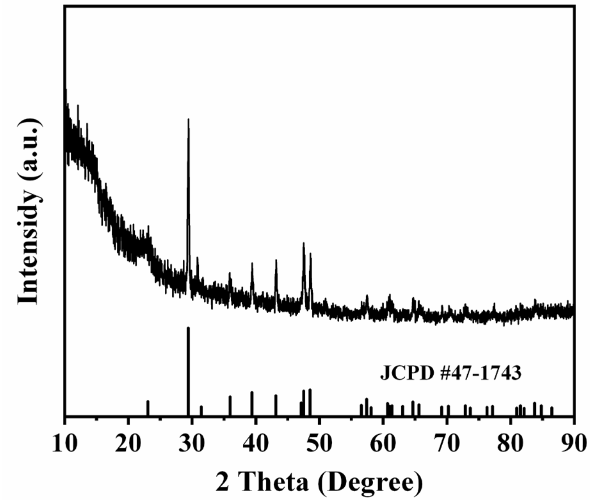

Figure 2. XRD pattern of the dried kelp before soaking into 6 mol/L KOH.

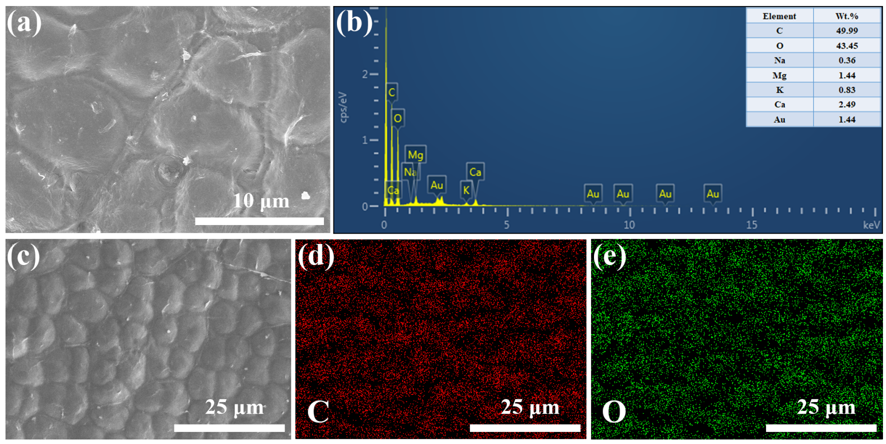

Figure 3. (a) SEM image, (b) EDX analysis, (c)-(e) elemental mapping images of C, O of the dried pure kelp.

MnO_2-based cathode for Zn-MnO_2 alkaline battery was prepared by coating the electrode paste containing MnO_2 powders, carbon powders, PVDF (dissolved in NMP in a ratio of 3:10) on a copper film with a thickness of 500 μm. The structure of the obtained MnO_2-based cathode was characterized by XRD measurement as shown in Figure 4. The two peaks at 43.3˚ and 50.4˚ are related to the (111) and (200) planes of Cu corresponding to the Cu film substrate of the as-prepared cathode (JCPD #04-0836). In addition, XRD pattern of the MnO_2-based cathode exhibits several small peaks at 37.1˚, 42.4˚, and 56˚ which correspond to (110), (101), and (102) planes of the MnO_2 (JCPD #30-0820) respectively, showing successful adhesion of the MnO_2-based paste onto the substrate. Moreover, the morphologic information of the fabricated electrode is obtained by SEM measurement in Figure 5(a). The active layer of the cathode is composed of MnO_2 and carbon particles, which are bound to form electrical pathways throughout the surface providing good electrical conductivity. EDX analysis further identified the composition of the electrode with C, O and Mn.

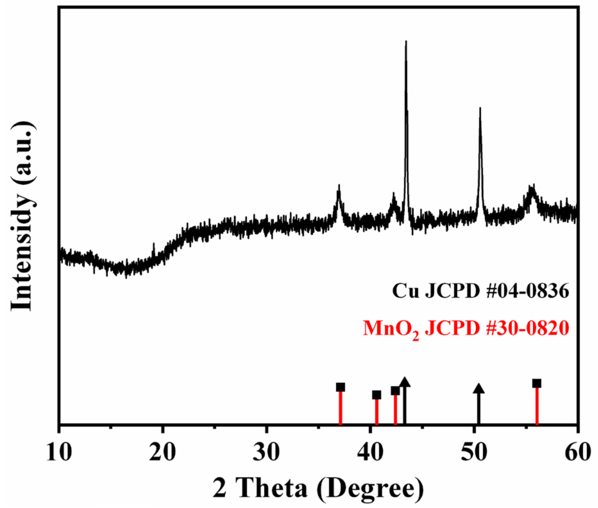

Figure 4. XRD pattern of the MnO_2-based cathode (fabricated by coating the MnO_2/C/PVDF/NMP on a Cu film).

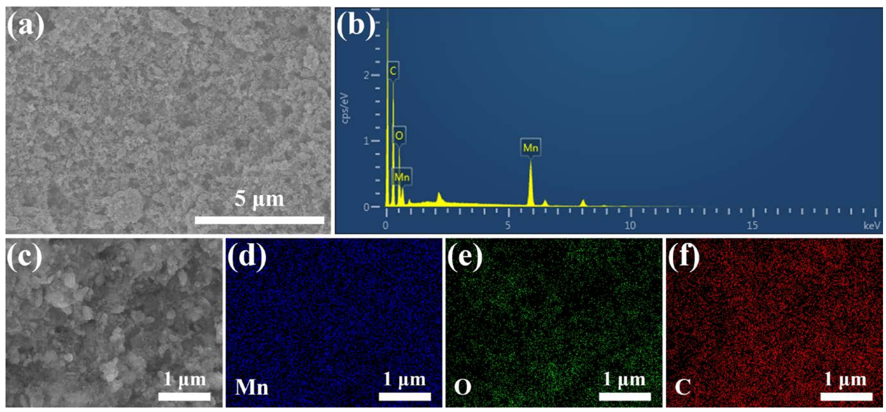

Figure 5. (a) SEM image, (b) EDX analysis, (c)-(f) elemental mapping images of Mn, O, C of MnO_2-based cathode.

Figures 5(c)-(f) are elemental mapping images of Mn, O, C of MnO_2-based cathode, indicating uniform distribution of the active materials of the electrode. Therefore, the resultant MnO_2-based cathode with good adhesion and uniform distribution of the active material paste onto the substrate is critical for the battery performance of the flexible Zn-MnO_2 battery.

Based on the prepared pure kelp immersed in the KOH electrolyte solution previously and the obtained MnO_2-based cathode, a flexible sandwich-type Zn-MnO_2 battery is fabricated. As illustrated in Figure 6(a), the flexible Zn-MnO_2 battery is assembled with a zinc film, an as-prepared MnO_2-based electrode paste coated Cu film cathode by laminating a pure kelp-KOH electrolyte membrane in between. A plastic film was used to enhance the integrity of the battery which was also used as the packing material. Figure 6(b) shows the photograph of the assembled Zn-MnO_2 battery. Figures 6(c)-(e) further demonstrates the good flexibility of each component of the battery which plays an essential role in the battery performance under bending deformation. Crosse-section SEM of the kelp electrolyte-based Zn-MnO_2 battery (Figure 7) is exhibited to illustrate its sandwich structure as well as the good battery integrity. Discharge curve of Zn-MnO_2 battery with the kelp-based electrolyte at a constant current density of 0.22 mA cm^{-2} (~6.4 mA·g^{-1}) is presented in Figure 8, which exhibits a specific capacity of 60 mA·h (~6.67 mA·h·cm^{-2}, ~767.3 mA·h·g^{-1}). Excitingly, due to the good electrolyte retention ability of the kelp-based electrolyte, integrated battery assembly, and successful package method, the resultant Zn-MnO_2 battery could discharge for 120 h (Figure 8), much longer than that of previously reported studies [17].

Benefiting from the good flexibility of each component of the as-fabricated Zn-MnO_2 battery as well as its promising battery performances (Figure 8), the kelp-based battery shows promising potential in practical applications. Figure 9(a) presents the open circuit potential (1.408 V) of a homemade flexible sandwich-type

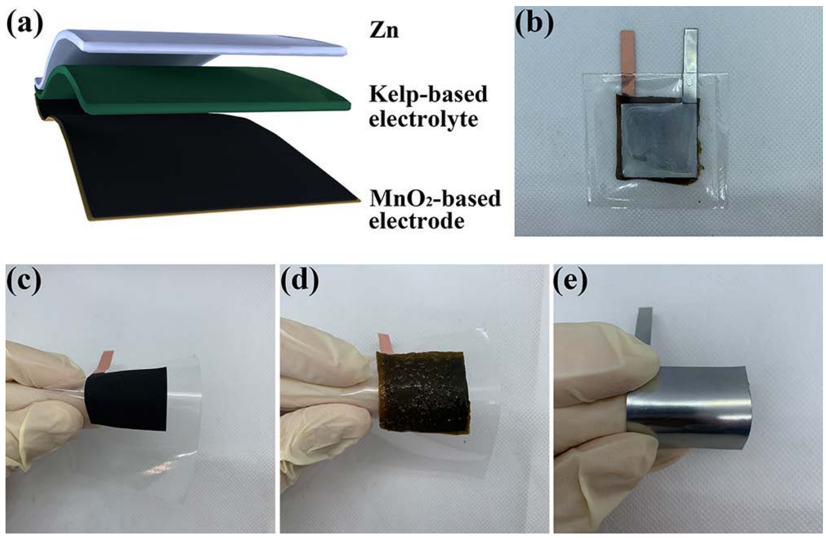

Figure 6. (a) Illustration of the battery structure of flexible sandwich-type Zn-MnO_2 battery fabricated with zinc film, MnO_2-based cathode and pure kelp-based electrolyte membrane. (b) Photograph of the assembled Zn-MnO_2 battery (30 × 30 mm^2). Flexible demonstration of (c) MnO_2-based cathode, (d) pure kelp-based electrolyte, and (e) zinc film.

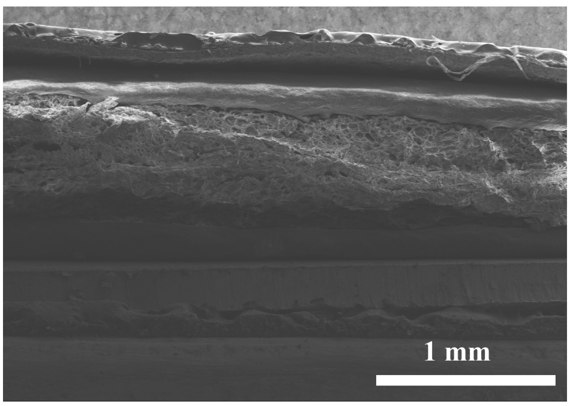

Figure 7. Crosse-section SEM of the kelp electrolyte-based Zn-MnO_2 battery.

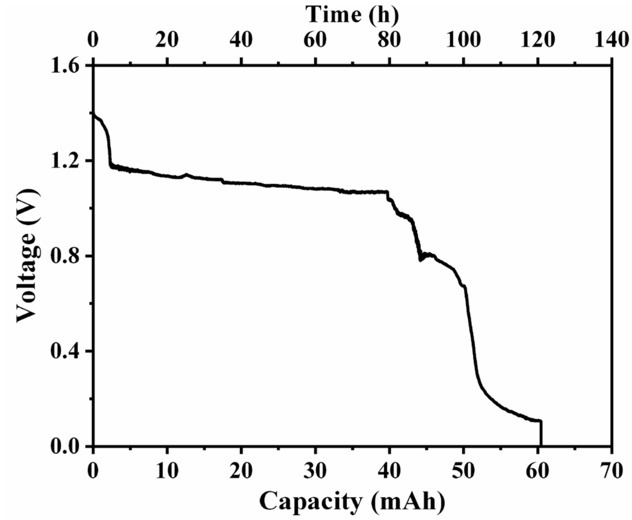

Figure 8. Discharge performance of the kelp electrolyte-based $Zn\text{-}MnO_2$ battery based on capacity and working time.

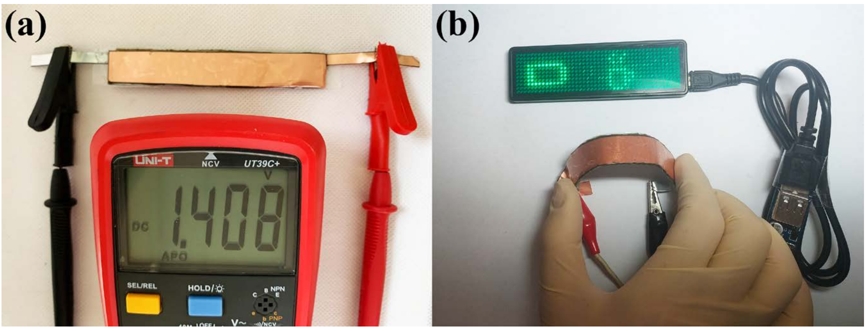

Figure 9. (a) Demonstration of the open circuit potential of the homemade flexible sandwich-type $Zn\text{-}MnO_2$ battery fabricated with zinc film, MnO_2-based cathode and pure kelp-based electrolyte membrane. (b) Demonstration of two of the fabricated $Zn\text{-}MnO_2$ battery in series under bending condition powering an LED screen.

$Zn\text{-}MnO_2$ battery fabricated with zinc film, MnO_2-based cathode, and the pure kelp-based electrolyte membrane. In addition, to further exemplify the viability for flexible and wearable applications, Figure 9(b) displays two of the fabricated $Zn\text{-}MnO_2$ batteries in series under bending condition which can power an LED screen. All of these results conclusively demonstrate the promising application of our fabricated flexible $Zn\text{-}MnO_2$ battery in flexible and wearable electronics.

4. Conclusion

In conclusion, a flexible alkaline $Zn\text{-}MnO_2$ battery is fabricated with a kelp-based electrolyte for the first time. In addition, XRD and SEM measurements on the pure kelp for the application of electrolytes are investigated for the first time to the best of our knowledge. Interestingly, benefiting from the good electrolyte retention capability of the pure kelp, the as-assembled $Zn\text{-}MnO_2$ battery exhibits a good specific capacity of 60 mA·h which can discharge for 120 h. Furthermore, each component of the battery shows outstanding mechanical flexibility, with which the resultant Zn-MnO_2 battery exhibits a relatively high OCP of ~1.4 V and can be bent into a ring-shape and power an LED screen. This study sheds light on the exploration of investigating a pure biomaterial (*i.e.* kelps) as electrolyte materials with non-toxicity, biodegradability, high safety, low cost and eco-friendliness for the application of flexible Zn-MnO_2 batteries. The successful construction of a kelp-based flexible Zn-MnO_2 battery shows promising potential for next-generation power supplies for wearable electronic devices.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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