



RAPID COMMUNICATION

A new type of secondary hybrid battery showing excellent performances



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Abstract

The zinc-based primary batteries have various merits including the low cost, high-security and reasonable energy, but their one-time use and low power performance limit the wider applications. Compared with the primary batteries, the supercapacitor has an extra higher cycling performance and power capability, but its specific energy is lower. Here we originally achieve a novel hybrid battery combined of a zinc-based primary battery and a supercapacitor through a unique assembly method. In this new structure, two symmetrical carbon nanotube/polyaniline nanoporous composites as supercapacitor electrodes are inserted in a zinc-manganese dioxide primary battery system with a way in series. Meanwhile, a special technique is used to form excellent conductive connections between the supercapacitor electrodes and the primary battery cathode and anode, respectively. This hybrid battery shows both a high specific power similar to that of the supercapacitor and a high specific energy comparable to that of the primary battery. It is more striking that the rechargeable character of this hybrid battery is much more excellent. Its specific capacity retained 75% after 500 cycles of charge-discharge at the high current density of 2 A g^{-1} while the coulombic efficiency kept at 100%. These notable improvements are attributed to the special design on the structure and chemistry system of the hybrid battery combining the merits of both the primary battery and the supercapacitor.

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Introduction

Primary batteries have been invented for more than 100 years and widely used as portable power sources for their

merits including high safety, good shelf life, easy to use and reasonable energy storage for various low energy consumption equipments such as wireless mouse, electronic watches, etc. [1]. Zinc is the most widely used metal as the anodes of the primary batteries for its good electrochemical performances, environmental-friendliness, abundant resource and low cost. Compared with the high chemical activity of lithium in water and the explosion risk of the lithium-based batteries

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using nonaqueous electrolyte and sealing packages, the water compatibility of Zn makes the Zn-based batteries based on aqueous electrolyte much easier to manufacture and safer to use, so the research on the Zn-based batteries is quite meaningful [2]. Many trials have been carried out on improving the flexible and capacity performances of some common Zn-based primary batteries, such as the Zn-carbon primary battery [3-5], the alkaline Zn-MnO₂ primary battery [6-8], assisted by some conductive fibers current collectors and solid electrolytes. However, the bad rechargeable ability greatly limits the wider use of the Zn-based primary batteries, so the studies on increasing their cycling performances are also very valuable. There have been some trials on improving the cycling properties of the alkaline Zn-MnO₂ primary batteries, but with limited effects [9-12]. As Xu et al. reported, a rechargeable zinc ion battery composed of a α -MnO₂ cathode, a Zn anode and a mild Zn²⁺ ions aqueous electrolyte showed an improved rechargeability [13]. As Parker et al. reported, the limited rechargeability of the primary zinc-air cell can be improved by using the wiring zinc in three dimensions as the anode [14]. In the above batteries, the electrodes and electrolytes need to be specially modified for performance improvements. Therefore, it is very necessary to further study on more easy and effective ways to enhance the cycling performances of the Zn-based primary batteries.

Compared with the Zn-based primary batteries, the supercapacitors have much better power abilities and extra higher cycling performances [15-18], but their specific energies are lower. A hybrid of the Zn-based primary battery and the supercapacitor has a great potential to combine the merits of these two devices.

Here we originally present a new simple structure combined of a Zn-MnO₂ primary battery and a polyaniline/carbon nanotube (PANI/CNT) supercapacitor. The used supercapacitor electrode material has a special nanoporous structure. This assembled hybrid battery shows an excellent cycling performance as well as both a high power ability like the supercapacitor and a high energy character like the primary battery. We also make a preliminary analyzation of the mechanism for these performance improvements.

Experimental section

Materials

Aniline (purity $\geq 99.5\%$) was purchased from Xilong Chemical Factory. MnO₂ (purity $\geq 85.0\%$) was purchased from Beijing Modern East Fine Chemical Products Co., Ltd. Carbon black (purity $\geq 99.9\%$) was purchased from Alfa Aesar. Zn metal sheet is obtained from a disassembled commercial Extra Heavy Duty (Zn-C battery) purchased from GP Batteries International Ltd.

Construction of the PANI/CNT supercapacitor system

To achieve this hybrid battery, we should choose a proper supercapacitor system. With an excellent conductivity and a high porous character, the CNTs are usually used as the supercapacitor electrode materials that showing a high double

layer capacitance and good cycling performance [19]. The PANI [20], a common conducting polymer, also can be made to supercapacitors showing a larger pseudo capacitance compared with the CNTs [21,22], but it has a worse cycle-life and mechanical property. Combining the merits of the above two materials, some PANI/CNT composite materials have been fabricated showing enhanced cycling and power performances as well as nanoporous, light-weight and flexible properties [23-25]. Therefore, this composite is a good choice as the supercapacitor electrodes to hybrid with batteries [26]. Hence, we choose the symmetrical PANI/CNTs in acid aqueous electrolyte as the supercapacitor system.

To get the PANI/CNT composite, we first use the super-aligned CNTs grown in array form to make a CNT network [27-29]. Because these CNTs have higher aspect ratio, they can be easily transformed to a freestanding CNT network as the following process. First, through chemical vapor deposition method, super-aligned CNTs were grown on silicon wafers in acetylene atmosphere using iron as the catalyst. Then, the CNTs were harvested from silicon wafers to mix with ethanol. After an ultra-sonication in 800 W for 10 min, the uniformly dispersed CNTs ethanol mixture was filtered through a micro-porous membrane with the aid of vacuum, and then was dried at 80 °C for 12 h in a vacuum oven. Finally, a CNT network was formed and easily peeled off from the membrane. The obtained CNT network has a nanoporous structure with a large special surface-area.

Then, we fabricate the PANI/CNT composite using the obtained CNT network as a template. As illustrated in Figure 1a, because the surface chemical bond of CNTs is appropriate for linking PANI, anilines can be polymerized to PANI in order along with the surface of CNTs through the following in situ chemical solution method. First, the CNT network was immersed in 1 mol L⁻¹ HCL aqueous solution containing 0.2 mol L⁻¹ aniline for ten minutes to be completely infiltrated, where ammonium per-sulfate equal in amount of substance with aniline was dripping in slowly as an oxidant for reaction. Second, at 0 °C for 24 h, aniline polymerized completely to PANI uniformly coated on the CNT network. Finally, we used deionized water, acetone and ethanol to clean the obtained PANI/CNT composite and dried it completely.

As Figure 1b demonstrates, this PANI/CNT composite has a thickness in 50 μm showing remarkable flexibility. This good mechanical strength should be attributed to the synergistic action of the strong support of the CNT network and the glued reinforcement of the PANI. Through the electrical measurement, this composite also shows an excellent electric conductivity of $4.6 \times 10^3 \text{ S m}^{-1}$. Its enhanced conductivity can be caused by the following two points. On one hand, the sufficient connections among the CNTs give a large amount of effective paths for electronic transport. On the other hand, the structure with PANI coated on the CNTs forms the good electrical contact between CNTs and PANI. Through the method reported in our previous work [25], we obtained the porosity of the PANI/CNT composite with a calculated value at about 70%.

The scanning electron microscopy (SEM) characterizations of microstructures were performed on the PANI/CNT composite using Sirion 200 with the resolution in 1.0 nm (FEI, USA). As shown in the SEM images in Figure 2a-b, the obtained PANI/CNT composite has a nanoporous structure

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