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High-performance all-solid-state flexible supercapacitors based on manganese dioxide/carbon fibers

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ABSTRACT

Flexible solid-state fiber supercapacitors are fabricated by directly electrodepositing ultrathin manganese dioxide (MnO_2) nanosheets on commercial carbon fiber yarns. The deposition process is well controlled and the composition of MnO_2 in fiber electrodes is optimized to enable fiber SCs to possess high specific capacitance. Conductive carbon fibers concurrently serve as current collectors in fiber SCs and as flexible substrates for the deposition of MnO_2. A single MnO_2/CFs fiber electrode exhibits a specific volumetric capacitance of 58.7 F cm^{-3} with a specific gravimetric capacitance of 428 F g^{-1} based on the MnO_2 mass. Two hybrid carbon fiber electrodes are assembled together in parallel with polyvinyl pyrrolidone/Na_2SO_4 gel, which is used as both an electrolyte and a separator. The assembled flexible device exhibits a high volumetric energy density of 3.8 mW h cm^{-3} at a power density of 89 mW cm^{-3} with a good flexibility (CV curves almost unchanged after 2000 bending times) and a superior long cycle stability (an 85.8% capacitance retention after 10000 cycles). Moreover, the integrated SCs could power a commercial light-emitting-diode (LED), demonstrating its strong potential for the practical applications of flexible energy storage devices.

1. Introduction

With the rapid growth of the demands for electronics with flexible, small, roll-up and long term cyclability characteristics, fiber-shaped energy storage devices are emerged as a kind of smart textiles which will revolutionize the functionality of our clothing and the fabrics in our surroundings [1–6]. Among various intelligent devices, fiber supercapacitors (SCs) are particularly attractive because of their high power density, long cycle life and fast charge/discharge rates [6–16]. Fiber SCs are shaped as one-dimensional wires with diameters ranging from micrometers to millimeters with small size and light weight. Compared with conventional planar SCs, fiber SCs have several advantages including a great design versatility to be fabricated into various desired shapes and located at different places, a high flexibility to be woven or knitted into smart textiles with excellent wearability and a good compatibility with other energy harvesting devices or sensors to form integrated multifunctional systems.

Based on the current progress in fiber SCs research, one of the key factors to improve the performance of wire-like devices is the design of fiber electrodes. Different from the electrode materials for conventional planar SCs, which can be fabricated in the form of bulk powder or thin film, the synthesis of fiber electrodes is usually constrained by the geometrical configuration and mechanical flexibility of the substrates. Typically, highly conductive fibers such as metal wires or carbon-based fibers are needed as current collector and the latter one can also be used as electrodes directly. To further increase the capacitance and energy density of fiber SCs, pseudocapacitive materials could be used, such as metal oxides, metal hydroxides and conductive polymer [17–19]. Researchers have explored many smart systems using different fiber electrodes, such as carbon nanotubes (CNTs) fiber [20], reduced graphene oxide (rGO) fiber [21], rGO on Au wire [22], PEDOT/CNTs fiber/Pt wire [23], rGO/CNTs fiber [24], MnO_2/rGO fiber [6] and so on. For example, CNT fiber SCs showed an energy density of 0.601 mWh cm^{-3} [20], and rGO fibers SCs displayed a value of 0.17 μW h cm^{-3} [21]. CuO/AuPd/MnO_2/Cu wire based fiber device exhibited a higher energy density of 0.55 mW h cm^{-3} [25], and the value of N-doped rGO/CNTs fibers SCs could reach to 3.5 mW h cm^{-3} [24]. Although the energy density can be generally increased by well designing the

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fiber-shaped structures, most of the reported systems usually challenge the established textile technology in scalable manufacturing. An effective tactic is to directly incorporate energy storage materials at the formation stages of textile fibers, which could not only provide sufficient and long-lasting energy supplies for their functions, but also take full advantage of their high flexibility to be woven or knitted into textiles of various shapes.

Commercial carbon fibers (CFs), usually made from polyacrylonitrile or pitch, are produced in a large quantity with billions of dollars market. Unfortunately, the carbonaceous fiber can hardly meet the requirement of high specific capacitance and energy density. It is envisaged that it is a practical and promising approach to efficiently incorporate pseudocapacitive materials including transitional metal oxides or conducting polymers into/onto weavable/knittable carbon fiber yarns, which combines the good capacitive energy storage properties of pseudocapacitive components with excellent electrical conductivity and mechanical flexibility of CFs. Manganese dioxide (MnO_2), as a good pseudocapacitive material, is widely used in SCs due to its high specific capacitance, low cost and environmental friendliness. Although Zhou's group synthesized a MnO_2-carbon core-shell fiber by dipping a common carbon fiber into $KMnO_4$ solution, the assembled parallel fiber SCs only shows a moderate energy density of 0.22 mW h cm^{-3} and remains 84% of the initial capacitance after 10000 charge-discharge cycles [26]. Further improvement on energy density and long term cyclability is still needed as well as good electrochemical properties under various bending configurations.

Herein, we fabricated a fiber-shaped, wearable, and all-solid-state SCs based on MnO_2/CFs hybrid fibers by a facile yet effective electrochemical deposition method. The deposition time was well controlled and the composition of MnO_2 in fiber electrodes was optimized to enable fiber SCs to possess high specific volumetric/gravimetric capacitance. Such a hybrid structure is expected to effectively avoid contact resistance caused by polymer binders and conductive additives as well as maximize the utilization of MnO_2 active materials. A single MnO_2/CFs fiber electrode exhibits a specific volumetric capacitance of 58.7 F cm^{-3} at 0.1 A g^{-1} with a specific gravimetric capacitance of 428 F g^{-1} based on the MnO_2 mass. Two hybrid carbon fiber electrodes were assembled together in parallel with polyvinyl pyrrolidone (PVP)/Na_2SO_4 gel, which is used as both an electrolyte and a separator [27–36]. The all-solid-state device displays a high volumetric energy density of 3.8 mW h cm^{-3} at power density of 89 mW cm^{-3} with a good flexibility (CV curves almost unchanged after 1000 bending times) and a superior long cycle stability (an 85.8% capacitance retention after 10000 cycles). Furthermore, the integrated SCs could power a commercial light-emitting-diode (LED), demonstrating its strong potential for energy storage applications.

2. Experimental section

2.1. Materials

All of the reagents were purchased from Sinopharm Chemical Reagents Co., Ltd., and used as received. CFs was purchased from Zhongfu-Shenying Carbon Fiber Co., Ltd.

2.2. Fabrication of MnO_2/CFs fiber electrodes

A bunch of CFs with a length of 2 cm was immersed in sulphuric acid (H_2SO_4) at room temperature for 2 h to improve its hydrophilicity. For the electrodeposition process, the treated CFs was used as the working electrode, and saturated calomel electrode (SCE) and platinum were used as reference and counter electrodes, respectively. Then nanostructured MnO_2 was electrochemically deposited onto the surface of CFs by an anodic electrodeposition as reported in our previous work [37]. A constant current of 0.5 mA was applied during the electrodeposition process and the deposition time varied from 100 s mg^{-1} to 500 s mg^{-1} based on the mass of CFs. Finally, the obtained MnO_2/CFs composites were rinsed with de-ionized (DI) water and dried in vacuum. The as-prepared hybrids with different deposition time were designated here as MnO_2/CFs-x (x stands for 100s, 200s, 300s, 400s, 500s).

2.3. Characterization and electrochemical measurements

The surface morphologies of the obtained composites were examined by field emission scanning electron microscopy (FESEM, Hitachi S-4800) equipped with energy dispersive spectrometer (EDS). X-ray diffraction (XRD) was obtained from ground-up samples of the fibers using a Rigaku D-max-2550 diffractometer with Cu Kα radiation ($\lambda = 0.154$ nm). Raman spectra were carried out with a LabRam-1B Raman spectroscope with He–Ne laser excitation at 632 nm. X-ray photoelectron spectroscopy (XPS) analysis was conducted with a 5000 C ESCA System (Mg Kα $h\nu = 1253.6$ eV) to characterize the chemical state of the samples. The contents of Mn element in the composites were evaluated by inductively coupled plasma-atomic emission spectrometer (ICP Leeman Prodigy). The electrochemical performances of a single MnO_2/CFs electrode were measured in a three electrode system in 1.0 M Na_2SO_4 aqueous solution with platinum mesh as the counter electrode and SCE as the reference electrode, respectively. Cyclic voltammetry (CV), galvanostatic charge-discharge curves and cycling stability measurements were conducted using PGSTAT302N AutoLab electrochemical workstation.

2.4. Fabrication of all solid-state fiber SCs

The all solid-state fiber SCs were fabricated through the assembly of two MnO_2/CFs fiber electrodes in parallel with a solid-state PVP/Na_2SO_4 electrolyte. The PVP/Na_2SO_4 gel electrolyte was prepared by mixing 4 g PVP (K30) and 3 g Na_2SO_4 in 40 mL DI water at 90 °C with 4 h of vigorous stirring [33,38,39]. Before assembly, each MnO_2/CFs fiber was dipped into the PVP/Na_2SO_4 gel. Then the symmetrical SCs were obtained by wrapping two MnO_2/CFs fibers-like electrodes in parallel with PVA film. The solidified PVP/Na_2SO_4 acted as both an electrolyte and a separator.

2.5. Determination of electrochemical performance of SCs

The volumetric capacitance of a single electrode in the three-electrode configuration was calculated from the charge-discharge curves using the following equation:

$$C_{v,electrode} = \frac{I\Delta t}{V_{electrode}\Delta t} \quad (1)$$

where I(A) is the discharge current, Δt(s) is the discharge time, ΔV(V) is the potential window, $V_{electrode}$(cm^3) is the volume of the MnO_2/CFs electrode.

The volumetric capacitance of the all solid-state MnO_2/CFs fiber SCs (two-electrode system) was determined from their charge-discharge curves by the following equation:

$$C_{v,cell} = \frac{I\Delta t}{V_{cell}\Delta V} \quad (2)$$

where I(A) is the discharge current, Δt(s) is the discharge time, ΔV(V) is the potential window, V_{cell}(cm^3) is the volume of the supercapacitor device.