



A flexible supercapacitor consisting of activated carbon nanofiber and carbon nanofiber/potassium-pre-intercalated manganese oxide



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HIGHLIGHTS

- K-preintercalation favors the K^+ diffusion into the interlayer structure of δ - MnO_2 .
- K-preintercalation enhances the pseudocapacitance utilization of δ - MnO_2 .
- K-preintercalated δ - MnO_2 is uniformly grown on CNF with ideal behavior for flexible ASCs.
- This ASC shows excellent cell capacitance retention and flexibility.

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ABSTRACT

Potassium-pre-intercalated δ -phase MnO_2 is uniformly grown on carbon nanofibers for the positive electrode of asymmetric supercapacitors. An electrospun CNF is chemically activated with KOH at 800 °C for the negative electrode, showing ideal capacitive behavior. The crystallinity of MnO_2 is significantly reduced by the pre-intercalation of K ions into its layered structure. This textural characteristic is beneficial to the K^+ diffusion into/out the interlayer structure, leading to effective utilization of the electroactive material of K_xMnO_2 . This unique composite electrode provides both ideal pseudo-capacitive behavior from K_xMnO_2 and excellent electric conductivity from the CNF network, exhibiting a fairly high specific capacitance value of 279 $F g^{-1}$ at 1 $A g^{-1}$ with ca. 82.3% capacitance retention from 1 to 32 $A g^{-1}$. A flexible ASC consisting of the positive $K_xMnO_2@CNF$ electrode, a paper separator, and the negative ACNF electrode is successfully assembled. This cell shows superior ASC performances: a high cell voltage between 0 and 2 V, excellent capacitance retention (10,000 cycles with 10% decay), and simultaneously reaching high specific energy and power of 21.1 $Wh kg^{-1}$ and 9.5 $kW kg^{-1}$. The charge storage behavior of this cell without bending and with a bending angle of 90° shows no apparent difference, demonstrating its potential in the next-generation flexible energy storage devices.

1. Introduction

The development of energy storage devices with thin and light-weight, flexibility, and safety has attracted enormous attention due to their critical role in flexible portable electronic devices such as curved mobile phones, wearable electronics, flexible displays [1–3]. Supercapacitors (SCs) with good flexibility, also called flexible electrochemical capacitors (FECs), have been regarded as promising power devices to achieve the application demands for flexible portable electronics since they showed unique characteristics of high power density, superb cyclic life, short charging time, maintenance-free, wide-

temperature operation, and excellent reliability [3]. Unfortunately, a relatively low energy density of FECs seriously limited their practical applications [4]. Thus, SCs of the asymmetric type are assembled to enlarge the cell voltage and improve the energy density without sacrificing the power density.

Among various SC electrode materials, manganese dioxide (MnO_2) has been widely considered to be one of the most promising materials because of its low cost, abundant resource and environmental friendliness [5–7]. In addition, MnO_2 exhibits promising capacitor properties, such as rapid charge-discharge characteristics, ideal capacitive behavior, good cycle stability, and high theoretical pseudo-capacitance

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($\sim 1370 \text{ F g}^{-1}$) [8]. For example, Qu et al. [9] assembled an ASC with a positive $\text{K}_{0.27}\text{MnO}_2 \cdot 0.6\text{H}_2\text{O}$ electrode and a negative AC electrode using K_2SO_4 as the electrolyte. This cell showed excellent cycle stability (less than 2% capacitance loss after 10,000 cycles) and a relatively high energy density (25.3 Wh kg^{-1}) but a low power density (140 W kg^{-1}). However, due to its relatively low electrical conductivity ($10^{-5} \sim 10^{-6} \text{ S/cm}$), the available specific capacitance of MnO_2 is much lower than its theoretical value [10–12] and significantly limits their application potential in SCs.

The other factors strongly influence the capacitive performances are the thickness and crystallographic structure of MnO_2 , which can be controlled by variation in the synthesis method and post-synthesis treatments [13]. In general, the optimal thickness of MnO_2 was reported to range from a few to tens of nanometers from practical application viewpoint. Moreover, amorphous MnO_2 has been demonstrated to exhibit more promising charge storage characteristics in comparison with the crystalline MnO_2 [14–16]. Accordingly, several investigations tried to create unique microstructures of MnO_2 -based materials for enhancing the utilization of electroactive MnO_2 with ideal capacitive responses [5,13–18].

Cation ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+$) pre-intercalation has been proposed to effectively reduce the crystallinity of MnO_2 and significantly reduce the distance of ion diffusion from the bulk electrolyte to the electrode to improve the utilization of MnO_2 in order to promote the pseudo-capacitance [19–24]. During the charging process, these intercalated ions can be easily expelled from the MnO_2 layer on the positive electrode. During the discharging process, the alkaline cations are easily re-intercalated into the layered MnO_2 . As a result, the crystallinity of MnO_2 is reduced to improve its bulk ion diffusion rate and redox reversibility of cation intercalation/de-intercalation.

Electrospinning has been reckoned to be an effective approach to produce continuous and flexible fibers as a binder-free electrode, which exhibits a controllable diameter, excellent flexibility, superior mechanical property, and low cost [25]. Hence, electrospun carbon nanofibers (CNF) are suitable for the electrode materials of Li-ion batteries [26,27], supercapacitors [28], and electrocatalytic reactions [29], which work as the support for metal oxides in the composite electrodes due to their conductive networks with abundant pores and channels. Basically, the metal oxides are easily coated on the CNF surface to form a core-shell structure in which the CNFs serves as the physical backbone support and offers the channel for efficient electron and ion transportation. For example, Zhi et al. [30] reported that the CNFs/ MnO_2 nanocomposite with 4 nm MnO_2 nanowhiskers exhibits high specific surface area ($102 \text{ m}^2 \text{ g}^{-1}$), good specific capacitance (311 F g^{-1} at a scan rate of 2 mV s^{-1}), good cycling stability (2.4% loss after 1000 cycles), high energy density (80.2 Wh kg^{-1}) and power density (57.7 kW kg^{-1}). Zhou et al. [31] showed that the porous CNF/CNT/ MnO_2 composites exhibit a high specific capacitance ($\sim 631.0 \text{ F g}^{-1}$ at current density of 0.9 A g^{-1}), excellent flexibility and cycle stability (over 95% after 1500 cycles). Obviously, MnO_2 -based CNF materials are promising electrode candidates for SCs, but how to accelerate the transport pathways of cations to the inner active sites to improve utilization of active materials but high reversibility is essential for developing practical SCs.

In this work, a positive electrode of $\text{K}_x\text{MnO}_2\text{@CNF}$ and a negative electrode of ACNF are assembled to be a flexible ASC which shows the high-voltage (2 V) capability in the aqueous electrolyte (0.5 M K_2SO_4), high specific energy and power (21.1 Wh kg^{-1} and 9.5 kW kg^{-1}), excellent capacitance retention (10,000 cycles with 10% decay), and good flexibility. The flexibility mainly results from the negative ACNF electrode and the electrospun CNF substrate *in-situ* grown with K_xMnO_2 . The electrospun CNF is chemically activated with KOH at 800°C (ACNF) to promote the specific capacitance with ideal double-layer capacitive responses. In addition, on the positive electrode, this CNF serves as the substrate support and provides the pathways of charge transport for $\delta\text{-K}_x\text{MnO}_2$ which acts as the redox-active material and

provides high pseudo-capacitance for promoting the energy density. Moreover, the neutral aqueous electrolyte of K_2SO_4 , which has been reported to be superior to other neutral aqueous electrolytes (i.e., Na_2SO_4 and Li_2SO_4) since the order of cations with respect to increasing the migration speeds of the hydrated ions in the bulk electrolyte and within the inner pores of active material is: $\text{Li}^+ < \text{Na}^+ < \text{K}^+$ [32,33]. This research reveals the application potential of our flexible ASC in the future wearable electronics and provides a deep insight for the preparation of promising conductive scaffolds for high-performance flexible supercapacitor electrodes.

2. Experimental

2.1. Preparation of carbonized nanofibers

Electrospun carbon nanofibers were synthesized according to our previous work [28]. Polyacrylonitrile (PAN) in 10 wt% was introduced and stirred in N, N-dimethyl-formamide (DMF) at 80°C for 30 min to form the precursor solution. The precursor solution was added into a 5-mL syringe with a stainless steel needle (24 gauge needle). The solution flow rate was controlled to be 0.7 mL h^{-1} and a high voltage (10 kV) was applied directly to the stainless steel needle. The distance between the needle tip and the collector was kept to be 20 cm. During the carbonization process, the furnace temperature was increased from room temperature to 280°C at a rate of 5°C min^{-1} and kept at this temperature for 2 h under an air flow. The carbon nanofibers (CNFs) were formed by carbonization at 1000°C under the N_2 atmosphere for 2 h.

2.2. Preparation of Mn oxide-based positive electrodes

The potassium-pre-intercalated MnO_2 -coated carbon nanofiber (denoted as $\text{K}_x\text{MnO}_2\text{@CNF}$) was synthesized by introduction of CNFs in a neutral K_2SO_4 solution, similar to our previous work [34]. The weight ratio of CNF:potassium manganite (KMnO_4): K_2SO_4 is 2:1:500. After the oxide decoration step, the $\text{K}_x\text{MnO}_2\text{@CNF}$ fabrics were taken out when the purple color of KMnO_4 had faded into golden brown at 65°C . The acquired $\text{K}_x\text{MnO}_2\text{@CNF}$ fabrics were washed in deionized water for several times to remove the residual reactants. In a controlled experiment, $\delta\text{-MnO}_2$ was decorated on CNFs without potassium pre-intercalation through a similar procedure, which was denoted as $\text{MnO}_2\text{@CNF}$.

2.3. Preparation of CNF-based negative electrodes

CNFs were chemically activated with potassium hydroxide (KOH). The weight ratio of CNFs:KOH is 1:4, mixed at 80°C for 2 h and dried at room temperature for 24 h [35–37]. The activated carbon nanofibers (denoted as ACNFs) were synthesized by chemical activation of the KOH-CNFs mixture which was heated from room temperature to 800°C at a rate of 5°C min^{-1} and kept at this temperature for 30 min under an N_2 flow. To remove the residual KOH, ACNFs were immersed in 0.5 M hydrochloric acid (HCl) for 30 min at room temperature and then, rinsed with distilled water until pH of the filtrated solution reached 6. The final ACNFs were dried at 80°C for 24 h.

2.4. Assembly of the flexible $\text{K}_x\text{MnO}_2\text{@CNF//ACNF}$ supercapacitor

A positive $\text{K}_x\text{MnO}_2\text{@CNF}$ electrode, a paper separator, and a negative ACNF electrode with the geometric area of 1 cm^2 were respectively soaked in a 0.5 M K_2SO_4 electrolyte overnight. A flexible asymmetric supercapacitor (ASC) was assembled in the sandwich structure with the above three components for the full-cell measurements. All solutions used in this work were prepared with $18 \text{ M}\Omega \text{ cm}$ DI water produced using a reagent water system (MILLI-Q SP, Japan), and all reagents were used as received.

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