



Asymmetric supercapacitors based on electrospun carbon nanofiber/sodium-pre-intercalated manganese oxide electrodes with high power and energy densities

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HIGHLIGHTS

- Na-preintercalation favors the Na^+ diffusion into the interlayer structure of $\delta\text{-MnO}_2$.
- Na-preintercalation enhances the pseudocapacitance utilization of $\delta\text{-MnO}_2$.
- Na-preintercalated $\delta\text{-MnO}_2$ is uniformly grown on CNF with ideal behavior for ASCs.
- The ASC shows only 7% capacitance decay in a 2 V, 10000-cycle stability test.

ARTICLE INFO

Keywords:

Carbon nanofibers
 $\delta\text{-Na}_x\text{MnO}_2$
 Sodium pre-intercalation
 Asymmetric supercapacitors

ABSTRACT

The sodium-pre-intercalated $\delta\text{-MnO}_2$ is *in-situ* grown on carbon nanofiber via a simple, one-step method for the application of asymmetric supercapacitors. The pre-intercalation of Na ions into the layered structure of $\delta\text{-MnO}_2$ reduces the crystallinity, beneficial to Na^+ diffusion into/out the interlayer structure and pseudocapacitive utilization of MnO_2 . This Na_xMnO_2 @CNF nanocomposite with desirable pseudo-capacitance from $\delta\text{-Na}_x\text{MnO}_2$ and high electric conductivity from CNF network shows a high specific capacitance of 321 F g^{-1} at 1 A g^{-1} with ca. 75.2% capacitance retention from 1 to 32 A g^{-1} . An ASC cell consisting of this nanocomposite and activated carbon as the positive and negative electrodes can be reversibly charged and discharged to a cell voltage of 2.0 V in 1 M Na_2SO_4 and 4 mM NaHCO_3 with specific energy and power of 21 Wh kg^{-1} and 1 kW kg^{-1} , respectively. This ASC also shows excellent cell capacitance retention (7% decay) in the 2 V, 10,000-cycle stability test, revealing superior performance.

1. Introduction

Supercapacitors, also called electrochemical capacitors (ECs), have been considered a promising energy storage system since they show several fascinating advantages compared to the secondary batteries and conventional capacitors. For example, they provide superb cyclic life, high power density, short charging time, maintenance-free and wide-temperature operation, and excellent reliability in comparison with rechargeable batteries [1]. However, the low energy density is the main drawback of supercapacitors, which significantly limits their application potential in energy storage.

According to $E = \text{CU}^2/2$ (C: cell capacitance, U: cell voltage),

promoting the energy density of supercapacitors can be achieved by enlargement in the cell voltage and/or cell capacitance. An effective way to extend the cell voltage is to construct the asymmetric supercapacitors (ASCs) which consist of two dissimilar capacitive electrode materials working in different potential windows; hence the energy density can be improved without sacrificing the power density. In addition, the ASCs with, at least, one electrode consisting of pseudo-capacitive materials (transition metal oxides or conducting polymers) with high specific capacitance are preferred since enormous amount of redox pseudo-capacitance can be provided by the faradaic reactions [2].

Among various transition oxides, manganese dioxide (MnO_2) is one

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of the most suitable electrode material candidates due to its high theoretical pseudo-capacitance ($\sim 1370 \text{ F g}^{-1}$), low-cost, abundance in nature, and environmental friendliness [3–6]. However, this material suffers from its poor conductivity ($10^{-5} - 10^{-6} \text{ S cm}^{-1}$). Consequently, the practical pseudo-capacitance of MnO_2 is significantly lower than the theoretical value and capacitance retention at high charge/discharge rates is relatively low [3,7]. Hence, many studies showed the optimal thickness of MnO_2 ranging from few to several nanometers to afford the best performance [3,8–11].

On the other hand, the crystallographic structure of MnO_2 was found to strongly influence the electrochemical behavior, which are designable by variation in the synthesis methods and post-synthesis treatments [12]. For example, the order of crystallographic structure with respect to decreasing specific capacitance is: $\delta \approx \alpha > \gamma > \lambda > \beta$ [13]. Clearly, the δ -type (the birnessite phase) MnO_2 exhibits the largest capacitance value among all of the crystallographic structures. Owing to the layered structure of $\delta\text{-MnO}_2$, this oxide offers more favorable pathways for intercalation/de-intercalation of protons or cations in comparison with monoclinic oxides [12]. However, protons or cations were reported to difficultly diffuse into/out of the $\delta\text{-MnO}_2$ interlayers during the charging/discharging processes because of good crystallinity [14]. Hence, $\delta\text{-MnO}_2$ with reduced crystallinity is considered to favor the cation diffusion towards the redox active sites [3,15,16]. Accordingly, a relatively open structure of $\delta\text{-MnO}_2$ with reduced crystallinity not only reduces the length of ion diffusion from the electrolyte to the redox active sites but also provides high utilization of pseudo-capacitance.

Cation pre-intercalation has been proposed to reduce the crystallinity of MnO_2 and to improve its bulk ionic diffusion characteristics and redox reversibility of cation intercalation/de-intercalation [12,17,18] and there is great interest in synthesizing cation-pre-intercalated MnO_2 recently [17,19–22]. For example, Na^+ -pre-intercalated MnO_2 , denoted as Na_xMnO_2 , was considered to be electrochemically active and highly reversible due to its layered structure and Na^+ distribution between layers, favorable for the accommodation of cations [18,23,24]. However, the proposed Na_xMnO_2 materials were synthesized via a solid-state reaction at high temperatures, which greatly increased the energy consumption. Thus, simple and cost-effective methods are worthy being developed.

Electrode materials synthesized by electrospinning generally feature large surface area, low cost, controllable diameter, excellent mechanical property, short ion transport lengths, and so on [25]. Carbon nanofibers (CNFs) have been prepared through the electrospinning technique for a long time, which act as a well conductive substrate to support the growth of metal oxides. For example, Wang et al. [26] proposed that $\delta\text{-MnO}_2$ could be grown on CNF by an *in-situ* method, exhibiting excellent electrochemical performance at temperatures ranging from 0 to 75°C . In addition, this composite possessed good cycling stability of 95.3% at 25°C and inferior capacity retention of 82.4% at 75°C . Tao et al. [27] reported that the CNT/CNF/ MnO_2 composite electrode (CNT: carbon nanotube) showed a high specific capacitance of 517 F g^{-1} at a scan rate of 5 mV s^{-1} by cyclic voltammetric evaluation due to the facilitated channels for electron and ion transport. Therefore, metal oxides can be successfully grown or deposited on the CNF surface to form a core-shell hybrid composite with improved electrochemical behavior. However, how to speed up the transport pathways of cations to the inner active sites with improved utilization of active materials is very essential for ECs.

Herein, sodium-pre-intercalated MnO_2 is firstly and *in-situ* grown on CNF at a mild temperature, denoted as $\text{Na}_x\text{MnO}_2\text{@CNF}$. Within the composite, CNF not only serves as the substrate support but also offers the pathways for electron transport. The $\delta\text{-Na}_x\text{MnO}_2$ acts as the redox-active material and provides high pseudo-capacitance. Moreover, due to the reduced crystallinity, the transport pathways of Na^+ to the active sites are further shortened by the pre-intercalation of Na^+ . There are several advantages of this *in-situ* method for growing $\delta\text{-Na}_x\text{MnO}_2$ on

CNF in comparison with previous studies [1,12,17]. Firstly, the required hydrophilic property of CNF can be simply achieved during the *in-situ* synthesis process since potassium manganite, a precursor and a strong oxidizing agent in this method, can directly oxidize CNF to form a hydrophilic surface. This simple process results in the conformal deposition of $\delta\text{-Na}_x\text{MnO}_2$ on the hydrophilic CNF without complicated steps (e.g., electrochemical-acidic pre-treatment for hydrophilic CNF, electrochemical deposition of MnO_2 , and pre-intercalation of Na^+). Secondly, the crystallographic structure of $\delta\text{-MnO}_2$ is not changed by the pre-intercalation of Na^+ instead of the phase transformation from $\alpha\text{-MnO}_2$ into the δ phase [12,17]. Therefore, the capacitive characteristics of $\delta\text{-MnO}_2$ without and with cation pre-intercalation can be evaluated and compared without the influences from the phase transform issue. Thirdly, the electrochemical activation step of common Mn oxides is not necessary for $\delta\text{-Na}_x\text{MnO}_2$ in order to reach an ideal and reproducible pseudo-capacitive signal. Finally, there is no need in binders (e.g., PVdF, Nafion, and so on) for CNF systems, further simplifying the electrode structure. Hence, the unique and novel $\text{Na}_x\text{MnO}_2\text{@CNF}$ nanocomposite possesses a high specific capacitance for the ASC application, resulting from the improved utilization of electroactive MnO_2 species. A positive electrode of $\text{Na}_x\text{MnO}_2\text{@CNF}$ and a negative electrode of activated carbon (AC) are assembled to be an ASC device which shows the high-voltage ($\sim 2 \text{ V}$) capability with high specific energy and power in the aqueous electrolyte ($1 \text{ M Na}_2\text{SO}_4 + 4 \text{ mM NaHCO}_3$).

2. Experimental

2.1. Electrode preparation

Carbon nanofibers were synthesized in the same way as our previous study [1]. Typically, 10 wt% polyacrylonitrile (PAN) was dissolved in N, N-dimethyl-formamide (DMF) at 80°C under stirring to form the precursor. The precursor solution was fed 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} . A voltage of 10 kV was applied directly to the stainless steel needle. The distance between the needle tip and the collector was maintained at 20 cm. Temperature of the furnace was initially increased from room temperature to 280°C at a rate of 5°C min^{-1} and kept at this temperature for 1 h under an air flow. After the nanofibers were synthesized, they were carbonized at 1000°C under the N_2 atmosphere for 1 h. The carbonized nanofibers were denoted as CNFs.

The sodium-pre-intercalated MnO_2 was decorated onto CNFs (denoted as $\text{Na}_x\text{MnO}_2\text{@CNF}$) by immersion of CNFs in a neutral Na_2SO_4 solution, according to our previous work [12]. The optimal weight ratio of CNF, potassium manganite (KMnO_4), and Na_2SO_4 is 2: 1: 200 at 65°C [26]. The $\text{Na}_x\text{MnO}_2\text{@CNF}$ nanocomposite was taken out when the purple KMnO_4 solution discolored (ca. 2 h). The obtained $\text{Na}_x\text{MnO}_2\text{@CNF}$ nanocomposites were rinsed with deionized water for several times to remove the residual reactants. In a controlled experiment, $\delta\text{-MnO}_2$ was deposited on CNF without Na pre-intercalation through a similar method, which was denoted as $\text{MnO}_2\text{@CNF}$.

2.2. Assembly of the asymmetric $\text{Na}_x\text{MnO}_2\text{@CNF}$ //AC supercapacitor

An ASC was assembled in the sandwich structure with one piece of 1 cm^2 $\text{Na}_x\text{MnO}_2\text{@CNF}$, a paper separator of 1 cm^2 , and one piece of 1 cm^2 AC with the electrolyte containing $1 \text{ M Na}_2\text{SO}_4$ and 4 mM NaHCO_3 , for the full-cell measurements. All solutions used in this work were prepared with $18 \text{ M}\Omega \text{ cm}$ DI water produced by a reagent water system (MILLI-Q SP, Japan), and all reagents were used as received.

2.3. Material characterizations

Morphologies of CNF, $\text{MnO}_2\text{@CNF}$, and $\text{Na}_x\text{MnO}_2\text{@CNF}$ were

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