Journal of Power Sources 255 (2014) 335–340

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Electrospun nanofiber of hybrid manganese oxides for supercapacitor: Relevance to mixed inorganic interfaces

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HIGHLIGHTS

- 3-Dimensional MnO_x nanofiber was formed by electrospinning.
- Upon calcination at different temperatures, MnO_x NFs became variable composition of Mn_3O_4 to Mn_2O_3.
- This study examined the supercapacitor performance depending on the phases of MnO_x.
- We found that mixed phase exhibited a higher capacity than that of respective single phase.
- The high specific capacitance was attributed to 3D structure and the reduced interfacial resistance.

ARTICLE INFO

Article history:
Received 3 December 2013
Received in revised form
5 January 2014
Accepted 6 January 2014
Available online 15 January 2014

Keywords:
Electrospun nanofiber
Manganese oxides
Mixed phase
Supercapacitor
Three-dimensional (3D) electrode

ABSTRACT

We prepare electrospun nanofibers (NFs) from a poly(N-vinylpyrrolidone)/manganese (II) acetate composite by electrospinning for application in supercapacitors. As-spun hybrid NFs are calcined at different temperatures to remove the polymer matrix, resulting in inorganic MnO_x NFs of variable compositional ratios of Mn_3O_4 to Mn_2O_3. Interestingly, the sample of MnO_x NFs that is calcined at 500 °C exhibits the highest electrochemical performance, reaching a high specific capacitance of 360.7 F g^{-1} at a current density of 1 A g^{-1}. This remarkable performance is attributed to the unique three-dimensional morphology and the reduced interfacial resistance of the mixed-phase MnO_x NFs within the matrix electrode and the electrolyte.

1. Introduction

Due to the exhaustion of natural resources and associated environmental issues as well as the increasing demand of energy for future portable devices and electric vehicles, there has been an intense interest in alternative energy conversion and storage systems with high efficiency, low cost, and environmental benignity [1–3]. Among many energy storage devices, electrochemical capacitors, also known as supercapacitors, have attracted considerable attention because of their high power density, fast charge–discharge rate, long cycle life, wide thermal operating range, and low maintenance cost. Therefore, the performance of electrochemical capacitors is complementary to those of secondary batteries and fuel cells [4–6].

Supercapacitors are generally classified into two types depending on their charge storage mechanism and the active materials used. Electric double-layer capacitors store electrical charges at the interface of a porous, carbon-based electrode and an electrolyte based on the non-Faradaic reaction [4,7,8]. On the other hand, pseudocapacitors utilize the Faradaic reaction of redox-active materials such as conducting polymers and metal oxides [4,9–11]. In particular, transition metal oxides that exhibit pseudocapacitive behavior, such as RuO_2 [12–14], MnO_x, NiO [15,16], CoO [17], and Fe_3O_4 [18], have been proposed as promising electrode materials for supercapacitors because of their high capacitance and good cycling stability. Among the above oxides, manganese oxide (MnO_x) is clearly noteworthy, displaying fine specific capacitance (200–600 F g^{-1}) and reversible charge–discharge feature with its natural abundance and low cost [6,19–22]. Despite these favorable features of MnO_x, its poor electric conductivity and stability often cause unsatisfactory performance in supercapacitors. In addition, various oxidation states of MnO_x result in a range of different crystalline

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http://dx.doi.org/10.1016/j.jpowsour.2014.01.011

phases with potentially different electrochemical behaviors. However, the relationship between phase structure and electrochemical properties of MnO_x has not been fully studied.

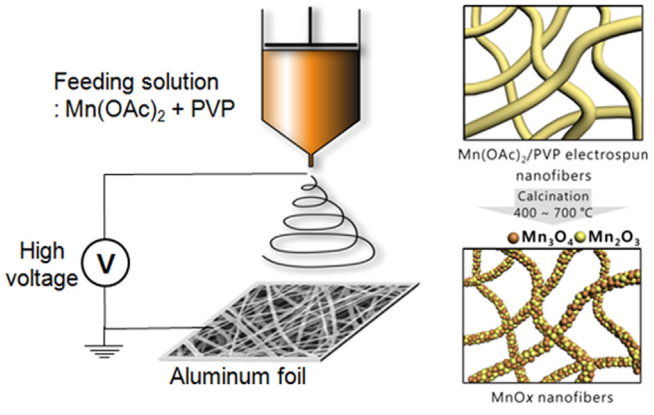
In order to improve supercapacitor performance, several approaches have been proposed, including developing new materials by deposition of electroactive metallic nanoparticles and conducting polymers, and creating new electrode structures [4,22–24]. As a representative approach, three-dimensional (3D), porous electrodes are known to exhibit superior capacitance because of increased specific surface area and enhanced access of electrolytes to the surface of the electrodes. In this regard, electrospinning can form porous, 3D electrodes from continuous, 1D nanofibers (NFs) of various materials [25–28]. Furthermore, electrospinning not only fabricates polymer and inorganic fibers with various dimensions, but also produces unique fiber structures such as hollow, core–shell, or porous structure [29–31].

In this report, we describe the fabrication of porous, 3D electrodes composed of MnO_x NFs by electrospinning for application in supercapacitors (Scheme 1). Specifically, a polymer matrix of poly(N-vinylpyrrolidone) (PVP) mixed with manganese (II) acetate ($Mn(CH_3COO)_2$ or $Mn(OAc)_2$) was employed to form continuous, 3D NFs of controlled dimensions. Upon calcination at different temperatures (400, 500, 600, and 700 °C), these NFs were transformed into hybrid MnO_x NFs with a varying degree of mixed phase of Mn_3O_4 and Mn_2O_3 in varying ratios. Interestingly, the relative composition of each phase was demonstrated to have a considerable influence on the supercapacitor performance by a series of electrochemical characterization measurements. For example, we confirmed that a mixed phase of Mn_2O_3 and Mn_3O_4 delivered a higher capacitance (360.7 F g^{-1}) than either of its individual material oxide taken individually, arising from the unique 3D morphology and the reduced interfacial resistance of the mixed phase within the matrix electrode and the electrolyte.

2. Experimental

2.1. Preparation of electrospun MnO_x NFs

Poly(N-vinyl pyrrolidone) (PVP) solution was prepared by dissolving PVP powder (M_w 1,300,000 g mol^{-1}) in deionized water (20 wt%). Then, $Mn(OAc)_2$/PVP solution was prepared by dissolving manganese acetate (20 wt%) in PVP solution. This solution was stirred for at least one day in order to obtain homogeneously distributed solutions. The solution obtained was injected from a syringe and syringe was fixed in syringe pump. The size of the needle in the electrospinning was 25 G, and the needle was connected to high-voltage power supply. The flow rate of the syringe pump was fixed at 10 μl min^{-1}, and the distance between the needle and collector was 10 cm and the applied voltage was 25 kV. The electrospun $Mn(OAc)_2$/PVP NFs were annealed at different temperatures (400, 500, 600 and 700 °C) to remove the polymer matrix and result in the MnO_x NFs.



Scheme 1. Schematic representation for the fabrication of the electrospun fiber and subsequent calcination process for hybrid MnO_x NF supercapacitors.

2.2. Structural characterizations

The morphology and fiber diameter of the prepared MnO_x NFs were investigated using a field emission scanning electron microscopy (FESEM, FEI, Nanonova 230) and transmission electron microscopy (TEM, JEOL JEM-2100 accelerating voltage of 200 kV, Gatan CCD camera). X-ray diffraction (XRD) measurements were employed by a high-power X-ray diffractometer (Rigaku Co., D/MAZX 2500V/PC) from 10° to 80°.

2.3. Electrochemical characterization

Electrochemical performance of the electrospun MnO_x NFs were carried out with a standard three-electrode test cell with 0.5 M Na_2SO_4 aqueous solution as electrolyte. Platinum wire and Ag/AgCl were used as a counter and reference electrode, respectively. The characterization of the electrochemical performance for the MnO_x electrode was conducted using a VMP3 electrochemical potentiostat (BioLogic Inc.). Cyclic voltammograms (CVs) and the galvanostatic charge–discharge test were carried out with a potential window from −0.2 to 0.8 V versus Ag/AgCl in 0.50 M Na_2SO_4 electrolyte with scan rates from 5 to 200 mV s^{-1} and a current density of 1 A g^{-1}. In order to internal resistance of MnO_x electrode, measurement of electrochemical impedance was performed in frequency range of 100 kHz–100 MHz.

3. Results and discussion

3.1. Characterization of electrospun MnO_x NFs

Initially, $Mn(OAc)_2$/PVP NFs were successfully fabricated by electrospinning using the procedures outlined in the experimental section. Fig. 1 shows the SEM images and diameter distribution of the as-spun $Mn(OAc)_2$/PVP NFs and the MnO_x NFs formed after calcination at temperatures from 400 to 700 °C. As shown in Fig. 1a, as-spun $Mn(OAc)_2$/PVP NFs were randomly oriented in a continuous, 3D, porous internal structure. The range of NF diameters in the sample was relatively narrow, and no beads were formed. The polymeric component (PVP) was completely degraded at ~400 °C in air, as determined by thermogravimetric analysis (TGA). Accordingly, the as-spun $Mn(OAc)_2$/PVP NFs were calcined above 400 °C in air (Fig. S1 in Supporting information). After calcination at different temperatures, the 3D porous structure was retained without significant structural deformation. However, the diameter of MnO_x NFs decreased after calcination due to the removal of the PVP matrix and the crystallization of MnO_x; for example, the average diameter of as-spun fiber decreased from 135 ± 18 nm to 72.3 ± 14.3 nm (400 °C), 64.2 ± 12.6 nm (500 °C), 52.7 ± 8.9 nm (600 °C) and 54.5 ± 6.9 nm (700 °C), respectively.

Various forms of manganese oxide such as α-MnO_2, δ-MnO_2, λ-MnO_2, Mn_2O_3, and Mn_3O_4 are known to exist depending on the conditions of annealing [32]. We further characterized the phase composition of MnO_x NFs after calcination by X-ray diffraction (XRD) (Fig. 2). The XRD patterns of MnO_x fibers calcined at different temperatures corresponded to either Mn_3O_4 (JCPDS 024-0734) or Mn_2O_3 (JCPDS 073-1826), or a combination of both. The NFs calcined at 400 °C adopted the tetragonal Mn_3O_4 phase exclusively (Fig. 2a). Above 400 °C, Mn_3O_4 transformed into the more oxidized