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Improved supercapacitor performance of MnO_2-electrospun carbon nanofibers electrodes by mT magnetic field

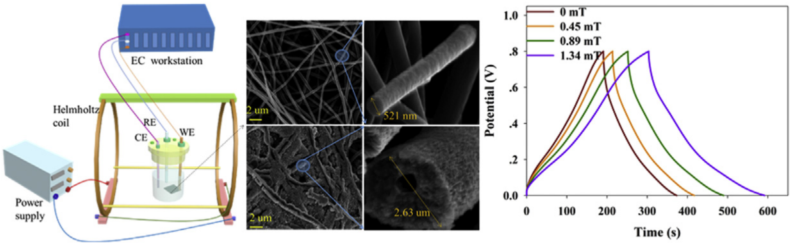
Zheng Zeng [1], Yiyang Liu [1], Wendi Zhang, Harish Chevva, Jianjun Wei*

Department of Nanoscience, Joint School of Nanoscience and Nanoengineering (JSNN), University of North Carolina at Greensboro, Greensboro, NC 27401, USA

HIGHLIGHTS

- Electrochemical deposited MnO_2-ECNFs as supercapacitor electrodes.
- Significant capacitance enhancement by mT magnetic field strength.
- Insight to the energy storage improvement.

GRAPHICAL ABSTRACT



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ABSTRACT

This work reports on a finding of mT magnetic field induced energy storage enhancement of MnO_2-based supercapacitance electrodes (magneto-supercapacitor). Electrodes with MnO_2 electrochemically deposited at electrospun carbon nanofibers (ECNFs) film are studied by cyclic voltammetry (CV), galvanostatic charge/discharge, electrochemical impedance spectroscopy (EIS), and life cycle stability tests in the presence/absence of milli-Tesla (mT) magnetic fields derived by Helmholtz coils. In the presence of a 1.34 mT magnetic field, MnO_2/ECNFs shows a magneto-enhanced capacitance of 141.7 F g^{-1} vs. 119.2 F g^{-1} (~19% increase) with absence of magnetic field at a voltage sweeping rate of 5 mV s^{-1}. The mechanism of the magneto-supercapacitance is discussed and found that the magnetic susceptibility of the MnO_2 significantly improves the electron transfer of a pseudo-redox reaction of Mn(IV)/Mn(III) at the electrode, along with the magnetic field induced impedance effect, which may greatly enhance the interface charge density, facilitate electrolyte transportation, and improve the efficiency of cation intercalation/de-intercalation of the pseudocapacitor under mT-magnetic field exposure, resulting in enhancement of energy storage capacitance and longer charge/discharge time of the MnO_2/ECNFs electrode without sacrificing its life cycle stability.

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1. Introduction

Electrochemical double layer supercapacitors have drawn a lot of attention due to fast charging/discharging rate, increased energy density and power density, and large life cycle stability [1–4]. However, regarding the energy storage capability, there is an emerging need to develop supercapacitors with high relative dielectric constant or redox reactions in the double layer and surface area of the electrode for higher energy density and larger life cycle stability [5–7]. Some of the electroactive metal oxides, e.g. ruthenium oxide (RuO_2) [8], manganese oxide (MnO_x) [9], nickel

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* Corresponding author.
E-mail address: j_wei@uncg.edu (J. Wei).

[1] Equal contribution.

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oxide (NiO_x) [10], cobalt oxide (Co_3O_4) [11], tin oxide (SnO_2) [12], zinc oxide (ZnO) [13], and vanadium (V) oxide (V_2O_5) [14] etc. were used in supercapacitor (so-called pseudocapacitor) electrodes to offer fast and reversible redox reactions, contributing to higher energy density capacity [15]. To increase surface area, carbon nanomaterials, such as carbon nanotubes (CNTs) [16], carbon nanofibers (CNFs) [17], graphene nanofoam (GF) [18], and reduced graphene oxide (rGO) [19] were used in supercapacitors, which not only provide unique size and surface dependent properties but also excellent intrinsic physical (e.g. electrical, thermal, chemical and mechanical) properties. Among these, electrospun carbon nanofibers (ECNFs) is known for its large porosity, high conductivity, low cost in production with freestanding nature, and good scaffolds to uniformly support nanostructured metal oxide [20]. Electrospinning is an efficient fiber production method which uses electric force to draw charged threads of polymer solutions or polymer melts up to form polymer nanofibers [21] which can be converted to porous ECNFs with subsequent carbonization [22]. Electrospinning has become a powerful and easy method to form carbon nanofibers in large scale for broad applications. It has been used for electrode material production or separator materials for supercapacitors [23–25], Li (or Na)-ion batteries [26–29], and preparation of electrical double-layer capacitor half-cells [30].

Recently, the influence of an external magnetic field over the capacitance of electrodes has won some attention due to effects of Lorentz force acting on moving charges/ions, charge density gradient modulation, electron state excitation and oscillatory magnetization [31–33], thus energy storage improvement. Two strategies of using magnetic field for enhancing the electrochemical process in capacitors have been demonstrated. One is to introduce magnetic nanoparticles into the electrode in the presence of an external magnetic field. For instance, Fe_2O_3/graphene nanocomposites [33], Fe_3O_4/active carbon nanocomposites [34], and Fe_3O_4/active carbon nanocomposites [35] demonstrated enhancement of the capacitance and energy density with an external magnetic field. The other one is to reconstruct the charge density and electric polarization in the magnetic material system. For example, ionic liquid was used in charge carrier engineering to achieve tunable dielectric permittivity [31].

During the past years, MnO_2 has been one of the most commonly used transition-metal oxides that have been used as pseudocapacitive electrode materials due to its unique characteristics, such as easy-for-deposition, stability and significantly enhanced energy storage performance [36,37]; however, little is known about the magnetic field effect on its energy storage. Herein, for the first time, we present a magnetization-induced capacitance enhancement in MnO_2/ECNFs nanocomposite electrodes fabricated by electrochemical deposition of MnO_2 on ECNFs. The MnO_2/ECNFs electrode was characterized by scanning electron microscopy (SEM), x-ray powder diffraction (XRD), energy-dispersive x-ray spectroscopy (EDX), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and superconducting quantum interference device vibrating sample magnetometer (SQUID VSM). The electrochemical performance of the MnO_2/ECNFs electrodes for capacitive energy storage was studied by cyclic voltammetry (CV), galvanostatic charge/discharge, electrochemical impedance spectroscopy (EIS), and life cycle stability tests in the presence/absence of milli-Tesla (mT) to sub-mT magnetic fields derived by Helmholtz coils.

2. Results and discussion

The morphologies of ECNFs and MnO_2/ECNFs were characterized by SEM (Fig. 1b,d). The ECNFs with nanofiber diameter of about 521 nm (Fig. 1c) are decorated by MnO_2 coating with thickness of ~2.1 μm making a total diameter of the fiber as about 2.63 μm (Fig. 1e). The charge current of 40 μA, the charge time of 3 h in an aqueous precursor solution containing 10 mM $MnSO_4$ and 100 mM Na_2SO_4 were applied to achieve the electrochemical deposition of the MnO_2 at the 1 cm^2 ECNFs film. The success of MnO_2 deposition was confirmed with Raman spectra (Fig. S1 Mn–O at the Raman shift of 627 cm^{-1}), XRD pattern (in Fig. S2, the well resolved peak at 37.1° is attributed to MnO_2), and FTIR spectra (in Fig. S3, Mn–O stretch is presented at the wavenumber of 648 cm^{-1} and 731 cm^{-1}) [38,39]. TGA shows the weight fraction of MnO_2 in the MnO_2/ECNFs electrode is about 53% (Fig. S4), which was further verified using EDX analysis by averaging different spectrum zones (Fig. S5).

As a pseudocapacitive electrode, the MnO_2/ECNFs electrode possesses combined contribution of spacers and redox reaction, i.e., the electrochemical double layer capacitance and the pseudocapacitance from MnO_2 for energy storage. The former stores charge electrostatically due to the adsorption of ions at electrode surfaces and is mainly determined by the electrode surface area. While, for the latter, the energy is stored in virtue of highly reversible redox reactions (e.g. electron transfer reactions) between Mn(IV)/Mn(III) species and cation intercalation/de-intercalation at the MnO_2/electrolyte interfaces [36,40,41]. The charge storage mechanism of the MnO_2/ECNFs electrode involving the KOH electrolyte can be expressed as [36,42]:

$$Mn(IV)O_2 + mH^+ + nK^+ \leftrightarrow Mn(III)Mn(IV)OOH_mK_n \tag{1}$$

Equation (1) represents the successive multiple surface redox reactions between the Mn(IV)/Mn(III) complexes leading to the pseudo-capacitive charge storage mechanism [42].

To measure the specific capacitance of the MnO_2/ECNFs electrode and magnetic field effect, CV was performed using the classical three-electrode method [43] in a 6.0 M KOH electrolyte solution. Fig. 2 shows the representative, stable cyclic voltammetry (CV) loops with or without an external magnetic field, which present a combination of both double layer and pseudocapacitive behaviors within the scan voltage from 0.0 V to 0.8 V. There are a pair of peaks at the voltage between 0.4 and 0.5 V vs. Ag/AgCl which might be attributed to the redox reaction of the Mn(IV)/Mn(III) species in the form of K^+ intercalation [41]. The overall specific capacitance is calculated from the integrated area of the CV loops (see details in Supplementary information, SI). In the absence of an external magnetic field, the specific capacitance of the MnO_2/ECNFs electrode was calculated to be 119.2, 105.8, 92.8, 71.0, 53.4 F g^{-1} at the voltage sweeping rates of 5, 10, 20, 50, and 100 mV s^{-1}, respectively. Compared to that of the ECNFs-only electrode (Fig. S6a), MnO_2/ECNFs shows higher capacitance because of the higher relative dielectric constant of MnO_2 and its pseudo-activity. In the presence of 1.34 mT magnetic field, the capacitance of the MnO_2/ECNFs magneto-supercapacitor electrode was obtained to be 141.7, 125.9, 110.2, 86.5, 67.0 Fg^{-1} at the same voltage sweeping rates of 5, 10, 20, 50, and 100 mV s^{-1}, respectively, which increased by about avg. 19% for all sweeping rates (Fig. 2b–d, Fig. S7). Since there is no measurable enhancement of capacitance of the ECNFs-only electrodes at the same range of voltage sweeping rates (Fig. S6) under the magnetic field, one can conclude that the magnetocapacitance enhancement of the MnO_2/ECNFs electrode is resultant from the magnetic field effect on the MnO_2 at the ECNFs substrate.

The effect of magnetization on the galvanostatic charge/discharge performance of MnO_2/ECNFs was studied under different current densities (0.5–20 A g^{-1}, Fig. 3abc & Fig. S8). The curvature of the charge step between the voltage of 0.0–0.4 V and larger growth of the discharge curve between the same range voltages suggest a combined contribution from pseudocapacitance and

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