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Electrochemical behavior of zinc oxide-based porous carbon composite nanofibers as an electrode for electrochemical capacitors

Chang Hyo Kim [a], Bo-Hye Kim [b,*]

[a] Department of Polymer Engineering, Graduate School, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 500-757, Republic of Korea
[b] Division of Science Education, Daegu University, 201 Daegudae-ro, Gyeongsan-si, Gyeongbuk-do 712-714, Republic of Korea

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ABSTRACT

Zinc oxide (ZnO)-based porous carbon composite nanofibers (ZnO–CCNFs) are prepared by one-step electrospinning and subsequent thermal treatment using zinc acetate, as the pore generator and ZnO precursor. In particular, the PAN-based nanofiber paper contains in-frame incorporated nitrogen surface functionalities, due to its large residual nitrogen content in the char. The N functionalities doped at the graphite edges enhances their capacitance by the pseudocapacitive effect.

Therefore, the ZnO–CCNFs showed higher capacitance (163 F g^{-1} at 1 mA cm^{-2}) and energy density (20.80–14.80 W h kg^{-1} in the power density range of 400–20,000 W kg^{-1}) than the control sample of carbon nanofibers (CNFs) in aqueous electrolyte. The combination of the high surface area of CNFs with the large capacity of surface functional groups such as N, O, and ZnO as the faradic electrode material affords the advantages of both the double layer capacitance and the pseudocapacitance, thereby offering potential applications for supercapacitors.

1. Introduction

The increasing demand for clean energy and the growing concern regarding air pollution and global warming have stimulated intense research into energy storage and conversion from alternative energy sources [1–4]. Electrochemical capacitors have attracted increasing attention as alternative energy storage systems for portable electronics, electric vehicles, and renewable energy systems operating on clean energy sources, such as solar and wind energy, due to their characteristics of high power density and durability [5–8]. Electrochemical capacitors may be divided into two categories according to the capacitance mechanism: electric double-layer capacitors (EDLCs) and pseudocapacitors (PCs) [9,10]. The energy storage mechanism of EDLCs is an electrostatic attraction with charge accumulation at the electrode/electrolyte double-layer interfaces [11], while PCs store energy by redox reactions on the electrode surface between the electrode materials and the electrolyte [10,12].

Porous carbon materials have attracted much attention due to their stable physical and chemical properties, large specific surface area, controlled pore structure, and high conductivity, which are beneficial properties for EDLC active materials [13–18]. However, the energy density of carbon materials as an EDLC electrode is much lower than that of secondary batteries, which limits the potential applications, while supercapacitors are ideal for applications that require short-term power boosts such as peak power assistance for batteries in electric vehicles [19,20]. To overcome the disadvantages of low energy density and specific capacitance, redox-active transition metal oxides such as oxides of Ru, Ni, Co, and Zn are commonly used as faradic electrode materials for PCs [21–23]. Among them, ZnO is a promising electrode material for supercapacitors, because of its good electrochemical activity and eco-friendly nature [24,25]. ZnO had also received special attention as an electrode material because of its high energy density of 650 Ag^{-1} [26]. However, although ZnO has received considerable attention as a desirable electrode material, the active materials are typically too insulating to support the fast electron transport required by the high rates [4]. Hence, the introduction of metal oxides in carbon materials should allow the utilization of both the faradaic capacitance of the metal oxide and the double layer capacitance of the carbon materials with large specific surface areas, thereby improving the capacitance and energy/power capabilities [27]. Among the many types of carbon materials, electrospun carbon nanofibers (CNFs) are one-dimensional nanostructures with a three-dimensional interconnected mesoporous texture, which can greatly affect the electrical properties of the

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* Corresponding author. Tel.: +82 53 850 6982; fax: +82 53 850 6989.
E-mail address: bohye@daegu.ac.kr (B.-H. Kim).

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supercapacitor. In particular, due to their high electrical conductivity ($\rho = (3\text{–}7) \times 10^{-3}\ \Omega$ cm), electrospun CNFs have been widely used as ideal electron pathways, resulting in high electrolyte accessibility and stability for developing high performance supercapacitors [28–30].

Here, we report the fabrication of ZnO–CCNFs by a simple and effective one-step electrospinning method, followed by stabilization and carbonization with the help of zinc acetate. We used zinc acetate to generate the porous structure as well as ZnO particles by the elimination of organic moieties during the thermal treatment. This work focuses on optimizing the effects of different zinc acetate contents and different carbonization temperatures on the electrochemical performance of the ZnO–CCNFs. The porous ZnO–CCNFs were morphologically and electrochemically characterized to evaluate their electrochemical utilization by cyclic voltammetry (CV), electrochemical impedance spectroscopy, and charge–discharge in aqueous electrolyte.

2. Experimental

2.1. Materials and fabrication

Polyacrylonitrile (PAN), zinc acetate, and dimethylformamide (DMF) were purchased from Aldrich Chemical Co. (USA) and used as received without further purification. Electrospinning solutions were prepared by dispersing a given amount of zinc acetate (10 and 20 wt% relative to PAN) in a 10 wt% PAN solution in DMF. The PAN/zinc acetate blend solution was electrospun into nanofibers (NFs) by using an electrospinning machine (NTPS-35 K, NTSEE Co., Korea). The NFs were stabilized in air at 280 °C to induce thermal stability and were carbonized at 800 and 1000 °C in a horizontal furnace under a flow of nitrogen at a heating rate of 5 °C min^{-1}. The carbonized samples at 800 °C were termed Zn(20)-800 and Zn(10)-800, with a concentration ratio of zinc acetate to PAN of 10 and 20 wt%, respectively. The carbonized sample at 1000 °C was termed Zn(20)-1000, and CNF-800 without any zinc acetate loading was also prepared as a control sample to compare the electrochemical properties.

2.2. Characterization

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a Shimadzu TGA 50 (Shimadzu, Inc.). The samples were heated up to 1000 °C at a rate of 10 °C min^{-1} in air. The surface morphology of the nano-structured materials was examined by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4700) equipped with energy dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) micrographs were obtained with a Tecnai-F20 system operated at 200 kV at the Gwangju center of the Korea Basic Science Institute (KBSI), Korea. Samples for analysis were prepared on a carbon-coated Cu grid by dip-coating in dilute-appropriate solutions (~1.0 wt% solid content). The compositional verification and elemental mapping were done by TEM equipped with EDS mapping in the scanning TEM (STEM) mode. X-ray diffraction (XRD) was obtained from ground-up samples of the fibers using a D-Max-2400 diffractometer and Cu Kα radiation (λ = 0.15418 nm). The specific surface area and the micropore size distribution of the samples were evaluated by using the Brunauer–Emmett–Teller (BET) theory and the micropore plot method. The chemical state of the surface and the elemental surface composition were characterized by X-ray photoelectron spectroscopy (XPS) on a VG Scientific ESCALAB 250 spectrometer with an Al Kα X-ray source (15 mA, 14 kV). The surface atomic ratios were calculated from the ratio of the corresponding peak areas after correction with the theoretical sensitivity factors based on the Scofield's photoionization cross-sections.

2.3. Cell fabrication and measurement

The electrodes of the supercapacitor cells were fabricated with two symmetric ZnO–CCNF electrodes (1.5 cm × 1.5 cm) using Ni foil as the current collector. All samples used as electrodes were cut into pieces of the web and directly used for the electrode, without the addition of any polymer binder, such as poly(vinylidene fluoride), or conducting agent, such as super-p, because they were fabricated as a web to enable adequate contact between the sample and the current collector. 6.0 M KOH was used as the aqueous electrolyte. CV of the unit cell was performed between −0.2 and 0.80 V for the aqueous electrolyte at 25 mV s^{-1}. The charge/discharge properties of the samples were measured using a WBCS 3000 battery cycler system (Won-A Tech. Co., Korea) at a current density of 1–20 mA cm^{-2}. The energy density was measured as a function of constant power discharge in the range of 400–20,000 W kg^{-1}. The ac impedance of the cell was measured over the frequency range of 100 kHz to 10 MHz using an electrochemical impedance analyzer (Jahner Electrik IM6e, Germany).

3. Results and discussion

Fig. 1 shows the TGA curve of the electrospun NF before thermal treatment, Zn(20) NF, using a heating rate of 10 °C min^{-1} in the temperature range from room temperature to 1000 °C. The mass was slightly decreased from about 100 to 200 °C due to the release of water. The mass drop from 200 to 350 °C, attributed to the pyrolysis of the fibers, was in agreement with the peak on the DSC curve of the Zn(20) NF and Zn(10) NF, as shown in Fig. 1 [31]. The sharp exothermic peak at about 300 °C indicates the cyclization of the nitrile group in PAN and corresponds to the oxidative stabilization process [32]. Furthermore, the exothermic peak was shifted downwards from 303.28 °C for Zn(0) NF to 248.32 °C for Zn(10) NF and then to 242.05 °C for Zn(20) NF with increasing zinc acetate concentration, as shown in the inset of Fig. 1. Although oxidative stabilization is critical for obtaining dimensional stability during high temperature thermal treatment, the stabilization includes complex chemical reactions and time-consuming steps. Therefore, reducing the oxidative stabilization time is important for cost-reduction and simplifying the process [33]. In this work, we could infer that the stabilization processes of the zinc

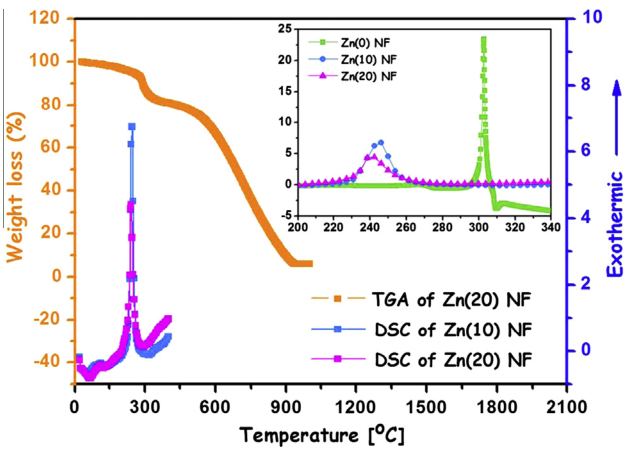

Fig. 1. TGA and DSC data of electrospun NFs.