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Barnacle-like manganese oxide decorated porous carbon nanofibers for high-performance asymmetric supercapacitors

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ABSTRACT

In this study, barnacle-like manganese oxide (MnO₂) decorated porous carbon nanofibers (PCNF) were synthesized using electrospinning and the chemical precipitation method for high-performance asymmetric supercapacitors. The porous structure of PCNF was acquired using poly(styrene-co-acrylonitrile) in the electrospinning solution. In order to obtain the optimized barnacle-like MnO₂ on PCNF (MnO₂-PCNF), the barnacle-like MnO₂ was synthesized using different synthetic times (namely, 1.5, 3.0, and 7.0 min) of the chemical precipitation. Among them, the optimized MnO₂-PCNF for 3.0 min exhibited the well-dispersed MnO₂ on the PCNF with the nano-size of 190–218 nm. The optimized MnO₂-PCNF showed the superior specific capacitance of 209.8 F g⁻¹ at 10 mV s⁻¹ and the excellent high-rate performance of 160.3 F g⁻¹ at 200 mV s⁻¹ with the capacitance retention of 98.7% at 100 mV s⁻¹ for 300 cycles. In addition, electrochemical performances of asymmetric cell (constructed activated carbon and MnO₂-PCNF) showed the high specific capacitance of 60.6 F g⁻¹ at the current density of 0.5 A g⁻¹, high-rate capacitance of 30.0 F g⁻¹ at the current density of 10 A g⁻¹, and the excellent energy density of 30.3–15.0 Wh kg⁻¹ in the power density range from 270 to 9000 W kg⁻¹. The enhanced electrochemical performance can be explained by the synergistic effects of barnacle-like MnO₂ nanoparticles with a high active area related to high specific capacitance and well-dispersed MnO₂ with a short ion diffusion length related to the excellent high-rate performance.

1. Introduction

In recent years, due to the characteristics of high power density, excellent cycling stability, fast energy-storage ability, and low operating temperature, electrochemical capacitors (ECs) have started to be widely used for various applications such as electric vehicles, portable electronic devices, and industrial power management [1–4]. In general, ECs are categorized into electric double-layer capacitors (EDLCs) and pseudo-capacitors (PCs) by different energy-storage mechanisms [5–7]. The principle of EDLCs is based on the physical adsorption of electrostatic charges in electrical double-layer between the electrode and the electrolyte. The principle of PCs is based on the chemical reaction with the faradaic redox reaction between the electrode and electrolyte. As compared to EDLCs, PCs have the attractive advantage of a higher energy density. Furthermore, PCs are composed of an electrode, an electrolyte, and a separator. Among those, electrode material is directly related to high-performance PCs that are commonly used for transition-metal oxides, such as manganese oxide (MnO₂), nickel oxide (NiO), cobalt oxide (Co₃O₄), vanadium oxide (V₂O₅), and ruthenium oxide

(RuO₂) [8–11]. Among transition-metal oxides, MnO₂ is a promising candidate as an electrode material for the high-performance PCs owing to its high theoretical specific capacitance (1380 F g⁻¹), as well as low cost, and eco-friendliness. However, despite its various advantages, MnO₂ is limited in its use as an electrode material in PCs due to the aggregation of MnO₂ and low electric conductivity, which results in a poor electrochemical performance [12–14]. To address these issues, carbon-based materials (graphite, graphene, carbon nanotubes (CNT), and carbon nanofibers (CNF)), characterized by a high electrical conductivity, a high specific surface area, and an excellent electrochemical stability, are employed as support materials for MnO₂ in PCs [15–17]. In particular, CNF is reported for support materials due to the high specific surface area (448 m² g⁻¹), low electrical resistivity (1.7 × 10² S m⁻¹), and superb physical/chemical stability, as well as the network structure [18–22]. The network structure consisting of one-dimensional nanofibers can afford the efficient electron transfer and a fast ion diffusion rate. For these reasons, many researchers have studied the MnO₂ and CNF composites in order to solve the above-mentioned problems. However, well-dispersed barnacle-like MnO₂ nanoparticles on porous

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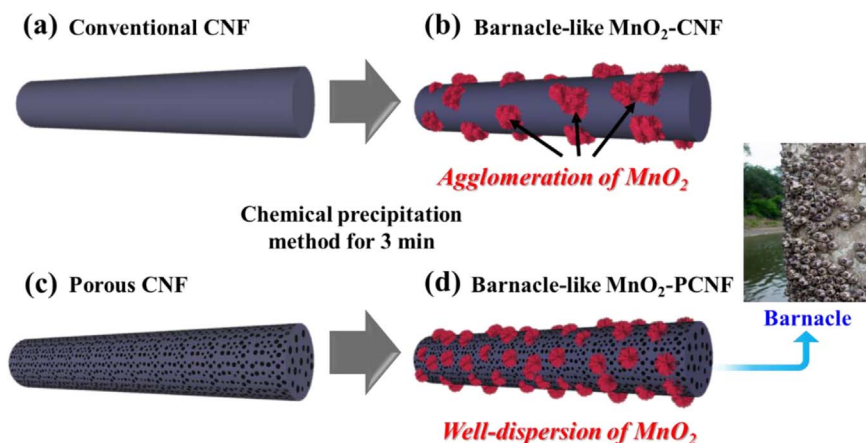


Fig. 1. A schematic illustration of (a) the conventional CNF by only the PAN polymer using electrospinning; (b) the MnO_2 -CNF3 using the chemical precipitation method; (c) the PCNF by the SAN polymer using electrospinning, and (d) the MnO_2 -PCNF3 using the chemical precipitation method.

carbon nanofiber (PCNF) have not yet been thoroughly studied for high-performance PCs.

Furthermore, one of key factors in an appropriate dispersion of the MnO_2 on CNF supports is development of a porous structure. The unique structure of well-dispersed MnO_2 nanoparticles on PCNF supports can lead to increase the active site and reduce the ion diffusion length for high-performance PCs. In the present study, we report synthesizing PCNF supports and well-dispersed barnacle-like MnO_2 nanoparticles on supports using electrospinning and the chemical precipitation method, and demonstrate their improved electrochemical performance.

2. Experimental

The barnacle-like MnO_2 decorated PCNFs were synthesized using an electrospinning and the chemical precipitation method. In order to synthesize the PCNFs, polyacrylonitrile (PAN, $M_w = 150,000$ amu, Aldrich) and poly(styrene-co-acrylonitrile) (SAN, $M_w = 165,000$ amu, Aldrich) were dissolved in *N,N*-dimethylformamide (DMF, 99.8%, Aldrich) under stirring for 5 h. Specifically, the SAN polymer was used for the formation of pore on the CNF supports. The electrospinning process was papered as follows. The syringe feeding rate was applied at 0.03 ml h^{-1} . The distance between the collector and the syringe needle was fixed at $\sim 15 \text{ cm}$ in the humidity of 10%. The voltage was maintained at $\sim 13 \text{ kV}$. The as-spun nanofibers were stabilized at 280°C for 2 h in air and then carbonized at 800°C for 2 h in nitrogen atmosphere (99.999%). The porous structure of CNF was formed by the decomposition of the SAN polymer during the carbonization process [23]. In order to decorate the barnacle-like MnO_2 on PCNFs, PCNFs were dispersed in 2 M sulfuric acid (H_2SO_4 , 95%, Aldrich) with stirring for 30 min at 80°C , which was followed by adding potassium permanganate (KMnO_4 , $M_w = 156.03 \text{ g mol}^{-1}$, 99%, Aldrich) to the prepared solution. To obtain the optimized amount of MnO_2 on PCNFs, three different types of samples were prepared: 1.5, 3, and 7 min during the synthetic time of the chemical precipitation method. All samples were then washed for several times using DI-water. In what follows, the three types of samples are referred to as MnO_2 -PCNF1.5, MnO_2 -PCNF3, and MnO_2 -PCNF7, respectively. For comparison, the barnacle-like MnO_2 decorated CNFs without the porous structure of CNF was synthesized for 3 min using the above-mentioned method (referred to herein as MnO_2 -CNF3).

The structural and morphological characteristics of all samples were investigated by field emission-scanning electron microscopy (FESEM; Hitachi S-4800) and transmission electron microscopy (TEM; JEOL, 2100 F, KBSI Suncheon Center). Furthermore, X-ray diffraction (XRD, Rigaku D/MAX2500V) with $\text{Cu K}\alpha$ radiation and X-ray photoelectron spectroscopy (XPS, ESCALAB250) with $\text{Al K}\alpha$ X-ray source were used to investigate the crystallinity and the chemical bonding states, respectively. The electrochemical measurements were performed using a

conventional three-electrode system with potentiostat/galvanostat (Autolab PGSTAT302N, FRA32M) in 0.5 M H_2SO_4 solution as the electrolyte. The three-electrode system was composed of a glassy carbon as the working electrode, an Ag/AgCl (saturated KCl) as the reference electrode, and a Pt wire as the counter electrode. To prepare the electrode, the slurry was mixed with the prepared samples as active materials, Ketjen black (Mitsubishi Chemical, ECP-600JD) as the conducting material, and poly(vinylidenedifluoride) (PVDF, Alfa Aesar) as the binder in the weight ratio of 7:1:2 in *N*-methyl-2-pyrrolidinone (NMP, 99.5%, Aldrich). The slurry was then coated on glassy carbon and dried in air at 60°C for 1 h. In the next step, cyclic voltammetry (CV) measurements were performed in the potential range of 0.0–1.0 V at the scan rates of 10, 30, 50, 100, and 200 mV s^{-1} . In addition, the electrochemical performances of asymmetric cell constructed by activated carbon (AC) and MnO_2 -PCNF3 were performed using a potentiostat/galvanostat in the 1 M Na_2SO_4 solution. The electrode of AC and MnO_2 -PCNF3 were prepared by a mixed slurry of the active material (AC and MnO_2 -PCNF3), the conducting material (Ketjen black, Mitsubishi chemical), and the binder (PVDF, Alfa Aesar) with the weight ratio of 7:1:2 in the NMP solvent. Prepared slurries were then casted on nickel foam as the current collector and dried at 80°C for 10 h in a dry oven. CV and charge-discharge performance were measured at the scan rate of 10 mV s^{-1} and the current density of 0.3, 0.5, 0.7, 1.0, 1.5, 2.0, 3.0, 5.0, and 10.0 A g^{-1} in the potential range of 0.0–2.0 V. In addition, to investigate the charge transfer and ion diffusion process, electrochemical impedance spectroscopy (EIS, PGSTAT302N by Eco Chemie, Netherlands) for AC// MnO_2 -CNF3 and AC// MnO_2 -PCNF3 was measured using the fresh electrode in frequency range of 100 kHz to 10 MHz.

3. Results and discussion

Fig. 1 shows a schematic illustration of an ideal synthetic process of barnacle-like MnO_2 -CNF3 and barnacle-like MnO_2 -PCNF3. The conventional CNF (Fig. 1(a)) is synthesized using the PAN polymer as the carbon precursor without the SAN polymer. MnO_2 -CNF3 (Fig. 1(b)) shows an agglomeration of barnacle-like MnO_2 on CNF due to the low surface area of CNF and the strong C-C bonding on the CNF surface. By contrast, PCNF (Fig. 1(c)) to obtain the porous structure of CNF is synthesized using the PAN polymer with SAN polymer as the pore forming agent. The micropores and mesopores in PCNF are formed by the decomposition of the SAN polymer during the carbonization process (see Table 1). MnO_2 -PCNF3 (see Fig. 1(d)) formed the well-dispersed barnacle-like MnO_2 on the PCNF due to the high surface area of PCNF by formed pore on the surface.

Fig. 2 shows the FESEM images of MnO_2 -CNF3, MnO_2 -PCNF1.5, MnO_2 -PCNF3, and MnO_2 -PCNF7. All samples showed the diameter in the range of 274.1–432.3 nm for MnO_2 -CNF3, 242.9–302.3 nm for

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