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Capacitive properties of hierarchically structured carbon nanofiber/graphene/MnO_2 hybrid electrode with nitrogen and oxygen heteroatoms

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ABSTRACT

Hierarchically structured carbon nanofiber/graphene/MnO_2(CGMn) hybrid with oxygen and nitrogen functionalities was fabricated in the form of a web via electrospinning as an electrode material for supercapacitors. The CGMn electrode exhibited a high capacitance (225 Fg^{-1} at 1 $mAcm^{-2}$), enhanced energy and power efficiency (15.8–13.6 $Whkg^{-1}$ in the power density range of 197–4000 Wkg^{-1}), and excellent capacitance retention (13% of the initial value at a discharge current of 20 $mAcm^{-2}$) in a 6 M KOH aqueous electrolyte, because of the combination of the double-layer capacitance and the pseudo-capacitive character associated with the surface redox-type reactions. The porosity and the number of heteroatoms of the CGMn composite were adjusted by changing the PMMA concentration and carbonization temperature. Therefore, the oxygen- and nitrogen-containing hierarchical porous CGMn hybrid prepared by a simple method is a promising candidate as an electrode material for supercapacitors.

1. Introduction

Generally, supercapacitors can be divided into electric double-layer capacitors (EDLCs) and pseudocapacitors (PCs) according to different charge-discharge mechanisms [1–3]. EDLCs are based on an electrostatic attraction with charge accumulation of electronic and ionic charges at the electrode-electrolyte interface, while PCs achieve Faradaic electrochemical storage via the redox reaction of electrode materials with the electrolyte. Porous carbon materials with large surface areas, suitable pore structures, and high conductivity can be used as EDLC active materials. Carbon materials often exhibit long durability, high power density, and good rate capability, but they have low specific capacitance because of their intrinsic charge storage mechanism [4–7]. Compared with EDLCs, PCs induced by transition-metal oxides have higher specific capacitance due to the reversible Faradaic redox reaction occurring in the electrode materials. However, the poor electronic conductivity and low surface area of transition-metal oxides in PCs limit their electrochemical performance such as cycling behavior and chemical reversibility in aqueous electrolytes [8–10]. Therefore, the combination of carbon materials and transition-metal oxides is expected to improve the capacitive performance by enhancing the specific capacitance, power and energy density, and rate capability. Based on the above considerations, many research groups have hybridized MnO_2 with carbon nanofibers (CNFs) to give good electrical conductivity and high capacitive performance [8–12]. Increasing the surface area of the electrode/electrolyte interface to enhance the charge transport is very important to improve the electrochemical properties of the electrode for maximizing the electrosorption efficiency. However, porous carbon-based electrochemical capacitors (ECs) still suffer from electrode kinetic problems of charge diffusion, because it is difficult for many of the micropores in the CNFs surface to be accessed by the solvated ions for diffusion into the micropores during high rate charge-discharge processes [12–14]. Wu et al. [15] investigated highly conductive electrospun CNF/MnO_2 coaxial nano-cables containing iron acetylacetonate for applization as pseudo-supercapacitors with high energy and power density due to the large specific surface area and high electronic conductivity introduced by iron acetylacetonate.

Herein, to avoid the above shortcomings of porous CNF electrode materials, we introduce surface heteroatoms such as oxygen

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and nitrogen into the CNF/graphene composites as a support for MnO_2. Generally, heteroatoms change the electron acceptor/donor characteristics of the carbon material, and thus can promote desirable interactions and improve the accessibility of the ions solvated with a polar solvent. Therefore, heteroatoms embedded in the porous CNFs are expected to increase not only the hydrophilicity of the carbons in aqueous electrolytes but also the interfacial capacitance by the pseudocapacitive effect [16–20]. Therefore, we focused on the hierarchically structured CGMn hybrids with heteroatoms using a simple electrospinning method in order to evaluate their electrochemical behaviors. The oxygen and nitrogen heteroatoms in CNF/graphene composites are mainly derived by a facile and economic method with heat treatment and concentration of the precursor such as poly(methyl methacrylate) (PMMA). The several methods to induce heteroatom-doped carbon materials include carbonization of nitrogen-containing polymers such as polyaniline and melamine, in situ CVD synthesis, and reaction of NH_3 gas. However, they are not suitable for commercial application because of their complicated preparation and relatively high cost. As a potential candidate for energy storage applications, the present research therefore demonstrates a simple method to produce advanced functional carbon materials with hierarchical porous structure controlled by PMMA concentration and carbonization temperature. The relationships among the porous structures and textures, nitrogen and oxygen contents, and the electrochemical properties in aqueous electrolytes, are discussed in detail. These results provide new insights into the pseudocapacitance arising from nitrogen, oxygen, and MnO_2 functionalities, and the double-layer capacitance of CGMn composites with suitable porosity for high-performance carbon electrode materials for supercapacitors.

2. Experimental

2.1. Materials and fabrication

Polyacrylonitrile (PAN), PMMA, manganese(II) chloride ($MnCl_2$), and dimethylformamide (DMF) were purchased from Aldrich Chemical Co. (USA) and used as received. Rice husk-derived graphene was prepared by activating agricultural waste using KOH at 550–700 °C [21]. Electrospinning solutions were prepared by dispersing an appropriate amount of $MnCl_2$ (3 wt%) in PAN/PMMA with different blend ratios (PAN:PMMA = 7:3 and 9:1) in a DMF solution. An appropriate amount of graphene (5 wt% relative to PAN and PMMA) was added to the electrospinning solutions, and the solution was sonicated for 2 h in a bath-type sonicator to homogeneously disperse the graphene. This mixture was continuously stirred at 60 °C until a homogeneous solution formed, after which it was cooled to room temperature. This solution was then spun into nanofiber (NF) webs using an electrospinning apparatus (NTPS-35K, Ntsse Co., Korea) operating at 20 kV. The electrospun NF webs were stabilized in flowing air at 280 °C for 1 h in an air atmosphere. The dried fibers were carbonized at 800 and 900 °C in a horizontal furnace for 1 h under a nitrogen flow at a heating rate of 5 °C min^{-1}. The samples were termed CGMn(3) and CGMn(1) with PAN/PMMA blend ratios of 7:3 and 9:1, respectively. Moreover, the carbonized samples were denoted as CGMn(3)-800, CGMn(1)-800 and CGMn(1)-900, where the numbers represent the carbonization temperature. To compare the electrochemical properties in aqueous electrolyte, samples of CG(3)-800 with PAN/PMMA blend ratios of 7:3 without $MnCl_2$ were synthesized at the same carbonized temperature of 800 °C.

2.2. Characterization

The surface morphology of the nano-structured materials was examined by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4700). A transmission electron microscopy (TEM) instrument equipped with energy dispersive X-ray spectroscopy (EDS) was used to investigate the microstructure. Selected area electron diffraction (SAED) micrographs were obtained with a Tecnai-F20 system operated at 200 kV. Samples for analysis were prepared on a carbon-coated Cu grid by dip-coating in appropriately dilute solutions (~1.0 wt% solid content). The specific surface area and the micropore size distribution of the samples were evaluated by using the Brunauer–Emmett–Teller (BET) theory. The chemical state of the surface was 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).

2.3. Cell fabrication and measurement

Two-electrode supercapacitor cells (two identical carbon electrodes without any reference electrode) were fabricated to simplify the fabrication procedure with two symmetric CGMn electrodes (1.5 cm × 1.5 cm) using Ni foil as the current collector. All CGMn electrodes were fabricated without adding any polymer binder or conducting agent for application as a web suitable for good contact between the sample and current collector. For the fabrication of the symmetric supercapacitor, the weight ratio of CGMn electrodes in positive (0.0058 g) and negative (0.0057 g) electrodes was 1:1. In the asymmetric assembly, the working electrode (CGMn(1)-800) was used as the positive electrode while the CNF carbonized at 800 °C (CNF-800) alone was used as the negative electrode. The aqueous electrolyte was 6.0 M KOH. Cyclic voltammetry (CV) of the unit cell was performed between 0 and 1.0 V for the aqueous electrolyte. 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 $mAcm^{-2}$. 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

The morphologies and structures of CGMn(1)-800, CGMn(1)-900, and CGMn(3)-800 were examined by FE-SEM images. All CGMn composites possess a fully interconnected structure between fibers, a round shape, and a well-controlled average diameter, as shown in Fig. 1. The average diameter of the CGMn fiber is gradually decreased from 540 nm to 300 nm as the temperature is increased from 800 to 900 °C (Fig. 1a–b), showing more mass loss from the extended carbonization temperature. The fiber diameter of CGMn decreases with increasing carbonization temperature, due to removal of non-carbon elements with increasing carbonizing temperature. The average fiber diameter of CGMn(1)-800 is about 540 nm, while that of CGMn(3)-800 is thinner at about 460 nm, as shown in Fig. 1c, because low spinning solution viscosity changes reduced the fiber diameter at higher PMMA concentrations [22]. In the case of CGMn(3)-800, the surface roughness increases and many small nanoparticles, as well as needle-like particles, are decorated on the surface of the NFs in Fig. 1d. In addition, the cross sectional field-emission SEM image in CGMn(3)-800 shows several mesopores induced by decomposition of the PMMA phase [23]. The carbonization temperature and PMMA content influence the fiber diameter and surface roughness in the process of electrospinning and heat treatment.

The microstructure and elementary composition of CGMn(3)-800 were further investigated using TEM and EDS with corresponding SAED, as shown in the inset in Fig. 2. The TEM images of all composites show many nanometer-sized dark particles