



Supercapacitive properties of nanoporous carbon nanofibers developed from polyacrylonitrile and tetraethyl orthosilicate



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ABSTRACT

Nanoporous carbon nanofibers (CNFs) are produced by incorporating tetraethyl orthosilicate (TEOS) into polyacrylonitrile (PAN) via electrospinning, and their electrochemical properties are investigated as an electrode in supercapacitors. TEOS is used as a pore generator in the PAN-based precursor for the CNFs with stabilized Si-related functional structures. The microstructures (e.g., nanometer-size diameters, high specific surface areas, narrow pore size distributions, and tunable porosities) and some of the surface functionalities of the CNFs are affected by the TEOS concentration. The electrode with these characteristics demonstrates better supercapacitor performance in terms of capacitance, energy, and power efficiency, which is attributed to the synergistic effect between the double-layer capacitance and the pseudo-capacitive effect.

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1. Introduction

Nanoporous carbon materials are a very attractive material due to their variety of forms and microtextures with unique properties for adsorbents, catalyst supports, and supercapacitor electrode materials [1–4]. The development of various carbonaceous electrode materials for supercapacitors has been an important issue in recent years in view of their large specific surface, controlled pore structure, ability to adjust the ratio of micropores to mesopores, good conductivity, and functionalization of the materials [5–8]. Supercapacitors 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, while PCs store energy via redox reactions on the electrode surface between electrode materials and the electrolyte [11]. Generally, the highly developed surface area and proper pore size distribution of the carbon electrodes play important roles in the electrochemical capacitance performance [12,13]. Although carbon electrode materials can obtain high capacitance, power density, and long cycle life, the energy density of carbon as an EDLC electrode is much lower than that of secondary batteries, which limits the application area [14]. Therefore, beside the pore size distribution, the introduction of heteroatoms such as oxygen and nitrogen

promotes desirable interactions and improves the accessibility of the ions solvated with a polar solvent, yielding an enhanced energy density and improving the power capabilities through pseudo-capacitive effects [15,16].

Here, we report the fabrication of nanoporous carbon nanofibers (CNFs) by a simple and effective one-step electrospinning method, followed by stabilization and carbonization with the help of tetraethyl orthosilicate (TEOS). In general, the additional activation step is not only time and energy consuming but pore formation has to be accompanied by significant mass loss, resulting in overall low yield [17]. Therefore, one of the interesting and versatile way to overcome these difficulties is sol-gel process for porous nano-composite of organic and inorganic materials. We used TEOS as the pore generator in the polyacrylonitrile (PAN)-based precursor for the CNFs with stabilized functional structures such as silicon oxynitride (SiO_xN_y) and silicon oxycarbide (SiO_xC_y). TEOS enhances the reaction rate catalytically in an air-stabilized process, and effectively creates suitable pores on the outer surface of CNFs during a thermal treatment by sol-gel reaction spontaneously. Recently we reported thin and bendable electrodes consisting of porous CNF via the electrospinning of PAN containing TEOS [18]. We could infer that the stabilization processes of TEOS incorporated nanofibers were kinetically higher than that of pure electrospun nanofibers due to the catalytic ability of TEOS [19]. This work focuses on optimizing the effects of different contents of TEOS on the electrochemical performance of the CNFs. The nanoporous CNFs with heteroatoms were morphologically and electrochemically characterized to evaluate their electrochemical utilization in aqueous electrolytes.

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2. Experimental

2.1. Materials and fabrication

Electrospinning solutions were prepared by dispersing a given amount of TEOS (10, 20, and 30 wt% to PAN) into 10 wt% PAN solution in the dimethylformamide (DMF). The PAN/TEOS blend solution was electrospun into nanofibers (NFs) by using an electrospinning machine (NTPS-35K, NTSEE Co., Korea). To produce a web, a voltage of 18 kV was applied to the positively charged capillary, and a tip-to-collector distance of 15 cm was maintained during the electrospinning process. The NFs were stabilized in air at 280 °C to induce thermal stability in the NFs and were carbonized at 800 °C in a horizontal furnace under a flow of nitrogen at a heating rate of 5 °C/min. The four samples were termed CNF, TP-10, TP-20, and TP-30, indicating concentrations of 0, 10, 20, and 30 wt% of TEOS to PAN, respectively.

2.2. Characterization

The surface morphology of the nano-structured materials was examined by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4700). The surface functionality of the CNFs was examined by Fourier transform infrared (FTIR) spectroscopy (Nicolet 200) in the range of 400–4000 cm^{-1} . Backscattering Raman measurement was carried out with a Renishaw in via-Reflex instrument at room temperature at the Gwangju center of the Korea Basic Science Institute (KBSI), Korea. A He–Ne laser was used to produce monochromatic red light of 633 nm wavelength at a power of approximately 15 mW on the sample surface. The chemical state of the surface was characterized by X-ray photoelectron spectroscopy (XPS) on a VG Scientific ESCALAB 250 spectrometer with an AlK X-ray source (15 mA, 14 kV). The porosity of the CNF webs was evaluated by using the Brunauer–Emmett–Teller (BET) method. The full range of pore sizes over a continuous scale was confirmed by density functional theory calculations (DFT PLUS for Windows).

2.3. Cell fabrication and measurement

The electrodes of the supercapacitor cells were fabricated with two symmetric CNF electrodes (1.5 cm \times 1.5 cm) using Ni foil as the current collector. All electrode samples were cut into pieces of the web and directly used for the electrode, without adding any polymer binder, such as poly(vinylidene fluoride), or conducting agent, such as super-p, because they were fabricated as a web that enables adequate contact between the sample and the current collector. 6.0 M KOH was used as aqueous electrolyte. Cyclic voltammetry (CV) of the unit cell was performed between 0 and 1.0 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} . In a symmetrical system, the specific capacitance C_m in farads per gram of sample (Fg^{-1}) is related to the specific capacitance of the cell, C , in terms of Eq. (1);

$$C_m = 2C/m \quad (1)$$

where C is the capacitance of the cell in farads (F), m is the weight (g) per electrode of samples. The energy density was measured as a function of constant power discharge in the range of 400–20,000 W kg^{-1} .

3. Results and discussion

Fig. 1a shows the properties of the spinning solution at various TEOS concentrations. The electrical conductivity of the spinning

solutions increased from 55 to 132.7 $\mu\text{S/cm}$ and the viscosity decreased from 1409 to 327.5 cP as the TEOS concentration was increased from 0 wt% to 30 wt%. FESEM images and fiber diameter distributions of the CNF webs produced at various TEOS concentrations are presented in Fig. 1b–d. When the TEOS concentration was increased from 10 to 20 to 30 wt%, the average fiber gradually became thinner, as the diameter decreased from 430 to 350 to 250 nm, respectively, and these samples exhibited continuous cylindrical morphologies. The viscosity and electrical conductivity changes reduced the fiber diameter at higher TEOS concentrations [20].

The IR spectra of CNF, TP-10, TP-20, and TP-30 are shown in Fig. 2a. In agreement with previous reports in the literature, the following three main observations were made [21,22]: (i) in case of TP-10, TP-20, and TP-30, the main bond of Si–O–C in the range of 1000–1250 cm^{-1} is composed of the C–O bond and Si–O cross-link bond, compared with CNFs [23]; (ii) the band at 1590 cm^{-1} is attributed to the C=C vibrations; and (iii) the broad band at ca. 3490 cm^{-1} is due to hydrogen bonded O–H stretching vibrations. The Raman spectra (Fig. 2b) of the three CNFs typically showed peaks in the range of 300–500 and 1300–1600 cm^{-1} . These Raman spectra exhibited two large peaks: one near 1340 cm^{-1} , which is a D peak from amorphous structures of carbon, and the other near 1603 cm^{-1} , which is a G peak from graphitic structures of carbon [24]. The broad band appearing between 300 and 500 cm^{-1} was attributed to a contribution from the amorphous Si–O–C-related structure [25]. The ratio of the integrated intensity of the D peak to that of the G peak (R) increased from 0.984 (TP-10) to 1.04 (TP-20) to 1.12 (TP-30) with increasing TEOS concentration from the Raman spectra [26], indicative of the formation of regions of more disordered carbons at higher TEOS concentrations. It is well known that the addition of silicon can increase the sp^3 -to- sp^2 ratio because silicon does not form π bonds [27]. Furthermore, the chemical state of nitrogen atoms could be assigned to two categories in the XPS spectrum (Fig. S1): N-6 (pyridinic nitrogen, N-(SiO_x)₃ 398.5 eV) and N-Q (quaternary nitrogen, nitrogen–oxygen (N–O) bonds, 401.1 eV) [28,29]. The results reveal TP series to be composed of SiO_xC_y , SiO_x , and SiO_xN_y structures. The introduction of these polar groups in the carbon matrix modifies the performance of the electro-chemical capacitor.

The CNF electrodes were cut into rectangles and attached to a nickel foil current collector in 6 M aqueous KOH electrolyte to evaluate the capacitance of the material in a two-electrode system. Fig. 3a shows the CV graphs of the CNF, TP-10, TP-20, and TP-30 electrodes at a scan rate of 25 mV s^{-1} . All of the CV curves displayed a box-like shape, indicative of their high potential as electrode materials for EDLC. The induced current of the TP-30 electrode was higher than that of the other CNFs, indicating that TP-30 has the largest capacitance among the materials employed here. The TP-10, TP-20, and TP-30 electrodes showed a much larger quasi-rectangular shape with some distortion at high voltages, whereas the CNF electrode showed a rectangular and symmetric shape. The shape of the voltammogram of TP-10, TP-20, and TP-30 is related to some surface functionalities, which can undergo fast redox reactions in aqueous electrolytes, resulting in a pseudo-capacitive contribution [30]. Fig. 3b shows the capacitance variation with different discharge current densities. As expected from the CV results, the TP-30 electrode had a higher specific capacitance (161.4 Fg^{-1}) at 1 mA cm^{-2} than that of the other electrodes, for example, 2.5-fold greater than that of the CNF electrode. The specific capacitance increased in the order CNF < TP-10 < TP-20 < TP-30, which demonstrated the benefit of the micropores for charge accumulation and the greater capacitance obtained for a large surface area and suitable pore size.

The texture parameters are summarized in Fig. 4. As shown in Fig. 4a, the specific surface area and mesopore volume fraction

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