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Activated carbon nanotubes/polyaniline composites as supercapacitor electrodes

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ABSTRACT

Chemically A-MWCNT (activated multiwalled carbon nanotube)/PANI (polyaniline) composites produced *via* ultrasonic polymerization of an aniline monomer in the presence of A-MWCNTs were investigated as potential electrode materials for supercapacitors. These composites were compared to pristine MWCNTs and MWCNT/PANI composites. The influence of the pore structure, which developed because of the polymerization process, was investigated by measuring N_2 adsorption/desorption isotherms at 77 K. The electrochemical properties of the materials were determined by cyclic voltammetry and galvanostatic charge–discharge cycling measurements in 1 M $NaNO_3$ electrolyte solution, using a three-electrode system at room temperature. The results suggested that the pore structure of the A-MWCNTs could effectively promote the homogenous-dispersion of aniline and consequently result in excellent cycling performance. Furthermore, interaction between the π-conjugated structure of carbon and the quinoid ring of the PANI matrix can lead to enhancement in the charge transfer process.

1. Introduction

Supercapacitors are energy storage devices that possess high power density and excellent cycling performance, and have attracted considerable attention because of their potential applications in a wide range of technologies such as hybrid electric vehicles, cellular phones, and portable devices [1,2]. Supercapacitors can also be used in hybrid electric vehicles as an auxiliary power source in combination with lithium ion secondary batteries. The electrode materials for supercapacitors are generally highly developed porous carbon materials such as activated carbons, carbon nanofibers, and mesoporous carbons [3–5]. However, supercapacitors with electrodes composed of carbon materials cannot provide as much energy density as faradaic pseudocapacitors, which indeed is the principal obstacle to their widespread application.

Recently, most of the research on supercapacitors has been focused on a pseudo-capacitive behavior and higher power/energy densities. Thus, incorporation of heteroatoms such as nitrogen and oxygen onto the carbon surface enhances the performance of the supercapacitor electrodes, suppresses destruction of the surface structure, and has proved to be an effective approach toward attaining-increased capacitance [6,7]. Additionally, when transition metal oxides such as RuO_2 and MnO_2 are incorporated in the electrode materials, supercapacitors exhibit markedly increased capacitance properties and show pseudo capacitive behavior (<1300 F/g) [8,9]. Conducting polymers have various advantages, namely high conductivity, high doping/undoping rate during cycling processes, excellent energy storage performance through their redox processes, and facile synthesis through chemical methods [10–14].

Among the various conducting polymers, PANI (polyaniline) is frequently used as an electrode material, not only because of its excellent specific capacitance but also because of its many advantages for practical applications, such as inexpensive preparation, ease of polymerization in aqueous media, and high stability in air [13,14]. However, the main drawback of using conducting polymers as supercapacitor electrodes is their poor stability during cycling owing to the huge volumetric change that occurs during the doping/undoping process.

Thus, the suitability of materials with high stability, high porosity parameters, and excellent capacitive behavior for use as fillers has been studied in order to solve the problem of poor stability of conducting polymers. MWCNTs (Multiwalled carbon nanotubes) have unique structural and electrochemical properties and high stability, and therefore, they have tremendous potential for application as filler materials for conducting polymer electrodes. Introduction of MWCNTs into the PANI matrix improves the

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stability during cycling as well as the textural properties of the pristine polymer [15–18]. Effective utilization of MWCNTs can be achieved by their homogeneous dispersal within the matrix as well as by the developed porous structure, which could be optimized by the preparation of chemically activated MWCNTs (A-MWCNTs) [19,20]. The strong chemical etching effect resulting from activation using KOH significantly increases the specific surface area of the MWCNTs and their specific capacitance. In order to further study the effects of introducing MWCNTs into a PANI matrix, some MWCNT-containing samples were additionally activated by KOH before the preparation of PANI composites.

In this work, we focus on the competitive effects of the porous structures and capacitive performance of A-MWCNTs used as the filler materials of a conducting polymer matrix. The A-MWCNT/PANI composites were fabricated by the polymerization of an aniline monomer in the presence of A-MWCNTs. Since the formation of the pore structure and its influence on the electrochemical performance of A-MWCNT/PANI composites are relevant to the application of these composites in supercapacitors, these factors are discussed in detail in comparison to the MWCNT/PANI case.

2. Experimental details

2.1. Materials and sample preparation

MWCNTs (purity: 90%), manufactured by CVD (chemical vapor deposition), were purchased from Nano Solution Co. Ltd (Korea). Prior to use, the pristine MWCNTs were purified by treatment with 5 M HNO_3 for 5 h at room temperature. Subsequently, these were washed with distilled water, and then dried in a vacuum oven for 24 h at 120 °C. To develop the pore structure, A-MWCNTs were prepared by heating a KOH/MWCNT [3:1 (w/w)] mixture at 5 °C/min rate to 900 °C in a tubular furnace under N_2 flow and then kept at that temperature for 1 h. A-MWCNTs were then obtained after washing with HCl and distilled water to remove the residual organic species (K^+ ions).

The A-MWCNT/PANI composites were synthesized by an *in situ* chemical polymerization method [18], whereby 3 mL of aniline as the precursor of PANI and 2.5 g of APS (ammonium persulfate) as the oxidizing agent for polymerization were dissolved in 30 mL of 1 M HCl. Then, 0.3 g of A-MWCNTs was added to the above solution; the resulting mixture was sonicated for 24 h at room temperature. The APS solution was slowly dripped into the A-MWCNT-containing aniline solution to initiate the polymerization reaction and then placed in an ice bath (0–5 °C) for 24 h. A dark-green suspension was obtained by filtering and washing to remove the residues this mixture with distilled water were in the form of A-MWCNT/PANI composites. Finally, the composites were treated by stirring for 3 h in a 2.0 M HCl solution, and then filtered and washed with distilled water and methanol to remove the excess acid. For comparison, pristine MWCNT/PANI composites were also polymerized under the same conditions.

2.2. Characterization

SEM (Scanning electron microscopy; Hitachi Co., S-4200) was used to observe the morphologies of the prepared samples. The textural properties were recorded from nitrogen adsorption/desorption isotherms at 77 K (BEL Co., BEL-SORP). The specific surface area, mesopore volume, and micropore volume were calculated using the BET equation, BJH method, and H–K method, respectively. The total pore volumes were estimated to be the liquid volume of N_2 adsorbed at a relative pressure (P/P_0) of 0.99. The working electrodes for supercapacitors were prepared by first mixing 90 wt% of active materials with 10 wt% of carbon black and 10 wt% of the binder PVDF (polyvinylidenefluoride). A small amount of NMP (*N*-methylpyrrolidone) was then added to the composites to make a homogeneous mixture. The mixture was finally cast onto a 1 cm^2 Ni-foam current collector in order to produce a working electrode. Electrochemical measurements (HS Technology Co., Iviumstat electrochemical analyzer) were performed at 25 °C with the conventional three-electrode system in 1.0 M $NaNO_3$ electrolyte solution. A Pt wire and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. CV (Cyclic voltammograms) were measured at scan rates of 2 and 10 mV/s from −0.2–0.8 V. Charge-discharge cycling performance tests were performed at different current densities, with cutoff potentials varying from −0.2–0.8 V.

3. Results and discussion

3.1. Morphologies

SEM images of the MWCNT, MWCNT/PANI, and A-MWCNT/PANI composites are illustrated in Fig. 1. The MWCNTs [Fig. 1(a)] are shown to be randomly oriented, and are present in a bundled form. After introducing PANI into the MWCNTs, the MWNT/PANI composites (Fig. 1b) assume thick bundled shapes, which is consistent with an earlier study [21]. The A-MWCNT/PANI has a homogeneous structure and resembles tree branches when compared with MWCNT/PANI. Moreover, their homogenous morphology becomes more complex on the introduction of PANI because of the well-dispersed A-MWCNT.

3.2. Textural properties

Fig. 2 shows the N_2 adsorption/desorption isotherms of all samples at 77 K. The behavior of the isotherms for the materials containing MWCNTs was between type II and type IV, indicating the maintenance of mesoporous structures. However, the isotherm of A-MWCNTs showed a significantly increased uptake at low relative pressures (<0.1), indicating the development of micropores. Before the activation process, the micropore structures of the MWCNTs were not detected. It is suggested that the adsorbed pore volumes of MWCNT/PANI are significantly decreased as compared with that of A-MWCNT/PANI. The pore volumes of the MWCNTs decreased upon the introduction of PANI, because the pore structures of the MWCNTs were blocked. The results suggest that the porosity parameter of A-MWCNT/PANI has a lower value than that of MWCNT/PANI, which may be attributed to the enhanced adsorption volume caused by chemical activation.

The details of the structural parameters of the pores are summarized in Table 1. The MWCNTs had a specific surface area of 211 m^2/g and a total pore volume of 0.810 cm^3/g; the corresponding values for the A-MWCNTs were 581 m^2/g and 1.571 cm^3/g, respectively. After the introduction of PANI into MWCNTs and A-MWCNTs, the specific surface area and total pore volume decreased because of the pore blocking effect. The specific surface area and total pore volume of A-MWCNT/PANI were higher than that of MWCNT/PANI, which could be attributed to the well-dispersed MWCNT particles as fillers in PANI composites.

Fig. 3 shows the micropore size distribution of all samples calculated by the H–K method. After producing A-MWCNTs by the activation process, the pore volumes significantly increase due to the increased micropore content; however, after introducing PANI, both the pore volumes and pore diameters decrease significantly because of the blocking of the MWCNT pore structure. The A-MWCNT/PANI composites have larger pore volumes (0.7–1.2 nm) than does MWCNT/PANI. The relationship between the capacitive