

Preparation and Characterization of Carbon Nanotubes-Based Composite Electrodes for Electric Double Layer Capacitors

Min-Kang Seo^{†,‡} and Soo-Jin Park^{‡,*}

[†]Jeonju Institute of Machinery and Carbon Composites, Jeonju 561-844, Korea

[‡]Department of Chemistry, Inha University, Incheon 402-751, Korea. *E-mail: sjpark@inha.ac.kr

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In this work, we prepared activated multi-walled carbon nanotubes/polyacrylonitrile (A-MWCNTs/C) composites by film casting and activation method. Electrochemical properties of the composites were investigated in terms of serving as MWCNTs-based electrode materials for electric double layer capacitors (EDLCs). As a result, the A-MWCNTs/C composites had much higher BET specific surface area, and pore volume, and lower volume ratio of micropores than those of pristine MWCNTs/PAN ones. Furthermore, some functional groups were added on the surface of the A-MWCNTs/C composites. The specific capacitance of the A-MWCNTs/C composites was more than 4.5 times that of the pristine ones at 0.1 V discharging voltage owing to the changes of the structure and surface characteristics of the MWCNTs by activation process.

Key Words : Multi-walled carbon nanotubes, Polyacrylonitrile, Composites, Activation, Electrochemical properties

Introduction

In recent years, electrochemical capacitors have been studied in terms of their practical application as high power devices, since they have higher power density than batteries and higher energy density than ordinary capacitors, as well as a long cycle life. Electrochemical capacitors can be divided into two types according to the energy storage mechanism: electrochemical double-layer capacitors (EDLCs) and redox supercapacitors. EDLCs are being considered for a variety of applications such as the capacitive deionization of water and as pulse power sources for cellular devices.^{1,2}

Activated carbons (ACs), activated carbon fibers (ACFs), carbon nanotubes (CNTs), graphite nanofibers (GNFs), and carbon aerogels (CAs) have been used as active electrode materials for EDLCs.³⁻¹⁰ Among them, CNTs, identified first by Iijima in 1991, are among the most attractive materials. Numerous studies pertaining to applications of CNTs have been carried out, focusing on the CNTs' novel hollow-tube structure, nanometer dimensions, high specific surface area, and excellent electronic semiconductivity and conductivity.¹¹⁻¹⁵ These properties, which not only facilitate the transportation of ions but also charging of the double layer, advantageous in the development of EDLCs⁵ and CNTs promise as candidate electrode materials for EDLCs. However, the specific capacitance of EDLCs based on CNTs is not very high at present; *e.g.*, the specific capacitance of CNTs-based EDLCs using organic electrolyte is only about 20-30 F/g.

In the present work, we prepare activated multi-walled carbon nanotubes/polyacrylonitrile (A-MWCNTs/C) composite films in an effort to improve the performance of CNTs-based electrodes for EDLCs. We also develop a simple process for fabrication of A-MWCNTs/C composites and evaluate these materials in terms of their potential to serve as

EDLC electrode materials.

Experimental

Materials. A MWCNTs/PAN dispersion was prepared at room temperature by mixing as-produced ILJIN Co. MWCNT powder with a 1.5 g/L dimethylformamide (DMF) solution of poly(acrylonitrile-methyl acrylate) (90:10) copolymer (Aldrich, Mw~100,000 g/mol).

Sample Preparation. The weight ratio of MWCNT powder to PAN copolymer was 40:60. Subsequent partial solvent evaporation from the MWCNTs/PAN dispersion at about 100 °C and then film casting at 85 °C in vacuum resulted in a ~10 μm thick MWCNTs/PAN composite films.

Physical or chemical activation^{16,17} of polyacrylonitrile or its copolymers was generally used for producing activated carbon with high specific surface area and high porosity, and it was expected that similar activation treatments of MWCNTs/PAN composite films could also be used for developing A-MWCNTs/C composite films. As-produced MWCNTs/PAN composite films were heat treated at 600, 800, and 1000 °C in nitrogen for 30 min and subsequently activated in CO₂ at the same temperature for 20 min in a tube furnace. During heat treatment and activation, the composite films did not exhibit significant shrinkage.

Characterizations. The morphology of the MWCNT powder, MWCNTs/PAN composite films, and A-MWCNTs/C composite films were characterized by scanning electron microscopy (SEM, JEOL JSM-840A using 5 keV beam energy) and high-resolution transmission electron microscopy (HRTEM) carried out using a JEOL model 2010 TEM with 100 keV beam energy.

N₂ adsorption isotherms at 77 K were measured using an ASAP 2010 (Micromeritics). The samples were degassed at

573 K for 12 h to obtain a residual pressure of less than 1×10^{-6} mmHg. The amount of N_2 adsorbed on the samples was used to calculate the specific surface area by means of the Brunauer-Emmett-Teller¹⁸ equations. The total pore volume was estimated to be the liquid volume of the nitrogen at a relative pressure of about 0.995, and the micro- and mesopore structures were analyzed by using D-P¹⁹ and BJH²⁰ equations.

Infrared spectra were recorded on a Digilab FTS (Bio-Rad) spectrophotometer equipped with an ATR attachment. A ZnSe crystal was used as the reflecting element and the angle of incidence of the infrared beam was 45° .

Electrochemical characterization of the composite electrodes was performed by computer-controlled potentiostat/galvanostat (Autolab PGSTAT 30 with GPES software) using a three-electrode assembly. A composite electrode was used as the working electrode, $Hg|Hg_2SO_4$ as the reference electrode, and platinum foil was employed as the counter electrode. Cyclic voltammetry (CV) of the composite electrodes was performed in a potential range of 0-0.9 V at a scan rate of 10 mV/s. The discharge capacitance (C) of the electrodes in EDLCs was calculated from the slope of the discharge on the basis of the following equation.^{21,22}

$$C = i \left(\frac{\Delta t}{\Delta V} \right) \quad (1)$$

where C is the capacitance of the cell in farads, i the discharge current in amperes (A), and $\Delta V/\Delta t$ the slope in volts per second (V/s).

All the electrochemical measurements were performed in 1 M H_2SO_4 electrolyte. For a symmetrical system, the specific capacitance C_m in farads per gram of the A-MWCNTs/C composite electrodes (F/g) was calculated from the capacitance of the cell C .

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

where m is the weight (g) per electrode of the A-MWCNTs/C composite film electrodes.

Results and Discussion

Morphologies. Figure 1 shows SEM and TEM images of MWCNTs, pristine MWCNTs/PAN, and A-MWCNTs/C composite films. Based on the SEM results, the diameter of the MWCNTs used in this study is 20 ± 5 nm and that for the as-prepared MWCNT/PAN composite film is estimated to be 40 ± 5 nm. The increased diameter indicates PAN copolymer adsorption by the MWCNTs. Also, the A-MWCNTs/C composite films activated at 1000 °C (Figures 1(c) and (d)) are found to have pores with 3-3.5 nm hydraulic radii and show mesoporous characteristics as the activation progressed although they roughly maintain their nanotubular morphology. However, the tubes become short and distorted. Many defects are generated and their surfaces become very rough.

Surface and Electrochemical Properties. Figure 2 shows cyclic voltammograms of pristine MWCNTs/PAN and A-MWCNTs/C composite films. A-MWCNTs/C composite film

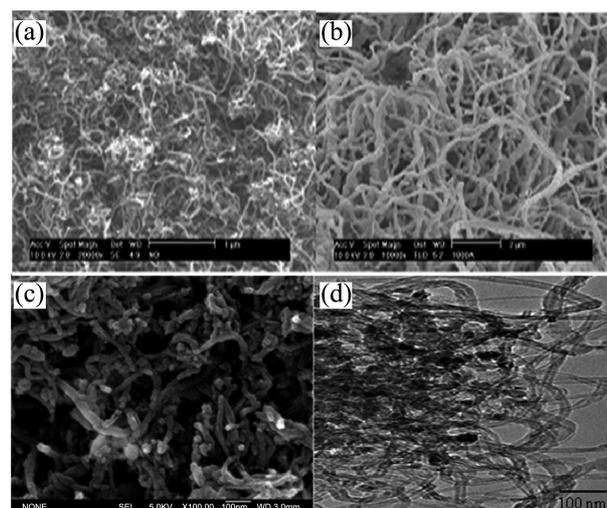


Figure 1. SEM and TEM images of MWCNTs (a), pristine MWCNTs/PAN (b), and A-MWCNTs/C ((c) & (d)) composites activated at 1000 °C.

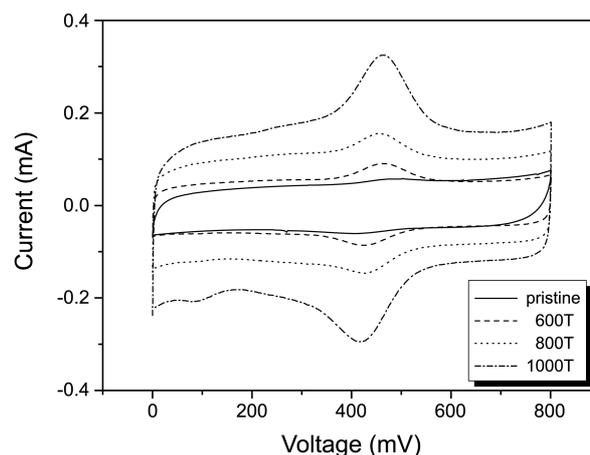


Figure 2. Cyclic voltammogram of A-MWCNTs/C composites as a function of activation temperature at 1 mVs^{-1} in 1 M H_2SO_4 electrolyte.

electrodes exhibit a rectangular cyclic voltammogram in a range of 0-800 mV/s. Cyclic voltammetric studies reveal that the activation leads to improvement of the capacitance of the EDLC's electrode. The increase in the specific capacitance for the A-MWCNTs/C composite film electrodes is attributed to a distinct increase in the BET area (double-layer capacitance).^{23,24} Consequently, the simple processing, highly accessible surface area, and high stability of A-MWCNTs/C composite films demonstrate that activation treatment offers potential advantages for the fabrication of an EDLC's electrode.

The results of the electrochemical capacitance experiment are listed in Table 1. The specific capacitance of the pristine MWCNTs/PAN composite films is 40 F/g and the A-MWCNTs/C composite films' specific capacitance is 180 F/g. The 4.5-fold higher specific capacitance of the A-MWCNTs/C composite films relative to that of the pristine MWCNTs/PAN composite films is attributed to the different

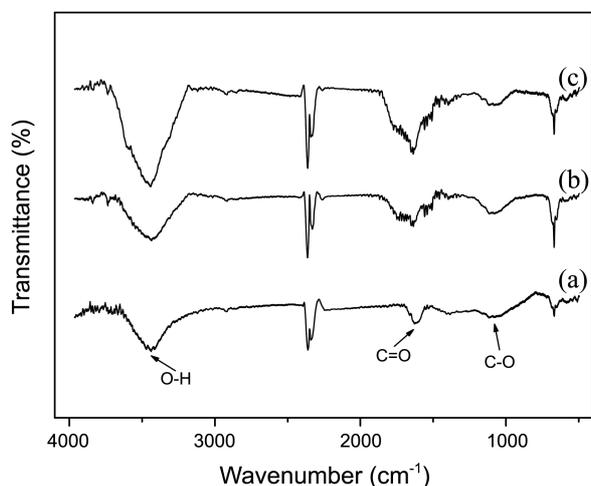
Table 1. Specific capacitance and textural properties of MWCNTs/PAN composite films at different activation temperatures

Specimens	Specific capacitance (F/g)	Specific surface area (m ² /g)	Mean pore diameter (nm)	Pore volume (cm ³ /g)	Relative volume ratio of microspores (< 2 nm) %
Pristine MWCNTs/PAN	40	190	7	0.62	13.84
A-MWCNTs/C at 600T	70	260	5	0.70	6.8
A-MWCNTs/C at 800T	100	290	3.5	0.78	5.4
A-MWCNTs/C at 1000T	180	360	3	0.94	3.2

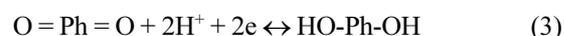
structure and surface characteristics of MWCNTs after the activation process.²⁵ The BET specific surface area, pore volume, and pore diameter distribution are crucial parameters with respect to EDLC electrode materials.²⁶ The A-MWCNTs/C composite films have higher BET specific surface area, pore volume, and lower volume ratio of microspores compared to those of the pristine MWCNTs/PAN composite films. Accordingly, we investigated the structures, morphologies, and surface characteristics of the activated MWCNT films by means of BET, BJH, SEM, TEM, and IR analyses.

Activation can introduce functional groups onto the surface of MWCNTs. Figure 3 shows the infrared transmission spectra of A-MWCNTs/C composite films. The functional groups in carbonyls, carboxyls, and carboxylic anhydrides are evident at about 1680 cm⁻¹. The band centered at about 1100 cm⁻¹ is associated with C-O stretching in ethers, hydroxyls or carboxylic anhydrides.²⁷ The peaks at about 1530 cm⁻¹ reflect the vibration of the carbocyclic plane of MWCNTs and can become sharper after activation due to the removal of amorphous carbonaceous materials. It is evident that there are many more carbonyl groups, carboxylic groups, hydroxyl groups, *etc.* in the A-MWCNTs/C composite films than in the pristine MWCNTs/PAN composite films, which may further enhance the specific capacitance of a polarizable electrode.

Some studies have found that the specific capacitance of

**Figure 3.** Infrared spectra of MWCNTs (a), pristine MWCNTs/PAN (b), and A-MWCNTs/C (c) composites activated at 1000 °C.

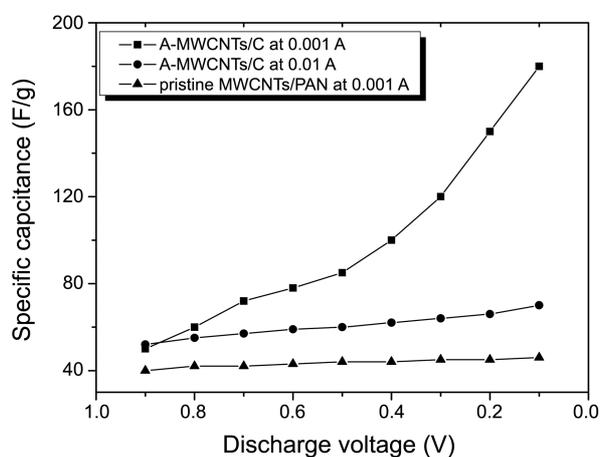
carbon materials can be enhanced by introducing various surface functional groups through thermal, chemical, or electrochemical routes.^{17,27,28} Certain electroactive groups, such as quinone, hydroxyl, and carbonyl groups, can provide the following redox transitions.



where Ph and R indicate phenyl and aliphatic groups, respectively.

The other functional groups, such as anhydrides and carboxyl groups, are ionic exchangeable or attractable to solvated ions.²⁹⁻³¹ Therefore, the number of ions involved in building the electric double layer should be increased, resulting in the increased charge density. Furthermore, a higher density of oxygen functional groups was reported to improve the wettability of the carbon surface in aqueous electrolytes, likely further increasing the utilization of specific surface area for double-layer capacitance.³¹

The specific capacitance of the A-MWCNTs/C composite films as a function of discharging voltage is shown in Figure 4. The specific capacitance of the A-MWCNTs/C composite films at 0.001 A discharge current is strongly dependent upon the discharging voltage, as a result of the non-linear discharging behavior.^{32,33} When the discharging voltage is changed from 0.8 to 0.1 V, the specific capacitance increased from 40 to 180 F/g. The non-linear constant current charging

**Figure 4.** Specific capacitance as a function of discharging voltage for A-MWCNTs/C composites activated at 1000 °C.

and discharging behavior of the A-MWCNTs/C composite films is attributed to either the broad pore size distribution³⁴ or the pseudocapacitance³⁵ introduced by the surface chemistry caused by the activation treatment.

Conclusions

A-MWCNTs/C composite film electrodes exhibited a rectangular cyclic voltammogram in a range of 0-800 mV/s. Cyclic voltammetric study revealed an increase in the specific capacitance of A-MWCNTs/C composite films from 40 to 180 F/g after activation. The activation of MWCNTs/PAN composite films led to the improvement of the capacitance of the EDLC's electrode. Simple processing, highly accessible surface area, and high stability of A-MWCNTs/C composite films demonstrated that the activation treatment afforded potential advantages for the fabrication of an EDLC's electrode.

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