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The surface chemical properties of multi-walled carbon nanotubes modified by thermal fluorination for electric double-layer capacitor

Min-Jung Jung[a], Euigyung Jeong[b], Young-Seak Lee[a,*]

[a] *Department of Applied Chemistry and Biological Engineering, Chungnam National University, Daejeon 305-764, Republic of Korea*
[b] *The 4th R&D Institute-4, Agency for Defense Development, Daejeon, 305-600, Republic of Korea*

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ABSTRACT

The surfaces of multi-walled carbon nanotubes (MWCNTs) were thermally fluorinated at various temperatures to enhance the electrochemical properties of the MWCNTs for use as electric double-layer capacitor (EDLC) electrodes. The fluorine functional groups were added to the surfaces of the MWCNTs via thermal fluorination. The thermal fluorination exposed the Fe catalyst on MWCNTs, and the specific surface area increased due to etching during the fluorination. The specific capacitances of the thermally fluorinated at 100 °C, MWCNT based electrode increased from 57 to 94 F/g at current densities of 0.2 A/g, respectively. This enhancement in capacitance can be attributed to increased polarization of the thermally fluorinated MWCNT surface, which increased the affinity between the electrode surface and the electrolyte ions.

1. Introduction

Electric double layer capacitors (EDLCs) possess certain advantages over traditional energy storage devices, including high power density in both charge and discharge modes and long cycle lives as high as 10^5 cycles. Because of these interesting characteristics, EDLCs have increased in popularity [1–3]. EDLCs play a very important role in complementing or replacing batteries in the energy storage field, such as for uninterruptible power supplies and load-leveling [4,5]. They can be fully charged and discharged in seconds, and thus, a much higher power delivery can be achieved; however, because the energy densities of EDLCs are lower than the energy densities of rechargeable batteries, it is difficult to use them in large capacity applications [6]. To increase the use of EDLCs, the effective amelioration of polarizable electrode materials is necessary.

Typically, porous carbon materials, such as activated carbon (AC), have been widely used as electrode materials for EDLC [7–9]. They usually have wide pore-size distributions ranging from micropores through mesopores to macropores; unfortunately, not all pore sizes are suitable for ion storage or rapid ion transfer. Furthermore, aggregates of AC particles have relatively poor electrical conductivity due to poor contact between the AC particles. Additionally, AC particles have relatively low intrinsic conductivity [10]. Carbon nanotube (CNT) materials have been developed for use as electrode materials for EDLCs because they have such desirable characteristics as high electrical conductivity, sufficient mechanical strength, and a reasonable specific surface area [11–16].

In previous studies, it has been reported that the surface modification of electrode materials could improve the interactions between electrolytes and electrodes at their interfaces, increasing the specific capacitances [17–19]. Various surface modification methods have been investigated, such as chemical treatment, plasma, flame, corona discharge, and direct fluorination [20–24]. Among these methods, direct fluorination is unique and one of the most promising methods; it changes the textural properties of carbon materials and introduces non-pseudofaradic reactive functional groups, i.e., C—F [25].

Based on the benefits of CNTs and fluorination of carbon materials, it is expected that the fluorination of CNTs will increase the specific capacitance of fluorinated CNT-based EDLCs. However, it is unknown how changing the textural and surface chemical properties of CNTs using fluorination will alter the electrochemical properties of the resulting electrodes because CNTs are higher-ordered carbon materials with a high degree of graphitization, which provides better chemical stability.

Therefore, this study adapted the concept of thermal fluorination from the previous study, using high temperature fluorination of multi-walled carbon nanotubes (MWCNTs) [26], in order to investigate how changing the textural and surface properties of MWCNTs alters the electrochemical properties of the resulting MWCNT-based electrode due to thermal fluorination at various temperatures.

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* Corresponding author. Tel.: +82 42 821 7007; fax: +82 42 822 6637.
E-mail address: youngslee@cnu.ac.kr (Y.-S. Lee).

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2. Experimental

2.1. Thermal–fluorination of MWCNTs

Multi-walled CNTs (MWCNTs, CM-250, 95%, Hanwha Nanotech, Korea) with inner diameters of 10–20 nm and lengths of 200 μm were used in this study as the electrode materials for EDLCs. The MWCNT surfaces were treated with a fluorination apparatus, which consisted of a reactor, a vacuum pump, and a buffer tank connected to gas cylinders. The samples were loaded into the reactor in a nickel boat and degassed at 150 °C for 1 h to remove impurities, such as water. The thermal–fluorination treatments were conducted at 30, 100, 200, and 400 °C for 10 min at 0.1 MPa, using fluorine (99.8%, Messer Grieheim GmbH) and nitrogen (99.999%) gas at a volume ratio of 2:8. After thermal fluorination, the samples were degassed to remove the unreacted gases. The untreated MWCNT was named R-C. The thermally fluorinated MWCNTs were referred to as 30TFC, 100TFC, 200TFC, and 400TFC, depending on the fluorination temperature.

2.2. Physicochemical characterization

To investigate the changes in the functional groups on the surfaces of the thermally fluorinated MWCNTs, X-ray photoelectron spectroscopic (XPS, VG Multilab 2000) analysis was performed using Mg $K\alpha$ radiation. The C1s peaks were deconvoluted using several pseudo-Vogit functions (sums of the Gaussian–Lorentzian function) with a peak analysis program obtained from Unipress Co., USA. The pseudo-Vogit function is given by the following equation [27]:

$$F(E) = H\left[(1-S)\exp\left(-\ln(2)\left(\frac{E-E_0}{\text{FWHM}}\right)^2\right) + \frac{S}{1+\left((E-E_0)/\text{FWHM}\right)^2}\right] \quad (1)$$

where $F(E)$ is the intensity at energy E, H is the peak height, E_0 is the peak center, FWHM is the full width at half-maximum, and S is the shape function related to the symmetry and the Gaussian–Lorentzian mixing ratio. Each component was considered to have a similar FWHM, i.e., 1.3 eV.

Field Emission scanning electron microscope (FE-SEM) images and Energy Dispersive X-ray (EDX) are observed to investigate surface morphology of thermally fluorinated MWCNFs by SEM apparatus (Hitachi S-5500, Japan, in KBIS Jeonju Korea).

The textural properties of the prepared samples were assessed via N_2 adsorption at 77 K using an ASAP2020 (Micromeritics, USA). The specific surface areas of the samples were evaluated using the Brunauer–Emmett–Teller (BET) equations.

2.3. Electrochemical characterization

The MWCNT based-electrodes for the EDLC were prepared as follows: the MWCNT suspension was mixed with 85 wt% MWCNT, 5 wt% carbon black (Super P, Timcal Ltd., Switzerland), and 10 wt% of the suspended polytetrafluoroethylene (PTFE, Aldrich) as a binder in isopropyl alcohol. The MWCNT-based electrodes were formed via vacuum filtration of the MWCNT suspension and then dried at 120 °C for 24 h.

The untreated and thermally fluorinated MWCNT-based electrodes were electrochemically characterized using a computer-controlled potentiostat–galvanostat (Ivium Technologies, Netherlands) equipped with a three-electrode assembly. The prepared MWNCT electrodes were used as the working electrode, and Ag|AgCl was used as the reference electrode. A platinum plate was used as the counter electrode. Cyclic voltammetry (CV) of the electrode materials was performed over the potential range of 0–1 V at a scan rate of 5 mV/s. The capacitance of the electrode was measured via a galvanostatic charge–discharge cycle in the potential range of 0–0.9 V at constant currents of 0.2–1.0 A/g. All electrochemical measurements were performed in a 1 M H_2SO_4 electrolyte.

An AC impedance spectrum analyzer combined with computer software was employed to measure and analyze the impedance behavior of the capacitors. In this work, the measurements were conducted at 0 V with an AC potential amplitude of 5 mV in the frequency range of 100 mHz to 30 kHz.

3. Results and discussion

3.1. Surface chemical properties of thermally fluorinated MWCNTs

XPS elemental analysis was conducted to compare the quantity of fluorine groups thermally generated at different fluorination temperatures. As can be observed in Table 1 and Fig. 1, three main peaks were identified, which are marked F1s, O1s, and C1s. The peaks at approximately 832–860 eV and 970–1000 eV are the F KLL and oxygen Auger peaks [28,29]. In the thermally fluorinated MWCNT samples, small Fe2p peaks were observed at approximately 712 eV [30]. Fe is present on the inside of the MWCNTs because it is commonly used as a catalyst in chemical vapor deposition (CVD) to manufacture MWCNTs [31]. In other words, the Fe was exposed to the surface of the MWCNT due to the surface etching effect of thermal–fluorination.

Fig. 2 shows SEM images and Fe EDX mapping of the thermally fluorinated MWCNTs. The FE-SEM images confirmed that the MWCNTs had average diameters of 10–15 nm and aspect ratios of ~1000. Additionally, the MWCNTs were tangled. The SEM images for the thermally fluorinated MWCNTs showed no changes in features compared to the control sample. Therefore, thermal fluorination did not change the shape of the MWCNTs. However, the Fe EDX mapping studies indicated the presence of Fe on the outside of the thermally fluorinated MWCNTs (Fig. 2b–e). Based on

Table 1
XPS surface elemental analysis parameters of thermally fluorinated MWCNTs.

Sample	Elemental content (atom percent)			F/C (%)
	C1s	O1s	F1s	
R-C	98.4	1.6	–	–
30TFC	93.0	2.1	4.9	5.3
100TFC	89.8	2.6	7.6	8.5
200TFC	85.3	1.7	13.0	15.2
400TFC	95.9	2.2	1.9	2.0

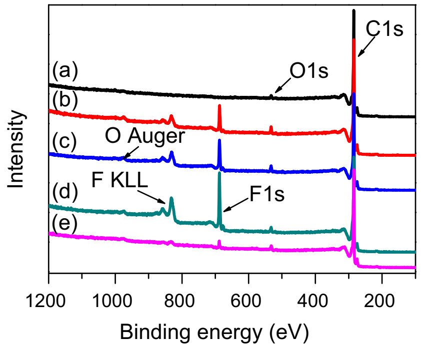

Fig. 1. XPS wide scan spectra of (a) R-C, (b) 30TFC, (c) 100TFC, (d) 200TFC and (e) 400TFC.