카본 나노튜브 첨가에 따른 Polyaniline/Carbon-MWCNT 복합 나노섬유 Web 전극의 전기화학적 특성

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Electrochemical Properties of Polyaniline/Carbon-MWCNT Nanofiber Composite Web Electrode with Addition of Carbon Nanotube

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1. Introduction

A supercapacitor is a crucial device in a energy storage/conversion system because it is applied to various areas such as electric vehicles, uninterruptible power supplies [1]. Many researchers have extensively studied electronically conducting polymers such as polypyrrole, polyaniline because they are used as electro-active materials for electrode of rechargeable batteries and capacitors [2,3]. The electrode by conducting polymer, however, has disadvantages of low cycle-life and slow kinetics of ion transport because the redox sites in the polymer backbone are not sufficiently stable for repeated redox processes [4]. It has been shown experimentally that the introduction of CNTs into a polymer matrix improves the electric conductivity as well as the mechanical properties of the original polymer matrix. Composites of carbon nanotube and polyaniline are prepared to enhance its electrochemical capacitance performance [5]. The high surface area and conductivity of CNTs might improve the redox properties of conducting polymers.

In this work, We, in this study prepared (1) polyacrylonitrile (PAN)-based activated carbon fiber web, (2) MWCNT embedded polyacrylonitrile (PAN)-based nanocomposite activated carbon fiber web by electrospinning, and (3) PANI/carbon-MWCNT nanofiber composite web by polymerizing polyaniline on the surface of carbon-MWCNT nanofiber web. The electrochemical characteristic was carried out about three cases.

2. Experimental

2. 1. Materials and co-electrospinning

The multi-walled carbon nanotubes (MWCNTs) used in this study was supplied by the Illjin Nanotech Co. (Korea). Polyacrylonitrile (PAN), N,N-dimethylformamide (DMF) and aniline as a monomer were purchased from Aldrich Chemical Co. And Ammonium peroxydisulfate (APS) used an initiator agent was purchased from Kanto Chemical Co. Tetrahydrofuran (THF) was used as solvent. The MWCNTs were sonicated for 30 min with homogenizer (Ulso Hi-tech, Korea) in order to disperse the

MWCNTs before mixing with PAN. The 10 wt.% composite solution was prepared by mixing PAN with MWCNTs dispersed in DMF. MWCNTs were dispersed in a PAN solution and co-electrospun, achieving a weight fraction of 3 wt.%. The composite solution was spun into fiber web through a positively charged capillary using an electrospinning apparatus (NT-PS-35K, NTSEE Co., Korea). The electrospun fiber was collected on an attached aluminum foil wrapped on a metal drum rotating at approximately 300 rpm.

2.2. Stabilization, activation and characterization

The electrospun nanocomposite fiber web was stabilized by heating up to 280℃ at a rate of 1℃/min and holding for 1 hr under an air atmosphere. The stabilized fiber webs were heated up to 800 ℃ at a rate of 5 ℃/min and activated by supplying 30 vol.% steam for 1 hr in a nitrogen carrier gas. The micro-textural characterization of the nanostructured materials was performed by SEM. The bulk electrical conductivity along the winding direction of the webs was measured by the four-point probe method.

2. 3. Preparation of PANI/carbon nanofiber composite web

The PANI/carbon and PANI/carbon-MWCNT nanofiber composite web were synthesized by chemically oxidative polymerizing aniline as a monomer on the surface of carbon or carbon-MWCNT nanofiber web.

2. 4. Electrochemical test

Two-electrode supercapacitor cells were fabricated with two 1.5 x 1.5 cm^2 electrodes, a polypropylene separator (Cellgard 3501, Scimat Co., UK), and a Ni 50 nm foil as a current collector soaked in 5 M H_2SO_4 aqueous solution. The electrochemical characteristics were evaluated by a galvanostatic charge/discharge andcyclic voltammetry (CV). The cell capacitance is calculated from the slope of the discharge on the basis of the equation (1)

$$C = i(t/V) \quad (1)$$

where C is the capacitance of the cell in farads; i is the discharge current in amperes (A); and t is the discharging time from 0.54 V to 0.45 V (about 50~60 % of the initial potential), V is the potential variation in the time range measured, the slope in volts per second (V/S). In a symmetrical system, the specific capacitance C_m in farads per gram of samples (F/g) is related to the capacitance of the cell C in terms of the equation (2)

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

where m is the weight (g) per electrode of samples.

The CV of the unit cells were performed in the potential range of 0 to 0.9 V at a scan rate ranging from 1 to 500 mV/sec.

3. Results and discussion

Fig. 1 is the SEM image of carbon naonfiber composite web. The SEM image, shown in Fig. 1(a), (b) reveals that the diameter in MWCNT/PAN nanocomposite fiber is distributed in the range of 100 to 500 nm. The nanocomposite fibers electrospun

were partially aligned along the winding direction of the drum winder. Fig. 1(c), (d) shows the SEM images of nanocomposite fibers activated at 800 ℃ for 60 min. The form of electrospun fibers was very straight, while the activated fibers containing MWCNT were wrinkled and showed that MWCNT was exposed on the surface of fibers. Fig. 1(e), (f) shows the SEM images of nanocomposite fibers synthesized by polymerizing aniline to use APS as an oxidant on the carbon nanofibers web. The effects of addition of MWCNT was studied by isotherms of nitrogen adsorption at 77 K and the electrical conductivities. The specific surface area of PAN nanofiber web was 1036 m^2/g, while that of MWCNT/PAN nanofiber web increased up to 2180 m^2/g. This is why CNT offers the creation of micropores as well as mesopores. Also, the addition of CNT leads to the electrical conductivity. The electrical conductivity of PAN nanofiber web was 0.42 S/cm and that of MWCNT/PAN nanofiber web was 0.98 S/cm. This is why CNT produces the excess free electrons due to well-developed structure. Potential cyclic voltammetric measurements of the nanostructured electrode supercapacitors were conducted within a potential window of 0 to 0.9 V to analyze the electrochemical behavior of the electrodes. Fig. 2(a) shows a cyclic voltammograms (CV) of nanostructured electrodes. The range of current for oxidation and reduction of PANI/ carbon-CNT electrodes were higher than PANI/carbon electrodes. Fig. 2(b) shows a cyclic voltammograms (CV) of nanostructured electrodes with various contents of PANI. The range of current for oxidation and reduction of PANI/carbon-CNT electrodes increased with increasing the content of PANI to carbon nanocomposite fiber. This is why addition of CNT brings out the increase of specific surface area and the polymerization of PANI on the carbon-CNT web maximize the effect of nonfaradaic and faradaic reaction. Fig. 3 shows the specific capacitances of the nanocomposite samples as a function of the content of PANI. The capacitance of the nanostructured electrodes is determined from the dc discharge with a 0.9 V potential window of capacitor device. The specific capacitances increases as the content of PANI increases.

4. Conclusions

The MWCNT/PAN-based novel nanocomposite carbon fibers was prepared by a co-electrospinning technique. After that, it was stabilized and activated oxidatively. The nanocomposite activated carbon fibers have been characterized by SEM, specific surface area, electrical conductivity and electrochemical measurements. The electrical conductivity and specific surface area increased with increasing MWCNT embedded. PANI/ carbon-MWCNT nanocomposite fiber web was synthesized by polymerizing aniline on the carbon-MWCNT fiber web. The specific capacitances increases as the content of PANI increases. The capacitance of 20 wt.% PANI/ Carbon-MWCNT nanocomposite fiber webs increased up to 287 F/g.

Acknowledgements

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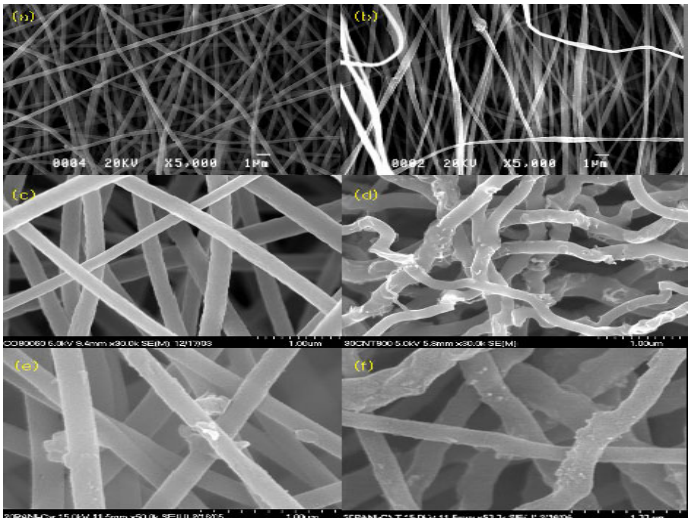

Fig. 1. SEM images of nanocomposite:
(a) Electrospun PAN web, (b) Electrospun PAN-MWCNT web, (c) Activated PAN web, (d) Activated PAN-MWCNT web, (e) PANI/Carbon, and (f) PANI/Carbon-MWCNT.

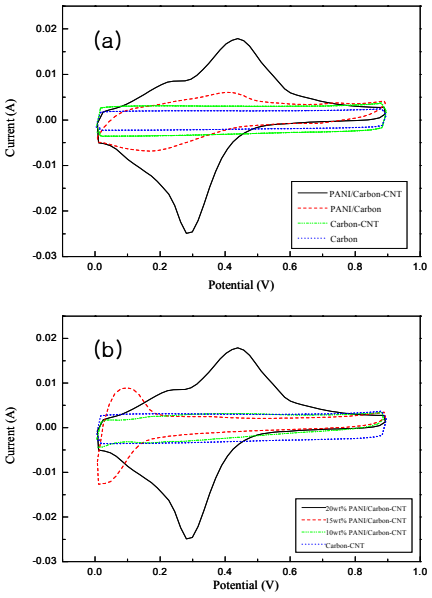

Fig. 2. Cyclic voltammgrams: (a) with the contents of CNT and (b) PANI.

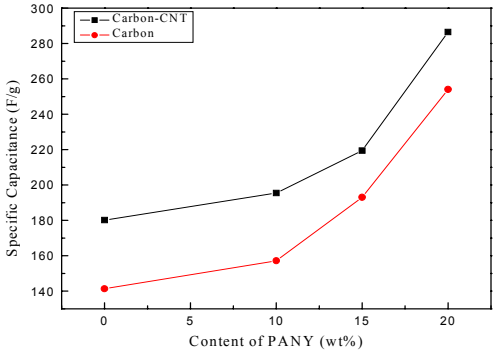

Fig. 3. Changes of specific capacitance of (a) carbon-CNT web (b) carbon web with the contents of PANI.