RuO_2/Carbon-CNT 복합 나노섬유 Web 전극에 있어서 카본 나노튜브 첨가에 따른 전기화학적 특성

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Effect of Carbon Nanotube on Electrochemical Properties of RuO_2/Carbon-CNT Composite Nanofiber Web

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1. Introduction

Electrochemical capacitors are charge storage devices having higher energy density than conventional dielectric capacitor. Besides, it has higher power density than battery [1]. Capacitor are divided into two type, that is, electrochemical double layer capacitor (EDLC) and pseudocapacitor. Pseudocapacitor is based on the faradaic mechanism, and a electrode material uses transition metals such as ruthenium, hydrous ruthenium, manganese, nickel oxides. Recently, the specific capacitance of amorphous ruthenium oxide as a supercapacitor has been recorded up to 720 F/g at 2mV/s scan rate in H_2SO_4 electrolyte [2]. The use of ruthenium oxide, however, has been hesitated because of very high expensive. Hence, many researchers have searched for the method minimizing ruthenium oxide. It has been studied the method doping/alloying Ru with other oxides, and dispersing RuO2 over high surface area substrates as such carbon and carbon nanotube (CNT) [3-5].

This work is focused on the preparation of (i) nanocarbon fiber web, (ii) carbon-CNT nanocarbon fiber web embedded CNT, (iii) RuO2/carbon fiber web composite impregnated RuO2, and (iv) RuO2/carbon-CNT composite nanofiber web. Both carbon fiber web and carbon-CNT fiber web is prepared by electrospinning. The electrochemical tests are carried out about four cases.

2. Experimental

2. 1. Materials and co-electrospinning

The multi-walled carbon nanotubes (called as CNT) was supplied by the Illjin Nanotech Co. (Korea). Polyacrylonitrile (PAN), N,N-dimethylformamide (DMF), ruthenium chloride hydrate ($RuCl_3 \cdot xH_2O$) and sodium borohydride ($NaBH_4$) were purchased from Aldrich Chemical Co. Tetrahydrofuran (THF) was used as solvent. Super-P carbon was used as an electron conductor. The collector used Ni mesh. The CNT was sonicated for 30 min with homogenizer (Ulso Hi-tech, Korea) in order to

disperse the CNT before mixing with PAN. The 10 wt.% composite solution was prepared by mixing PAN with CNT 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 RuO_2/carbon composite

The RuO_2/carbon and RuO_2/carbon-CNT composite were prepared as follows. At first, the $RuCl_3$ solution dissolved in distilled water immersed to the carbon or the carbon-CNT web. The reduction of ruthenium oxide on the surface of web was carried out by $NaBH_4$ aqueous solution. After that, it was washed by methanol over several times, and then dried in a vacuum oven.

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 6 M KOH 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 images of carbon naonfiber composite web. The SEM image, as shown in Fig. 1(a), (b) reveals that the diameter in CNT/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 activated at 800℃ for 1 hr. The electrospun fibers was formed very straight, while the activated fibers containing CNT were wrinkled and showed that CNT was exposed on the surface of fibers. Fig. 1(e), (f) shows the SEM images of nanocomposite synthesized by impregnating Ru on the carbon composite. The effects of addition of CNT 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 CNT/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 CNT/PAN nanofiber web was 0.98 S/cm. This is why CNT produces the excess free electrons due to well-developed structure. Fig. 2 shows cyclic voltammograms (CV) of nanostructured electrodes within a potential window of 0 to 0.9 V. The range of current for non-faradaic process of carbon-CNT electrodes were higher than carbon electrodes, and it shows the range of current for faradaic process of RuO_2/carbon-CNT electrodes were much higher than the other electrodes such as carbon, carbon-CNT, RuO_2/carbon electrodes. This is why addition of CNT brings out the increase of specific surface area and the impregnation of Ru 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 RuO_2. 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 RuO_2 increases. Addition of both 20 wt.% RuO_2 and 3 wt.% CNT brings out four times electrochemical performance compared to pure carbon because of the combination of both double layer and pseudocapacitance. On the other hand, The case of The addition of only CNT brings out the electrochemical performance of 50 to 140 F/g because of the synergic effect of double layer capacitance.

4. Conclusions

The CNT/PAN-based novel nanocomposite carbon fibers was prepared by a co-electrospinning technique. The electrical conductivity and specific surface area increased with increasing CNT embedded. PANI/ carbon-CNT nanocomposite fiber web was synthesized by impregnating Ru on the carbon-CNT composite. The specific capacitances increases as the content of RuO_2 increases. The capacitance of 20 wt.% RuO_2/ carbon-CNT nanocomposite fiber webs increased up to 530 F/g.

Acknowledgement

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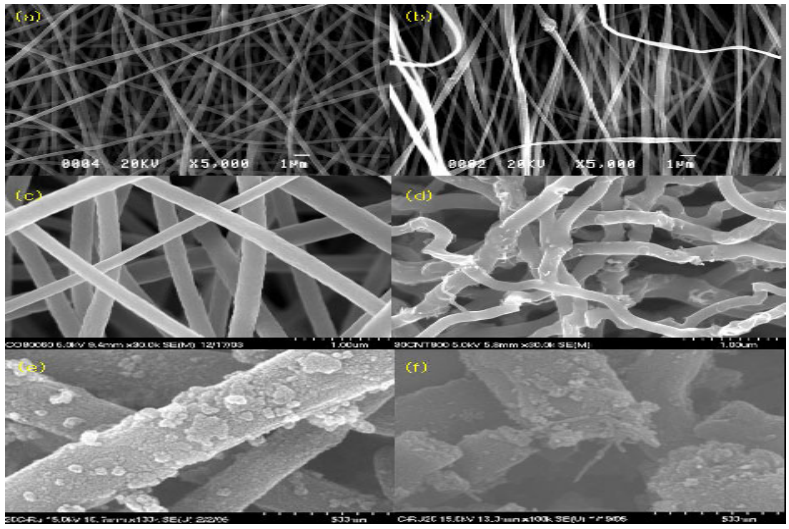

Fig. 1. SEM images of nanocomposite:
(a) Electrospun PAN web, (b) Electrospun PAN-CNT web, (c) Activated PAN web,
(d) Activated PAN-CNT web, (e) RuO_2/carbon, and (f) RuO_2/carbon-CNT.

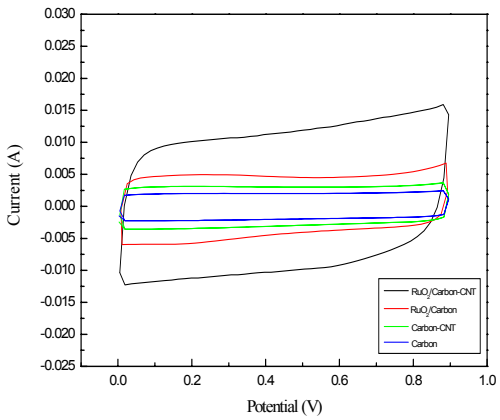

Fig. 2. Cyclic voltammgrams with the contents of CNT and RuO_2.

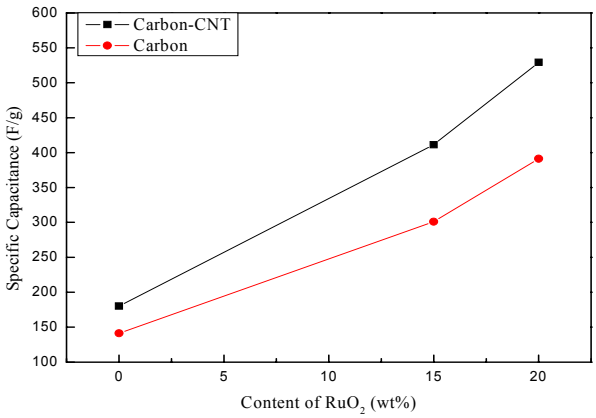

Fig. 3. Changes of specific capacitance of (a) carbon-CNT web (b) carbon web with the contents of RuO_2.