# Supercapacitor performances of carbon nanotube composite carbon fibers from electrospinning

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**Abstract**

10 wt.% of PAN was dissolved in *N,N*-dimethylformamide (DMF) and 1 wt. % of the multi wall carbon nanotubes (MWCNTs) was evenly dispersed in PAN solution by using ultrasonic mixer. The 1 wt.% addition of MWCNT increased the specific capacitance by two times more from 82 to 160 F/g. The specific capacitance of carbon nanofiber(CNF)/carbon nanotube(CNT) composite capacitors was about 90 F/g at the current density of 500 mA/g. This value is even larger than the capacitance from the CNF electrode at the current density of 5 mA. The relatively high capacitance at the high current density is a practical importance for applications to supercapacitor in motor vehicle.

**Introduction**

Recent developments in large-scale synthesis of carbon naotubes(CNTs) have accelerated the applications of the materials to the area of electrical energy storage systems.

An advantage of the electrospinning5 is to produce a web structure consisting of nanofibers. Electospinning process[1] is capable of carrying carbon nanotube in a continuous nanostructured carbon composite fiber web with superior electrochemical properties such as discharging capacitance and electrical conductivity, and performances of the electrodes for a supercapacitor. The supercapacitor has been considered as one of the most attractive rechargeable power devices because it offers high power density, high-rate charge/discharge ability, and long cycle life compared with commercialized rechargeable batteries[2-3].

**Experimental**

10 wt.% of PAN was dissolved in *N,N*-dimethylformamide (DMF) and 1 wt. % of the MWCNTs was evenly dispersed in PAN solution by using ultrasonic mixer. The solutions were pun into fiber web by using an electrospinning apparatus consisting of a 25 kV DC power supply (HYP-303D, Han Young Co., Korea) equipped with the positively-charged capillary from which the polymer solution was extruded and with a negatively-charged drum winder to collect the fibers as webs. The electrospun fiber web was stabilized at 280 °C for 1 h under air flow, and then activated at 900 °C for 60 minutes by supplying 30 vol.% of steam in the carrier gas of $N_2$. A sandwich type capacitor cell was prepared with a pair of the activated webs separated by a separator (Selgard 3106) and current collectors made of Ni foil. Capacitance measurements were undertaken in a 30 wt.% KOH aqueous solution.

**Results**

Figure 1 shows SEM micrographs of various nanocomposite activated carbon fibers. Not only carbon nanofibers (CNF) but also CNTs in the nanofibers (CNF/CNT) were partially aligned parallel to the winding direction and longitudinal direction of the component fiber. The average diameters of the CNF and CNF/CNT fibers were 300 nm and 400 nm, respectively. When the electrospinning is processed to make the electrode, the electrode is produced without a need of second processing to add a binder and an electric conductor. Therefore, the webs from electrospinning can be used with an improvement of an ease of handling, an increase in the efficiency due to large specific surface area, an enhancement of the conductivity due to the increased density of the contact points, and the low cost of preparations of the electrode. The activated carbon nanofibers (ACNFs) produced by the electrospinning give a high specific surface area from shallow pores. The shallow pores will be formed from the nanosize in diameter through the activation process, and they would lead to high specific capacitance at high current density due to the short moving distance of the ions in the pores.

The surface characteristics of the CNF and CNF/CNT nanostructured activated carbon fibers were evaluated using a surface area analyzer by the measurement of the $N_2$ adsorption isotherms at 77 K (Table 1). The Brunauer-Emmett-Teller (BET) surface area and micropore volume fraction of CNF/CNT were 2 and 3 times higher, respectively, than that of CNF. However, average pore diameter decreased with additions of CNT indicating more micropores formed in the CNF/CNT composite fibers. The micro pores could be created by the CNT exposed outside of the composite fiber. The increases of the specific surface area and the pore volume fraction would contribute to the enhancements of the specific capacitance.

The galvanostatic charge/discharge of a capacitor built from the CNF and CNF/CNT nanocomposite electrodes is presented in Fig. 2(a). The capacitance gave rise by two times more from 82 F/g to 160 F/g by introduction of 1 wt.% CNT in the CNF at the current of 10 mA. The specific capacitance of the CNF and CNF/CNT electrode reduced by 33 % and 42 % with an increase in discharge current density from 5 mA to 500 mA, respectively (Figure 2 (b)). The larger reduction 42% of the CNF/CNT electrode would be resulted form the hindered accessibility of the ions in the micro pores

in the CNF/CNT composite electrodes with more fraction of micro pores than in the CNF only. However, the specific capacitance of CNF/CNT capacitors was about 90 F/g at the current density of 500 mA/g. This value is even larger than the capacitance from the CNF electrode at the current density of 5 mA. The relatively high capacitance at the high current density is a practical importance for applications to supercapacitor in motor vehicle.

Figure 3(a) shows a cyclic voltammograms (CV) of CNF and CNF/CNT nanostructured electrodes at scan rate of 10 mV/s. The cyclic voltamogram of the CNF/CNT electrode was found be a rectangular shape representing not only an absence of Faradic reactions and but also low electrical resistance of the electrodes.

The electrochemical behavior of the electrodes could be more clearly understood by ac impedance measurement (Figure 3 (b)). The impedance data represent that the charge transfer resistance of the CNF/CNT is smaller than that of CNF. The ideal capacitance will give rise to a straight line parallel to the imaginary axis (Z") at lower frequency, however, a real capacitor with a series of resistances, the slope of the impedance line in the mass transfer region has a finite slope (the so called Warburg impedance), representing existences of the diffusive resistances of the ions outer Helmholtz plane in the electrolyte solution. The impedance of CNF/CNT electrode showed higher slope than that of CNF only, implying higher slope of charge density from the inner Helmholtz plane for the CNF/CNT electrode and resulting faster mass transfer.

## Conclusions

The 1 wt.% of MWCNT addition in 10wt.% PAN solution for composite carbon nano fibers led to not only increases in electrical conductivity but also specific surface area, which influence drastic increases in capacitance at high current density.

## References


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Table 1. The BET characteristics of the CNF and CNF/CNT activated carbon webs.

| Sample | BET surface Area ($m^2/g$) | Average pore diameter (Å) | Pore size distribution (%) | | Total pore volume (cc/g) |
|---|---|---|---|---|---|
| | | | Micro | Meso | |
| CNF | 680 | 12.7 | 31 | 69 | 0.31 |
| CNF/CNT | 1200 | 8 | 89 | 11 | 0.55 |

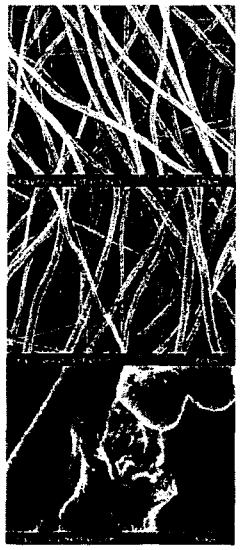
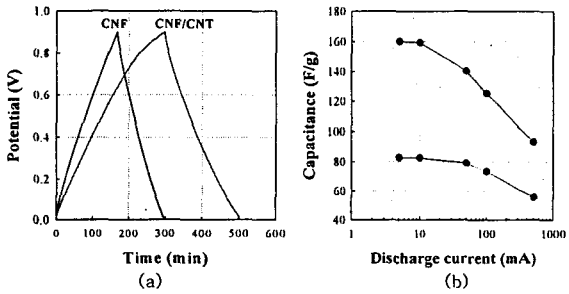


Figure 1. SEM micrographs of activated carbon nanofibers.

(a) PAN-based activated carbon nanofibers,

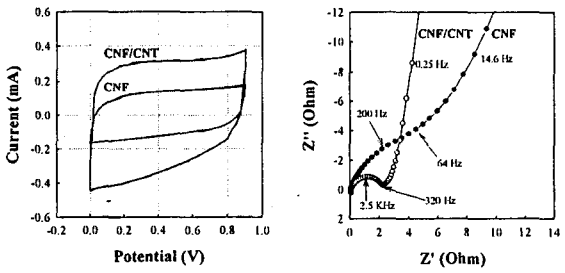
(b) carbon nanocomposite fibers of 1 wt.% CNT in PAN-based nanofibers

(c) high magnification of (b) and the white triangle indicated the CNTs in PAN nanofiber.




(a) (b)

Figure 2. (a) Galvanostatic charge/discharge of an electrochemical supercapacitor and (b) dependence of specific capacitances on the discharge current density of CNF and CNF/CNT nanocomposite electrodes. Capacitance measurements were undertaken in a 30 wt.% KOH electrolyte aqueous solution.




(a) (b)

Figure 3. (a) Cyclic voltammograms of CNF and CNF/CNT electrodes in 30 wt.% KOH electrolyte aqueous solution at potential sweep rate of 10 mV/s and (b) complex-plane impedance plots of the samples (AC signal level, 20 mV; frequency range, 1 mHz - 1 MHz).