Processing and Performance of Electric Double-Layer Capacitors with Block-Type Carbon Nanotube Electrodes

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Two kinds of block-type porous materials of carbon nanotubes were fabricated. One was fabricated by hot-pressing without any binding materials, the other was synthesized through carbonization of a cured mixture of carbon nanotubes and phenol-formaldehyde resin. The specific surface area and total volume of the open pores were measured. Both are suitable for fabricating polarizable electrodes of electric double-layer capacitors (EDLCs). In addition, the block-type carbon nanotube electrodes enable one to fabricate a box-type cell. A cell with large capacitance, 150 F at 1.0 V, was developed by using sulfuric acid as the electrolyte.

Since the discovery of carbon nanotubes by Iijima, many theoretical and experimental investigations on their novel structure, fascinating properties, and potential applications have been carried out. Carbon nanotubes have a narrow distribution of size, high strength, highly accessible surface area, low resistivity, and high stability. Such properties give carbon nanotubes potential applications in many areas such as reinforcement material and catalyst carrier.[1—7]

Electric double-layer capacitors (EDLCs) based on activated carbons have been widely studied because of their large capacitance, long cycling life, and freedom from toxic materials.[8—12] The activated carbon electrodes were classified in two categories: sheet-type electrodes and block-type electrodes. The capacitor using sheet-type electrodes consists a pair of wound-activated-carbon on current collectors. The block-type electrodes enable one to fabricate a box-type capacitor which has space merit.[13]

Potential application of carbon nanotubes for EDLCs is of current great interest. Recently, sheet-type carbon nanotube electrodes with a thickness of only 25.4 μm have been developed by some authors.[14] As mentioned above, this is of interest for processing block-type carbon nanotube electrodes. Here we report our findings on the processing of such electrodes and the performances of the various kinds of electric double-layer capacitors.

Experimental

Preparation of Block-Type Carbon Nanotube Electrodes. Carbon nanotubes used in this experiment were produced by a process of catalytical pyrolysis of C_2H_4/H_2 with Ni particles as the catalyst. Nitric acid treatment was employed to remove the catalyst particles. After nitric acid treatment, the TEM image of the carbon nanotubes with the diameter of 20—30 nm was taken and is shown in Fig. 1. The entangled structure is the main feature of catalytically grown carbon nanotubes.

Two kinds of processes for the fabrication of carbon nanotube electrodes were developed. One synthesis process is hot-pressing.

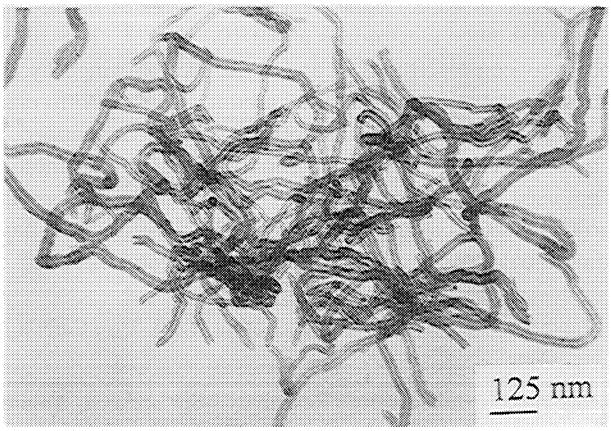


Fig. 1. TEM image of carbon nanotubes.

Carbon nanotubes, without any binder materials, were hot-pressed at 2273 K and 25 MPa in argon to attain block-type porous materials (named as electrodes A). The other synthesis process is similar to the method for activated carbon electrodes developed by Y. Kibi et al.[9] The electrodes are obtained by carbonization of cured mixtures of carbon nanotubes (CNTs) and phenol-formaldehyde (PF) resin. The tested electrodes (named as electrodes B), in which the starting material composition was CNTs/PF = 80/20 in weight ratio, were carbonized at 850 °C under nitrogen flow. In addition, the block-type activated carbon electrodes with the surface area of 1500 $m^2\,g^{-1}$ and bulk density of 0.5 $g\,cm^{-3}$ (Taike Electric Co., Ltd., Daqing, China) were used for comparison. They were named as electrodes C.

Capacitor Characteristics. The d.c. capacitance measurements were carried out in a test cell. Two identical block-type carbon nanotube electrodes were assembled in a test cell. First, each of the electrodes was immersed in a 38 wt% solution of sulfuric acid. A separator was sandwiched between electrodes. A pair of graphite collectors was attached to the electrodes for electric current collecting.

For measuring d.c. capacitance, the test cells were charged at a constant voltage of 1.0 V for 30 min. Then each of the cells was

discharged at a constant current of 10 mA until the 1.0 V decreased to 0 V. The d.c. capacitance was calculated from the discharge process by using the following equation.

$$C = I\Delta t/\Delta V = 10 \times 10^{-3}\Delta t/(0.6 - 0.4) = 0.05\Delta t,$$

where C is the capacitance in Farads (F), and Δt, the time period from the decrease from 0.6 to 0.4 V in seconds.

The charging current after 30 min at 1.0 V was taken as apparent leakage current (I_L). The equivalent series resistance was measured by applying an alternating current at 10 mV amplitude in the frequency of 1 kHz.

Results and Discussion

Properties of Block-Type Carbon Nanotube Electrodes. The SEM images of the carbon nanotube electrodes A and B are shown in Fig. 2. Both electrodes consist of randomly entangled carbon nanotubes. The pores in the electrode are connected spaces in the entangled carbon nanotube network. So the pore structure of our electrode is free of dead end pores. It indicates that the sulfuric acid aqueous solution can be impregnated into almost all the pores.

As listed in Table 1, the BET surface area of block-type carbon nanotube electrode is about 100 $m^2\,g^{-1}$. The difference between electrodes A and B can be explained by the excess of pores formed by the carbonization of PF in electrodes B, see Fig. 3. Most nanotubes we used are capped. It can be seen clearly from Fig. 1. So the cavity of the nanotube is not used at this stage. It should be effective to increase the surface areas by using open nanotubes. Some authors have pointed out that the nitric acid oxidation[15] and oxygen[16] or carbon dioxide oxidation[17] can be employed to increase the surface area. This is due not only to the oxidation of the nanotube surfaces, but also to the opening of the nanotube caps. So further treatments are needed to obtain higher surface areas. It remains under investigation.

Table 1. The Physical Properties of the Block-Type Carbon Nanotube Electrodes

Electrode	Bulk density	Resistivity	Surface area	Volume
	$g\,cm^{-3}$	Ω cm	$m^2\,g^{-1}$	$cm^3\,g^{-1}$
A (hot-press)	0.9	$2—3\times10^{-4}$	ca. 100	ca. 0.3
B (CNTs/PF)	1.05	$4—5\times10^{-4}$	ca. 150	ca. 0.45

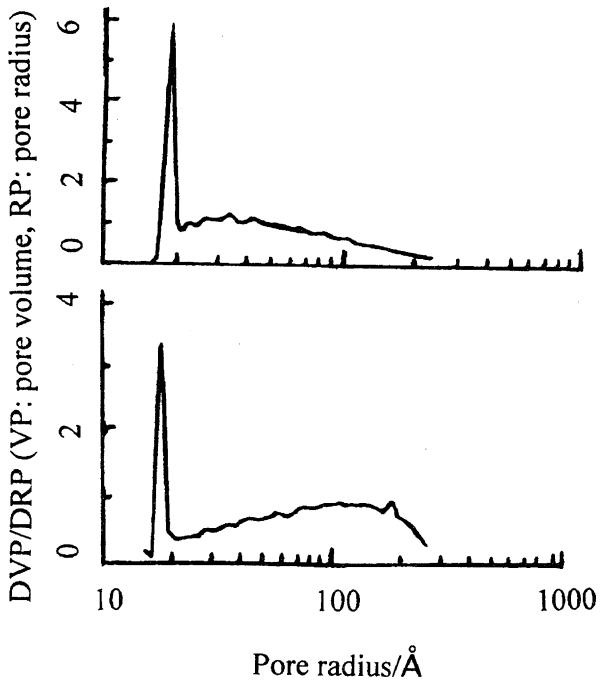
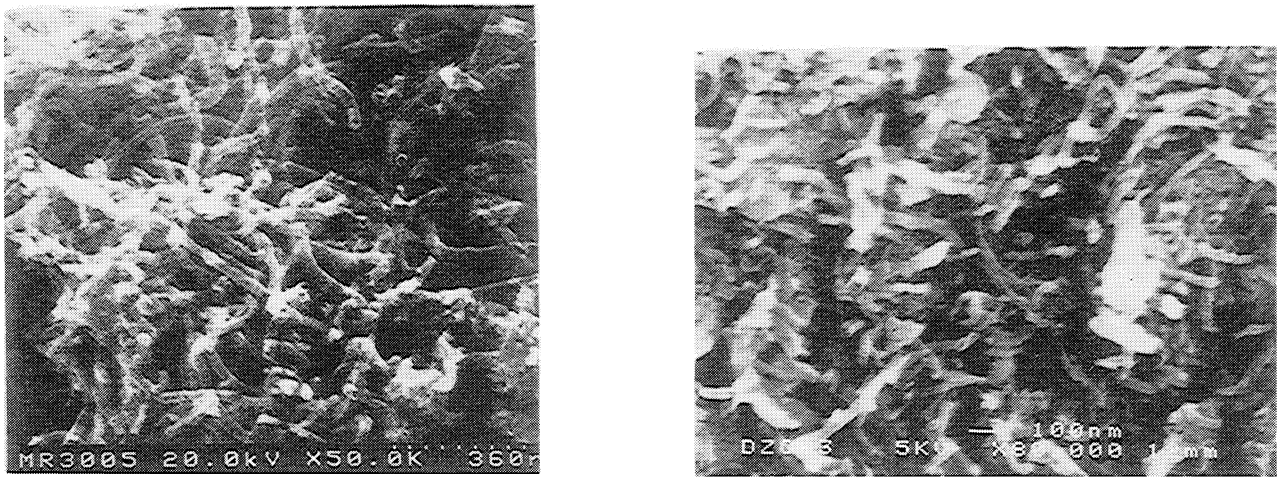


Fig. 3. Pore size distribution of block-type electrodes. Up: hot-press, Down: CNTs/PF.

As can also be seen in Fig. 3, most pore diameters are between 4—50 nm. This provides an advantage over activated carbon because micropores with below 4 nm diameter take a majority part in activated carbon electrodes. It is very similar to the data presented by C. Niu[14] though carbon nanotubes with different diameters were used. For the pores in the electrodes are connected spaces in the network. It can be deduced that the diameter of pores has no strong relation



(a) Electrodes A (hot-press) (b) Electrodes B (CNTs/PF)

Fig. 2. SEM image of block-type electrodes.

Table 2. The Capacitor Characteristics of the Test Cells

Electrode	Size	Capacitance	C_p	C_v	I_L	ESR
	mm	F	$F\,g^{-1}$	$F\,cm^{-3}$	mA	Ω
A (hot-press)	8×8×3	7.5	86.8	78.1	< 0.6	2.75
B (CNTs/PF)	20×20×2.4	45.8	90.8	95.3	< 1.7	1.17
C (activated carbon)	8×8×3	6	125	62.5	< 1.0	4

to the diameter of carbon nanotubes. In fact, it was found that there is no substantial change in pore size distribution even utilizing carbon nanotubes with 50—100 nm diameter. Moreover, in contrast with activated carbons, carbon nanotubes have high thermal stability. The analysis of electrode A by hot-pressing at 2273 K shows there is no substantial decrease in the specific area or total pore volume. If the same process was carried on activated carbons, the specific area of activated carbons probably decrease so dramatically that the second-phase activation process is needed. So the methods of fabricating carbon nanotube electrode are simpler and almost unlimited.

The resistivity of the carbon nanotube electrodes measured by conventional four-probe method is on the order of 10^{-4} Ω cm, which is about one order of magnitude lower than that of activated carbons.[16] The resistivity of electrodes B is higher than that of electrodes A due to using binding materials that bring impurities into the structure.

Capacitor Performance. Table 2 lists the capacitor characteristics of the test cells. The typical d.c. charge/discharge curve for a test cell with electrodes B is shown in Fig. 4. Electrically, each cell is actually two EDLCs in series. The measured capacitance should be about 1/2 the value of capacitance of each electrode. Based on the electrode materials only, it can be calculated that a specific capacitance (C_p) about 90 $F\,g^{-1}$ and an energy density about 12.5 $kJ\,kg^{-1}$ are achieved. With comparison to the 104 $F\,g^{-1}$ by C. Niu, we concluded that similar values were obtained on sheet-type and block-type electrodes. Also, this value is very close to carbon aero-gels with surface area ca. 700 m^2 which exhibit a specific capacitance of 95 $F\,g^{-1}$, but somewhat lower than the reported optimum value of more than 150 $F\,g^{-1}$ with activated carbon.[18] However, the bulk densities of electrodes formed by activated carbon are mostly in the range of 0.2—0.8 $cm^3\,g^{-1}$. So the carbon nanotube capacitor performances are even better if high volumetric capacitance (C_v) and low ESR were considered. This can be verified by comparing carbon nanotube electrodes with electrodes C, see Table 2. It indicates that the block-type carbon nanotubes are good candidates for fabrication of EDLCs along with sheet-type ones.

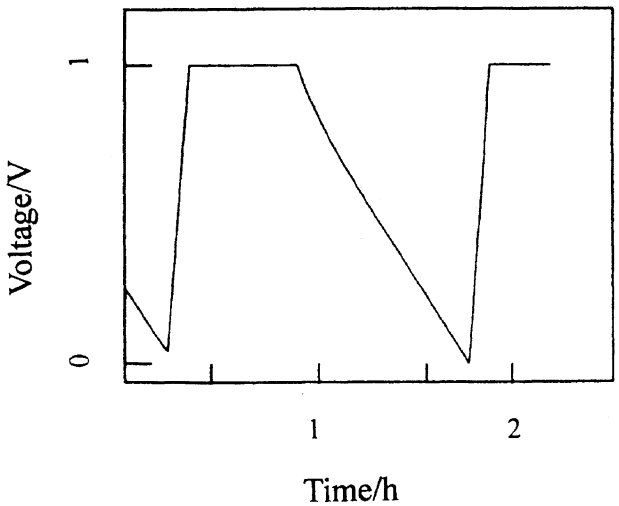


Fig. 4. Typical charge and discharge curve for a test cell with electrodes B. The charge is at constant 1.0 V and discharge current is 10 mA.

The block-type carbon nanotube electrodes are suitable for fabricating a box-type capacitor as developed in lead/acid battery and activated carbon capacitor. The test cell with capacitance of greater than 150 F at 1.0 V was fabricated in the author's lab by simply enlarging the cross section area of electrodes to 40×40 mm. Higher operation voltage can be obtained by stacking the cells in series. Use is expected as a new energy storage device and as a new supplementary power source.

Traditionally, EDLCs have been optimized in two versions — minimum self-discharge rate for low-current applications and minimum ESR for high-current applications. On carbon nanotube capacitors, the apparent leakage current of lower than 1.5 mA was obtained on a single cell device. It is actually the sum of a charging current and a self-discharge current. The self-discharge current could be measured by open-circuit voltage-decay and it was estimated to be about 30 $\mu A\,cm^{-2}$. ESR is directly related to the electrode thickness and is inversely proportional to its cross sectional area. The value of 1—3 Ω is reasonable if one considers that the electrode thickness is about 3 mm. If it was to be designed for high-current applications, the thickness can decrease to 0.5 mm with enough strength remaining.

Conclusions

EDLCs based on block-type carbon nanotube electrodes with a specific capacitance of 90 $F\,g^{-1}$ were fabricated in this experiment. Results show the block-type electrodes are suitable for the fabrication of EDLCs like sheet-type ones. Moreover, the block-type electrodes enable one to fabricte a box-type capacitor which has space merit.

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