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Short communication

Study of electrochemical capacitors utilizing carbon nanotube electrodes

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Abstract

Several types of block-form porous tablets of carbon nanotubes are fabricated to use as polarizable electrodes in electrochemical capacitors (ECs). These tablets are prepared by using moulded mixtures comprising carbon nanotubes and phenolic resin powders. Comparison of the effect of different processing on the performance of the capacitors is specifically investigated. Using these polarizable electrodes, ECs with a specific capacitance of about 15 to 25 F cm^{-3} are obtained with 38 wt.% H_2SO_4 as the electrolyte.

Keywords: Carbon nanotubes; Electrical properties; Electrochemical capacitors

1. Introduction

Electrochemical capacitors (ECs) or 'supercapacitors' have many potential advantages in electrical devices by virtue of their large capacitance, high power and long cycle life. Various types of polarizable electrodes based on activated carbons have been developed, namely, paste type, activated-carbon fibre cloth type, activated-carbon fibre sheet type, activated carbon–carbon composite type [1–5]. Recently, high-power ECs based on carbon nanotube sheet electrodes have been developed [6].

Carbon nanotubes have a novel structure, a narrow distribution of size in the nanometer range, highly accessible surface area, low resistivity, and high stability [7–11]. These features suggest that carbon nanotubes are suitable materials for polarizable electrodes. In order to fabricate ultrahigh capacitors (100 to 1000 F), it is of great interest to process carbon nanotube solid electrodes. The present paper reports the processing of carbon nanotube solid electrodes and the effect of chemical treatment on the performance of these electrodes in ECs.

2. Experimental procedures

2.1. Preparation of carbon nanotube electrodes

Carbon nanotubes were produced catalytically with Ni particles as the catalyst. Nitric acid treatment was employed to remove the catalyst particles before use. A transmission electron micrograph (TEM) of carbon nanotubes after such nitric acid treatment is shown in Fig. 1. The nanotubes have a diameter of 20 to 30 nm and a length of several microns to several tens of microns.

Several processes for the fabrication of carbon nanotube tablets were developed. The flow chart of these processes is given in Fig. 2. A mixture of carbon nanotubes (CNTs) and phenolic resin (PF) powders in a CNTs: PF weight ratio of 85:15 was moulded under a certain pressure at 100°C for 15 min (electrode (a)). A second version was obtained by carbonization of the moulded mixtures at 850°C for 2 to 4 h under nitrogen flow (electrode (b)). Finally, electrode (b) was immersed in a hot mixture of concentrated sulfuric acid and nitric acid for 15 min and then washed with distilled water and dried under vacuum at 100°C to give electrode (c).

2.2. Capacitor characteristics

The DC capacitance measurements were carried out in a unit test cell at 25°C. The unit cell contained two carbon nanotube electrodes 22 mm in diameter and 1.2 mm in

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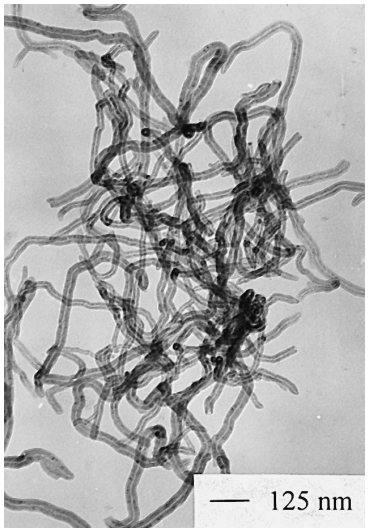

Fig. 1. TEM image of as-produced nanotubes.

thickness. The separator was made of glass fibre, which retains the electrolyte solution (38 wt.% H_2SO_4). A pair of graphite discs was attached to the electrodes to collect the electric current. The gasket was made of a thermoplastic resin.

To measure DC capacitance, the test cells were charged to 0.9 V at a constant current of 100 mA, then held at this voltage for 30 min. Each of the cells was discharged at a constant current of 10 mA until the voltage decreased to 0 V. The DC capacitance was calculated according to:

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

where: C is the capacitance in Farads (F); i is the discharge current in ampere (A); Δt is the time period (in seconds) for the potential change (ΔV, in volts). By comparing the linearity of the voltage change with respect to time during the discharge period, the capacitance (C_1, C_2) was calculated by the potential change from 0.6 to 0.4 V and from 0.6 to 0.2 V, respectively.

The DC current after 30 min charging at 0.9 V was taken as the apparent leakage current (I_L). The DC resistance was calculated from the voltage drop at the initial stage of discharge.

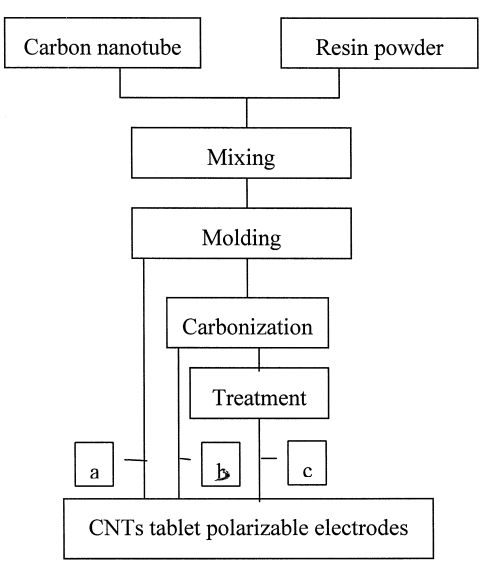

Fig. 2. Fabrication process of CNT tablets.

3. Results and discussion

3.1. Properties of carbon nanotube electrodes

A scanning electron micrograph (SEM) of the carbon nanotube electrode is shown in Fig. 3. The electrode consists of randomly entangled carbon nanotubes. The pores in the electrode are connected spaces in this network, i.e., the pore structure is free of dead-end pores. The electrodes have a bulk density of around 1.0 g cm^{-3} and good strength. The volumetric specific surface area (BET) is about 120 m^2 cm^{-3}. This is lower than that of activated carbon powders and carbon cloth, but of the same order as that of high bulk density carbon aerogel.

3.2. Capacitor performance

Using the new polarizable electrodes, ECs with specific capacitance of about 15 to 25 F cm^{-3} (the volume of the capacitor), low apparent leakage currents and low DC resistance are obtained with a single cell device when the discharge current is about 10 mA.

For electrode (a), the DC resistance is the highest for an electrode containing 15% binders. The binders deteriorate the performance. Thus, it is necessary to carry out a carbonization process. After carbonization, the resistance decreases dramatically, (electrode (b)). The capacitance of electrodes (a) and (b) are similar. For electrode (c), however, chemical treatment enhances the capacitance, see Fig. 4. That is, discharge is increased and this effect is considered to be related to the surface condition of the carbon nanotubes.

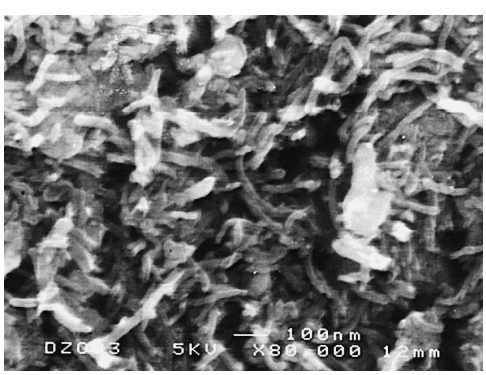

Fig. 3. SEM image of CNT electrode.

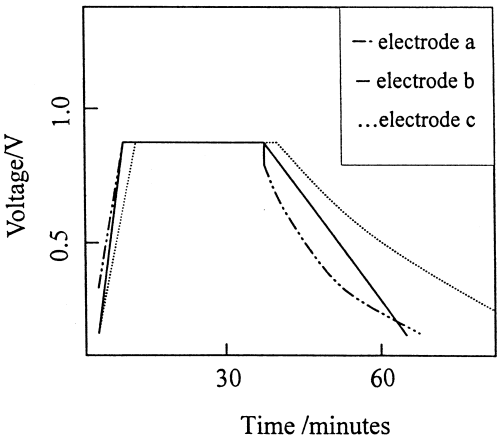

Fig. 4. Charge and discharge curve of capacitors with electrode (a), (b) and (c).

Table 1
Properties and capacitor characteristics of carbon nanotube electrodes

Electrode	Bulk density	Capacitance $C_1[C_2]$ (F)	I_L (mA)	DC resistance (Ω)
a	1.2	14.1 [16.8]	1.5	8
b	1.05	16.1 [16.25]	1.2	0.8
c	0.98	24.1 [26.6]	1.2	1.0

It is well known that the capacitance performance of carbon fibre is dependent upon the surface condition of the fibre. There are several methods for introducing oxygenated groups on to the surface of carbon [12,13]. In this study, nitric acid treatment on as-produced carbon nanotubes and chemical treatment on electrode (b) create acid sites on the surface of the carbon nanotubes. It is estimated that there are around 10^{21} sites per gram [14]. The acid sites are composed of functional groups such as –COOH, –OH, and $>C=O$, and provide hydrophillic sites on the surface to produce cation-exchange properties. As some authors have reported [15,16], higher capacitance can be achieved through the attachment of a variety of surface function groups using either thermal, chemical or electrochemical treatments.

The functional groups import an enhancement effect with a somewhat retarded current. In order to distinguish this kind of effect, a comparison was made of the linearity of the discharge curves of three types of electrodes. For ECs, Posey and Morozumi [17] have pointed out that the voltage drops suddenly at the initial period of discharge. This voltage drop is caused by a gradient of potential throughout the pores in the electrodes. Then, the voltage decrease should be linear because the pore effect is finite. The voltage drop is proportional to the electrolyte resistance in the pores. If the values of C_1 and C_2 are compared, it can be seen that the discharge curve of electrode (b) is very linear (Fig. 4). There are, however, some differences with electrodes (a) and (c) which are probably caused by the chemical treatment of these electrodes. The infrared spectra of electrodes (a), (b) and (c) are shown in Fig. 5. Electrodes (a) and (c) have the same surface structure of carboxy and ester groups with aliphatic alcohol and ketone compounds. On carbonization at 850°C in a N_2 atmosphere, the alcohol and ketone compounds are removed and the carboxy and ester groups are converted to phenolic hydroxy and quinone groups. Thus, the discharge curve of the carbonized electrode (b) exhibits different behaviour to electrode (a) or (c).

Besides introducing functional groups, chemical treatment with concentrated nitric acid and sulfuric acid is also considered to remove impurities and to expand the pore size. This conclusion is based on the decrease in the bulk

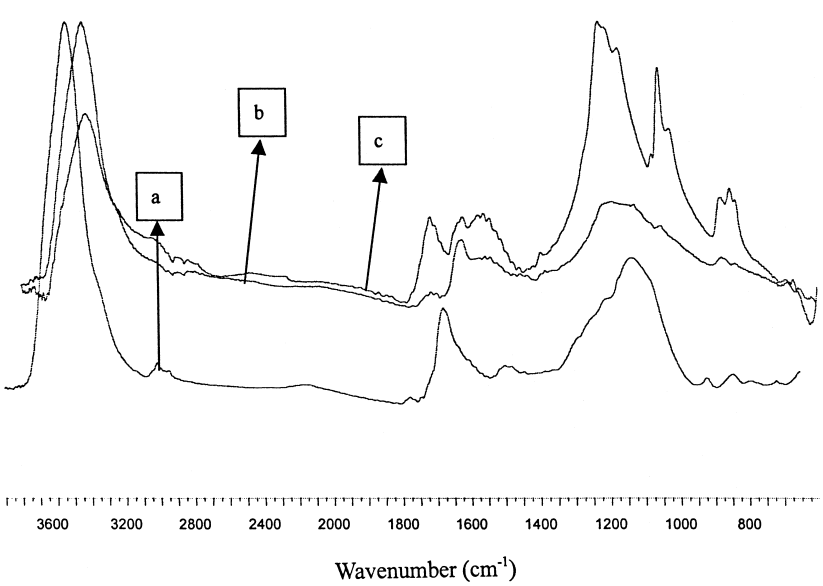

Fig. 5. Infra-red spectra of electrodes (a), (b) and (c).

density of electrodes after such treatment (Table 1). Thus, the superior capacitance of electrode (c) with respect to that of electrode (b) is likely to be the result of a combination of these factors.

It is practical to fabricate supercapacitors from carbon nanotube solid electrodes because the electrodes exhibit high bulk density, high strength, and excellent electric conductivity. In fact, a single cell with a capacitance of over 100 F was easily fabricated in the author's laboratories by using electrodes with a large diameter, viz., 45 mm. The only problem is the price of carbon nanotubes. At present, the authors can achieve in daily production of only about 100 of multi-walled carbon nanotubes quite cheaply.

4. Conclusions

ECs based on carbon nanotube solid electrodes with specific capacitances of about 25 F cm^{-3} are obtained with 38 wt.% H_2SO_4 as the electrolyte. Chemical treatment of the carbon nanotubes and the electrode enhances the performance of the capacitors. This improvement is related to the surface condition of the carbon nanotubes. It is practical to fabricate ultrahigh capacitors by using such techniques.

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