

Effects of binders on the performance of electric double-layer capacitors of carbon nanotube electrodes^{*}

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Received September 15, 2004; revised November 8, 2004

Abstract Polarizable electrodes of electric double layer capacitor (EDLCs) were made from carbon nanotubes. Effects of different binders, which are phenolic resin (PF) and polytetrafluoroethylene (PTFE), on the properties of polarizable electrodes are studied. Results indicate that the microstructure, pore size distribution and specific capacitance of the electrodes with PTFE binder are superior to those electrodes with PF binder after carbonization. The suitable binder (PTFE) for carbon nanotubes electrodes is proposed.

Keywords: carbon nanotubes, electric double-layer capacitors, phenolic resin, polytetrafluoroethylene.

Electric double layer capacitors (EDLCs) or 'supercapacitors' have many potential advantages in electrical devices due to their large capacitance, high power and long cycle life^[1,2].

Activated carbons, which exhibit a large specific surface area (higher than 1000 m²/g), have been widely used as polarizable electrodes of the capacitors^[1-3]. However, generally less than 1/3 of the surface area of these carbons is available to the electrolyte for the reason that they contain a large number of micropores. Moreover, the pores of activated carbon or carbon fiber are dead end (like cavities) and not connected to each other, and their availability is also low.

Carbon nanotubes (CNTs) have a novel structure, a narrow distribution of diameter in the nanometer range, a highly accessible surface area, and low resistivity, and they also have high stability^[4-6]. These features suggest that carbon nanotubes are suitable materials for polarizable electrodes^[7-9]. As for the CNT polarizable electrodes with an ideal structure, their surface is uncovered; pores in the nanotube network are all connected and fully available; micropores almost do not exist; all the surfaces of CNTs contribute to the build-up of a double layer between the conductors/solutions.

The structure of the real CNT electrodes, pre-

pared from a suspension of CNTs in a binder solution or with suspended binder (which is a general approach for preparing block-formed electrodes), may not be entirely ideal since a binder will choke the spaces between the CNTs. Although a higher mechanical stability is attained, the capacitance of the polarizable electrode is diminished by the blocking of a large part of the CNT's high surface area. However, this drawback may be obviously reduced if a suitable binder is selected.

The present paper reports the processing of carbon nanotube solid electrodes and the effects of different types of binder, phenolic resin (PF) and polytetrafluoroethylene (PTFE), on the microstructure, pore size distribution and performance of the electrodes in EDLCs.

1 Experimental procedure

1.1 Preparation of CNT electrodes

In our experiment, CNTs were produced catalytically with Ni particles as the catalyst. Nitric acid treatment was employed to remove the catalyst particles before use. A transmission electron microscopy (TEM) of CNTs after such nitric acid treatment is shown in Figure 1. The multi-walled CNTs have a diameter of about 30 nm and a length of from several microns to tens of microns.

^{*} Supported by the Major State Basic Research Development Program of China (Grant No. 10332020)

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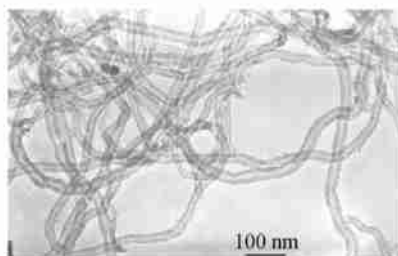


Fig. 1. Transmission electron microscopy (TEM) of as-produced CNTs.

The flow chart of the processes for the fabrication of CNT tablet polarizable electrodes is given in Figure 2. A full mixture of CNTs and phenolic resin (PF), prepared by mixing CNTs with ethanol solved PF (the CNTs to PF weight ratio is 90 :10), was dried, ground and molded under a certain pressure at 150 °C for 15 min to form the tablet ($\Phi 22 \text{ mm} \times 0.7 \text{ mm}$). Electrode (I) was obtained by carbonization of such a tablet at 850 °C for 2 h under nitrogen flow; A full mixture of CNTs and polytetrafluoroethylene (PTFE), prepared by mixing CNTs with PTFE suspending liquid (the CNTs to PTFE weight ratio is 90 :10), was dried, ground and molded under a certain pressure at 150 °C for 15 min to form the tablet ($\Phi 22 \text{ mm} \times 0.7 \text{ mm}$). Electrode (II) was obtained by carbonization of such a tablet at 850 °C for 2 h under nitrogen flow.

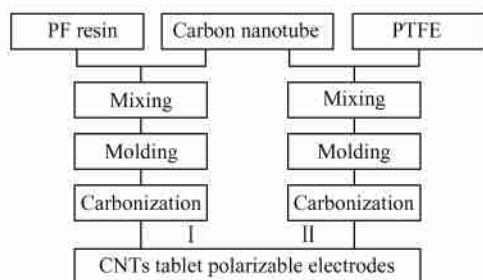


Fig. 2. Fabrication process of CNT tablet polarizable electrodes.

1.2 Capacitor characteristics

The DC capacitance measurements of EDLC were carried out in a test capacitor unit, which contained two CNT polarizable electrodes, with aluminum foil as current collector and microporous separator "celgard 2400" as separator. A 1 M solution of lithium perchlorate (LiClO_4) in a mixture of ethylene carbonate (EC) and propylene carbonate (PC) (1 :1 by volume) was used as an electrolyte solution. H_2O in the solution was removed by vacuum treatment and the H_2O content was less than 30 ppm before being used. Both the polarizable electrodes and the separa-

tor were wetted enough to maintain the electrolyte solution. The gasket was made of a thermoplastic resin.

The measuring method of DC capacitance is the same as that of Ref. [7]. The charge/discharge range of the test capacitor unit was 0.0–2.8 V with a constant current of 10 mA. The equivalent series resistance (ESR) of the capacitor unit was measured by applying an alternating current of 10 mV amplitude at a frequency of 1 kHz.

1.3 Apparatus

The morphology and microstructure of the products were observed using field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The specific area and the pore size range of CNT polarizable electrodes were measured by the BET method and the B.J.H. method^[8], respectively. The apparatus employed was SORPTOMAT-IC1990, Thermo Quest Italia S.P.A.

2 Results and discussions

It is indicated in Table 1 that the specific capacitance of electrode II is about twice as high as that of electrode I, attaining about 42 F/g. This result is due to the differences of surface structure and the pore size distribution between the two electrodes.

Table 1. Performance of the polarizable electrodes made of CNTs

	Specific area (m^2/g)	Relative volume of micropores (<2 nm)%	Specific capacitance of polarizable electrode (F/g)	Equivalent series resistance (ESR)
Electrode I	147.75	19.97	21.6	3.92
Electrode II	145.29	6.21	41.8	2.93

Fig. 3 is SEM images of electrode I and electrode II under a magnification of 5000 times. Figure 3 (a) indicates that the surface of electrode I is flat and has sparse cracks. Figure 3 (b) indicates that the surface of electrode II is rougher and has more furrows and burrows compared to electrode I. Fig. 4 is SEM images of electrode I and electrode II under a magnification of above 60000 times, and the randomly entangled CNTs contained in the electrodes can be identified. Figure 4 (a) indicates that the surface of electrode I is still flat, the CNTs are embedded in the surface and the spaces between them are unopened. Figure 4 (b) shows that in the surface of electrode II, the CNTs are protruding and thus their surface is uncovered, the spaces in the network of

CNTs are connected to form the pores that are free of dead-end. These differences of structure indicate that the CNTs' surface in electrode II can be more effectively utilized compared to those in electrode I.

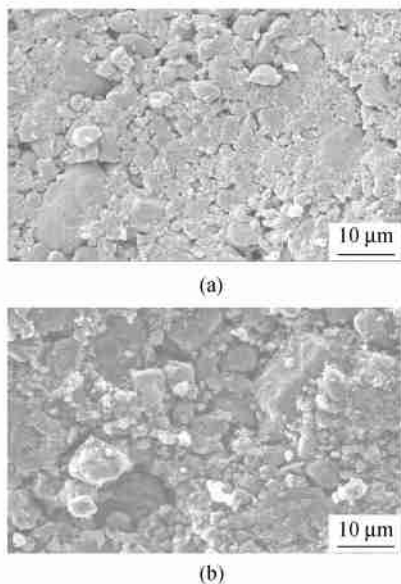


Fig. 3. Scanning electron microscopy (SEM) of the electrodes. (a) electrode I; (b) electrode II.

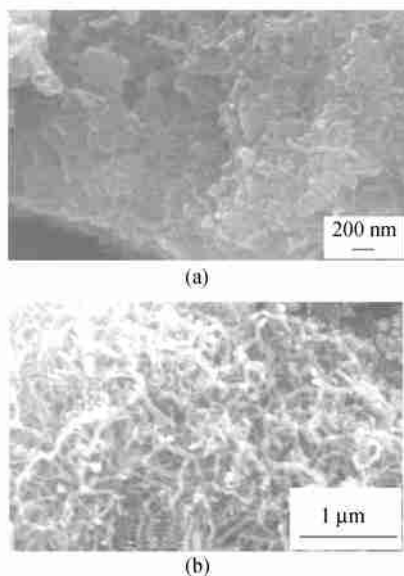


Fig. 4. Scanning electron microscopy (SEM) of the electrodes. (a) electrode I; (b) electrode II.

The structural differences between electrode I and electrode II are the result of the different physical and chemical characteristics of the two binders.

During the fabrication of electrode I, under a certain pressure at 150 °C, PF will melt, flow, fill

the pores in the electrode, fill the spaces between the CNTs and cement them together, as shown in Figure 5 (a). Although the PF binder decomposed during the carbonization process, the remaining glassy carbon was still abundant (holding about 50 wt % of the mass of PF^[10]). A qualified strength of the electrode was attained, but many pores and a large part of CNT surfaces were still blocked. Thus the surface of electrode I was flat and the spaces between the CNTs were blocked, as shown in Figure 3 (a) and Figure 4 (a).

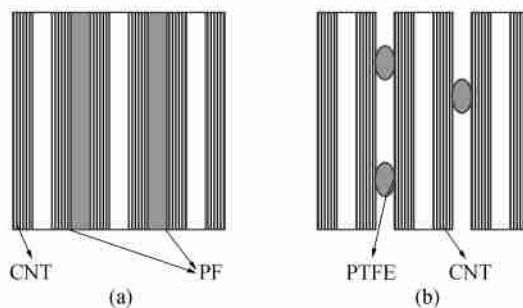


Fig. 5. Schematic diagram of connection states between CNTs with (a) PF and (b) PTFE binders.

PTFE has a high chemical stability and will hardly be dissolved by any solution. To ensure the PTFE, fine particles were uniformly distributed among the CNTs, and electrode II was fabricated via a full mixture of CNTs and PTFE suspending liquid. Since PTFE cannot melt at 150 °C but its ductility can enhance under heating, during the molding process, PTFE particles did not melt and fill the pores in the electrode, but they could firmly bind the adjacent CNTs together due to the effect of pressing and their enhanced ductility. As shown in Figure 5 (b), the connection parts between the CNTs formed by PTFE particles only hold a small part of the CNT surface, thus a large part of CNT surface is uncovered and the spaces between CNTs are mostly open. After carbonization the PTFE binder decomposed and a large part of its mass was lost, which can result in further enlargement of the pores in the electrode and the free spaces between the CNTs. Thus, the surface of electrode II is rough, the CNTs are protruding and the free spaces in the network of CNTs are connected, as shown in Figure 3 (b) and Figure 4 (b).

Such structural difference between electrode II and electrode I can also lead to the difference of pore size distribution between them.

As listed in Table 1, electrode I has a specific surface area of $147.75 \text{ m}^2/\text{g}$. The pore-size-range graph of electrode I is illustrated in Fig. 6 (a), and the calculated relative volume ratio of the micropores is about 20%. Although the specific area is of the same order as that of high-bulk density carbon aerogel^[7], and the ratio of micropores is much lower than that of activated carbon, the performance of the electrodes will still be limited for the reason that the redundant glassy carbon, formed by PF decomposing, not only blocks the surface of many CNTs but also brings in many micropores that are not available for the double layer.

The pore-size-range graph of electrode II is illustrated in Figure 6 (b). The calculated relative volume ratio of micropores from it is about 6.2%, as listed in Table 1. Because many pores in the electrodes are unfilled and a large part of spaces between the CNTs are opened, the relative volume ratio of micropores in electrode II is also obviously lower than that in electrode I.

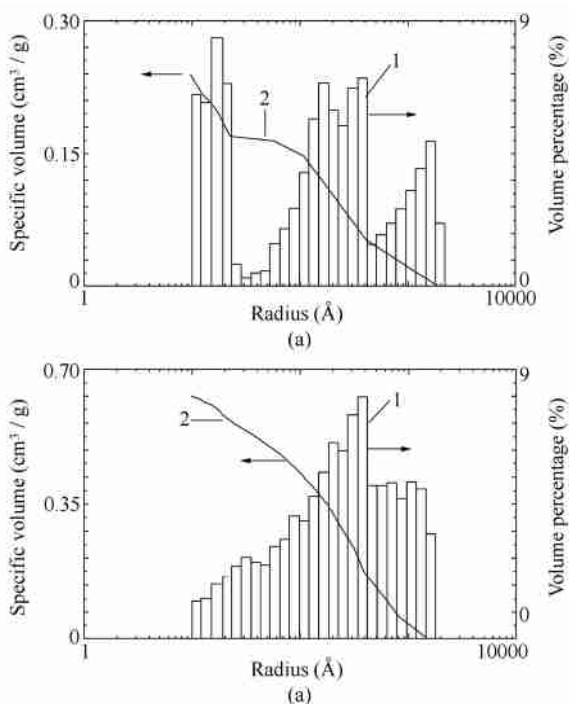


Fig. 6. Pore size distribution of the electrodes. (a) electrode I; (b) electrode II. (1. the relative volume (%) curves; 2. the cumulative volume (cm^3/g) curves.)

Table 1 indicates that the specific surface area of electrode II is slightly lower than that of electrode I. The reason lies in that the micropores of electrode

II are obviously fewer than those of electrode I. The decrease of micropores may lead to the decrease of total specific area for the reason that they represent part of the total pore volume^[11].

Comparing electrode II to electrode I, the relative volume ratio of micropores decreases from about 20% to about 6.2% but the specific surface area decreases very little, as listed in Table 1. It can be inferred from Ref. [11] that micropores take a greater portion of the specific surface area of the electrode than mesopores or macropores do, if their relative volume ratios are equal. If the electrodes have an invariable surface area, the decrease of the relative volume ratio of micropores results in a greater increase of the area that is available for building up the double layer. Thus a larger area of electric double layer can be formed in electrode II compared to electrode I.

The ESR of the EDLC based on electrode II is lower than that of the EDLC based on electrode I, as listed in Table 1. It is likely that the improvement of pore distribution of electrode II is beneficial to the transmission of the solvated electrolyte ions and helps to reduce the ESR of EDLC^[12].

Some co-workers even found that PTFE binder had superiorities for CNT electrodes^[8,9]. However, in their work, CNT electrodes with PTFE binder were fabricated from ball milling CNTs and PTFE powder, the electrodes were not carbonized, since the strength of electrodes could not be secured after carbonization due to the non-uniform distribution of PTFE binder. The main drawback of CNT electrodes with uncarbonized PTFE binder lies in the high internal resistance of EDLCs^[8,9]. Certainly, the CNT electrodes with uncarbonized PF binder also result in high internal resistance of EDLCs^[7]. In this study, the CNT electrodes with PTFE binder were fabricated from fully mixing CNTs with PTFE suspending liquid. The strength of electrode can be secured after carbonization, and the superior performance of CNT electrodes with PTFE binder was further realized.

Moreover, the specific capacitance can be further elevated if some other ways are combined, such as reducing the layers of CNT-walls and reducing the thickness of polarizable electrodes, etc^[13].

3 Conclusions

Electric double layer capacitor was fabricated from CNT electrodes.

Experimental results indicate that PTFE is a superior binder compared to PF for CNT electrodes. The CNT electrode with PTFE binder has superior structure and pore size distribution, which can bring about superior capacitor performance.

References

- 1 Nishino A. Capacitors: operating principles, current market and technical trends. *Journal of Power Sources*, 1996, 60(2): 137—147.
- 2 Kibi Y., Saito T. and Kurata M. Fabrication of high-power electric double-layer capacitors. *Journal of Power Sources*, 1996, 60(2): 219—224.
- 3 Moromoto T., Hiratsuka K. and Sanada Y. et al. Electric double-layer capacitor using organic electrolyte. *Journal of Power Sources*, 1996, 60(2): 239—247.
- 4 Iijima S. Helical microtubes of graphitic carbon. *Nature*, 1991, 354(6348): 56—58.
- 5 Issi J., Langer L. and Heremans J. et al. Electronic properties of carbon nanotubes: experimental results. *Carbon*, 1995, 33(2): 941—948.
- 6 Dai H., Wong E. W. and Lieber C. M. Probing electrical transport in nanomaterials: conductivity of individual carbon nanotubes. *Science*, 1996, 272(5261): 523—526.
- 7 Ma R. Z., Liang J. and Wei B. Q. et al. Study of electrochemical capacitors utilizing carbon nanotube electrodes. *Journal of Power Sources*, 1999, 84(1): 126—129.
- 8 Zhang B., Liang J. and Xu C. L. et al. Electric double-layer capacitors using carbon nanotube electrodes and organic electrolyte. *Materials Letters*, 2001, 51(6): 539—542.
- 9 Wang D. Z., Chen G. M. and Xu C. L. et al. Effect of binders in block-formed carbon nanotube electrodes on performances of electric double layer capacitors. *Journal of Chinese Inorganic Materials (in Chinese)*, 2001, 16(4): 672—676.
- 10 Rosy A. and Pilki C. K. S. Synthesis and thermal characterization of chemically-modified phenolic resins. *Journal of Applied Polymer Science*, 1994, 54(4): 429—438.
- 11 Peigney A., Laurent C.H. and Fakhaut E. et al. Specific surface area of carbon nanotubes and bundles of carbon nanotubes. *Carbon*, 2001, 39(4): 507—514.
- 12 Song H. K., Jung Y. H. and Lee K. H. et al. Electrochemical impedance spectroscopy of porous electrodes: the effect of pore size distribution. *Electrochimica Acta*, 1999, 44(20): 3513—3519.
- 13 Liu C. Y., Bard A. J. and Wudl F. Electrochemical characterization of films of single-walled carbon nanotubes and their possible application in supercapacitors. *Electrochemical and Solid State Letters*, 1999, 2(11): 577—578.