SCIENCE CHINA
Technological Sciences

April 2012 Vol.55 No.4: 913–920
doi: 10.1007/s11431-011-4708-2

Effect of electrochemical oxidation on carbon nanotube electrodes of electric double layer capacitors

QIAO YingJie[1], LI ChenSha[1,2*], CHEN XingJuan[3] & JIAO CaiShan[3]

[1] *Department of Materials Science, Harbin Engineering University, Harbin 150001, China;*
[2] *Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China;*
[3] *Chemistry Engineering Department, Harbin Engineering University, Harbin 150001, China*

Received July 11, 2011; accepted December 9, 2011; published online February 25, 2012

Electrochemical oxidation of the carbon nanotube (CNT) polarizable electrodes of electric double layer capacitors (EDLCs) was studied. It indicated that electrochemical oxidation elevated the available surface area of the electrodes and introduced some kinds of functional group on the CNT surfaces. The specific capacitances of the polarizable electrodes with organic electrolyte could be enhanced from 22.4 F g^{-1} to 78.2 F g^{-1} after electrolysis oxidization. The enhancement of the specific capacitance depends on the extent of electrochemical oxidation. Using acidic electrolyte for electrochemical oxidation has different effects on modifying the performances of the CNT polarizable electrodes compared to using basic electrolyte.

carbon nanotubes, electrodes, electrolytic oxidation, transmission electron microscopy, specific surface

Citation: Qiao Y J, Li C S, Chen X J, et al. Effect of electrochemical oxidation on carbon nanotube electrodes of electric double layer capacitors. Sci China Tech Sci, 2012, 55: 913–920, doi: 10.1007/s11431-011-4708-2

1 Introduction

Energy storage devices are classified according to energy and power density. Power density is related to the strength of a given current and voltage combination (wattage), while energy density is related to the duration of time that wattage can be applied. Batteries are currently the most common form of electrical energy storage. They are typically able to store higher energy density than supercapacitors, but they deliver less power compared to traditional dielectric capacitors. However, due to their short cycle life and low power densities [1], batteries are not suitable for many lightweight power source applications. Electric double layer capacitors (EDLC), commonly called supercapacitors or ultracapacitors, are intermediate systems that bridge the power and energy gap between traditional dielectric capacitors with a high power and batteries with a high energy.

An EDLC is composed of two non-faradic electrodes and an electrolyte. Its function is to store charges at an electric double layer interface that consists of space charges in an electrode bulk and physical adsorption of counter ions in an electrolyte [2]. They have many potential advantages in electrical devices by virtue of their large capacitance, high power and long life cycle.

The energy storage mechanism for an EDLC is mainly accounted for by the double-layer capacitance formed near the electrode surface. The specific capacitance depends on the surface texture, the specific area and the distribution of apertures of the polarizable electrode [3]. For the organic electrolyte, because of its larger molecular structure, the dissolved electrolyte ions cannot enter the micropores with diameters less than 2 nm and electric double layers cannot be formed. High specific area and low ratio of micropores can help elevate the specific capacitance of EDLCs. The

---

*Corresponding author (email: lichnsa@mail.tsinghua.edu.cn, lichnsa@163.com)

activated carbon and carbon fiber have been most widely used in electrode materials for EDLCs, and their surface areas can be higher than 1000 $m^2 g^{-1}$ [4]. But 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, leading to much lower actual values of specific capacitance than estimated from the specific surface area. Moreover, the activated carbon in itself does not have a high enough electrical conductance to act as a fully suitable material for the polarizable electrodes, the grain boundary resistance between the activated carbon particles decreases the power density of EDLC.

Carbon nanotubes (CNTs) have a novel tube shaped structure and a narrow distribution of diameters in the nanometer range, which are expected to be suitable for forming the double layer between the surface and the electrolyte. CNTs have highly accessible surface area, high electrical conductivity, and high chemical stability [5, 6]. These features suggest that CNTs are suitable materials for polarizable electrodes [5–8]. The single-walled CNTs seem most suitable as an EDLC electrode material because they are composed of only a single carbon network layer. However, the single-walled CNTs have some undesirable physical properties for the EDLC performance. Such as, not all single-walled CNTs inevitably exhibit metallic high conductivity, because they have three chiral structures of a graphene sheet, two of which are semi-conductive [9]. Furthermore, the diameters of the single-walled CNTs are usually much smaller than those of the multi-walled CNTs. When the diameter is smaller, the electronic conductivity depends more strongly on the chirality of a graphene sheet [10]. Thus here we focused on the multi-walled CNTs as a CNT material for the EDLC electrode material.

For the CNT polarizable electrodes with ideal structure, the surfaces of all CNTs are uncovered. Pores in electrodes are spaces in the entangled nanotube network, thus they are all connected. These spaces are large compared with the dimension of CNTs, so that micropores do not exist and all the surfaces of CNTs are contributed to the build-up of a double layer between the conductor and the solution, moreover, electrolyte access will be easier than in the case of activated carbon containing many pores which are like cavities and difficult to access. For the real electrodes, the structure may not be entirely ideal. The materials for carbon-based capacitors are generally prepared from a suspension of carbonaceous materials in a binder solution or with suspended binder, which is applied to the formation of rigid electrodes [11]. A binder will always tend to obstruct the pores. With the binder, a higher mechanical stability is attained but the capacitance and thus the measured performance of the polarizable electrode are strongly diminished by block of a large part of the carbon's high surface area that provides the major contribution to a high double-layer capacitance.

Electrochemical oxidation is usually used in modifying the carbon materials, such as activating carbon fibers [12, 13]. In this work, electrochemical oxidation was studied to change the structure, modify the surface characteristics and improve the performances of the CNT polarizable electrodes. Experiment results indicated that electrochemical oxidation can greatly enhance the specific capacitance of the CNT polarizable electrodes, and the enhancement of specific capacitance depends on the extent of electrochemical oxidation. However, acidic electrolyte and basic electrolyte used in electrochemical oxidation process have different effects on modifying the performances of the CNT polarizable electrodes.

2 Experiments

2.1 Preparation of CNT electrodes

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, JEOL-200CX) was employed to observe the microstructure of CNTs, as shown in Figure 1. The multi-walled CNTs had a diameter of 20 to 30 nm and a length of several microns to several tens of microns.

The flow chart of the processes for the fabrication of the CNT tablet polarizable electrodes is given in Figure 2(a). A full mixture of CNTs and phenolic resin (PF), prepared by mixing CNTs with ethanol dissolved PF (a CNTs: PF weight ratio of 85:15), was dried, hand grinded and molded under a certain pressure at 150°C for 15 min to form the tablets (ϕ22 mm×0.7 mm). The as-prepared CNT electrodes were obtained by carbonization of the tablets at 850°C for 2 h under nitrogen flow.

The electrochemical procedure used a CNT electrode, immobilized in a platinum plate as an anode within the electrolytic cell. The cathode was a graphite bar, electrolyte was aqueous solution of HNO_3 (or NaOH) of 1 mol L^{-1} concentration. When a current of 500 mA flowed through the electrolyte, the anions were discharged on the positively charged CNT electrode surface and the reactant generated

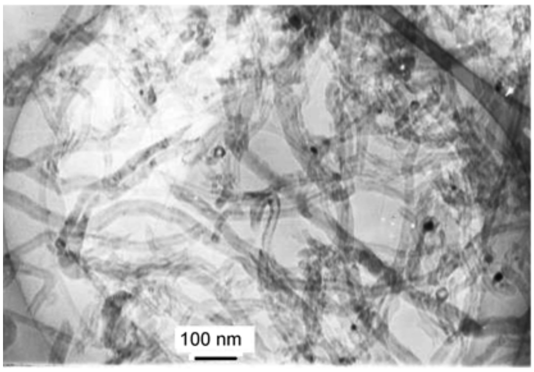

Figure 1 Transmission electron micrograph (TEM) of the as-produced CNTs.

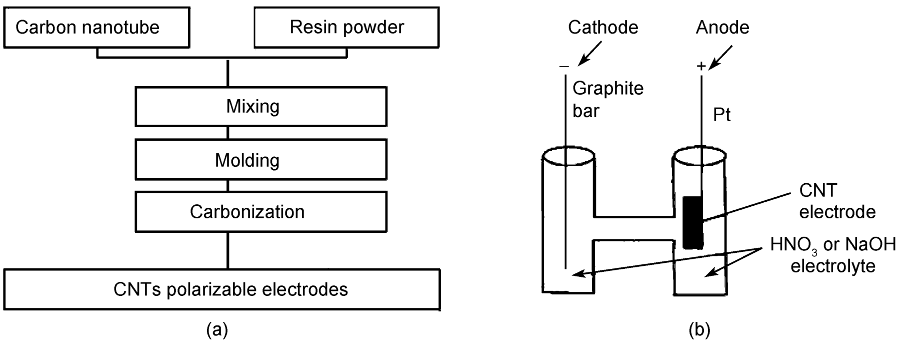

Figure 2 (a) Fabrication process of CNT tablet polarizable electrodes; (b) process of electrolysis treating the polarizable electrodes.

could react with the CNT electrode. The extent of electrochemical oxidation was as follows [14]:

$$Q=i\Delta t/m, \tag{1}$$

where Q was the extent of electrochemical oxidation (C g^{-1}); i was the current in Ampere (A); Δt was duration time (in seconds); m was the mass of each electrode (g).

A field emission scanning electron microscopy (FE-SEM, AMRAY-1910) was employed to observe the morphology of electrodes. “PERKINELMER Spectrum GX FT-IR System Jeol-200CX” infrared spectrum apparatus was employed to measure the functional groups. The specific area and the pore size distribution of the CNT polarizable electrodes were measured by BET method and B.J.H. method [7, 15], the employed apparatus was SORPTOMATIC1990.ThermoQuest Italia S.P.A.

2.2 Capacitor characteristics

The employed apparatuses for electrochemical measurements were “Solartron S11278 Interface/1255B” frequence response analyser and “Arbin” battery-testing instrument. The d.c. capacitance measurements of EDLC were carried out in a test capacitor unit, as shown in Figure 3. The unit cell contained two CNT polarizable electrodes, with aluminum foil as current collector and Celgard-2400 membrane as separator. A 1 mol L^{-1} 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 organic 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 separator were wetted enough to maintain the electrolyte solution. The gasket, which was the cylindrical shell of the test capacitor, was made of polytetrafluoroethylene (PTFE) resin.

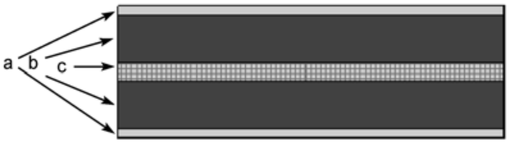

Figure 3 Schematic diagram of the test capacitor unit. a, Current collectors; b, electrodes; c, separator filled with electrolyte.

The measuring method of d.c. capacitance was as that of ref. [6]. To measure d.c. capacitance, the test cells were charged to 2.8 V at a constant current of 10 mA, then discharged at this current until the voltage decreased to 0 V, this process was cycled 100 times, the characteristics of the test cells remained constant during these cycles, d.c. capacitance was calculated from the slope of the $V(t)$ plot.

$$C=i\Delta t/\Delta V, \tag{2}$$

where C was the capacitance in Farads (F); i was the discharge current in ampere (A); Δt was the time period (in seconds) for the potential change (ΔV, in volts). The capacitance of every polarizable electrode C_E was calculated as follows [16]:

$$C_E=4\times C. \tag{3}$$

In our work, specific capacitance of every polarizable electrode was normalized to per unit mass, F g^{-1}.

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.

3 Results and discussions

3.1 Variation of structure of polarizable electrode treated by electrolysis in acid solution

Figures 4(a) and 4(c), the SEM images of the as-prepared electrode and the electrolytically oxidized (in HNO_3 solution) electrode under a magnification of 5000 times, indicate that the electrodes were constituted by many masses; Figures 4(b) and 4(d), the SEM images of the as-prepared electrode and the electrolyzed (in HNO_3 solution) electrode under a magnification of 100000 times, indicate that the masses were constituted by many CNTs. Moreover, Figure 4(a) indicates that the surface of the as-prepared electrode was flat and there were sparse cracks to divide the masses; Figure 4(c) indicates that the surface of the electrolyzed (in

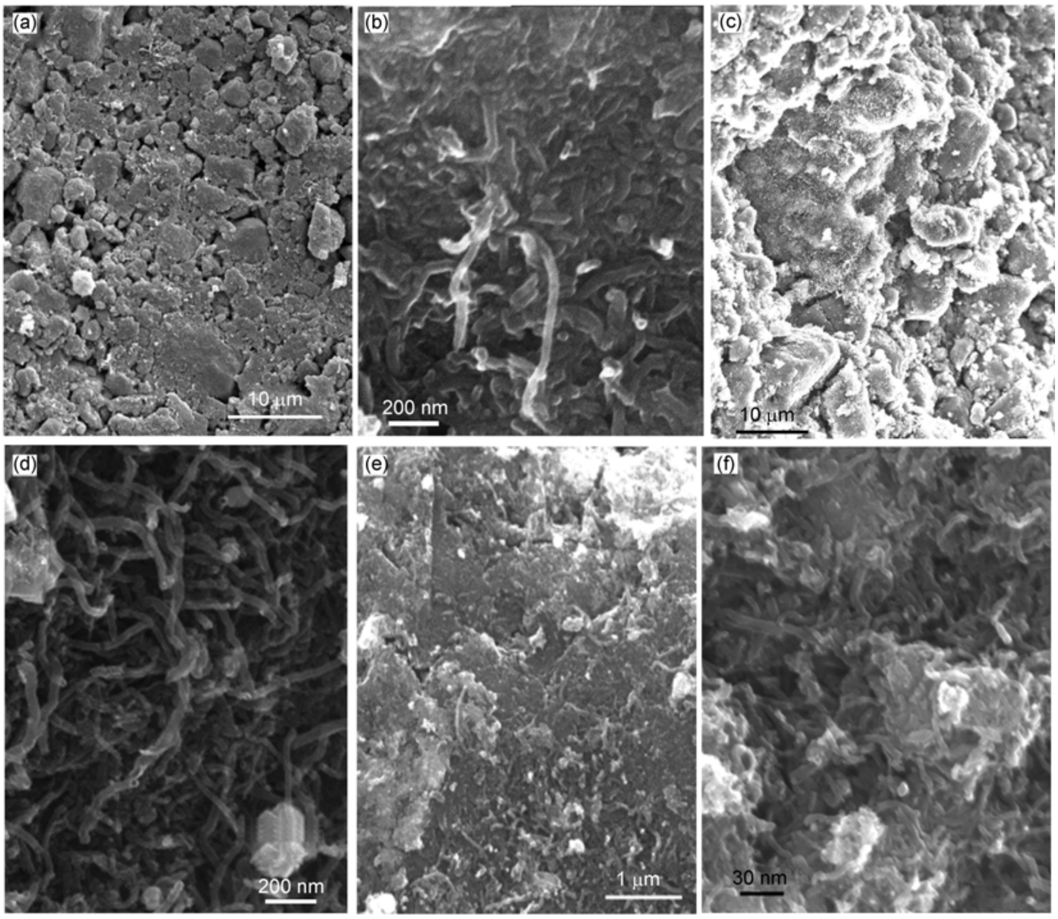

Figure 4 Scanning electron micrograph (SEM) of the electrodes. (a), (b) Images of the as-prepared electrode magnified by 5000 times and 100000 times respectively; (c), (d) images of the electrolytically oxidized (in HNO_3 solution) electrode magnified by 5000 times and 100000 times respectively, the extent of electrochemical oxidation of 6080 C g^{-1}; (e), (f) images of the electrolytically oxidized (in NaOH solution) electrode magnified by 25000 times and 100000 times respectively, the extent of electrochemical oxidation of 6080 C g^{-1}.

HNO_3 solution) electrode became rougher and had more furrows and burrows, the masses were also protruding; Figure 4(b) indicates that the surfaces of the masses in the as-prepared electrode were still flat, CNTs were embedded and the spaces between them were obstructed. Figure 4(d) shows that in the masses of the electrolyzed (in HNO_3 solution) electrode, CNTs were protruding and thus their surfaces were uncovered, the spaces in the network of CNTs were opened and connected.

The structure difference between the as-prepared electrode and the electrolyzed (in HNO_3 solution) electrode is considered to be the result of selective oxidation:

It can be known from Figure 4 that during the molding process of tablet, CNTs were cemented together to form secondary particles (masses), secondary particles were cemented together to form the tablet. External pores should be formed by the spaces between the secondary particles and internal pores formed mainly due to the spaces between CNTs. Under the applied pressure and temperature, PF melted and flowed to consolidate the tablet, but it also filled the external pores and the spaces between CNTs even if its amount was decreased. During the carbonization process, the PF binder decomposed, remaining amorphous carbon, which held about 50 wt% of the initial PF [17], still blocked many external pores and a large part of CNTs' surfaces. Thus the surface of the as-prepared electrode was flat and the spaces between CNTs were unopened, as shown in Figures 4(a) and 4(b).

According to the different oxidation rates existing between CNTs and other carbonaceous parts [18], electrochemical oxidization of the CNT electrodes by electrolyzing them in acid solution is considered to remove the redundant amorphous carbon and to expand the pore size. Hydro-molecules released electrons at the anode and generated free oxygen atoms during the electrolysis process. Free oxygen atoms could oxidize carbon atoms and the following reaction occurred in the anode [19]:

$$\mathrm{C(solid)} + \mathrm{H_2O} \rightarrow \mathrm{C(solid)O(adsorption)} + 2\mathrm{H^+} + 2\mathrm{e} \quad (4)$$

$$2\mathrm{C(solid)O(adsorption)} \rightarrow \mathrm{CO_2} + \mathrm{C(solid)} \quad (5)$$

where C, O, H^+, H_2O and CO_2 respectively denote carbon atom, oxygen atom, hydrogen ion, water molecule and carbon dioxide molecule. The reactivity of amorphous carbon is higher than that of CNTs [18]. Free oxygen atoms oxidized the amorphous carbon which was generated through the decomposition of organic binder, resulting in its fading and being stripped off from the external pores and the CNT networks. Thus the surface of the electrolyzed (in HNO_3 solution) electrode was rougher and had more furrows compared to the as-prepared electrode, while CNTs in the electrolyzed (in HNO_3 solution) electrode were protruding and the spaces in the network of CNTs were free of obstruction.

The variation of the structure of polarizable electrode oxidized by electrolysis led to the variation of surface area and pore size distributions. Table 1 indicates that the specific surface area of the electrode decreased a little after electrochemical oxidation. The reason was that many small pores vanished with the redundant amorphous carbon removed. The decrease of small pores may lead to the decrease of total specific area for reason that they represent part of the total pore volume [16, 20]. However, due to many pores in electrode being expanded and a large part of the spaces between CNTs being opened, the relative volume ratio of mesopores was obviously increased and that of micropores was obviously decreased after electrochemical oxidation. The measured relative volume ratio of micropores of the as-prepared electrode and the electrolyzed (in HNO_3 solution) electrode was about 20.86% and 6.5% respectively, as listed in Table 1.

3.2 Surface characteristics of CNTs in the electrode after electrolytic oxidation in acid solution

Inspection of infrared transmission spectra of the CNT electrodes is shown in Figure 5. For the as-prepared CNT electrode, there were three bands: one at about 1630 cm^{-1}, associated with >C=O functional groups in quinones or ketones [21], one at about 1380 cm^{-1}, associated with C–H in methyls [22], a broad band centered around 3400 cm^{-1}, associated with hydroxy groups. For the electrolyzed (in HNO_3 solution) electrode, there were two new bands of interest: the band at 1715 cm^{-1}, associated with >C=O in carboxyls or carboxylic anhydrides, a broad band centered around 1221 cm^{-1} associated with C–O stretching in ethers, phenols, carboxyls and carboxylic anhydrides [21].

For the as-prepared electrode, quinones or ketones might be introduced when CNTs were treated by nitric acid before they were used in fabricating electrodes [23], and the methyls might be a residual product during the carbonization of the PF binder. The decomposition temperatures of quinones and ketones are above 900°C [21], thus these two radicals can be retained after carbonization of electrodes under 850°C. The hydroxyl groups should also be introduced when CNTs were treated by nitric acid before use [23], but they should be decomposed during carbonization process for reason that their decomposition temperature was from 600°C to 700°C [21]. Thus the signature of hydroxyl groups might be caused by moisture absorption.

For the electrolyzed (in HNO_3 solution) electrode, some functional groups could be added [19, 23]: free oxygen atoms generated during the electrolysis process could combine with water molecules to generate free radicals of –OH that could connect pi bonds and dangling bonds of carbon atoms on the outer walls of CNTs to generate phenols; free oxygen atoms could also connect two adjacent carbon atoms with hook-bonds to generate ethers; there were carbon atoms with two or three free bonds in the defects of the CNT walls, those with two free bonds could connect the free oxygen atoms to form carbonyls (>C=O) and those with three free bonds connected the oxygen atoms and the free radicals of –OH to form carboxyls (–COOH). Carbonyls (>C=O) could also connect H^+, OH^- and free oxygen atoms to form carboxyls（–COOH）or –C–OH. Dehydration reaction might occur between the adjacent carboxyls to generate carboxylic anhydrides.

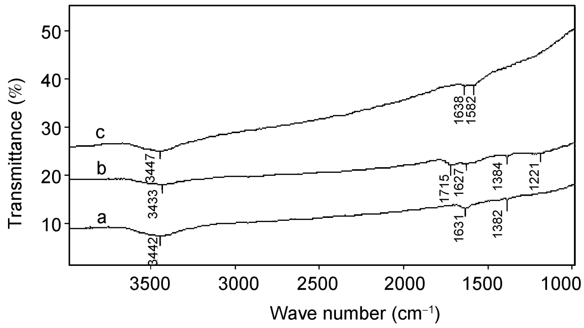

Figure 5 Infrared spectra of the electrodes. a, The as-prepared electrode; b, electrolyzed electrode in HNO_3 solution; c, electrolyzed electrode in NaOH solution. The extent of electrochemical oxidation was 6080 C g^{-1}.

Table 1 Performances of the CNT polarizable electrodes

	Specific area (m^2 g^{-1})	Relative volume ratio of micropores (<2nm) (%)	Specific capacitance of polarizable electrode (F g^{-1})
Electrode (a)	147.59	20.86	22.4
Electrode (b)	143.66	6.52	78.2
Electrode (c)	146.34	17.89	24

Electrode (a): As-prepared CNT electrode; electrode (b): electrolysis oxidized with the extent of electrochemical oxidation being 6080 C g^{-1} in HNO_3 solution; electrode (c): electrolysis oxidized with the extent of electrochemical oxidation being 6080 C g^{-1} in NaOH electrolyte.

3.3 Specific capacitance of polarizable electrode treated by electrolysis in acid solution

It is indicated in Table 1 that the specific capacitance of the electrolyzed (in HNO_3 solution) electrode was higher than that of the as-prepared electrode for the above two times.

The superior specific capacitance of the electrolyzed (in HNO_3 solution) electrode with respect to that of the as-prepared electrode was first of all due to the improvement of the structure and the pore size distribution:

The above discussed structure differences between the two electrodes, as shown in Figure 4 and Table 1, indicate that the surfaces of CNTs in the electrolyzed (in HNO_3 solution) electrode could be more effectively utilized compared to those in the as-prepared electrode, and a larger area of electric double layer could be formed in the electrolyzed (in HNO_3 solution) electrode.

As listed in Table 1, the specific surface area of the electrolyzed (in HNO_3 solution) electrode decreased very little compared to that of the as-prepared electrode, but the relative volume ratio of micropores decreased from 20.86% to 6.52%. It is known from ref. [24] that micropores should take a greater portion of the specific surface area of the electrode than mesopores or macropores do if their relative volume ratios are equal. For the electrodes with basically equal surface area, the obvious decrease of the relative volume ratio of micropores should result in a greater increase of the area that is available for building up double layer, thus effectively elevating the specific capacitance.

Secondly, the functional groups should import an additive enhancement of the specific capacitance of the polarizable electrode. As some authors have reported [6, 12], higher capacitance can be achieved through the attachment of a variety of surface function groups using thermal, chemical or electrochemical treatments. The functional groups on the CNT surfaces can be attractable for the dissolved electrolyte ions [21, 25, 26]. The process is due to physical adsorption, by electrostatic forces between the carbon surface and the electrolyte ions. Therefore, the numbers of electrolyte ions involved in building the double layer match the charge density increased. In addition, the increase in oxygen functional groups content might improve the wettability of the CNT surfaces in the electrolyte, resulting in a corresponding increase of the real area of the built-up double layer [25]. Therefore, the capacitance per available area of the electrolyzed electrode (in HNO_3 solution) should also be higher than that of the as-prepared electrode.

A series of experiments of electrolytic oxidizing CNT electrodes in HNO_3 of 1 mol L^{-1} with different extents of electrochemical oxidation were made, the results of specific capacitances of the polarizable electrodes and ESRs of the capacitor units are shown in Figure 6.

Figure 6 indicates that the specific capacitance increased as the extent of electrochemical oxidation increased, attaining 78.2 F g^{-1}, which was about 2.5 times higher than the specific capacitance of the untreated polarizable electrode, at the extent of electrochemical oxidation of 6080 C g^{-1}.

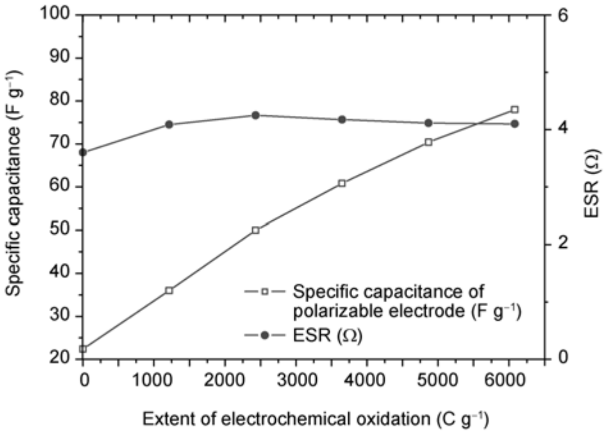

Figure 6 Specific capacitances of the polarizable electrodes and the equivalent series resistances (ESRs) of capacitor units at different extents of electrochemical oxidation. Electrodes were electrolyzed in HNO_3 solution.

The amorphous carbon generated by the carbonization of organic binder should not be excessively consumed for reason that they were responsible for maintaining the strength and shape of electrodes. Experiment indicated that no matter how much the current intensity was used during the electrolysis oxidizing process, when the extent of electrochemical oxidation was above 6250 C g^{-1}, the strength of the electrodes began to seriously weaken, resulting in the electrodes being broken. This indicates that the consuming extent of the amorphous carbon in the electrodes depended on the extent of electrochemical oxidation.

Figure 6 shows that the ESR of capacitor units increased a little after electrolytic oxidation. It was very likely that the presence of surface functional groups retarded the motion of electrolytes and thus increased the resistance of electrolytes along the axial direction of pores. In addition, surface functional groups were strong polar sites that would adsorb electrolyte ions and thus hindered their migration in pores [25], resulting in the increase of the resistance of the electrolyte-filled electrodes. The ESR attained a maximum value of 4.25 Ω at 2432 C g^{-1}, then slightly decreased. It might be due to the expanding of pores in the electrodes caused by the continued electrolytic oxidation, the expanded pores were beneficial for the transmission of the dissolved electrolyte ions [27, 28].

The ESR of a capacitor unit is determined by the resistance of the electrolyte-filled polarizable electrode and separator, the bulk resistance of electrolyte and the contact resistance between polarizable electrode and current collector [27]. The electrolyte-filled electrodes only share a small part of the total resistance of capacitor unit. Therefore, the ESR of capacitor unit increased only a little (under 20%).

3.4 Performances of the polarizable electrode treated by electrolysis in basic solution

Experiment indicated that when the CNT electrodes were electrolyzed in the NaOH solution, the surface of the electrode was stripped off layer by layer during the electrolysis process, the residues stripped from the electrode were deposited in the bottom of the electrolytic cell and the electrode was gradually worn. The observation by SEM showed that after electrolysis in the NaOH solution, the electrode surface was still flat and the spaces between CNTs were unopened, as shown in Figures 4(e) and 4(f).

If carbon materials are electrolyzed in basic solution, the OH^{-1} ions are adsorbed by the activated carbon atoms in the surface of the carbon material. The adjacent carbon atoms adsorbing the hydroxyl ions can interact to generate oxygens, resulting in the number of the activated carbon atoms being increased. The reaction process is as follows [19]:

$$\mathrm{C(solid)} + \mathrm{OH}^- \rightarrow \mathrm{C(solid)OH(adsorption)} + \mathrm{e} \quad (6)$$

$$\mathrm{4C(solid)OH(adsorption)} \rightarrow \mathrm{4C(solid)} + 2\mathrm{H_2O} + \mathrm{O_2}\uparrow \quad (7)$$

When the CNT electrodes were electrolyzed in the NaOH solution, the hydroxyl ions were integrated with the amorphous carbon atoms, which were generated by the decomposition of organic binder during the carbonization process, to form the state of “C(solid)OH(adsorption)”. The amorphous carbon atoms became unstable after the “C(solid) OH(adsorption)” decomposed to release H_2O and O_2. This reaction process was widespread in the CNT electrode during the electrolysis process in the NaOH solution, led to the amorphous carbon, which are generated by the decomposition of organic binder and responsible for consolidating CNTs and maintaining the strength and shape of the CNT electrode, being gradually stripped off. Thus CNTs were stripped off layer by layer and the electrode was worn. The stripping proceeded gradually from the surface to the interior of the electrode, the ratio between the stripped CNTs and the stripped amorphous carbon was the same as the ratio between CNTs and the amorphous carbon in the electrode. Therefore the surface structure and pore size distribution of the CNT electrode electrolyzed in the NaOH solution are similar to those of the as-prepared CNT electrode, as shown in Figure 4 and Table 1.

Figure 5, the infrared transmission spectra of the CNT electrodes, shows that compared to the as-prepared CNT electrode, a new peak around 1580 cm^{-1}, which is associated with carboxyl in carbonates [21], appeared. The carbonates should be generated during the process of electrolyzing the CNT electrode in the NaOH solution and were absorbed by the electrode. Moreover, the peak around about 1380 cm^{-1}, associated with C–H in methyls, was obscured. The reason might lie in that much amorphous carbon, which contained residual methyls, generated by the carbonization of PF was stripped off, resulting in the C–H being difficultly measured.

For reason that the surface structure, pore size distribution and surface characteristics of the CNT electrodes were not effectively improved after being electrolyzed in the NaOH solution, their performances were thus not greatly enhanced. Figure 7 shows that the specific capacitance of the CNT electrodes was not obviously elevated after being electrolyzed in the NaOH solution (below 40%). The variation of the specific capacitance had no regular relation with the extent of electrochemical oxidation. Moreover, even the CNT electrodes were electrolyzed in the heated NaOH solution (70°C), their specific capacitances have no obvious differences with those electrolyzed in the NaOH solution with room temperature. The specific capacitance of the CNT electrode which was electrolyzed with the extent of electrochemical oxidation of 6080 C g^{-1} was about 24 F g^{-1}, as listed in Table 1.

4 Conclusions

At present, the authors have achieved producing CNTs in batches by a process of catalytic pyrolysis of organic gas at low cost. Therefore, it is practical to fabricate EDLCs from the CNT electrodes.

By the method of electrolytic oxidation in acid solution, the structure, pore size distribution and surface characteristics of the CNT electrode were greatly improved. The specific capacitances of the CNT polarizable electrodes were enhanced by nearly 2.5 times, attained 78.2 F g^{-1} with organic electrolyte. In the other researchers reports, acid oxidation of the CNT polarizable electrode and electrochemical oxidation of carbon fiber polarizable electrode only enhanced the specific capacitances by less than one time [6, 12].

However, acidic electrolyte and basic electrolyte used in electrochemical oxidation process have different effects on modifying the performances of the CNT polarizable electrodes. When basic electrolyte was used in electrochemical

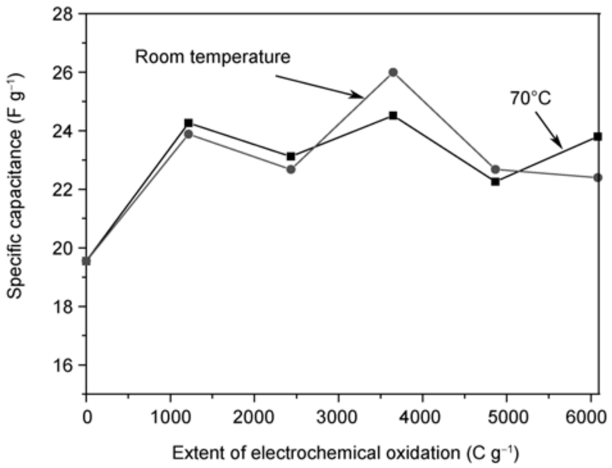

Figure 7 Specific capacitances of the polarizable electrodes at different extents of electrochemical oxidation. Electrodes were electrolyzed in the NaOH solution. The room temperature was 25°C.

oxidation process, the structure, pore size distribution and surface characteristics of the CNT electrode were less improved, the performances of the CNT polarizable electrodes were also less enhanced.

The results in this work indicate that electrochemical oxidation is a promising method to enhance the performances of the CNT polarizable electrodes and fabricate ultrahigh capacitors based on CNTs.

This work was supported by the Major State Basic Research Development Program of China (Grant No. 10332020).

1 Christen T, Carlen M W. Theory of Ragone plots. J Power Sources, 2000, 91(2): 210–216

2 Conway B E. Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications. New York: Kluwer Academic Publisher, 1999

3 Inagaki M, Konno H, Tanaike O, et al. Carbon materials for electrochemical capacitors. J Power Sources, 2010, 195(SI24): 7880–7903

4 Nakamura M, Nakanishi M, Yamamoto K. Influence of physical properties of activated carbons on characteristics of electric double-layer capacitors. J Power Sources, 1996, 60(2): 225–231

5 Issi J, Langer L, Heremans J, et al. Electronic-properties of carbon nanotubes-experimental results. Carbon, 1995, 33(7): 941–948

6 Ma R Z, Liang J, Wei B Q, et al. Study of electrochemical capacitors utilizing carbon nanotube electrodes. J Power Sources, 1999, 84(1): 126–129

7 Zhang B, Liang J, Xu C L, et al. Electric double-layer capacitors using carbon nanotube electrodes and organic electrolyte. Mater Lett, 2001, 51(6): 539–542

8 Obreja V V N. On the performance of supercapacitors with electrodes based on carbon nanotubes and carbon activated material - A review. Physica E, 2008, 40(7): 2596–2605

9 Saito R, Fujita M, Dresselhaus G, et al. Electronic-structure of chiral graphene tubules. Appl Phys Lett, 1992, 60(18): 2204–2206

10 Dresselhaus M S, Dresselhaus G, Eklund P C. Science of Fullerenes and Carbon Nanotubes. New York: Academic Press, 1996

11 Richner R, Muller S, Wokaun A. Grafted and crosslinked carbon black as an electrode material for double layer capacitors. Carbon, 2002, 40(3): 307–314

12 Mommas T, Liu X, Osaka T, et al. Electrochemical modification of active carbon fiber electrode and its application to double-layer capacitor. J Power Sources, 1996, 60(2): 249–253

13 Sheveleva I V, Zemskova L A, Zheleznov S V, et al. Effect of modification on electrochemical and sorption properties of woven carbon materials. Russ J Appl Chem, 2007, 80(6): 924–929

14 Yue Z R, Jiang W, Wang L, et al. Surface characterization of electrochemically oxidized carbon fibers. Carbon, 1999, 37(11): 1785–1796

15 Sun Y, Webley P A. Preparation of activated carbons from corncob with large specific surface area by a variety of chemical activators and their application in gas storage. Chem Eng J, 2010, 162(3): 883–892

16 Qu D Y, Shi H. Studies of activated carbons used in double-layer capacitors. J Power Sources, 1998, 74(1): 99–107

17 Antony R, Pillai C K S. Synthesis and thermal characterization of chemically-modified phenolic resins. J Appl Polym Sci, 1994, 54(4): 429–438

18 Park Y S, Choi Y C, Kim K S, et al. High yield purification of multiwalled carbon nanotubes by selective oxidation during thermal annealing. Carbon, 2001, 39(5): 655–661

19 He F, Wang M Z. Carbon Fibers and Their Composite Materials (in Chinese). Beijing: Science Press, 1995

20 Hasegawa G, Aoki M, Kanamori K, et al. Monolithic electrode for electric double-layer capacitors based on macro/meso/microporous S-containing activated carbon with high surface area. J Mater Chem, 2011, 21(7): 2060–2063

21 Figueiredo J L, Pereira M F R, Freitas M M A. Modification of the surface chemistry of activated carbons. Carbon, 1999, 37(9): 1379–1389

22 Zoltan D, Bela P, Jozsef N J. Possible coupling reactions of functional silanes and polypropylene. Polymer, 1999, 40(7): 1763–1773

23 Jia Z J, Wang Z Y, Liang J, et al. Production of short multi-walled carbon nanotubes. Carbon, 1999, 37(6): 903–906

24 Peigney A, Laurent C, Flahaut E, et al. Specific surface area of carbon nanotubes and bundles of carbon nanotubes. Carbon, 2001, 39(4): 507–514.

25 Hsieh C T, Teng H H. Influence of oxygen treatment on electric double-layer capacitance of activated carbon fabrics. Carbon, 2002, 40(5): 667–674

26 Lin C C, Yen C C. RF oxygen plasma treatment of activated carbon electrodes for electrochemical capacitors. J Appl Electrochem, 2007, 37(7): 813–817

27 Song H K, Jung Y H, Lee K H, et al. Electrochemical impedance spectroscopy of porous electrodes: the effect of pore size distribution. Electrochim Acta, 1999; 44(20): 3513–3519

28 Segalini J, Daffos B, Taberna P L, et al. Qualitative Electrochemical Impedance Spectroscopy study of ion transport into sub-nanometer carbon pores in Electrochemical Double Layer Capacitor electrodes. Electrochim Acta, 2010, 55(SI 25): 7489–7494