

Carbon-based nanocomposite EDLC supercapacitors

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ABSTRACT

EDLC cells based on activated carbon as host material electrodes were fabricated and tested. The MWCNT additive was added into the host material to form a nanocomposite and the effect of the MWCNTs concentration on improving the performance of the EDLC cells was explored. 1M TEABF₄-PC solution was used as organic electrolyte. The nanocomposites functioned differently in improving the specific power and energy density of EDLC cells., where impedance spectroscopy, cyclic voltammetry and galvanostatic charge-discharge measurements were performed to characterize the EDLC cells.

Keywords: Supercapacitors, EDLC, carbon, multical carbon nanotubes

1 INTRODUCTION

A supercapacitor known as electrochemical double layer capacitor (EDLC) is an electric device with power and energy densities between those of a traditional capacitor and battery [1]. As the demand for energy storage devices with a high power and a long durability increases, the supercapacitor becomes more and more important. The EDLC supercapacitor differs from a traditional capacitor in that its electrodes are composed of a porous conductor such as activated carbon, which has a huge surface area, and it accumulates and keeps the charges on the thin layer of electrode/electrolyte interface via electrostatic force or non-faradic effect, so that it possesses a huge capacitance (> 100F/g), and has higher power and much longer recycle lifetime (>100000 cycles) than rechargeable batteries [2]. However, up to now the energy density of EDLC supercapacitors was not so high [1,2].

Carbonaceous materials such as carbon aerogel [3,4], powder [5,6] and carbon fiber are the most commonly used materials as electrodes in EDLC devices, as carbon can have high surface area, is chemically and thermally stable, of relatively low cost and environmentally friendly. A method to increase EDLC performance includes creating novel carbon nanocomposite electrodes [7], which increasing the conductivity and surface area of the electrodes.

In this report, a series of carbon based symmetric electrodes for EDLCs were explored, using a commercial, activated carbon powder as the basic active material and

carbon nanotubes as a conductive filler. The performances of organic electrolyte based on LiPF₆ or Et₄NBF₄ in mixed solvents were also explored, which have an electrochemical window of more than 3V [8,9]. A VersaSTAT MC analyser was used to carry out impedance spectroscopy, cyclic voltammetry and galvanostatic charge-discharge tests on the devices.

2 EXPERIMENTAL DETAILS

2.1 Carbon electrodes

Activated carbon powder (AC) with a surface area of 1000m²/g was used as the host electrode material. Multiwall carbon nanotube powder (MWCNT) was added without modification, in a series of investigations at a weight percentage of 0.15 wt%, 1 wt% and 7 wt%, respectively. PVDF (Poly(vinylidene fluoride)) was added as a binder at 5 wt.% of total solid component. The carbonaceous film had an areal density of 4~5 mg/cm².

2.2 Fabrication of capacitors

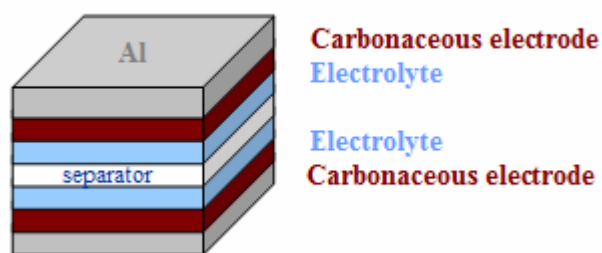


Figure 1. Diagram of an EDLC supercapacitor cell

Figure 1 presents a diagram of the type of supercapacitor cells fabricated in this study. The electrolyte was 1M Et₄NBF₄ (Tetraethylammonium tetrafluoroborate or TEABF₄) in PC (propylene carbonate). Both the salt and solvent were from Sigma-Aldrich, Et₄NBF₄ was 99% pure, PC was anhydrous, 99.7% pure.

To assemble a capacitor cell, two rectangle strips of the carbonaceous material coated Al were cut out and combined with the carbon side face to face, a separator was soaked with electrolyte solution and was sandwiched in between. Thus a symmetric electrode EDLC cell was

formed, with the electrodes overlap area defined as the working area, which was fixed to 2cm^2 in all the devices.

2.3 Electrochemical characterization of capacitors

The performance of different EDLC cells was determined by impedance spectroscopy, cyclic voltammetry and galvanostatic charge-discharge tests, using a VersaSTAT MC analyser. During the electrochemical tests, the EDLC cells were put under a pressure of 0.5Kg/cm^2 to ensure a good electrical contact of carbon-Al, and a fixed gap between the two electrodes. The devices were characterized in a 2-terminal configuration like in most commercially packaged electrical capacitor devices. No reference electrode was used in the tests.

3 RESULTS AND DISCUSSION

3.1 Impedance spectroscopy analysis

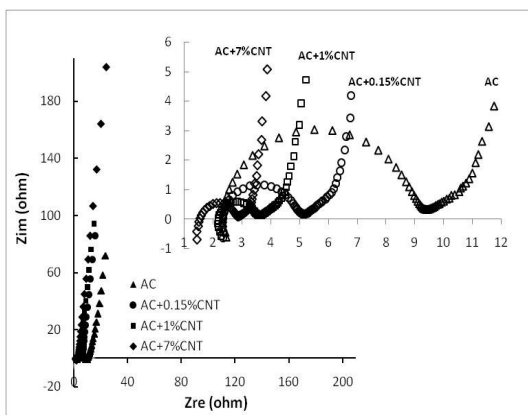


Figure 2. (a) Nyquist plots for the EDLC cells with AC, AC+0.15%CNT, AC+1%CNT and AC+7%CNT electrodes at a dc bias of 0.2 V, sinusoidal signal of 20 mV over the frequency range from 1000 kHz to 0.01 Hz. Z_{re} : real impedance. Z_{im} : imaginary impedance. Inset shows an enlarged scale graph in the high frequency region.

The Electrochemical Impedance Spectroscopy (EIS) measurements were carried out at a DC bias of 0.2 V with sinusoidal signal of 20 mV over the frequency range from 1MHz to 10mHz. Figure 2 shows the corresponding Nyquist plot for four devices with AC, AC+0.15%CNT, AC+1%CNT and AC+7%CNT carbonaceous electrodes. In the region of high frequency to medium frequencies, only small amounts of charge complexes can overcome the activation energy to migrate with the alternating potential. The Z_{im} - Z_{re} semicircle is developed by the moving charge-complexes close to the Helmholtz plane and is represented by an interfacial contact capacitance (C_c) and charge

transfer resistance (R_c) [10]. The semicircle has 2 intersection points on the real axis, the Z_{re} value at the left end of the semicircle represents the equivalent series resistance (ESR) of the capacitor, which is the combination of the carbon-Al contact resistance, the bulk solution resistance of the electrolyte and the resistance of the electrode material itself; ESR values are similar for all electrodes except for the AC+7%CNT electrode which has a very low ESR. The diameter of the semi-circle represents the charge transfer resistance R_c : they are 7.1Ω , 2.8Ω , 1.4Ω and 1.2Ω for the AC, AC+0.15%CNT, AC+1%CNT and AC+7%CNT electrodes, respectively. This indicates that the conductive MWCNT can reduce the charge transfer resistance. On the right side of the semicircle, a $\sim 45^\circ$ Warbury region was observed, which is the result of the ion diffusion into the bulk of the electrodes, all of which have a pore size distribution [11]. At lower frequency range, the curve is almost vertical, indicating the capacitive nature of the device.

3.2 Cyclic voltammetry analysis

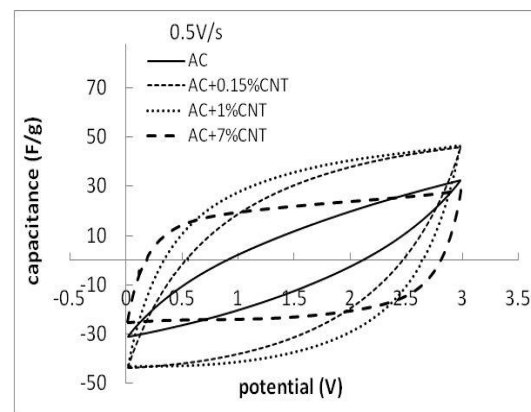
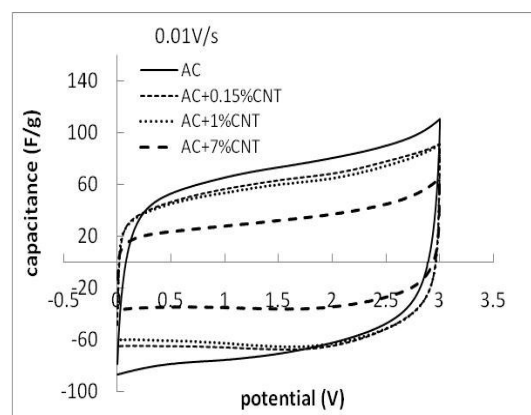


Figure 3. Cyclic voltammograms of EDLC cells with AC, AC+0.15%CNT, AC+1%CNT and AC+7%CNT electrodes using 1M TEABF₄-PC electrolyte at two extreme scan rates: (a) 0.01V/s, (b) 0.5V/s

The cyclic voltammetry (CV) response of the three devices was conducted between 0 and 3V at a range of scan rate from 0.01V/s to 0.5V/s, and the results are presented in Figure 3. For each cell, there are two typical CV curves at two extreme scan rates, from which a normalized specific capacitance, C , can be derived according to the following equation:

$$C = \frac{i}{m\nu}$$

where i is the current, ν is the scan rate, m is the mass of one electrode (the current collectors not included). The curves are regular and symmetric to the 0 horizontal axis, with a Faradaic fraction [12] of ~0.05 in the 0-3 V scanned region, indicating a non-redox or non-faradic property of the cell.

At the low scan rate, the capacitances of all AC+CNT electrodes are lower than the AC only electrode, the higher the CNT percentage the lower the capacitance is. This can be justified by the fact that at the low charge/discharge rate, all surface area of AC is used in which case the high energy storage capacity of the AC carbonaceous material is confirmed. On the other hand, at the high scan rate, the capacitance of AC+CNT is higher than the AC electrode, and the CV shape is more like rectangle, indicating the fast charge-discharge process in the AC+CNT electrodes. In the fast charge-discharge case, only the AC+CNT electrodes are effective, where the presence of CNTs brings this charge efficiency. It can be concluded that the MWCNT have formed a continuous electrically conductive network, which might short the electric circuit in the gaps and some pores so that charges cannot diffuse into deep gaps and pores, as MWCNTs are more conductive and the unmodified CNT is lower in surface area than AC. As a result, the total capacitance is reduced.

3.3 Galvanostatic charge-discharge analysis

In order to examine the device rate performance and the power and energy density relationship, galvanostatic charge-discharge cycling between 0 and 3V at various current densities was carried out and it is shown in Figure 4. Two typical plots of constant current charge-discharge are presented at two extreme current densities. At low the current density of 2 mA, the performance of the four electrodes is in the order of AC>AC+0.15%CNT>AC+1%CNT>AC+7%CNT, which is consistent with their CV behaviour at low scan rate. At the high current density of 50 mA, the performance of the CNT containing AC electrodes is better than that of the AC alone. The IR drop at the turning point of charge-discharge indicates the energy loss due to the internal DC resistance; the data show that the IR drop changes with CNT content

according to the following sequence: AC<AC+0.15%CNT<AC+1%CNT<AC+7%CNT.

Two key factors of a supercapacitor, namely its gravimetric power and energy density, are evaluated from the discharge curves of the galvanostatic cycles at different current densities according to [13]:

$$E = I \int \frac{Vdt}{2m}, \quad P = \frac{E}{\Delta t_d}$$

where I is the current density, m is the mass of one electrode (the current collectors not included), Δt_d is the time elapsed during discharge. From this, it can be concluded that the addition of 0.15% and 1% conductive CNT can improve the capacitor performance especially in the high power region, but at 7%CNT content the energy density was greatly reduced.

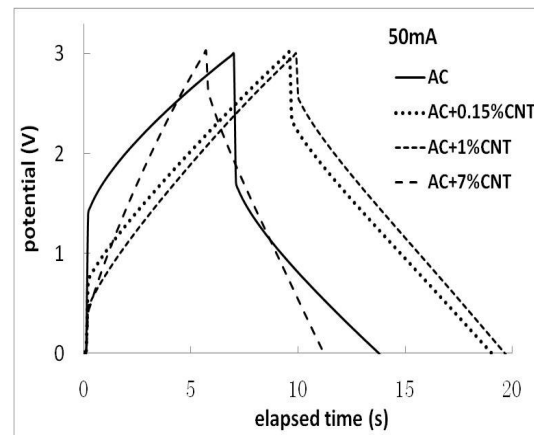
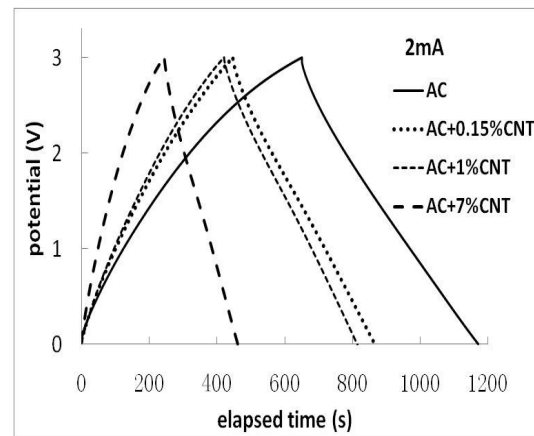


Figure 4. Galvanostatic charge-discharge curve of EDLC cells with AC, AC+0.15%CNT, AC+1%CNT and AC+7%CNT electrodes using 1M TEABF₄-PC electrolyte at two extreme constant current densities: (a) 2 mA, (b) 50mA.

4 CONCLUSIONS

Electrochemical analysis of the EDLC cells shows that activated carbon is suitable material for supercapacitor electrodes, whereas a small amount of conductive MWCNT can improve its performance through the reduction of charge transfer resistance in the electrode/electrolyte interface. At higher CNT content, the specific energy density is reduced, as the unmodified CNT is lower in surface area than AC. The MWCNTs might form a highly conducting network in the bulk carbon electrode and thus prevent charges from diffusing into the deep bulk of carbon electrode.

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