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Activated carbon–carbon nanotube nanocomposite coatings for supercapacitor applications

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ABSTRACT

Electrochemical double layer capacitor cells were fabricated based on electrodes with activated carbon (AC) coating as the host material, targeting large energy storage. Highly dispersed multiwall carbon nanotubes (MWNTs) were added to form nanocomposite coatings, used as electrodes targeting high-power performance for very low content of MWNTs. 1 M tetraethylammonium tetrafluoroborate–propylene carbonate solution was used as organic electrolyte. The resulting cells were characterized using impedance spectroscopy, cyclic voltammetry, and galvanostatic charge–discharge tests. It was concluded that at optimum composition of AC–MWNT coatings both power and energy densities are raised whereas further increase of the MWNT content would increase the power density but decrease the energy density.

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1. Introduction

As the demand for energy storage devices with higher power and longer durability than batteries increases, the supercapacitor becomes more and more important. An electrochemical double layer capacitor (EDLC) supercapacitor differs from a traditional capacitor in that it contains double the number of charged layers, by including a separator membrane, and its electrodes are composed of a porous conductor such as activated carbon (AC), which has a huge surface area and it accumulates the opposite charges on the thin layer of electrode/electrolyte interface via electrostatic forces or the non-faradic effect, so that it possesses a large capacitance, and has higher power and much longer charge–discharge (CD) lifetime (>100,000 cycles) than rechargeable batteries [1] since there is no faradic reaction involved in the charge storage process; however, up to now its energy density has been less than ideal [1,2]. Attempts to increase the energy density of supercapacitors by increasing the pore area of various activated carbonaceous electrodes have resulted in the reduction of power density, due to an increase of the electrode material resistance. Much of today's EDLC research is concerned with increasing their energy density with the minimum sacrifice in power capability [3].

Carbonaceous materials such as aerogels [4,5], AC powders [6,7] and carbon fibre mats are the most commonly used materials as electrodes in EDLC devices, as AC can have high surface area, is chemically and thermally stable, of relatively low cost and environmentally friendly. Carbon can be activated [5,8] to form extremely large surface area. On the other hand, the electrical conductivity of AC is low, usually 0.1–1.0 S cm^{-1}, due to its high area porosity [9,10]. Large resistance inevitably results in an increase in power loss and energy dissipation.

As a result, recent research has targeted conductive fillers [11–14] to increase the power of supercapacitors. Multiwall carbon nanotubes (MWNTs) can be used to increase electrical conductivity as they are metallic. Bordjiba et al. [11] mixed polyacrylonitrile powder and MWNTs, and subjected the mixture to carbonization; the so produced aerogels were used as electrodes in supercapacitors with KOH electrolyte, from which the aerogel with 3% MWNTs yielded a maximum capacitance of 210 F/g in cyclic voltammetry (CV) at 5 mV/s or in CD at 0.7 mA/cm^2. Similarly, Noked et al. [12] achieved similar results with KOH electrolyte for cells based on AC–MWNT monolithic electrodes produced from the carbonization and activation of polyvinylidene–MWNT solutions. Aqueous electrolytes may result in high specific capacitance due to the small size of ions and their ability to migrate through the smallest pores of the carbonaceous electrode and effective use of a very large proportion of the electrode surface area; however, they have a limited maximum voltage window, only from −0.2 V to −1 V (with reference electrode Ag/AgCl) in the cited study [11], which limits considerably both energy and power density, as they are both proportional to V^2.

The focus of the present study has been to raise the energy density–power density curve. Novel EDLCs have been fabricated comprising nanocomposite electrodes including AC and MWNTs at different concentrations to explore the effect of the electrode composition on both energy and power densities. The electrode materials were selected on the hypothesis that the large surface area AC would provide the high-energy density and the well-dispersed MWNTs would provide a highly conductive network for high-power density. An important novel feature is the use of a high strength organic electrolyte to achieve a wider voltage window: the tetraethylammonium tetrafluoroborate ($TEABF_4$)–propylene carbonate (PC) electrolyte has a large electrochemical window of more

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than 3 V [15–17]. The fabricated cells were tested in impedance spectroscopy, CV and galvanostatic CD tests. The resulting cells demonstrated excellent supercapacitor performance, including high-energy and high-power densities, where the added MWNTs had significant effects on both power and energy performance.

2. Experimental part: materials and procedures

2.1. Carbon electrodes

The AC powder was from Sigma-Aldrich. According to the product specification, this AC product was an acid-washed (hydrochloric acid), granular carbon with a surface area of 1000 m^2/g and a particle size distribution as follows: greater than 74 micron: 10–15%; greater than 10 microns: 70–75%. It was used as the electrode host material. MWNT powder was added without modification, with a series weight percentage of 0.15 wt%, 1 wt% and 7 wt% CNTs (carbon nanotubes). Poly(vinylidene fluoride) was added as a binder at 5 wt.% of total solid component. The CNTs used in this study were Elicarb® MWNTs from Thomas Swan Ltd. They had an average length of tens of microns, 10–30 nm outer diameter and >92% purity, as provided by the manufacturer. These MWNTs have also been found to have high electrophoretic mobility and zeta potential [18]. The MWNTs were dispersed in l-methyl-2-pyrrolidinone by first sonicating for half hour and then vigorously stirring for 1 h using a Wiggenhauser homogenizer. The MWNT solution was then added into the AC. The ingredients were mixed to form a slurry, which was coated onto aluminium foil using a film applicator. The coating was then dried in an oven at 120 °C for 4 h. The dried carbonaceous electrode had a thickness of about 150 μm and a loading of 4–5 mg/cm^2.

2.2. Fabrication of capacitor cells

Fig. 1 presents a diagram of the type of supercapacitor cells fabricated in this study. The electrolyte was 1 M Et_4NBF_4 ($TEABF_4$) in PC. Both the salt and solvent were from Sigma-Aldrich, Et_4NBF_4 was 99% pure, PC was anhydrous, 99.7% pure. To assemble a capacitor cell, two rectangular strips of the carbonaceous material coated Al were cut out and combined, with the carbon side face to face, and 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 2 cm^2 in all the devices.

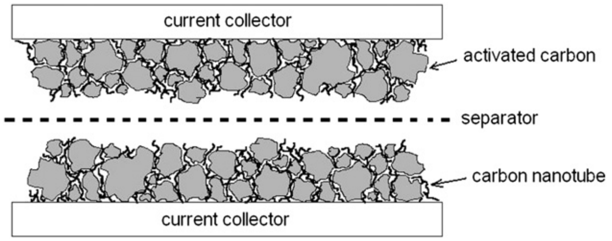

Fig. 1. Diagram of an EDLC supercapacitor cell.

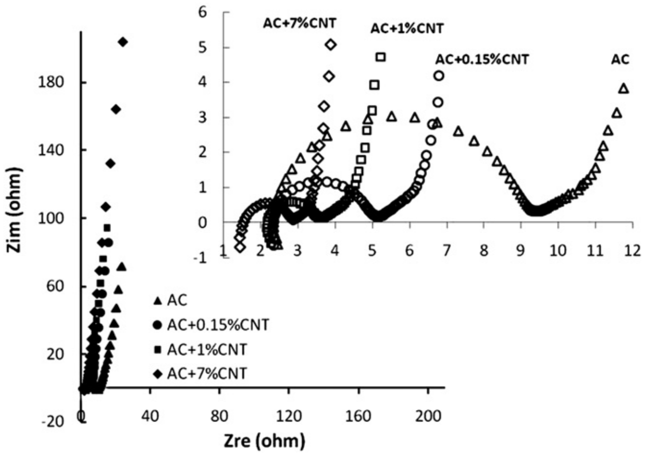

Fig. 2. Nyquist plots for the EDLC cells with AC, AC + 0.15%CNT, AC + 1%CNT and AC + 7%CNT electrodes at a dc bias of 0.2 V, sinusoidal signal of 20 mV over the frequency range from 1 MHz to 0.01 Hz. Z_{re}: real impedance. Z_{im}: imaginary impedance. Inset shows an enlarged scale graph.

2.3. Electrochemical characterization of the capacitor cells

The performance of the different EDLC cells was determined by impedance spectroscopy, CV and galvanostatic CD tests, using a VersaSTAT MC analyser. During the electrochemical tests, the EDLC cells were put under a pressure of 0.5 kg/cm^2 to ensure good electrical contact of carbon–Al, and a fixed gap between the two electrodes. The devices were characterized in a 2-terminal configuration as in most commercially packaged electrical capacitor devices. No reference electrode was used in the tests. The cell and electrode capacitances, C_c and C_e respectively, were determined in CV and CD tests as follows:

$$CV, CD : C_c = \frac{1}{2m}\frac{I}{{}^{dV}/_{dt}} \tag{1}$$

$$Average\, C_{c\ \ in\ \ CV} = \frac{1}{2m}\frac{\int IdV}{\Delta V dV/dt} \tag{2}$$

$$C_e = 4C_c \tag{3}$$

where m is the mass of carbonaceous electrode, I is the current, V is the potential difference, and t is time.

3. Results and discussion

The electrochemical impedance spectroscopy (EIS) measurements were carried out over the frequency range from 1 MHz to 10 mHz. Fig. 2 shows the corresponding Nyquist plot for four devices with AC, AC + 0.15%CNT, AC + 1%CNT and AC + 7%CNT electrodes. Fig. 3 presents the equivalent electric circuit model used to interpret the EIS data [19], consisting of an inductor, *L1*, an equivalent in-series-resistance, *ESR*, a resistance in parallel, *Rc*, and three constant-phase elements, *CPE1*, *CPE2* and *CPE3*, the impedance of which is given by the equation:

$$Z = \frac{1}{Q(2\pi fj)^n} \tag{4}$$

where Z is the impedance and f is the frequency of AC. If the power index is n = 1, then the CPE is a capacitor of capacitance Q; if the power index is n = 0, then the CPE is a resistor of resistance 1/Q; if the power index is n = 0.5, then the CPE is a Warburg element corresponding to a curve at 45° slope in the Nyquist plot (usually just after the semicircle in the Nyquist plot). Table 1 presents the parameter values of the equivalent electric circuit model, determined from the EIS data of Fig. 2.

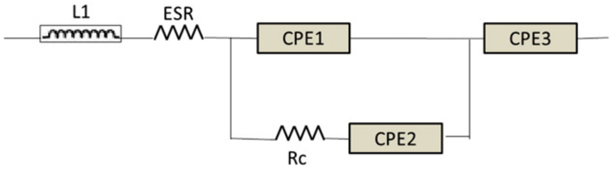

Fig. 3. Equivalent electric circuit used to interpret the EIS data.

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