Fabrication and electrochemical properties of carbon nanotube film electrodes

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Abstract

Carbon nanotube (CNT) film electrodes were fabricated by a novel process involving the electrostatic spray deposition (ESD) of a CNT solution. Acid treated CNTs were dispersed in an aqueous solvent through sonication and then the CNT solution was electrostatically sprayed onto a metallic substrate by the ESD method. The CNT film electrodes showed well-entangled and interconnected porous structures with good adherence to the substrate. A specific capacitance of 108 F/g was achieved for the electrodes in 1 M H2SO4. In addition, the CNT film electrode showed good high rate capability.

Keywords: Carbon nanotubes; Electrochemical properties

1. Introduction

Recently, research into electrochemical capacitors (ECs) has received a great deal of attention, because of their potential use in high power energy storage devices [1]. In these ECs, the energy stored is either capacitive or pseudocapacitive in nature. The capacitive or non-Faradaic process is based on charge separation at the electrode/solution interface, whereas the pseudocapacitive process consists of Faradaic redox reactions which occur within the active electrode materials [2]. The most widely used active electrode materials are carbon [3], conducting polymers [4] and transition metal oxides [5].

Carbon-based ECs, which are frequently referred to as electrochemical double layer capacitors (EDLCs), whose mechanism of energy storage primarily involves charge separation at the carbon/electrolyte interface [6], have been the subject of intensive investigation, because of their low-cost, high cycling life and high capacitance. They include carbon blacks, glassy carbon, activated carbons, carbon microbeads, carbon fibers, carbon cloths, carbon aerogels and carbon nanotubes [7].

Carbon nanotubes (CNTs), which were first discovered in 1991 [8], are of great interest for many applications, such as batteries, hydrogen storage, flat panel displays, chemical sensors, etc., because of their nanometer size and interesting properties, including their good electrical conductivity and mechanical strength. Furthermore, their high accessible surface area, narrow distribution of mesopore sizes, low resistance and high chemical stability suggest that CNTs are suitable materials for use as electrodes in ECs [9]. In recent years, ECs based on CNT electrodes have been reported using either aqueous or organic electrolytes. Niu et al. [9] prepared sheet type CNT electrodes by the filtration of a dispersed CNT solution and reported a maximum specific capacitance of 113 F/g with respect to the unit cell in 38 wt.% H2SO4 solution. Frackowiak et al. [10] investigated the electrochemical characteristics of an MWNT pellet electrode prepared by pressing a mixture
of CNTs with a binder. The specific capacitance of the electrode in 6 M KOH ranged from 4 to 135 F/g with respect to the unit cell, depending on the synthetic route used for the preparation of the CNTs or/and their pretreatment. Zhang et al. [11] prepared MWNT electrodes by molding CNTs with a binder and reported a specific capacitance of 18.2 F/g with respect to the unit cell and a specific energy of up to 20 kW/kg in an organic electrolyte system, due to their high operating voltage.

Since the as-produced CNTs in the form of soot are rather difficult to use directly for practical applications, much effort has been made to transform them into a macrosopic electrode form, especially for electrochemical applications such as ECs. Currently, two kinds of CNT electrodes are widely used; binder-free and binder-enriched. When they are mixed with polymeric binders, the CNTs are mechanically and electrically tight, however, the binder-enriched CNT film electrode may contain impurities which can degrade its electrochemical performance [12,13].

In order to prepare a binder-free electrode, the filtration method [14], the electrophoretic deposition method [15] and the drop-drying method [16] involving the use of CNT dispersed in solvents are frequently used. These methods enable the simple assembly of the individual CNTs, but are known to have some inherent problems associated with them, such as the poor control of the mass and thickness and the poor surface morphology and uniformity of the CNT film [17]. Furthermore, CNT film electrodes prepared by these methods are reported to have relatively high contact resistance between the CNTs and current collectors. CNT film electrodes with CNTs directly grown on a substrate are known to have a small contact resistance between the CNTs and the substrate [13]. Recently, Emmenegger et al. reported that the directly grown CNT on aluminum substrate showed promising electrochemical characteristics for electrochemical double layer capacitor [18,19].

In this paper, we report on the preparation of a CNT film electrode by a novel fabrication method involving electrostatic spray deposition (ESD). Recently, the ESD technique has been used for preparing thin films of metal oxide, such as lithium manganese oxide and lithium cobalt oxide, which are used for the cathode materials of a lithium battery [20,21]. The principle of the ESD technique is the atomization of a precursor solution in the needle of a syringe into an aerosol under the application of the high DC potential difference between the needle tip and the substrate, which results in a well defined trajectory of spray droplets being directed towards the heated substrate along the electric field [22]. Several physical and chemical processes are involved in the ESD of a metal oxide layer, and these occur either sequentially or simultaneously. The possible sequential steps are: (1) spray formation; (2) droplet transport, evaporation, disruption; (3) the preferential landing of droplets; (4) discharge, droplet spreading, penetration of the droplet solution, drying; (5) surface diffusion, reaction [23].

For these metal oxide thin films, metal salt solutions have traditionally been used as the precursor solutions. In this work, however, we employed a CNT suspension in aqueous media as the precursor solution, instead of a metal salt solution, to electrostatically deposit the CNT film onto a metallic substrate. This simplifies the preparation of the CNT film electrodes and has several advantages, viz. the preparation of a binder-free CNT film electrode with a uniform film surface morphology, easy control of the mass and thickness and a low operating temperature. In this paper, we report the synthesis and electrochemical characterization of a CNT film electrode prepared by the ESD technique for electrochemical capacitor applications.

2. Experimental

Two kinds of commercial multi-wall nanotubes (MWNTs) were obtained from ILJIN Nanotech Co., Ltd. (South Korea). The first kind of MWNTs, which are referred to as “CNT-A”, have a diameter of about 5 nm, a length of 10–20 µm, and a BET surface area of 400 m²/g. The other kind, which are referred to as “CNT-B”, have a diameter of 10–20 nm, a length of 10–50 µm and a BET surface area of 200 m²/g. The process of fabrication of the CNT film consists of two steps. The first step involves the dispersion of the CNTs in aqueous media. To introduce a hydrophilic functional group onto the surface of the CNTs, the MWNTs were treated with nitric acid (Duksan Chem., 98%) in a glass beaker at 80 °C for 4 h. The treated MWNTs were then rinsed with distilled H₂O several times, filtered and then dried in an oven. The resulting black powders were sonicated in distilled H₂O for 1 h at concentrations of 0.04 and 0.12 wt.% of the CNTs. Then, the CNT dispersion was mixed with ethanol (Duksan Chem., 99%).

The second step involves the electrostatic spraying of a MWNT precursor solution onto the substrate. A schematic view of the ESD set-up used in this study is shown in Fig. 1. It is composed of a precursor solution feeding unit, a power supply unit and a temperature control unit. Here, the solution was electrostatically sprayed downwards toward the substrate. The resulting precursor solution of MWNTs was pumped at a flow rate of 1–10 ml/h into a stainless nozzle placed about 2–10 cm above the substrate, which was heated to 80–200 °C. The voltage between the spraying nozzle and the substrate was maintained at 6–20 kV.

The nominal area of the CNT film was 1 × 1 cm². Pt coated Si wafers were used as the current collecting substrate. The amount of deposited CNTs was measured by weighing the electrode with a microbalance (Sartorius Ultra-Microbalance SC4, Germany) before and after the spraying of the CNTs. The morphology of the deposited CNTs was investigated by scanning electron microscopy (SEM, SIRION™, FEI COMPANY). Electrochemical measurements were made in a three electrode electrochemical cell in which the CNT film electrode was used as the working electrode, a platinum plate as the counter
electrode, and a saturated calomel electrode (SCE) as the reference electrode. Cyclic voltammetry was performed for the purpose of electrochemical characterization using a potentiostat/galvanostat (VMP2, Princeton Applied Research, USA). The electrolyte was 1 M H2SO4 and the potential window and potential scan rate were in the ranges of $-0.2$ to $0.8 \text{ V}_{\text{SCE}}$ and 10–500 mV/s, respectively.

3. Results and discussion

Fig. 2 shows the typical SEM images of the CNT (CNT-A) film electrode. It has mesopores with a distance of several tens of nanometers between the individual CNTs (see inset of Fig. 2a). The presence of well-entangled and interconnected porous structures with good adherence to the substrate is clearly seen. Fig. 2b shows the vertical section of the CNT film and reveals that the film has very good film thickness uniformity and a flat surface. It does not show any of the droplet-shape clumps frequently observed in the binder-free CNT films prepared by other techniques [17]. This could be attributed to the formation and spraying of the tiny aerosol CNT droplets with an excess positive charge in the ESD method and the uniform dispersal of the liquid droplets on the substrate.

The relationship between the amount of sprayed solution, the film thickness and the mass of the deposited CNTs can be seen in Table 1. Electrodes S1–S3 were fabricated by spraying a solution containing 0.04 wt.% of the CNTs. Both the mass of the deposited CNTs and the CNT film thickness increased linearly as the amount of sprayed solution was increased. Electrodes S4 and S6, prepared with a solution containing 0.12 wt.% of the CNTs, also showed the same tendency. Electrodes S5–S8 show that the ESD method is capable of preparing CNT film electrodes reproducibly with respect to the mass of the deposited CNTs and the CNT film thickness.

The cyclic voltammograms of the CNT (CNT-A) film electrode shown in Fig. 3a were mostly featureless in the potential window of $-0.2$ to $0.8 \text{ V}_{\text{SCE}}$, indicating that the CNTs exhibit typical electric double layer capacitive behavior with a pair of broad redox peaks. This type of redox
response has been observed for other types of carbon materials [24] and CNTs [25]. The origin of the redox peaks may be the oxidation/reduction of the COOH, –OH, and >C=O surface functional groups induced by the acid treatment. It is known that these functional groups enhance the capacitance of CNT electrodes [10].

The specific capacitance of the CNT film electrode was calculated from the voltammetric charge by CV curve in Fig. 3a according to Eq. (1)

\[ C_p = \frac{q_a + q_c}{2m\Delta V} \]

where \( C_p \), \( q_a \), \( q_c \), \( m \), and \( \Delta V \) are the specific capacitance of the CNT film electrode, the anodic and cathodic voltammetric charges on the anodic and cathodic scans, the mass of the deposited CNT film, and the potential range of the CV, respectively. The specific capacitance is plotted as a function of the potential scan rate in Fig. 3b.

The specific capacitance was 108 F/g at a potential scan rate of 10 mV/s, and it decreased slightly to 103 F/g at a potential scan rate of 100 mV/s. With a further increase in the potential scan rate to 500 mV/s, the specific capacitance decreased to 92 F/g (85% of the specific capacitance at 10 mV/s). It should be noticed that the MWNTs used in this study were not chemically or thermally treated for the purpose of improving the EDLC properties.

This result indicates that the MWNT film electrode prepared by the ESD technique has a high rate capability, which is comparable to that of CNTs directly grown on a graphite substrate (from 2 to 100 mV/s, specific capacitance drops by 17.8%) [13] and that of a CNT film electrode prepared by the vacuum filtration of an SWNT suspension (from 5 to 500 mV/s, specific capacitance drops by 14.3%) [26].

Fig. 4 shows the geometric capacitance of the prepared CNT film electrode as a function of the mass of the CNTs. In all cases, CNT-A was used and the potential scan rate was fixed at 70 mV/s. The geometric capacitance was calculated by multiplying the specific capacitance of the CNT film by the mass of the CNTs for each sample. It shows that the geometric capacitances of the CNT film electrode are linearly proportional to the mass of the deposited CNTs. This result implies that, in this study, the specific capacitance of the CNT film electrode shows a slight decrease as the mass of the deposited CNTs increases, because the CNT film electrode retains its well-entangled and interconnected porous structures.

Fig. 5 compares the specific capacitance of the two different CNT film electrodes prepared with CNT-A (BET surface area of 400 m²/g) and CNT-B (BET surface area of 200 m²/g), respectively. The specific capacitances of the CNT film electrodes made with CNT-A and CNT-B were 108 and 62 F/g at potential scan rate of 10 mV/s, respec-
The specific capacitance of the CNT film electrodes made by the ESD technique was proportional to the specific surface area of the CNTs used in this study, as expected [6]. The CNT film electrode prepared with CNT-B showed a 16% decrease in specific capacitance from 62 F/g at 10 mV/s to 52 F/g at 500 mV/s, which is almost the same as the 15% decrease in the specific capacitance observed for the CNT film electrode made with CNT-A under identical test conditions.

The volumetric capacitance of the CNT film electrode prepared with CNT-A was calculated from the estimated film thickness of 27.9 μm. Since the geometric capacitance of this electrode was 79.9 mF/cm², the volumetric capacitance was 2.9 F/cm³. Compared with the volumetric capacitance of activated carbon electrodes showing ~40 F/cm³ [18], relatively low volumetric capacitance of the CNT film electrode was due to its small mass density. The CNT film electrode showed the well-entangled and interconnected porous structures with good adherence to the substrate, which is expected to be an ideal substrate for the electrochemical capacitors from the view of electrical conductivity and ion transport. High volumetric capacitance of the CNT film electrodes could be achieved for metal oxide/CNT nanocomposite electrodes, in which the external surface of the CNTs were deposited with a thin layer of metal oxides at the nanometer scale [27–29].

The binder-free CNT film electrode fabricated by the electrostatic spray deposition of a CNT solution possessed well-entangled and interconnected porous structures with good adherence to the substrate, and showed promising electrochemical properties as an electrode for EDLC applications. Its range of potential applications can be extended to nanotechnology devices, such as field emitter devices, sensitive chemical sensors and field effect transistors, because of its thickness uniformity and flat surface morphology.

4. Conclusion

In the present study, we demonstrated a novel method of fabricating a binder-free CNT film electrode using the electrostatic spray deposition (ESD) technique. The CNT film electrode prepared by ESD showed well-entangled and interconnected porous structures on the nanometer scale with good adherence to the substrate. Its vertical section is characterized by good film thickness uniformity and a flat surface. The cyclic voltammograms of the CNT film electrode were mostly featureless in 1 M H₂SO₄ solution in the potential window of −0.2 to 0.8 V SCE, indicating typical electric double layer capacitive behavior. The specific capacitance was 108 F/g at a potential scan rate of 10 mV/s, and it decreased slightly to 103 F/g at a potential scan rate of 100 mV/s.

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