

# PREPARATION AND CHARACTERIZATION OF ACTIVATED CARBON/CNT ELECTRODE PREPARED BY ELECTROSTATIC SPRAY DEPOSITION TECHNIQUE

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## Abstract

Composite electrodes which comprise a activated carbon of large surface area(1600m<sup>2</sup>/g) and a conductive carbon nanotubes(CNTs) of small surface area (200m<sup>2</sup>/g) have been prepared by electrostatic spray deposition and investigated for their capacitive properties in aqueous H<sub>2</sub>SO<sub>4</sub> electrolytes. With the addition of sonochemically well dispersed CNTs to the activated carbon, equivalent series resistance(ESR) was reduced dramatically with 5wt% CNTs contents. Maximum specific capacitance exists at the composition believed to correspond to the percolation threshold for CNTs.

## 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. 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. 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, 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. In carbon based ECs, electrodes of 60~300  $\mu\text{m}$  thickness are fabricated using carbon paste or slurry containing 5~20wt% binders. Electrophoretic deposition (EPD) of carbon nanotubes was reportedly to be very effective in processing of CNT thin film on conductive substrates for EDLCs.

In this paper, we report on the preparation of an activated carbon electrode with CNTs as a conducting agent 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. 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. In this work, however, we employed a suspension of Activated carbon and CNT in ethanol base as the precursor solution, instead of a metal salt solution, to electrostatically deposit the Activated carbon/CNT film onto a metallic substrate.

## Methods

### *Materials*

Activated carbon with a specific surface area of 1600 m<sup>2</sup>/g was used as the base material for the composite electrode. Commercially available MWNTs(ILJIN Nanotech Co., Ltd.) which were deposited by the CVD method, were added to the activated carbon to act as a conducting material. In order to remove the catalyst, the MWNTs were acid-treated, then rinsed with distilled water for several times, filtered, and then dried in an oven. These electrode materials were mixed with polyvinylidene fluoride (PVDF) binder and then sonicated for 30 minute in ethanol base to prepare well dispersed solution. All the composite electrode contained 2.5wt% content of PVDF binder. The CNTs concentration of the Activated carbon-CNT(AC/CNT) composite electrodes was varied from 0wt% to 20wt%. Activated carbon-MWNTs stable suspensions which prepared sonication were electrostatically sprayed onto a heated Ti substrate.

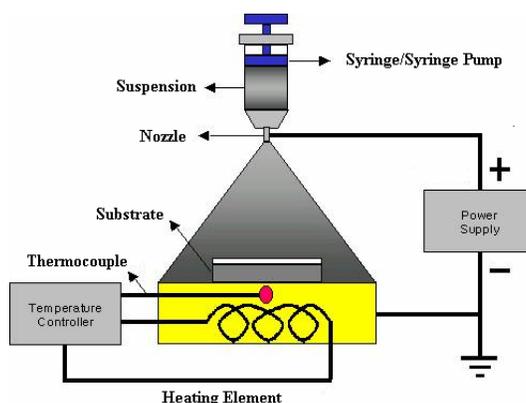
### *Electrochemical experiment*

The capacitance measurements were performed using a typical three-electrode cell configuration. The AC/CNT composite electrode with a geometric area of 1cm<sup>2</sup> was used as the working electrode. A platinum foil served as the counter electrode and a saturated calomel electrode(SCE) was used as the reference electrode. An H<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. Electrochemical characterizations were carried out using cyclic voltammetry, galvanostatic cycling and electrochemical impedance spectroscopy. Their morphological characteristics were investigated by Scanning electron microscopy(SEM).

## Results and Discussion

### *Electrostatic Spray Deposition(ESD) method*

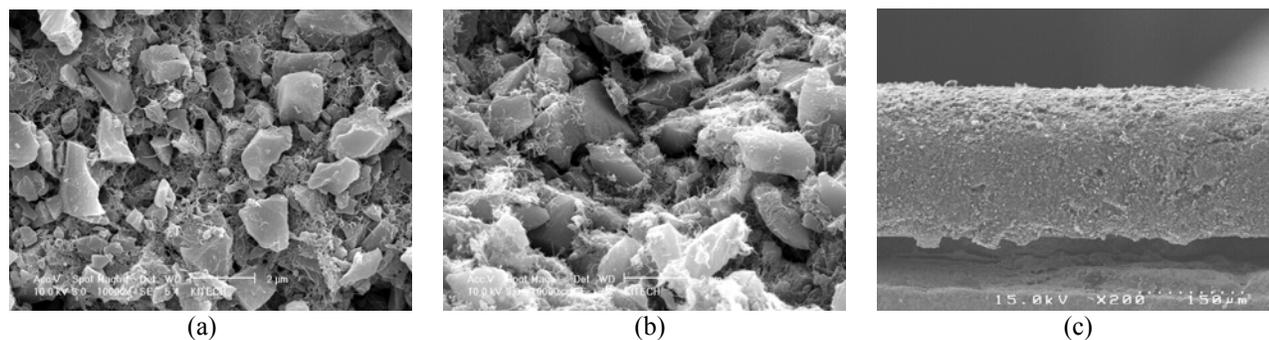
A schematic view of the ESD set-up used in this study is shown in Fig. 1. It is composed of a precursor solution feeding unit, a power supply unit and a temperature control unit. Here, the AC/CNTs dispersion solution was electrostatically sprayed downwards toward the substrate. The resulting precursor solution of AC/CNTs was pumped at a flow rate of 16~32ml/h into a stainless nozzle placed about 2– 10cm 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. 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. Furthermore, ESD method has several advantages with fabrication a uniform film surface morphology, easy control of the mass and thickness and a low operating temperature.



**Figure 1.** Schematics of Electrostatic Spray Deposition (ESD) Technique

### *Morphology of AC/CNTs composite*

Fig. 2 shows SEM images of AC/CNTs composite electrode which were prepared with ESD technique. In the Fig. 2, with 5wt% CNT contents, the Activated carbon and CNTs are ideally mixed with each other and the MWNTs attached to entire Activated carbon surface and interconnect to Activated carbon and MWNTs. This SEM investigation indicates that the MWNTs percolate throughout the overall electrode materials as the conducting agent. Furthermore, It is clear that Electrostatic spray deposition process produced the well-mixed AC/CNTs composite electrode with interconnected, three dimensional pore structures with good adherence to the substrate with small quantity of polymeric binders.

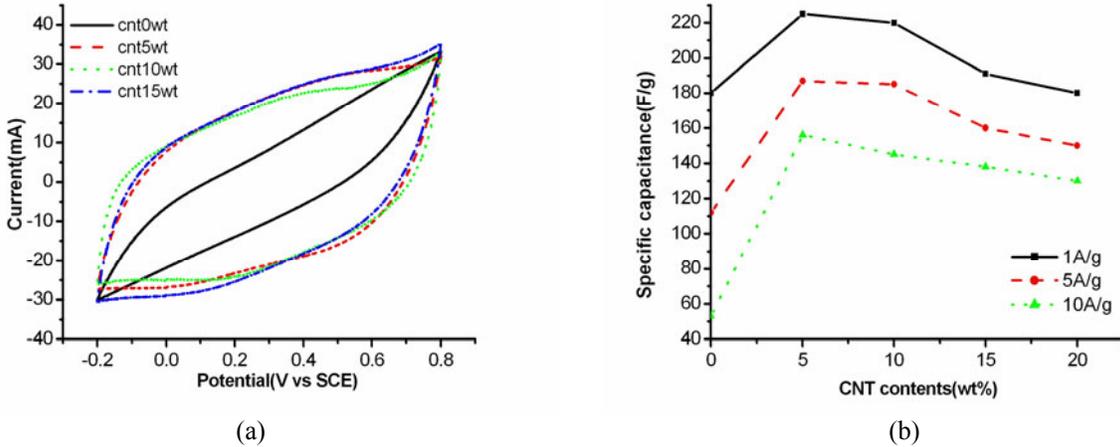


**Figure 2.** SEM image of 95wt% Activated carbon/ 5wt% CNT composite electrode, (a) plain view and (b), (c) cross sectional view

Fig. 2(c) shows the cross sectional view of the entire AC/CNTs electrode which was electrostatically deposited on Ti substrate. With ESD technique, the EDLC electrodes were fabricated with uniform thickness and good packing morphology. Electrode thickness and CNT deposit mass could be controlled easily by controlling the quantity of the sprayed solution and spraying time.

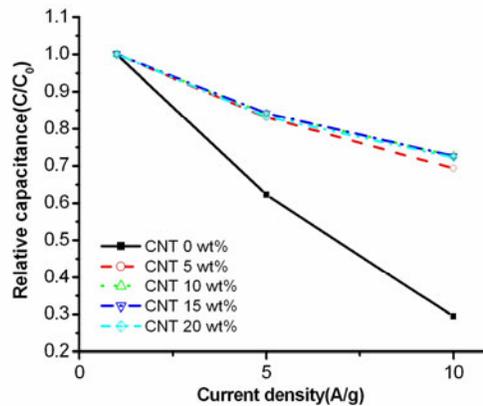
**Cyclic Voltammogram and capacitance profile**

Fig. 3(a) presents the change of the CV behavior of the active material versus the CNTs weight content in the active material, at the sweep rate of 200mV/s. With 0wt% CNTs content, there is no rectangular shape in the CV behavior. But when the CNTs content is increased up to 5wt%, even at the high scan rate, cyclic voltammogram with rectangular-like shape is observed and the capacitive current is much larger than that of 0wt% CNTs content. This implies that CNTs enhance the electronic conductivity of the electrode.



**Figure 3.** Electrochemical characterization of AC/CNT electrode. (a)cyclic voltammograms of AC/CNT electrode at the scan rate of 200mV/s, (b)specific capacitance variation with different CNTs content at a various current density

Plots of specific capacitance versus current density are given in Fig. 3(b). A maximum capacitance is formed at CNTs=5wt% for each current density in the range of 1A/g to 10A/g. the maximum specific capacitance are 223F/g for 1M H<sub>2</sub>SO<sub>4</sub> electrolyte at current density of 1A/g. the overall specific capacitance decreases with increasing CNTs due to reduction in the total surface area, as CNTs has a much smaller specific surface area than AC. When the current density is increased, the ionic migration of the electrolyte limits the accessibility to the whole porosity, leading to decrease of capacitance as compared with low current density.

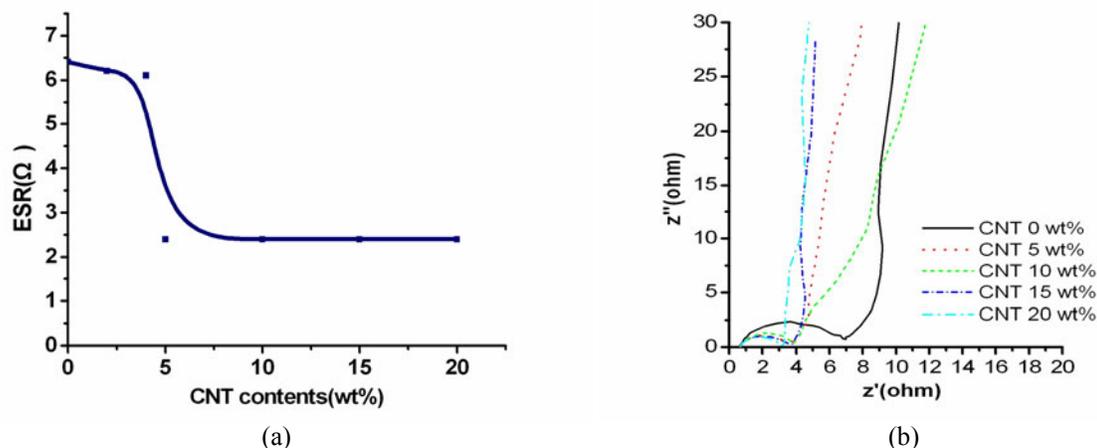


**Figure 4.** Variation of the relative capacitance  $C/C_0$  where  $C_0$  measured at 1A/g

For the CNTs content higher than 5wt%, with the relative capacitance in the Fig. 4, the loss of capacitance become constant and the reduction ratio is around 25% at high current density. With these results, when the CNTs content is under the 5wt%, the electronic conductivity is not effective and only a portion of the AC particle contribute to the overall capacitance. In this case, the overall capacitance increases with increasing CNTs. On the other hand, When the CNTs content is over the 5wt%, the electronic conductivity is ensured the entire electrode and the overall capacitance decreases with increasing CNTs due to the reduction of surface area of active materials.

### Electrochemical impedance spectroscopy measurements

Fig. 5(a),(b) presents the influence of CNTs content in the active material on the equivalent series resistance and Nyquist plot of the AC/CNT composite electrode. When the CNTs content is lower than 5wt%, little decrease can be seen but there is not significant change of the ESR. On the other hand, when the CNTs content is more than 5wt%, a sharp decrease of ESR is observed down to 2.5Ω. For higher CNTs content, i.e. 10wt% and 20wt%, it tends to be constant around 2.5Ω. Nyquist plot of AC/CNT composite electrode also presents the electrode resistance( $Z'$ ) is almost identical when the CNT content is higher than 5wt%. This indicates that the electronic conductivity of AC/CNTs composite electrode increased dramatically in 5wt% CNT content and when the CNTs content is over the 5wt% , there is no changes on internal resistance and ionic and electronic conductivity.



**Figure 5.** Electrochemical impedance spectroscopy(EIS) of AC/CNTs composite electrode

(a)Equivalent series resistance(ESR) with CNTs content. (b)Nyquist plot of AC/CNTs composite electrode with CNT content

It seems that the uniform dispersion of CNTs in the solution makes the interconnected pore structure which percolates throughout the entire active materials. Furthermore, the 3-D interconnected structure of AC/CNTs composite electrode effectively enhance the electronic conductivity of electrode. From the above, it is proposed that the optimum CNTs content to make percolation threshold is 5wt% in our system.

### Conclusions

EDLC with activated carbon and CNTs have been prepared using the novel technique of electrostatic spray deposition(ESD) technique. With ESD method, uniformly-mixed and 3-D interconnected AC/CNTs composite electrode could be fabricated. The prepared AC/CNTs composite electrodes have been studied by CV, galvanostatic charging-discharging and electrochemical impedance spectroscopy. When the CNTs content is higher than 5wt%, rectangular-like shape could be seen in the CV behavior and the ESR of the electrode dramatically decreased. Furthermore, the highest specific capacitance could be obtained in 5wt% CNT content. From these result, electrode with 5wt% CNT addition prepared with ESD technique optimizes the AC/CNTs composite electrode both the electronic conductivity percolation and electrode resistance.

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