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A comparative study on electrosorption behavior of carbon nanotubes electrodes fabricated via different methods

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ABSTRACT

The carbon nanotubes (CNTs) electrodes were fabricated via electrophoretic deposition (EPD), press and screen printing methods, respectively. The electrochemical properties and electrosorption performance of the CNTs electrodes were tested, respectively. Inhere, screen printing, as a conventional method for fabricating supercapacitor electrodes, was used for fabricating the CDI electrodes for the first time. Such a comparison is reasonably envisaged not only to be used to further understanding the influence of fabrication method on the electrode performance, but also to form a fundamental basis for CDI applications.

1. Introduction

Capacitive deionization (CDI) is a promising deionization technology for removing ionic species from aqueous solutions without high power consumption and secondary pollution [1–7]. When wastewater was pumped to flow through two opposite electrodes with an electric field applied, the charged ions in the solution were forced to move toward the surface of electrodes with countercharges. As a result, the contaminated solution was purified.

Generally, porous carbon materials have been reported to be widely used in CDI process due to their good conductivity, high surface area, and suitable pore size distribution [8–11]. Among various carbon species, carbon nanotubes (CNTs), with high ratio of surface area to volume and good chemical stability are regarded as a suitable candidate for CDI electrodes [12–14]. It is known that the electrosorption capacity of CNTs electrode strongly depends on its morphology and structure, which are related to the electrode fabrication method. By now several methods, such as electrophoretic deposition (EPD), press and screen printing, have been employed to deposit CNTs to the conductive substrate to fabricate the CNTs electrode [15–18]. Zou et al. [18] used press method to fabricate the ion-selective CNTs film as CDI electrodes. A higher salt removal efficiency than that of traditional CNTs electrode was achieved. The CNTs electrodes were fabricated via EPD method for CDI [16]. The electrodes exhibited a comparable electrosorption capacity in NaCl solution to other conventional carbon electrodes. Therefore, the electrode fabrication methods play an important role in the electrosorption performance of CNTs electrodes by influencing their morphology and structure.

In this work, we fabricated the CNTs electrodes using three different methods: EPD, press and screen printing, and their electrosorption performance in NaCl solution was investigated. Screen printing, as a conventional method for fabricating supercapacitor electrodes [19,20], was used for fabricating the CDI electrodes for the first time. Such a comparison is reasonably envisaged not only to be used to further understanding the influence of fabrication method on the electrode performance, but also to form a fundamental basis for CDI applications.

2. Experimental

2.1. Materials

Multi-walled CNTs were purchased from Nanotech Port Co. Ltd. (Shenzhen, China) with detailed specifications as follows: length (1–2 μm), diameter (10–20 nm) and purity (≥95%). Polyvinyl alcohol (PVA), ethyl cellulose (EC) and terpilenol were purchased from Sinopharm Chemical Reagent Co. Ltd. All the reagents were used without further purification.

2.2. Fabrication

The CNTs electrodes were prepared by EPD method [16]. In brief, CNTs were dispersed in a mixture solution of acetone and ethanol (volume ratio 1:1) and 10 mg $Al(NO_3)_3{\cdot}9H_2O$ was added into the suspension to increase the deposition rate and improve the adhesion of the powder particles to the substrate. The EPD was

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conducted by applying a constant DC voltage of 40 V for 30 min. Then the as-deposited CNTs film electrode, named as sample 1, was dried in the air at 40 °C for 2 h.

The press method was described as follows: firstly, 2.7 g PVA was dissolved into 97.3 g deionized water under stirring at 90 °C for 4 h. Then the carbon slurry was prepared by mixing 800 mg CNTs and 100 mg carbon black with 2.7 g PVA solution, and stirred in an agate bowl till the CNTs were homogeneously dispersed in the mixture. The carbon slurry was pressed on the graphite paper. Finally, the as-CNTs electrode, named as sample 2, was dried at 80 °C for 2 h in an oven.

The CNTs electrodes were prepared by screen printing method [19]. In brief, 1 g EC was added into 20 g terpilenol, and dissolved under stirring at 80 °C. Then the carbon slurry was prepared by mixing 850 mg CNTs and 100 mg carbon black with 1.05 g EC solution, and stirred in an agate bowl till the CNTs were homogeneously dispersed in the mixture. The CNTs were screen-printed on the graphite paper and then heated at 100 °C for 1 h. The obtained CNTs electrode was named as sample 3.

2.3. Characterization of CNTs electrodes

The surface morphology and structure of CNTs electrodes were examined by scanning electron microscopy (SEM, JEOL JSM-LV5610). The contact angles of water on the surface of the prepared electrodes were measured with the sessile drop method by a contact angle goniometer (JC2000D, Powereach) using digital micrographs of deionized water droplets. The cyclic voltammetry (CV) was investigated by using Autolab PGSTAT 302N electrochemical workstation in a three-electrode mode, including a standard calomel electrode as reference electrode and a platinum foil as counter electrode. 1 M KCl solution was used as electrolyte. The specific capacitance can be obtained from CV curves using the following equation:

$$C = \tilde{i}/(v \times m) \tag{1}$$

where $\tilde{i}$ is the average current (A), v is the scan rate (V s^{-1}) and m is the mass of electrodes (g).

2.4. Batch-mode electrosorption experiments

The electrosorption performance of CNTs electrodes fabricated using different methods was investigated by batch-mode electrosorption experiments with a continuously recycling system [21]. In each experiment, the analytical pure sodium chloride (NaCl) was employed as the target solution with a volume of 50 mL and the flow rate was 40 mL/min. A direct voltage of 1.2 V was applied on the opposite electrode. The initial conductivity of NaCl solution was 50 μS/cm, and the atmosphere temperature was kept at 298 K. The relationship between conductivity and concentration was obtained according to a calibration table made prior to the experiment [22]. The concentration variation was continuously monitored and measured at the outlet of the unit cell by using an ion conductivity meter.

In our experiment, the salt removal and electrosorption capacity are defined as follows:

$$\eta = \frac{\Phi_0 - \Phi}{\Phi_0} \times 100\% \tag{2}$$

where Φ_0 is initial solution conductivity and Φ is the final solution conductivity.

$$\Gamma = \frac{(C_0 - C_e) \times V}{m} \tag{3}$$

where C_0 is initial NaCl concentration (mg L^{-1}), C_e is the final NaCl concentration (mg L^{-1}), V is the volume of NaCl solution (L) and m is the mass of electrodes (g).

3. Results and discussion

Figure 1 shows SEM images of CNTs electrodes fabricated via different methods. It can be observed that CNTs in all the samples entangle with each other and show a good network structure with many mesopores, which provides more tunnels for the entering of the solution and allows hydrated ions easily to move onto the surface of the film [23]. However, different from Figure 1a, there are some particles in Figure 1b and c, which should be carbon black or binders used in press and screen printing methods. These particles may block the pores of the CNTs porous network, which is not beneficial to the electrosorption.

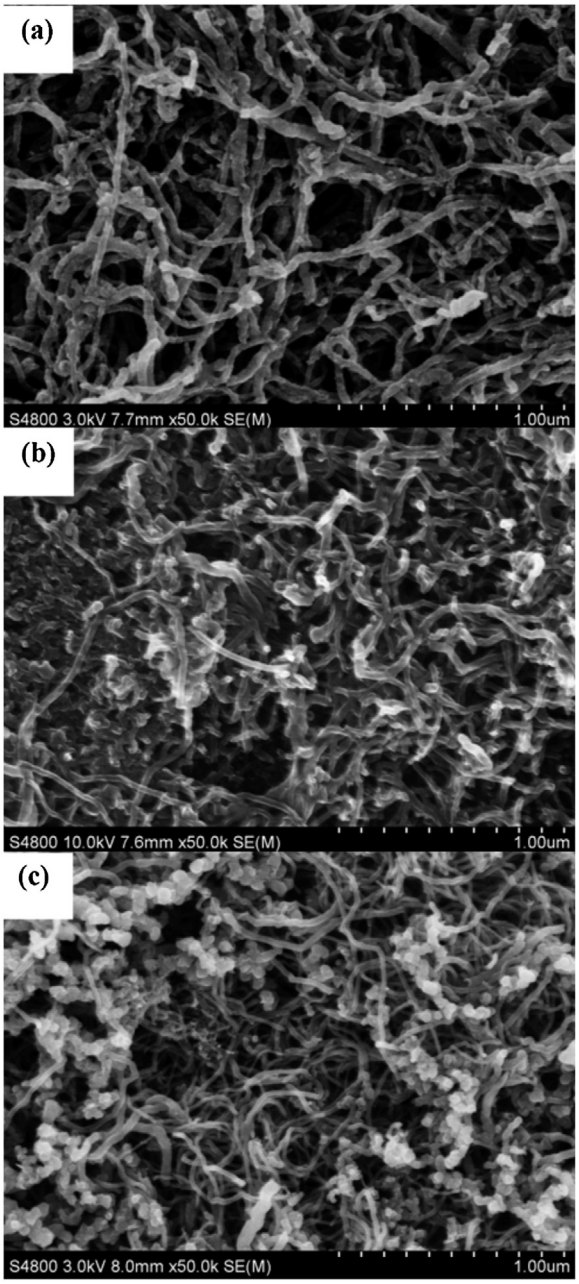

Figure 1. Typical SEM images of (a) sample 1, (b) sample 2 and (c) sample 3.