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Characteristics of NiO coating on carbon nanotubes for electric double layer capacitor application

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ABSTRACT

Nickel oxide (NiO) nano-structures were synthesized on random carbon nanotubes (CNTs) growing on a carbon cloth substrate processed using vacuum annealing and oxygen plasma treatment for the electric double layer capacitor electrode application (EDLC). From the electrochemical measurement analytical results the NiO nano-structure/CNT composite electrode with carbon cloth substrate exhibits low internal resistance features. The specific NiO/CNTs/carbon cloth electrode capacitance can reach up to 162.41 F/g in contrast with 53.75 F/g for the CNTs/carbon cloth electrode in 1 M KOH solution. These results indicate that NiO nano-structures formed onto CNTs/carbon cloth electrodes are suitable materials for EDLC applications.

1. Introduction

The electrochemical capacitor is an energy storage device that possesses relatively higher energy, greater power density, and more rapid energy storage than traditional capacitors and batteries [1,2]. In actual use its sustainability and stability demonstrate superior capacitor behavior [3]. Two major types of electrochemical capacitors are classified by their energy storage mechanisms: the electric double layer capacitor (EDLC) [4] and pseudo-capacitor [5]. The EDLC is based on the charge storage in an electric double layer at the interface between the electrode and electrolyte solution [6]. The pseudo-capacitor occurs at the active electrode with the faradaic redox reaction principle [7].

Porous structure carbonaceous materials are often used as electrode material for EDLCs because the ELDC capacitance arises from the charge separation at the electrode and electrolyte interface [8]. On account of the porous structure advantages, the increasing effective contact area between the electrode and electrolyte results in more electrolyte ions in contact with the electrode surface, leading to better electrochemical performance. Carbon nanotube (CNT) [9] electrode material is suitable for electrode use. The high CNT aspect ratio provides a large effective surface area. CNT also exhibits good electrical conductivity and high chemical stability [10]. To enhance the capacitance transition metal oxides such as RuO_2 [11], NiO_x [12], MnO_x [13] and IrO_2 [14] have been studied as electrode materials for pseudo-capacitor applications because they have high energy density and possess many oxidation numbers which can contribute fast, reversible redox reactions at or near their solid electrode surfaces [15]. Compared with other transition metal oxides, nickel oxide (NiO) is easy to obtain, low cost and can be prepared using several methods such as liquid crystal templating electro-deposition [16], simple liquid-phase process [17], electro-deposition thermal treatment [18] and sol-gel prepared nickel hydroxide techniques [19]. It has been reported that a combination of NiO and CNTs can obtain good electrochemical characteristics [20], giving the NiO/CNT composite developmental potential in industrial applications.

In this work we report on a simple NiO nano-structure formation coated onto a CNT/carbon cloth surface as an electrode for EDLC applications. The carbon cloth is used as a flexible, lightweight, anti-corrosive substrate with good conductive advantages [21]. The same carbon cloth component has relatively stronger adhesion to CNTs that resists separation from each other in electrolyte for a long time. The Ni film was first deposited onto the CNTs using e-beam evaporation. The Ni/CNTs were then treated with a vacuum annealing process and oxygen plasma to form uniform NiO nano-structures on the CNT surface. The electrochemical

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properties were measured using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and a galvanostatic charge-discharge experiments. The results show that the NiO/CNT composites coated onto carbon cloth formed using this simple method is a promising electrode for EDLC applications.

2. Experimental

The carbon cloth was cut into 15 × 15 mm^2 pieces. To grow the CNTs we first used an e-beam evaporator to coat a buffer layer of Al for 5 nm and a catalyst layer of Fe for 3 nm onto the carbon cloth surface. The CNTs were grown onto the carbon cloth surface using thermal chemical vapor deposition (TCVD). C_2H_2 gas as the carbon source was introduced into the TCVD system for 20 min under a working pressure of 5.3 mbar at 750 °C.

Prior to the NiO nano-structures forming onto the CNT/carbon cloth, Ni film (20 nm) was coated onto the CNTs/carbon cloth using an e-beam evaporator. The Ni film was annealed at 750 °C for 60 min using a vacuum annealing process to form the Ni nanoparticles. An oxygen plasma treatment was then used to form the NiO nano-structures onto the CNT/carbon cloth. The applied RF power was 25 W with flowing oxygen at a pressure of 0.53 mbar at a flow rate of 20 sccm at 300 °C for 30 min. NiO/CNTs/carbon cloth, CNTs/carbon cloth and carbon cloth electrodes were prepared for comparison.

The surface morphologies of the carbon cloth, CNTs/carbon cloth and Ni nanoparticles coated onto CNTs/carbon cloth before and after oxygen plasma treatment were observed using a scanning electron microscope (SEM). The detailed NiO nanoparticles structure was revealed using a transmission electron microscope (TEM). To confirm the proportion of elements in the NiO/CNT/carbon cloth composite, carbon, nickel, and oxygen were analyzed using an energy dispersive spectrometer (EDS).

The electrochemical characteristics were measured by a three-electrode system which was equipped with a working electrode (carbon cloth, CNTs/carbon cloth, and NiO/CNTs/carbon cloth), an Ag/AgCl (saturated KCl) reference electrode, and a platinum wire counter electrode in 1 M KOH solution. The EIS was measured by a sinusoidal alternating voltage frequency set between 0.01 Hz and 10 kHz with ac oscillation of 10 mV at a constant potential of 0 V versus the Ag/AgCl electrode. The CVs were measured with an electrical potential range from −0.25 to 0.25 V at scan rates of 1, 5, 30, and 50 mV/s. The charge-discharge were measured at a constant current of 0.5 mA with the voltage limits set between −0.25 and 0.25 V and was measured for 100 cycles to test the electrode stability.

3. Results and discussion

The carbon cloth, CNTs/carbon cloth, and NiO/CNTs/carbon cloth morphological features are shown in Fig. 1. Fig. 1 (a) shows the carbon cloth surface morphology is smooth. Fig. 1 (b) shows the random CNT growth on the carbon cloth. The inset in Fig. 1 (b) shows a partial magnification section of random CNTs. It shows that the number density of the random CNTs is high, exhibiting greater contact possibility between the electrode and electrolyte. Fig. 1 (c) shows a top view image of the Ni nanoparticles coated onto CNTs after annealing for 60 min. The inset in Fig. 1 (c) shows the Ni nanoparticles distributed uniformly and continuously onto the CNT surface. The nanoparticle diameter is about 50 nm. Fig. 1 (d) shows the surface morphology of the NiO nano-structures formed onto the CNTs after oxygen plasma treatment. Some CNTs were etched during the oxygen plasma treatment process. The probable reason may be the oxygen plasma treatment time was too long [22]. The inset in Fig. 1 (d) shows magnification of the NiO nanoparticles formed onto CNTs. The NiO nanoparticle diameter is about 50 nm.

TEM observations of the NiO nanoparticles are shown in Fig. 2. Fig. 2 (a) shows the elliptical shape of the NiO nano-structures. Fig. 2 (b) reveals the core–shell NiO nanoparticles after oxygen plasma treatment from Ni nanoparticles. The nano-structure has

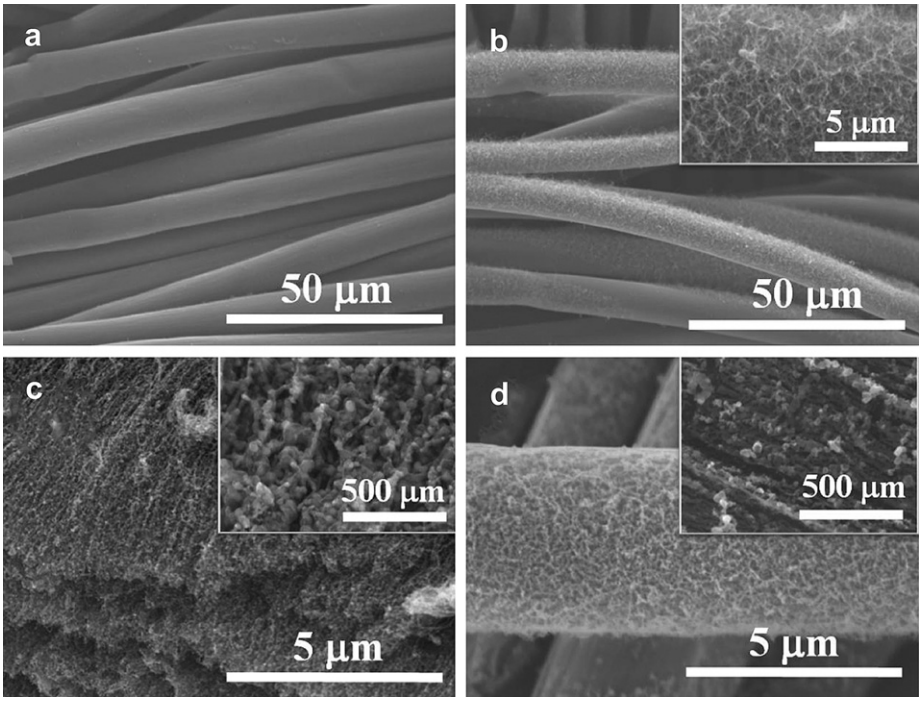

Fig. 1. (a) The SEM image of the carbon cloth. (b) The SEM image of the CNTs grown on the carbon cloth. The inset of (b) is the SEM image at high magnification. (c) The SEM image of the Ni nanoparticles coated on CNTs after annealing for an hour. The inset of (c) is the SEM image of Ni nanoparticles at high magnification. (d) The SEM image of NiO nanoparticles formed on CNTs after oxygen plasma treatment. The inset of (d) is the SEM image of NiO nanoparticles at high magnification.