Polypyrrole (PPy)/carbon nanotube (CNT) hybrid composite electrode on ceramic fabric for supercapacitor applications

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1. Introduction

Recently, there has been increased research interest in the development of ultrathin, flexible, and safe energy storage devices. Electrochemical capacitors have many potential applications in the power source field. [1-5] Porous carbon materials for electric double layer capacitor (EDLC) have long cycle life and good mechanical properties, but unsatisfactory specific capacitance. Metal oxides also were used for active material of pseudo capacitor. Conducting polymers for pseudo capacitor have high flexibility and relatively high specific capacitance. [1-5] However, conducting polymers commonly have poor mechanical stability because of the considerable volume change caused by the repeated intercalation and depletion of ions during charging and discharging. There have been many attempts to synthesize composite materials to compensate for the limitation of each individual material in electrochemical capacitors. Carbon nanotubes (CNTs) have been considered to be a very attracting material for composites. Composites of CNTs and conducting polymers are even more interesting and promising, since they combine two relatively cheap materials to benefit from the large pseudo capacitance of the conducting polymers coupled with the conductivity and mechanical strength of the CNTs. [1-4] In this study, a composite electrode consisting of CNTs and a conducting polymer was prepared for a supercapacitor, in which the conducting polymer was used as a conductive binder. Flexible, thermally stable, and porous nonwoven ceramic fabric was used as the substrate for the electrode. Aligned CNTs on the ceramic fabrics were prepared by the thermal vapor deposition (CVD) process and PPy was subsequently coated on the surface of the CNTs on the ceramic fabrics by chemical polymerization.

The CNTs provided a high surface area combined with the high electrical conductivity required for the active material. PPy provided not only additional capacitance as an active material, but also enhanced the adhesion between the CNTs and ceramic fabrics. Furthermore, PPy also acts as a conducting binder for connecting every individual CNT, in order to collect all of the residual capacitance. The procedure used for the preparation of the PPy-CNT composite electrode on the ceramic fabrics is represented in Fig. 1. The electrochemical properties of the PPy-CNTs composite electrode were investigated by cyclic voltammetry and galvanostatic charge/discharge tests.

2. Preparation

2.1. Preparation of CNTs on ceramic fabric

The ceramic fabric (10x10mm) was used as a substrate for the growth of the CNTs. The original ceramic fabrics contain some polymer binder which was completely removed by dissolution in acetone, dichloromethane, and ethanol under sonication. the CNTs on ceramic fabric was synthesis from Fe-precursor by using thermal CVD process. [6]

2.2. Preparation of PPy or PPy-CNTs composite on ceramic fabric

The ceramic fabric or CNT-ceramic fabric was immersed in Py/ACN solution and then in $FeCl_3$ aqueous solution for chemical polymerization. After the polymerization process, the PPy or PPy-CNT composite on the fabric was washed several times with ethanol and then dried in an oven at 50℃ for 24h.

2.3. Instrument

The weight of PPy and CNTs were measured by a micro-analytical balance (Mettler-Toledo AX205 Delta range, Greifensee, Switzerland). Thermal chemical vapor deposition (Thermal CVD, SNTEK, Thermal CVD System, Korea) was used for the growth of the CNTs. The composition of Fe dispersed on the ceramic fabric was observed by energy dispersive x-ray microanalysis (EDX, JEOL JSM-7000F, Japan). The surface morphology of the prepared electrodes were observed by scanning electron microscopy (SEM, JEOL JSM-7000F, Japan) and high resolution transmission electron microscopy (HRTEM, JEM-3011, Japan). Two electrochemical cells were fabricated with symmetric electrodes (1x1cm), bare ceramic fabric (2x2cm) as a separator, and Au plate (1x5cm) as a current collector for all electrochemical analysis. The electrochemical characteristics were evaluated using galvanostatic charge-discharge and cyclic voltammetry. The specific capacitance of the electrodes was gavanostatically measured at a potential ranging from 0 to 1~2 V at a current density ranging from 1 mA•cm^{-2}. The cyclic voltammetry of the unit cell was performed over the voltage range of -1~1 V at a scan rate of 25mV•s-1. All electrochemical measurements were carried out at room temperature using 1 M 1M $LiClO_4$/PC as the electrolyte. Cyclic voltammetry and the galvanostatic charge-discharge test of the prepared electrodes were performed using a potentiostat (VSP, Princeton Applied Research, USA), and the specific capacitances of the prepared electrodes were obtained from the following equation:

$$C = i \cdot \Delta t \cdot \Delta V^{-1}$$

where i is the current and △t is the time interval for the change in voltage, △V

3. Results and discussion

A PPy-CNT composite electrode was successfully fabricated on a ceramic fabric by CVD and chemical polymerization and its capacitive characteristics were studied. The specific capacitance of the PPy-CNTs on the ceramic fabric was 152.78 F g−1 at 1 mA•cm-2 and its stability was well retained even after 1000 redox cycles. The ceramic fabric serves as a suitable substrate for the growth of the CNTs and chemical polymerization, due to its chemical and thermal stability. Moreover, the CNTs and porous structure of the ceramic fabrics provide the electrode with a high surface area. PPy not only participated in the electrochemical redox process an active material, but also provided electron conducting pathways for individual CNTs. The adhesion of the interface between the CNTs and ceramic fabrics was also enhanced by the deposition of PPy.

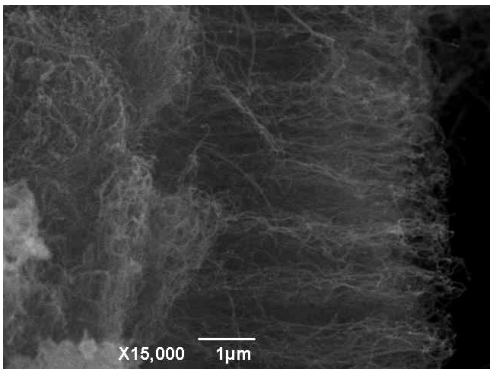

Fig. 1. SEM images of CNTs on ceramic fabrics

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