Synthesis and Electrochemical Performance of Polypyrrole-Coated Iron Oxide/Carbon Nanotube Composites

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Abstract

In this work, iron oxide (Fe_3O_4) nanoparticles were deposited on multi-walled carbon nanotubes (MWNTs) by a simple chemical coprecipitation method and Fe_3O_4 -decorated MWNTs (Fe-MWNTs)/polypyrrole (PPy) nanocomposites (Fe-MWNTs/PPy) were prepared by oxidation polymerization. The effect of the PPy on the electrochemical properties of the Fe-MWNTs was investigated. The structures characteristics and surface properties of MWNTs, Fe-MWNTs, and Fe-MWNTs/PPy were characterized by X-ray diffraction and X-ray photoelectron spectroscopy, respectively. The electrochemical performances of MWNTs, Fe-MWNTs, and Fe-MWNTs/PPy were determined by cyclic voltammetry and galvanostatic charge/discharge characteristics in a 1.0 M sodium sulfite electrolyte. The results showed that the Fe-MWNTs/PPy electrode had typical pseudo-capacitive behavior and a specific capacitance significantly greater than that of the Fe-MWNT electrode, indicating an enhanced electrochemical performance of the Fe-MWNTs/PPy due to their high electrical properties.

Key words: multi-walled carbon nanotube, iron oxide, polypyrrole, supercapacitor

1. Introduction

Electrochemical capacitors or supercapacitors have attracted increased interest due to their high power density compared to that of conventional capacitors [1-3]. Electrochemical capacitors have been developed to provide power pulses for a wide range of application areas including transportation, consumer electronics, medical electronics, and military devices [4]. According to the energy storage mechanism, two kinds of electrochemical capacitors have been examined: 1) electric double layer capacitors (EDLC) using carbon having a very high surface area as the electrode material [5]; 2) conducting polymers [6] or metal oxide based pseudo-capacitors [7].

In pseudo-capacitors, charge is stored by the electrical charge transport in redox reaction on the electroactive species. These species in pseudo-capacitors formed metal oxides and conducting polymers on the electrode surface, accelerating the redox reactions [8,9].

Polypyrrole (PPy) is one of the most important conducting polymers; it is used in a wide range of applications owing to its relatively facile processability, mechanical flexibility, low cost, electrical conductivity, and thermal and chemical stability [10].

Carbon nanotubes (CNTs), as EDLC electrode materials, have attracted much attention because of their high electrical conductivity, unique entangled network, and dominant porous character [11]. Nowadays, significant interest has been generated in research that mixes CNTs with various inorganic and organic substances by physical and chemical approaches to prepare multifunctional composites. A variety of CNT composites have been prepared and investigated [12,13]. Recently, extensive efforts have been made to prepare functional PPy-CNT composites that exhibit enhanced electrical, thermal or mechanical properties relative to PPy or to CNTs alone [14].

Much research on supercapacitors is aimed at increasing both the power and the energy densi-

ty as well as lowering fabrication costs while using environmentally friendly materials. The development of advanced composite materials based on the use of metal oxide-carbon nanotubes for supercapacitor electrodes has been studied in the hope that these materials can provide improved capacitive behaviors due to their enhanced stability, high conductivity, and pseudo-capacitance [15,16].

In this work, a novel PPy-coated Fe_3O_4 / multi-walled CNT (MWNT) nanoparticle composite (Fe-MWNT/PPy) has been prepared by the coprecipitation of Fe^{3+} and Fe^{2+} and the in situ polymerization of pyrrole. The characterization and electrochemical performance of Fe-MWNTs/PPy are performed to determine its potential use as a supercapacitor electrode.

2. Experimental

2.1. Materials

MWNTs produced via chemical vapor deposition method were purchased from Nano Solution Co. (Korea, degree of purity: ≥ 95 wt%, diameter: 10-25 nm, length: 10-50 μm). Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), pyrrole, ammonium persulfate (APS), and ammonium hydroxide aqueous solution (NH_4OH , 25 wt%) were obtained from Aldrich.

2.2. Preparation of Fe-MWNTs

The pristine MWNTs were purified by impregnating them with 5 M HNO_3 for 5 h at room temperature. Purified MWNTs was washed using distilled water until pH 7.0 was obtained. After vacuum filtration, the sample was dried for 24 h at 120°C in a vacuum oven.

Fe-MWNTs were prepared by suspending 1.0 g of purified MWNTs in 200 mL of distilled water containing 1.0 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 2.7 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at 50°C under an N_2 atmosphere. Then, 0.5 mL of NH_4OH solution was slowly added to the above solution under continuous stirring to promote complete growth of the nanoparticle crystals. Subsequently, the composites were centrifugally separated from the solution, washed with distilled water until a pH 7.0 was reached, and dried at 100°C for 12 h in vacuum. The chemical reaction of the Fe_3O_4 precipitation is as follows [17].

2.3. Preparation of Fe-MWNTs/PPy

To prepare Fe-MWNT/PPy, the obtained Fe-MWNTs were dispersed in 150 mL of 0.1 M HCl solution. Subsequently, 1 mL of pyrrole was added. After the solution was stirred mechanically for 10 min, it was mixed with an aqueous solution of APS. The polymerization of pyrrole was allowed to proceed for 5 h at approximately $0-5^\circ\text{C}$. Then, the final product was washed with copious amounts of water and absolute ethanol and was dried under vacuum at 80°C for 24 h.

2.4. Characterization

The structures of the MWNTs and Fe-MWNTs were characterized using X-ray diffraction (XRD, BRUKER D2 PHASER)

with $\text{CuK}\alpha$ radiation. The XRD patterns were obtained in 2θ ranges between 20° and 80° at a scanning rate of $5^\circ/\text{min}$.

The surface characteristics of the MWNTs, Fe-MWNTs, and Fe-MWNTs/PPy were determined using X-ray photoelectron spectroscopy (XPS, VG Scientific Co., ESCALAB MK-II) with an $\text{Al K}\alpha$ ($h\nu = 1486.6$ eV) X-ray source.

For the electrochemical investigation, cyclic voltammetry (CV) and galvanostatic charge-discharge tests were performed using an electrochemical analyzer (Iviumstat, Ivium Technologies) to evaluate the electrochemical performance in the potential range between -0.9 V and 0 V in the 1 M Na_2SO_3 electrolyte solution.

3. Results and Discussion

Fig. 1 shows XRD patterns of the MWNTs and Fe-MWNTs. Diffraction peaks assigned to the MWNTs at $2\theta = 26.5^\circ$ and 43° can be clearly seen in the XRD curves of the MWNTs and Fe-MWNTs, indicating that the MWNT structure was not destroyed after the successive deposition of Fe_3O_4 . The XRD patterns exhibit typical characteristic peaks of Fe_3O_4 at $2\theta = 30.2^\circ$, 35.4° , 46.6° , 53.7° , 57.3° , and 62.8° , which is in agreement with the standard values (JCPDS card no. 75-0033). The grain size of the Fe_3O_4 particles was calculated from the major diffraction peak (311) using the Debye-Scherrer equation [18].

$$L_c = \frac{K\lambda}{\beta_{1/2} \cos \theta} \quad (2)$$

where L_c is the particle size (nm), K is the Scherrer constant ($= 0.9$), λ is the X-ray wavelength ($\text{CuK}\alpha = 0.154$ nm), θ is the angle at the peak maximum, and $\beta_{1/2}$ is the width (radians) of the peak at half the height. According to equation, the deposited Fe_3O_4 particles have an average grain size of 14 nm.

The MWNTs, Fe-MWNTs, and Fe-MWNTs/PPy were also characterized using XPS analysis. Fig. 2 shows the wide scan spectrum, in which the photoelectron lines at binding energies of about 285, 533, 400, and 711 eV are attributed to C_{1s} , O_{1s} , N_{1s} , and Fe_{2p} , respectively. The peaks at 285 eV correspond

Fig. 1. X-ray diffraction curves of multi-walled carbon nanotubes (MWNTs) and Fe-MWNTs.

Fig. 2. X-ray photoelectron spectroscopy curves of multi-walled carbon nanotubes (MWNTs), Fe-MWNTs, and Fe-MWNTs/PPy.

Fig. 3. Cyclic voltammetry curves of multi-walled carbon nanotubes (MWNTs), Fe-MWNTs, and Fe-MWNTs/PPy at the scan rate of 50 mV/s in 1 M Na₂SO₃ electrolyte.

with the sp^2 hybridized carbon of the MWNTs [19]. The N_{1s} spectrum of Fe-MWNTs/PPy shows its peak at a binding energy of about 400 eV, which is characteristic of amine-like or neutral pyrrolium nitrogens ($-NH-$ structure) [20]. In the case of Fe_{2p} , the core-level spectra of the Fe-MWNTs and Fe-MWNTs/PPy show very similar peaks at a binding energy of about 711 eV. It can be suggested that there is no significant chemical reaction between PPy and Fe-MWNTs, and that Fe-MWNTs are used as a template for the polymerization of conducting PPy.

The electrochemical performance of MWNTs, Fe-MWNTs, and Fe-MWNTs/PPy was measured using CV and charge-discharge curves in 1 M Na₂SO₃ electrolyte solution. Fig. 3 presents the CV curves of each electrode between a potential from -0.9 to 0 V at a scan rate of 50 mV/s. It can be seen that the MWNT electrodes have symmetrical, rectangular-shaped voltammograms, which is a characteristic feature of EDLCs. However, anodic peaks and cathodic peaks were observed in the CV for the Fe-MWNTs and Fe-MWNTs/PPy electrodes, which is attributed to the redox reactions of Fe_3O_4 . The possible mechanism is as follows [21]:

Fig. 4. Charge/discharge curves of multi-walled carbon nanotubes (MWNTs), Fe-MWNTs, and Fe-MWNTs/PPy with 0.2 A/g in 1 M Na₂SO₃ electrolyte.

The galvanostatic charge-discharge curves of MWNT, Fe-MWNT, and Fe-MWNTs/PPy electrodes were investigated at 0.5 A/g; the corresponding results are shown in Fig. 4. It can be seen that the curve of the MWNT electrode is very symmetrical, indicating that the MWNT electrode has perfect EDLC behavior. However, the shapes of the charge-discharge behavior of the Fe-MWNT and Fe-MWNTs/PPy electrode did not show the characteristics of a pure electrochemical double-layer capacitor, which is in agreement with the result obtained from CV in Fig. 3.

The specific capacitance can be measured by the galvanostatic charge-discharge behavior, according to the following equation [22]:

$$C_{sp} = \frac{Q}{\Delta V \times m} = \frac{I \times t}{\Delta V \times m} \quad (5)$$

where I is the current of charge-discharge, t the discharge time, ΔV the potential window, and m the mass load of active materials. The calculated specific capacitances of the MWNTs, Fe-MWNTs, and Fe-MWNTs/PPy are 20, 60, and 73 F/g, respectively. It is obvious that the specific capacitance of the Fe-MWNTs/PPy is improved by the coating of PPy, which enhances the electric conductivity, lowers the resistance, and facilitates the charge-transfer of the composites.

4. Conclusions

In this work, Fe-MWNTs/PPy was successfully prepared by the coprecipitation of Fe^{3+} and Fe^{2+} and the in situ polymerization of pyrrole. From the CV results, the prepared Fe-MWNT and Fe-MWNTs/PPy electrodes showed pseudo-capacitive characteristics in terms of their electrochemical reversibility and reactivity. Charge-discharge measurement of the prepared electrodes at 0.5 A/g yielded specific capacitances of 20, 60, and 73 F/g for MWNTs, Fe-MWNTs, and Fe-MWNTs/PPy, respective-

ly. Among these electrodes, the Fe-MWNTs/PPy electrode exhibited excellent capacitive performance and had a high specific capacitance from -0.9 to 0 V in 1 M Na₂SO₃ electrolyte due to pseudo-capacitance stemming from the redox reaction of Fe₃O₄ and the high electric conductivity and increased charge transfer between Fe-MWNTs and PPy.

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