Nickel oxide/carbon nanotubes nanocomposite for electrochemical capacitance

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Abstract
We have fabricated supercapacitor electrodes with nickel oxide (NiO)/carbon nanotubes (CNTs) nanocomposite formed by a simple chemical precipitation method. The presence of CNT network in the NiO significantly improved (i) the electrical conductivity of the host NiO by the formation of conducting network of CNTs and (ii) the active sites for the redox reaction of the metal oxide by increasing its specific surface area. This increased the specific capacitance by 34% at a percolation limit of 10 wt.% of CNTs. In addition, we also found that the power density and cycle life were improved. We will further show that the specific surface area of the composite is closely related to the specific capacitance.

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1. Introduction

The supercapacitor (also called electrochemical capacitors) has several advantages of high power density, long cycle life, short charge time, and safety over the battery, and attracts great interests for energy storage devices [1,2]. Although the activated carbons are commercially available, a new material with high capacitance is always desirable [3–5]. Nanocomposites of conducting polymers and carbon nanotubes (CNTs) have been attempted for this purpose [6–8]. Transition metal oxides have been also considered as the promising materials for supercapacitors [9–21]. Noble metal oxides, such as RuO2 and IrO2 have been identified as the ideal electrode materials for supercapacitors because of their remarkable specific capacitance, good electrical conductivity, and high chemical stability [9,10]. However, the high cost and scarce source of these materials retarded their commercial acceptance. Recent researches have been focused on cheap transition metal oxides. A sol–gel method has been introduced to produce the porous nickel oxide (NiO) but the long process time and poor controllability have been a serious drawback for further application [11]. The electrochemical method has an advantage of controllability but is not suitable for mass production [12–15]. Other approach is required to improve such drawbacks if possible.

NiO electrode has high resistivity, which is a serious drawback to apply for practical applications to supercapacitors. It is crucial to enhance the electrode conductivity in order to improve the energy density and power density of electrodes. Moreover, the specific surface area of electrodes is directly related to the specific capacitance. However, the specific surface area of the NiO is in general not high enough for high capacitance. The carbon nanotube has been known to yield high conductivity and large specific surface area [22–25]. Adding CNTs in NiO electrode is therefore expected to provide a chance to improve the performance of the NiO and supercapacitors. In this report we propose a nanocomposite
consisting of nickel oxide and carbon nanotube and apply it to an electrode material for supercapacitors. The nanocomposite was prepared by a simple chemical precipitation followed by thermal annealing. This approach is easy to control and straightforward, which is suitable for production in large quantity. We find that the conductivity of the nanocomposite is greatly improved by with an addition of CNTs in the NiO, giving rise to high capacitance, high power density, and long cycle life.

2. Experimental

The nanocomposite was prepared by a simple chemical precipitation followed by thermal annealing. The CNTs used were multi-walled CNTs produced thermal chemical vapor deposition (CVD) process, which were provided from Iljin Nanotech, Korea. The pristine CNTs were refluxed in 68 wt.% HNO3 for 20 h for the purpose of effective dispersion, and then washed by filtering. The refluxed CNTs were suspended by ultrasonication for 3 h in deionized water. The nickel acetate tetrahydrate $[\text{Ni(CH}_3\text{COO)}_2\cdot 4\text{H}_2\text{O}]$ powder was added to get 0.2 M solution of nickel acetate in the CNT suspension. Ammonium hydroxide of 0.5 M was then dropped into this suspension to get nickel hydroxide on CNTs. The obtained suspension was further centrifuged to separate the nanocomposite of nickel hydroxide and CNTs. The obtained nanocomposite was then mixed again with deionized water with a volume ratio of 1:1. The electrodes were formed by dip-coating on Ni-foam into the nanocomposite suspension, where the Ni-foam was served as a current collector. After dried in air, these samples were annealed at 280–320 °C for 1.5 h.

The X-ray diffractionometry (XRD), field-emission scanning electron microscopy (FE-SEM) and four probe techniques were used to characterize structural and electrical properties of samples. Charge/discharge, ac impedance, and cyclic voltammetry (CV) test were executed to characterize the electrochemical properties. The Brunauer–Emmett–Teller (BET) surface area of the bare NiO and NiO/CNT nanocomposite was measured by a surface area analyzer (Micrometrics ASAP2010, USA) by the $N_2$ adsorption isotherms at 77 K. A unit cell for the capacitor was fabricated with two electrodes separated by a thin polymer (Celgard) in 2.0 M KOH aqueous solution as the electrolyte.

The cell was charged at a constant voltage of 0.9 V for 10 min, and then discharged at a constant current density of 10–100 mA/g. The discharge capacitance of the test cell was then calculated by $C = \frac{I_d \times \Delta t}{\Delta V}$, where $I_d$ is the constant discharge current, and $\Delta t$ is the discharge time, $m$ is the mass of electrode materials and $\Delta V$ is the voltage change at a constant current discharge.

The ac impedance of a unit cell in the frequency range from 100 kHz to 10 mHz was measured by an Electrochemical Impedance Analyzer (Zahner Electrik, USA). Cyclic voltammetric measurement of a unit cell was also performed with a Potentio-Galvanostat (EG&G 273A, USA).

3. Results and discussion

Fig. 1(a) shows the field-emission scanning electron microscope image of the pristine multi-walled CNTs. The pristine CNTs are a few micrometers in length and some of them are even longer. Only 5 wt.% of carbonaceous particles are included in the sample, which was estimated from the thermogravimetric analysis (TGA). The diameters are widely distributed in the pristine sample with smaller ones of 30–40 nm and larger ones of about 60–70 nm. The CNTs are randomly entangled and cross-linked. Fig. 1(b) shows the FE-SEM image of bare NiO powder. The primary NiO powder consists of small particles, and some primary particles aggregate into large secondary particles. The CNTs are well dispersed in the NiO and form a network among NiO powders, as shown in Fig. 1(c). We note that the CNT diameters are in the range of 20–30 nm, which are smaller than those of the pristine sample, and furthermore the CNTs are more severely curved in the nanocomposite. This indicates that the CNTs were damaged to some extent and the originally bundled CNTs were dispersed into individual CNTs during the reflux and sonication process [24,25]. The bare NiO and NiO/CNT nanocomposite clearly show the diffraction peaks from various directions of NiO in the X-ray diffraction pattern, as shown in Fig. 1(d). This suggests that the prepared NiO nanoparticles are crystalline. The CNT peak is also clearly seen near 26° in the NiO/CNT nanocomposite, which is typical for multi-walled CNTs [26]. The XRD peak widths are used to estimate the average sizes of the NiO crystallites in the bare NiO and NiO/CNT nanocomposite from the Scherrer equation,

$$d = \frac{K \lambda}{(\beta \cos \theta)}$$

where $\lambda$ is the full width at half-maximum in terms of 2θ, $\lambda$ is the incident radiation wavelength, $\theta$ is the angle of the diffraction, $K$ is a constant (taken as 0.9), and $d$ is the crystallite size [18].

According to Eq. (1), average sizes of the NiO crystallites in the bare NiO and NiO/CNT nanocomposites are about 17 and 10 nm, respectively. The CNTs with high specific surface area can act as a template for a nucleation of the NiO, and furthermore the reflux and sonication process creates more defect sites on the CNT walls, thus creating more effective nucleation sites. Therefore, we expect the size of NiO crystallites in the nanocomposite to be smaller than that of the bare NiO. The NiO crystallites with smaller sizes should be beneficial for higher specific surface area and more active sites for redox action of the NiO [27,28].

Fig. 2(a, b) show the cyclic voltammetry behavior of the bare NiO and NiO/CNT (10%) nanocomposite, respectively. Both CV curves reveal no current peaks and furthermore...
they are nearly symmetric with respect to the zero-current line. This indicates that both electrodes have the characteristic of a capacitor with constant charging and discharging rates over a complete cycle. The NiO/CNT nanocomposite electrode shows more rectangular shape in the CV curve and therefore closer to an ideal capacitor than the bare NiO does, following similar properties of CNTs [26]. The charging and discharging rates of the NiO/CNT nanocomposite is much faster than those of the bare NiO. This property is related to not only the redox reaction rate but also the resistivity of the electrode. Since CNTs have much higher conductivity than NiO, it is easy to imagine that the NiO/CNT nanocomposite reveals good conductivity compared to that of NiO. This will be discussed in the following paragraph.

Fig. 3 (a) shows dependence of specific capacitance on the discharge current density for the bare NiO and NiO/CNT (10%) nanocomposite. The specific capacitances of the bare NiO and NiO/CNT (10%) nanocomposite are 122 and 160 F/g, respectively at a discharge current density of 10 mA/g. In general, the specific capacitance decreases gradually with increasing discharge current density due to large IR drop at a large discharge current density that leads to the small specific capacitance. However, the specific capacitance is quite independent of the discharge current density in the NiO/CNT (10%) nanocomposite, whereas the specific capacitance of the bare NiO decreases with increasing discharge current density. This difference originates from the internal resistance of electrodes. The respective specific capacitance of the bare NiO and NiO/CNT (10%) nanocomposite drops by 34% and 13% even at very high discharge current density of 100 mA/g, which is caused by the severe IR drop of the resistive electrodes.
Fig. 3. (a) Specific capacitance of the bare NiO and NiO/CNT (10%) composite as a function of the discharge current density. (b) Cycle test of the specific capacitance of the bare NiO and NiO/CNT (10%) composite.

Fig. 3(b) shows the cycle test of two samples. The specific capacitance of the NiO/CNT nanocomposite is slightly increased at 60 cycles, which is probably due to insufficient activation process. The NiO/CNT (10%) nanocomposite reveals stable specific capacitance over 100 cycles. This suggests that the NiO/CNT nanocomposite is similar to the activated carbons in terms of stability, which usually swell and shrink in the electrolyte and thus have no long cycle life [1,6].

The complex-plane impedance plots of unit cells of the bare NiO and NiO/CNT nanocomposite are shown in Fig. 4(a). The intercept at the real impedance ($Z'$) axis of those plots indicates the combined series resistance of electrodes, electrolyte, current collectors, and the contact resistance between electrodes and current collectors. The electrical resistances of electrolyte and current collectors of both devices are equivalent. The intercept of the NiO/CNT (10%) nanocomposite is about 5 Ω, whereas this value for the bare NiO is about 93 Ω. The enhancement of the conductivity of the NiO/CNT nanocomposite is huge even with a CNT composition of only 10 wt.%. The conductivity enhancement is dramatically seen in the typical four-point probe dc measurement, as shown in Fig. 4(b). The resistivity decreases exponentially with increasing CNT compositions and reaches the resistivity of bare CNTs at a CNT composition of 30 wt.%, which is a percolation limit, where the electrical resistivity of NiO/CNT nanocomposites is closely similar to that of CNTs. The improvement of the electrode resistance is directly related to the power density. Since the power density is expressed by $V^2/4R$, where $V$ is the voltage between two electrodes and $R$ is the equivalent series resistance, we expect the power density to be improved by about 19 times in the NiO/CNT nanocomposite. The average increase of the power density from the Ragone plot is determined to be roughly 18 times, in excellent agreement with the predicted value. The conductivity enhancement is also related to the capacitance and energy density. The capacitance is increased by 30% in the NiO/CNT nanocomposite, which is linearly proportional to the energy density. This suggests that the energy density is less closely related to the electrode resistance.

Fig. 5(a) shows the dependence of specific capacitance on the mass fraction of CNTs in the NiO/CNT nanocomposite. The specific capacitance increases when the mass fraction of CNT increases up to 10%, and then decreases with further increasing CNT mass fraction. This strongly suggests...
that the specific capacitance of the NiO/CNT nanocomposite originates not only from electric double layer capacitance that is mainly related to specific surface area but also from pseudocapacitance that is closely related to redox reaction of NiO. The specific surface area of the NiO/CNT nanocomposite, however, increases rapidly up to 200 m²/g at 10% of the CNT mass fraction and then increases slowly to saturate to 251 m²/g of the bare CNT. The increasing rate of the surface area becomes smaller after 10% of CNT mass fraction. After 10% of CNT mass fraction, the reduction of the NiO mass fraction in the NiO/CNT nanocomposite affects the specific capacitance more severely than the increment of surface area by the CNT mass fraction. This is a strong evidence that the specific capacitance of the NiO/CNT nanocomposite is dominated by the redox reaction of NiO. The role of CNTs is to supply more active sites for the redox reaction of NiO by increasing the specific surface area, in addition to reduce the electrode resistivity.

Fig. 5(b) shows the dependence of the specific capacitance on annealing temperature. The specific capacitance of the bare NiO and NiO/CNT nanocomposite is very sensitive to the annealing temperature. When the annealing temperature increases from 280 to 290 °C, the specific capacitance increases, which may result from an effective formation of NiO for redox reaction. The specific capacitance decreases with further increasing annealing temperature to 320 °C. This may result from the increment of the size of NiO crystallites that decreases surface area in turn and thereby decreases the number of active sites of NiO.

4. Conclusions

We have provided a simple chemical precipitation method for formation of the NiO/CNT nanocomposite. The CNTs in the NiO/CNT nanocomposite form electrically conductive network, decreasing the resistivity of electrode materials, and thereafter decreasing the ESR of supercapacitors. In our case, the percolation limit is achieved at a CNT mass fraction of 30%. However, this limit can be reduced if one improves the dispersion of CNTs in advance for formation of the NiO/CNT nanocomposite. The CNTs with high specific surface area is required to form high electrical double-layer capacitance and more active sites for redox reaction of metal oxides. Our approach provides a clue for practical applications of metal oxides by improving the electrochemical properties.

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References