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Letter

Carbon nanotube–zinc oxide electrode and gel polymer electrolyte for electrochemical supercapacitors

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ABSTRACT

The electrochemical supercapacitors (ESs) were assembled with carbon nanotube (CNT) and zinc oxide (ZnO) composite as the electrode and gel polymer as the electrolyte. The CNT film was fabricated using screen-printing method and ZnO was deposited by ultrasonic spray pyrolysis (USP) in different time from 2 to 30 min. The analysis of cyclic voltammetry (CV) shows that the ESs of CNTs with ZnO deposited for 5 min exhibited the optimized electrochemical capacitive properties, and the specific capacitance reaches 126.3 F/g by CV test, much better than that of the pure CNTs.

1. Introduction

Electrochemical supercapacitors (ESs) are regarded as ideal energy storage devices to meet the urgent needs in electric and electronic devices, such as hybrid electric vehicle-based green transportation, backup energy sources, since they have high power density and long cycle life [1,2]. The performance of the ESs is closely related with the electrode and electrolyte. Carbon nanotubes (CNTs) have attracted much attention as a good candidate as the electrodes in ESs, due to their chemical stability, high conductivity, large specific surface area, etc. [3–5]. To further improve capacitive performance of ESs, the metal oxide, such as RuO_2, NiO_x, and IrO_2, have been introduced into CNT electrodes [6]. However, most of the metal oxides suffer from the poor high-rate capability and expensive cost [7]. Therefore, further scan of metal oxide suitable for ESs is necessary. Currently much interest has been focused on zinc oxide (ZnO) due to its excellent optical and electrical properties, which has enabled its application in electronic and optoelectronic devices, such as solar cells, gas sensors, short-wavelength light-emitting diodes [8,9]. However, the potential application of ZnO combined with CNTs as the electrode materials in ESs is seldom discussed.

Liquid electrolytes including aqueous and organic solutions are extensively chosen as the electrolytes [10]. However, devices with liquid electrolytes have to risk the liquid leakage, pollution to the environment and loss of electrolyte through drying. As a result, solid state electrolyte is in great need to replace the liquid one because of its high ionic conductivity, wide operation temperature and electrochemical window and no leak [11,12]. As a kind of solid electrolyte, gel polymer such as poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA) and polyaniline (PANI) with alkali or inorganic acid is widely investigated [12–14]. Nevertheless, poly(vinyl alcohol) (PVA) with polyacid as an electrolyte is scarcely reported so far.

In this work, ZnO–CNT composite and PVA–phosphomolybdic acid (PMA) gel polymer are employed as the electrode and electrolyte of ESs, respectively. CNTs are first screen-printed on conductive copper and nickel alloy substrates and then ZnO is deposited on CNTs by a low-cost and simple ultrasonic spray pyrolysis (USP) method. The capacitive properties of the as-made ESs are investigated.

2. Experimental

The CNTs (Shenzhen Nanotech Port Co., Ltd.) were mixed with ethyl cellulose (Sinopharm Chemical Reagent Co. Ltd.) and terpineol (Fluka), and stirred in an agate bowl till the CNTs were homogeneously dispersed in the mixture. CNTs were screen-printed on CuNi alloy with the thickness of 10 μm and then heated at 100 °C for 1 h. A precursor solution was prepared by mixing zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$, Fluka] and distilled water. ZnO was deposited on the CNTs from the precursor solution by USP (402AI) at a frequency of 1.65 MHz. The flow rate of air used as a carrier gas was 2 ml/min. The substrates of CNTs were kept at 400 °C and the CNT–ZnO electrodes with ZnO deposited in 2, 5, 10, 20 and 30 min (named as CNT–ZnO-2, CNT–ZnO-5, CNT–ZnO-10, CNT–ZnO-20, CNT–ZnO-30) were obtained. The mixture of PVA (15 wt%) and PMA (30 wt%) was employed as the gel polymer electrolyte. The experimental cells were assembled as two symmetrical electrodes laminated together with the electrolyte in between. The surface morphology and structure of the CNTs and CNT–ZnO were observed by scanning electron microscopy (SEM, JSM-5910LV), and X-ray diffraction spectroscopy (XRD, Siemens D5005) with Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 20 mA, respec-

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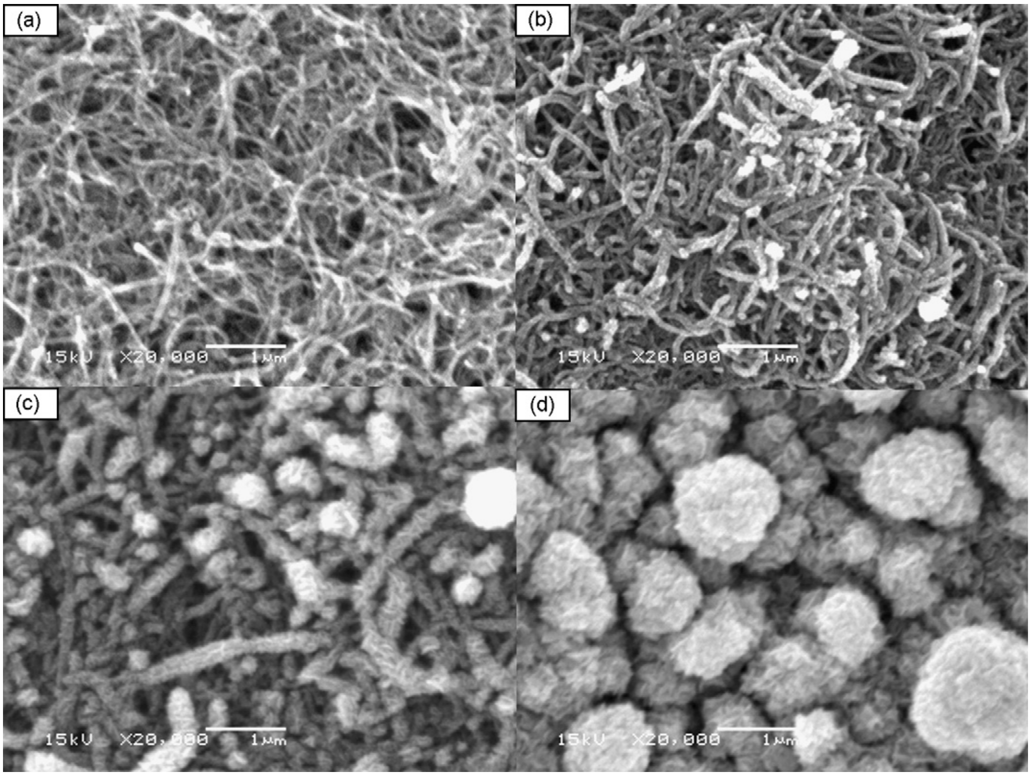

Fig. 1. SEM images of (a) the CNTs screen-printed on Cu–Ni substrate and the CNT–ZnO composite electrodes with ZnO deposited in (b) 5 min, (c) 10 min and (d) 30 min.

tively. The capacitive properties of the ESs were studied by cyclic voltammetry (CV, CHI 1111A).

3. Results and discussion

Fig. 1(a) shows the SEM morphology of the CNTs screen-printed on Cu–Ni, randomly entangled, and diameter of the CNTs is about 10 nm. Fig. 1(b)–(d) is SEM images of the CNT–ZnO composite with ZnO deposited in different time. As can be seen in Fig. 1(b), ZnO scatters on the CNTs in the CNT–ZnO-5 sample. With the increase of deposition time, the amount of ZnO increases. The particles of ZnO settle down on the walls of the CNTs and wrap them outside (Fig. 1(c)). In longer deposition time, especially 20 and 30 min (Fig. 1(d)), the ZnO particles tend to agglomerate and cover the CNT film surface.

The XRD patterns of the electrodes in Fig. 2 are analyzed by PCPDFWIN databases. For CNT–ZnO-2 and CNT–ZnO-5 samples, the CNTs are dominating in the composite. $2\theta = 26.2^\circ$ corresponding to $\{0\,0\,2\}$ *d*-spacing of the CNTs can be observed and three peaks at 2θ of 44.0°, 51.2° and 75.3° correspond to the $\{1\,1\,1\}$, $\{2\,0\,0\}$ and $\{2\,2\,0\}$ planes of carbon [PDF #43-1104], respectively. The peaks in the XRD profiles at $2\theta = 38.3^\circ$ and 65.1° are caused by the chemical residual impurity (ethyl cellulose and terpineol). With the increase of deposition time, the peaks of CNTs become weaker and the ZnO peaks tend to be sharper due to the domination of ZnO over the surface of the electrodes. The diffraction peaks of CNT–ZnO-30 are in accordance with ZnO [PDF #79-0205] and no CNT peaks are observed, indicating that the ZnO is well formed and almost cover the CNT film by USP process.

Capacitive characteristics of the experimental cells are investigated by CV measurements. The potential range is set at −0.5 to 0.5 V with the scan rate of 50 mV/s. The cyclic voltammograms are presented in Fig. 3. ESs can be divided into two types: electric double-layer capacitor and redox supercapacitor. For the former type, double-layer capacitance arises from charge separation at the electrode/electrolyte interface. While for the latter one, reversible Faradic reactions contribute to the pseudo-capacitance [15]. The specific capacitance (C_{sp}) of the ESs is calculated by

$$C_{sp} = \frac{2I}{s \times m} \tag{1}$$

where I is the charge current, s is the scan rate, and m is the mass of the electrode. For the cell with CNT electrodes, the value of capacitance (Table 1) is 92.7 F/g. And peaks are observed during the cycle, which is supposed to be the redox reactions caused by the organo-functional group of the residual organic materials in the electrodes. For the CNT–ZnO-2 and CNT–ZnO-5 electrodes, the capacitances

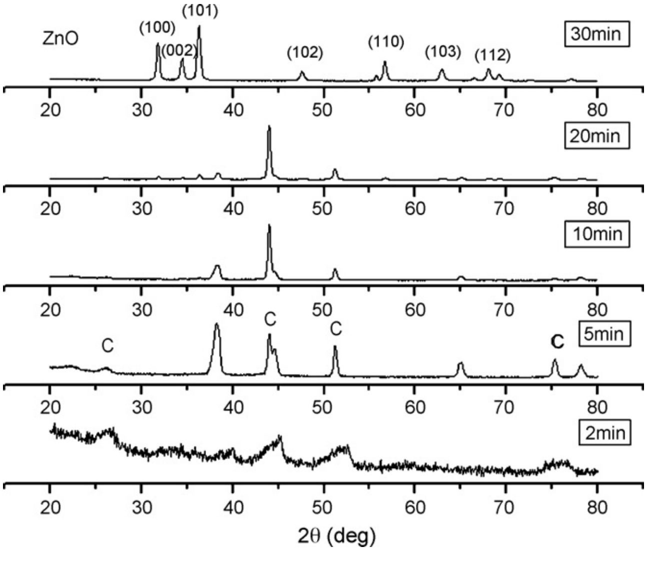

Fig. 2. XRD patterns of CNT–ZnO composite films.

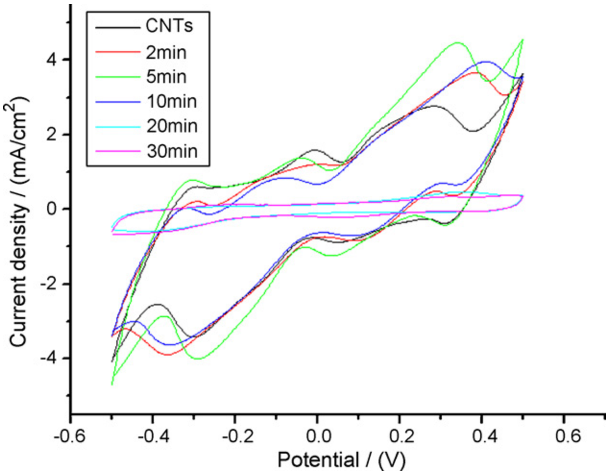

Fig. 3. Cyclic voltammograms of the ES cells with different CNT–ZnO composite electrodes.

Table 1
Specific capacitance C_{sp} calculated by CV curves.

Samples	C_{sp} (F/g)
CNTs	92.7
CNT–ZnO-2	99.7
CNT–ZnO-5	126.3
CNT–ZnO-10	96.9
CNT–ZnO-20	13.8
CNT–ZnO-30	12.4

gradually increase to 99.7 and 126.3 F/g, respectively. However, the C_{sp} of CNT–ZnO-10 sample decreases to 96.9 F/g, still higher than that of pure CNTs. The pseudo-capacitance derived from the Faradic reactions caused by ZnO contributes to the increase of the total capacitance.

However when the deposition time of ZnO further increases to 20 and 30 min, the capacitor behavior deteriorates. As can be seen in Fig. 3, the charge current density of CNT–ZnO-20 and CNT–ZnO-30 is apparently lower even than that of the pure CNTs, and the capacitances decrease to 13.8 and 12.4 F/g consequently. The CNTs are totally covered by ZnO which has a relatively high resistance and thus lower the conductivity of the electrodes significantly. Furthermore, the accumulation of ZnO destroys the net structure formed by CNTs and thus lowers the specific surface area, which disturbed the protons and electrons to be adsorbed on the surface of the electrode.

4. Conclusions

In summary, ES cells with high capacitance have been developed based on CNT–ZnO electrode and PVA–PMA gel electrolyte. CNT–ZnO electrodes exhibit better capacitive performance as compared to the pure CNTs. When ZnO is deposited in 5 min, CNT–ZnO electrode has the optimized performance with the specific capacitance of 126.3 F/g. However, excess ZnO in CNT–ZnO composite will result in agglomeration of ZnO and decrease the specific area of the electrodes, and thus deteriorate the capacitive performance.

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