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Electrochemical behaviors of graphene–ZnO and graphene–SnO_2 composite films for supercapacitors

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ABSTRACT

Graphene, graphene–ZnO and graphene–SnO_2 films were successfully synthesized and used as electrode materials for electrochemical supercapacitors, respectively. The screen-printing approach was employed to fabricate graphene film on graphite substrate while the ZnO and SnO_2 were deposited on graphene films by ultrasonic spray pyrolysis. The electrochemical performances of these electrodes were comparatively analyzed through electrochemical impedance spectrometry, cyclic voltammetry and chronopotentiometry tests. The results showed that the incorporation of ZnO or SnO_2 improved the capacitive performance of graphene electrode. Graphene–ZnO composite electrode exhibited higher capacitance value (61.7 F/g) and maximum power density (4.8 kW/kg) as compared with graphene–SnO_2 and pure graphene electrodes.

1. Introduction

Carbon and metal oxide materials are two hotspots as electrode materials for electrochemical supercapacitors (ESCs), in which energy is stored due to the formation of an electrical double layer at the interface of the electrode or due to electron transfer between the electrolyte and the electrode through fast Faradic redox reaction. If integrating the two kinds of materials into the electrodes of ESCs, their capacitive performance will be enhanced largely because most of the metal oxide can contribute pseudocapacitance to the total capacitance apart from the double-layer capacitance from carbon materials [1–3]. As a rising star in carbon family, graphene has attracted a great deal of attention in recent years. Chemical approaches, for the large-scale production of highly conducting graphene sheets, which speed up the application of graphene, have become reality [4–6]. Due to its good conductivity, superior chemical stability, large surface-to-volume ratio, suitable pore size distribution and good capacitive performance, graphene has competed with carbon nanotubes (CNTs), activated carbon, etc. to be used as the electrode of ESCs. Stoller et al. [7] evaluated the electrochemical characteristics of graphene as the electrode of ESCs and a specific capacitance of 135 F/g in 5.5 M KOH aqueous electrolyte had been achieved. Vivekchand et al. [8] studied the capacitive behavior of graphene and a better capacitive performance of graphene up to 117 F/g in aqueous H_2SO_4 solution under a potential from 0 to 1 V and 75 F/g in PYR_{14}TFSI ionic liquid with an operating voltage extended to 3.5 V had been obtained as compared with single-walled and multi-walled CNTs. Wang et al. [9] employed graphene as the electrode of ESCs which exhibited a maximum specific capacitance of 205 F/g in an aqueous electrolyte solution and kept excellent long cycle life along with ~90% specific capacitance retained after 1200 cycle tests. Lv et al. [10] fabricated the graphene by vacuum-promoted low-temperature (200 °C) exfoliation of graphite oxide and a high capacitance up to 264 F/g in aqueous system had been obtained. These distinguishable electrochemical behaviors of graphene may be caused by residual oxygen-containing groups in the graphene because the chemically prepared graphene contains a considerable amount of oxygen [11,12] and the fully accessible surface to electrolyte ion because both sides of a broad range of graphene sheets can be exposed to the electrolyte [9].

Currently one obvious challenge is to utilize these 2D carbon nanostructures as conductive carbon mats to anchor metal oxide materials to form new nanocomposite hybrid materials with potential application in optoelectronics and energy conversion devices. Lambert et al. [13] studied the synthesis of TiO_2-graphene nanocomposite by hydrolysis of TiF_4 in the presence of an aqueous dispersion of graphene oxide. Williams et al. [14] fabricated TiO_2-graphene nanocomposite by UV-assisted reduction of graphene oxide in TiO_2 suspensions. Paek et al. [15], Wang et al. [16] and Yao et al. [17] fabricated the graphene–SnO_2 composite electrode

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materials and studied their application in lithium-ion batteries. Li et al. [18] reduced graphene oxide with $SnCl_2$ to gain graphene/SnO_2 composite which achieved a better capacitive behavior with a specific capacitance of 34.6 F/g in 1 M H_2SO_4 solution. In our previous work [19], graphene–ZnO composite film was fabricated by ultrasonic spray pyrolysis (USP) and a higher specific capacitance about 11.3 F/g had been obtained by comparison to pure graphene or ZnO electrode. However, as promising hybrid electrode materials for ESCs, the exploration on graphene-metal oxide composite materials is not nearly enough so far.

In this work, we comparatively study the electrochemical characteristics of graphene–ZnO, graphene–SnO_2 and pure graphene electrodes in 1 M KCl electrolyte solution. Such a comparison between the performances of graphene-metal oxide composite materials is reasonably envisaged not only to be useful for understanding the individual contribution from graphene and metal oxides but also to form a fundamental basis for ESCs applications. The graphene films were screen-printed on graphite sheets used as current collector, and the metal oxides were deposited on the surface of graphene by USP method. The electrochemical tests show that graphene–ZnO composite film performs a better capacitive behavior as compared with pure graphene or graphene–SnO_2 electrodes.

2. Experimental

Graphene was synthesized via hydrazine reduction of exfoliated graphite oxide as described in our previous works [20]. The as-synthesized graphene was mixed with ethyl cellulose (Sinopharm Chemical Reagent Co. Ltd.) and terpineol (Fluka) in an agate bowl until the graphene homogeneously dispersed in the mixture. After that, the mixed slush was coated on graphite sheets by screen-printing approach and then heated for 1 h at the temperature of 100 °C. The specific surface area of the screen-printed graphene electrode measured by Brunauer–Emmett–Teller method (Micromeritics Tristar 3000) from N_2 adsorption–desorption isotherms is about 25.4 m^2/g. This value is higher than 14.2 m^2/g of pristine graphene in our previous works [20] and shows that the screen-printing method does not harm the specific surface area of graphene electrode. ZnO and SnO_2 were deposited onto the graphene film by USP (402AI) at a frequency of 1.65 MHz using 0.3 M zinc acetate (Sinopharm Chemical Reagent Co. Ltd) and 0.3 M tin acetate (Sinopharm Chemical Reagent Co. Ltd.) aqueous solution, respectively. The substrates' temperature, the flow rate of air as carrier gas and deposition time were set at 430 °C, 2 ml/min and 5 min, respectively.

The surface morphology, structure and composition of the samples were characterized by transmission electron microscopy (TEM, JEM-2100), field-emission scanning electron microscopy (FESEM, Hitachi S-4800), energy dispersive X-ray fluorescence spectrometer (EDX, S-4700), and X-ray diffraction spectroscopy (XRD, Siemens D5005), respectively. The electrochemical impedance spectrometry (EIS), cyclic voltammetry (CV) and chronopotentiometry experiments were investigated by using CHI 660C in a three-electrode mode, including a standard calomel electrode as reference electrode and a platinum foil as counter electrode. The experiments were operated at room temperature with 1 M KCl solution as electrolyte. The specific capacitance (C_{sp} in F/g) could be obtained from the CV process according to Eq. (1) or from the charge–discharge process according to Eq. (2):

$$C_{sp} = \frac{\bar{i}}{\nu \times m} \tag{1}$$

where $\bar{i}$ is the average current (A), ν is the scan rate (V/s) and m is the mass of electrode (g):

$$C_{sp} = \frac{i \times t}{\Delta V \times m} \tag{2}$$

where i, t and ΔV are the constant current (A), charge/discharge time (s), potential difference (V), respectively.

3. Results and discussion

Fig. 1(a) shows the TEM image of graphene nanosheets consisting of three or four carbon atom layers [20]. The corrugated and scrolled sheets resemble crumpled silk veil waves. Graphene layers interact with each other to form an open pore system, through which electrolyte ions easily access the surface of graphene to form electric double layers [10]. The graphitic laminar structure can be confirmed in ordered region as shown in the selected area electron diffraction pattern (SAED) in the inset of Fig. 1(a). The hexagonal symmetry of diffraction spots verifies the well crystalline structure of the graphene nanosheets [21].

Fig. 1(b) shows the FESEM image of as-synthesized graphene nanosheets. It can be seen that most of graphene nanosheets are curled and entangled together. Fig. 1(c) and (d) draw the FESEM images of graphene–ZnO and graphene–SnO_2 electrodes. It is clearly observed that the graphene nanosheets are covered by densely packed and irregularly shaped ZnO or SnO_2 grains, spreading in a large-scale.

The existence of Zn and Sn in the composite films has been proved by the peaks of Zn and Sn in EDX data (not shown here), respectively. XRD analysis in Fig. 2(a) further shows that both of ZnO and SnO_2 appear excellent crystal structures. Graphene nanosheets exhibit a strong (0 0 2) diffraction peak at $2\theta = 26^\circ$ and a (1 0 0) diffraction peak at 44.5° [22]. The peak at 38.3° is caused by the chemical residual impurity (ethyl cellulose and terpineol) [23]. The peaks at 54.8° and 65.1°, as shown in the XRD pattern of graphene–ZnO film, correspond to the (1 1 1) and (2 0 0) planes of ZnO [PDF#77-0191], respectively. Correspondingly, the three peaks at 51.9°, 54.6° and 65° in the XRD profile of graphene–SnO_2 film are ascribed to the (0 0 2), (0 2 1) and (1 1 2) planes of SnO_2 [PDF#29-1484].

CV curves were conducted at a scan rate of 50 mV/s under the potential from −0.5 to 0.5 V. Fig. 2(b) shows CV curves of various electrodes. The shapes of CV loop in our experiment are close to rectangle, indicating a good capacitive behavior in the ESCs [24]. It can be seen that the capacitive performance of graphene–ZnO electrodes obviously better than those of graphene–SnO_2 and pure graphene electrodes. The specific capacitances of graphene–ZnO, graphene–SnO_2 and graphene electrodes calculated from CV curves are 61.7, 42.7 and 38.9 F/g, respectively. It means that the contribution from ZnO to the total capacitance is higher than the one from SnO_2, apart from the double-layer capacitance from graphene. The CV properties of graphite substrate is also measured and compared in Fig. 2(b) and it shows that the capacitive contribution from graphite substrate to the whole electrode is very low.

EIS were conducted at a frequency range of 0.1 Hz to 100 kHz. Fig. 3 shows the Nyquist diagrams of the electrodes. A semicircle arc and a straight line have been observed. The high-frequency arc corresponds to the charge transfer limiting process and is ascribed to the double-layer capacitance (C_{dl}) in parallel with the charge transfer resistance (R_{ct}) at the contact interface between electrode and electrolyte solution. R_{ct} can be directly measured as the semicircle diameter [25]. It is noticed that graphene–SnO_2 electrode has higher R_{ct} (1.5 Ω) than graphene–ZnO electrode (0.6 Ω) but both values are much smaller than the one of pure graphene electrode (2.5 Ω), indicating that the incorporation of ZnO or SnO_2 improves the charge transfer performance of graphene electrode. At low fre-