Journal of Alloys and Compounds 660 (2016) 99–107

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Deposition of MnO_2 nanoneedles on carbon nanotubes and graphene nanosheets as electrode materials for electrochemical capacitors

Chien-Te Hsieh*, Dong-Ying Tzou, Wen-Yen Lee, Jo-Pei Hsu

Department of Chemical Engineering and Materials Science, Yuan Ze University, 32003 Taoyuan, Taiwan

ARTICLE INFO

Article history:
Received 30 July 2015
Received in revised form
31 October 2015
Accepted 3 November 2015
Available online xxx

Keywords:
Electrochemical capacitors
Manganese oxide crystals
Graphene sheets
Carbon nanotubes
Specific capacitance

ABSTRACT

Hierarchical carbon nanotubes (CNTs) and graphene nanosheets (GNs) supported MnO_2 nanoneedles have been synthesized through a facile chemical-wet route without any further thermal treatment. The electrochemical capacitive performances of MnO_2-based composite electrodes are analyzed using cyclic voltammetry, galvanostatic charge–discharge cycling, and impedance spectroscopy. It is found that the electrochemical utilization of MnO_2 nanoneedles is effectively enhanced by the synergistic effect that combines the MnO_2 crystals and the carbon supports, raising more active sites available for formation of charge transfer and electric double-layer in the hybrid architecture. The maximal specific capacitance of capacitors attains as high as 440 F g^{-1}. The specific energy of MnO_2/GN capacitor can reach as high as ~40 Wh kg^{-1} at a specific power of 20,000 W kg^{-1}, analyzed by the Ragone plot. The improved performance can described to the fact that the robust design of hybrid structure is capable of (i) maximizing the utilization of MnO_2 nanoneedles and (ii) leading to fast chemical reaction kinetics including ionic electro-sorption and charge transfer. This method provides a straightforward approach to deposit MnO_2 onto GNs as electrode materials for various energy-storage devices.

1. Introduction

Over the past two decades, lithium-ion batteries and electrochemical capacitors (ECs) have received great attention as the key energy storage systems for the applications in portable consumer electronics and electric vehicles [1,2]. Recently, manganese dioxide (MnO_2) has been admitted as a potential electrode material in EC applications due to its natural abundance, low toxicity, environmental compatibility, cost effectiveness, and high theoretical specific capacitance ~1300 F g^{-1} [3,4]. Basically, a Mn^{4+}/Mn^{3+} redox pair involving a single-electron transfer is responsible for the MnO_2 pseudocapacitive behavior [5]. It is generally recognized that the energy storage mechanism of MnO_2-based ECs mainly originates from the accumulation of ionic charges in the redox reaction and the double layer at the electrode/electrolyte interface. Accordingly, pioneering studies have reported synthesis of MnO_2 nanostructures by using different fabrication routes such as hydrothermal synthesis [6–8], microwave-assisted synthesis [9], assembling flocculation method [10], $MnCO_3$ and carbon nanotube (CNT)-based template synthesis [11,12], *in situ* redox reaction [13], and facile physical mixing method with the spent battery powder [14]. However, two major challenges appear when applying MnO_2 as electrode materials because of its rigid metal oxide nature and poor conductivity [3]. First, a dramatic volume expansion would occur in host matrix of bulk MnO_2 electrodes during one cyclic charging/discharging process, inducing rapid capacity decay [7]. Thus, nanostructural MnO_2 has been confirmed to be a promising candidate to minimize the volume change. Second, the poor conductivity of MnO_2 seriously hinders its electrochemical applications due to its discontinuous charge-transfer pathway. This drawback becomes more serious when assembling thick-film MnO_2 electrodes.

To achieve a better performance of ECs, one strategy to maximize the utilization of MnO_2 electroactivity is the design to enable the synergistic effects from MnO_2 nanostructures and excellent electronic conducting supports such as CNTs and graphene nanosheets (GNs). Both CNTs and GNs have been commonly studied as electrode materials for ECs owing to their high surface area, inert, and electric conductance that are responsible for store and release energy by nanoscopic charge separation at electrochemical interface between an electrode and electrolyte [3,15,16]. Thus, several approaches of using MnO_2/CNT (CNT-M) and MnO_2/GN (GN-M)

* Corresponding author.
E-mail address: cthsieh@saturn.yzu.edu.tw (C.-T. Hsieh).

http://dx.doi.org/10.1016/j.jallcom.2015.11.021
0925-8388/

composites as electrode materials for ECs have been reported in the literature [17,18]. This achievement directs us at the facile synthesis of CNT-M and GN-M electrode materials for high-performance ECs. Herein, we present an efficient chemical-wet method for preparing both composites, in which needle-like MnO_2 was deposited over the CNT and GN supports. Comparing with the other synthesis methods, the chemical-wet method does not require complex and accurate control of experimental conditions, showing a commercial feasibility in industrial scale. The ECs equipped with CNT-M and GN-M composites were electrochemically characterized by cyclic voltammetry (CV), charge–discharge cycling, and electrochemical impedance spectroscopy (EIS). Most importantly, the merit of the present work is to shed some light on how the application of one- and two-dimensional carbon nanostructures (i.e., CNTs and GNs) plays a significant role in anchoring needle-like MnO_2, showing superior electrochemical performance including high specific capacitance, low inner resistance, and excellent cycleability.

2. Experimental

The synthesis of MnO_2 nanostructures was carried out chemically starting with aqueous solutions of $KMnO_4$ and $MnSO_4 \cdot H_2O$. Herein 0.1 M $KMnO_4$ was slowly dropped into 0.15 M $MnSO_4 \cdot H_2O$ solution, and then the aqueous solutions were stirred and well mixed at ambient temperature. The chemical-wet synthesis process was performed for 6 h, thus producing precipitate in the bottom of the solution. The as-prepared precipitate was carefully washed by distilled water several times. The washing was done until the pH of the washed water was 7. After the filtration, the wetted precipitate was dehydrated in vacuum oven at 110 °C overnight. As for the preparation of CNT-M and GN-M samples, the chemical-wet synthesis was similar to the previous method with little modification. First, 2 g of carbon supports (i.e., CNTs and GNs) was poured into 0.15 M $MnSO_4 \cdot H_2O$ solution. The ionic adsorption process was performed for 3 h, ensuring a homogeneous dispersion of carbon slurry. Herein the CNTs were grown by using catalytic chemical vapor deposition, in which Ni particles and ethylene served as metallic catalyst and carbon source, respectively [19]. The GNs were prepared by using a modified Hummers' method, followed by thermal reduction in H_2-containing atmosphere. The synthesis of GNs has been reported elsewhere [20]. Second, 0.1 M $KMnO_4$ was gently plunged into the carbon slurry. The stirring process was also done at room temperature for 6 h, and the MnO_2-based composites were then collected and washed by distilled water until the pH value of the distilled water reached at 7. Similarly, the MnO_2-based composites were dried at 110 °C overnight. The schematic representation of the structural MnO_2 samples was illustrated in Fig. 1.

The phase purity of as-synthesized materials was examined by X-ray diffraction (XRD) with Cu-Kα radiation, using an automated X-ray diffractometer (Shimadzu Labx XRD-6000). The morphology and structural properties of MnO_2-based samples were further elucidated by scanning electron microscopy (FE-SEM, JEOL JSM-6701F) and transmission electron microscopy (TEM, JEOL, JEM-2100). A thermogravimetric analyzer (TGA, Perkin Elmer TA7) was adopted to calculate the amount of MnO_2 deposited on the carbon supports. The TGA analysis was carried out under an air atmosphere at a heating rate of 10 °C min^{-1} with the temperature range of 30–1000 °C. Fourier transformed infrared (FTIR) spectroscopy was used to study the surface chemistry of the carbon samples. The FTIR spectra were obtained using a Nicolet Avatar 360 FTIR spectrometer. For each sample, 32 scans in the spectral ranges were recorded with a resolution of 4 cm^{-1}.

The EC electrodes for evaluating the electrochemical performance of as-synthesized MnO_2-based materials were fabricated by dropping MnO_2-based powders onto carbon paper. Afterward, the working electrodes were assembled by pressing the MnO_2-containing carbon papers onto stainless steel foil as current collector. The electrochemical properties of ECs equipped with MnO_2 composites were investigated in a three-electrode configuration system at room temperature using 1 M Li_2SO_4 as the electrolyte solution. The electrolyte solvent used in this present work was distilled water. The selection of Li_2SO_4 electrolyte originates from the reasons that Li_2SO_4 is an excellent lithium ion conductor in the high temperature, but it is also a proton conductor in a hydrogen-containing atmosphere. Li_2SO_4 could be a good proton conductor at intermediate temperatures (600–850 °C) and so its structural and electrical properties have been intensively researched [21,22]. Herein Pt wire and Ag/AgCl electrode were used as the counter and the reference electrode, respectively. An epoxy resin was used to seal the electrode and the sealed electrode allowed an area *ca.* 2 cm^2 to be exposed to the electrolyte solution. The mass loading of electrode materials was well controlled within 0.01–0.012 g cm^{-2}. The CV measurements of MnO_2 composite electrodes were conducted within the potential range of 0–1 V vs. Ag/AgCl at sweep rate of 30 mV s^{-1}. The galvanostatic charge–discharge experiments were performed at different current densities of 0.1–1 A g^{-1}. The specific capacitance (C_S) of ECs has been evaluated using the following formula:

$$C_S = i\,\Delta t / m\,\Delta V \quad (1)$$

where i is the current used for charge/discharge, Δt is the time elapsed for the charge or discharge cycle, m is the mass of active electrode, and ΔV is the voltage interval of the charge or discharge. The three-electrode cells were also used to examine their impedance behavior, using an EIS analyzer (CH Instrument, Inc., CHI 608C). The potential amplitude of ac was set at 5 mV, and the frequency was from 0.001 Hz to 100 kHz. The above electrochemical tests were carried out at ambient temperature.

3. Results and discussion

3.1. Characterization of MnO_2-based nanocomposites

The schematic representation of the formation of different MnO_2-based structures is depicted in Fig. 1. The typical corresponding FE-SEM micrographs of MnO_2, CNT-M, and GN-M samples are shown in Fig. 2. It can be seen the formation of flower-like nanoclusters of MnO_2 with an average diameter of 300 nm through the chemical-wet route. There are a number of nanowhiskers, which protrude out of the clusters. As observed from Fig. 2(c) and (d), both CNT-M and GN-M samples appears as the MnO_2 nanoneedles decorated with the carbon supports.

The MnO_2 nanoneedles are uniformly dispersed over the surface of CNTs and GNs. The microstructures of fresh MnO_2, CNT-M, and GN-M samples were also characterized by TEM, as shown in Fig. 3. The MnO_2 precipitates are basically composed of a number of nanoneedles and nanowhiskers, forming flower-like nanoclusters. The size of the primary MnO_2 cluster is approximately 200–300 nm (see Fig. 3(a)), and the nanoneedles and nanowhiskers have an average diameter of 5–10 nm, as shown in the inset of Fig. 3(a). It has shown from Fig. 3(b) and (c) that the needle-like MnO_2 are randomly deposited over the surface of CNTs and GNs. This morphology transformation from the MnO_2 clusters to the nanoneedles could be attributed to the oxide group distributions upon surface chemistry of carbon, i.e., surface heterogeneity.

FTIR spectra of different carbon supports were recorded in the range of 4000–500 cm^{-1} in a transmittance mode, as shown in Fig. 4. It can be seen that both GN and CNT supports possess oxygen