Electrochimica Acta 117 (2014) 528–533

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Manganese dioxide nanosheet arrays grown on graphene oxide as an advanced electrode material for supercapacitors

Ying Liu[a], De Yan[a,*], Yanhong Li[a,b,c], Zhiguo Wu[a], Renfu Zhuo[a], Shuankui Li[a], Juanjuan Feng[a], Jun Wang[a], Pengxun Yan[a,b], Zhongrong Geng[c]

[a] *School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, People's Republic of China*
[b] *Key Laboratory of Solid Lubrication, Institute of Chemistry and Physics, Chinese Academy of Science, Lanzhou 730000, People's Republic of China*
[c] *School of Mechatronic Engineering, Lanzhou Jiaotong University, Lanzhou 730070, People's Republic of China*

ARTICLE INFO

Article history:
Received 4 September 2013
Received in revised form 25 October 2013
Accepted 20 November 2013
Available online 4 December 2013

Keywords:
Hydrothermal method
Manganese dioxide nanosheet
Graphene oxide
Supercapacitors

ABSTRACT

A simple hydrothermal method has been provided for synthesis of the MnO_2-GO hybrid with birnessite-type manganese dioxide (MnO_2) nanosheet arrays on graphene oxide (GO) flakes. To assess the properties of the as-synthesized hybrid for use in supercapacitors, cyclic voltammetry (CV) and galvanostatic charging/discharging (GCD) measurements are performed. The MnO_2-GO hybrid exhibits enhanced specific capacitance (213 F g^{-1} at current density of 0.1 A g^{-1}), rate capability (even 80 F g^{-1} at 10 A g^{-1}) and capacitance retention ratio (98.1% at 1 A g^{-1} after 1,000 cycles) compared with the GO and MnO_2. Furthermore, the electrochemical impedance spectroscopy (EIS) demonstrates the electrochemical resistance of MnO_2 nanosheet which directly grows on GO is reduced, indicating easier access for intercalation/deintercalation of charges in MnO_2-GO hybrid.

1. Introduction

Over the past few years, considerable effort has been devoted to the development of alternative energy storage/conversion devices with high power and energy densities because of the ever-increasing environmental problems and the up-coming depletion of fossil fuels [1]. As an intermediate system between dielectric capacitors and batteries, supercapacitors have attracted a great deal of attention owing to their higher power densities relative to secondary batteries [2,3]. Nevertheless, the disadvantages of them, such as low energy density and high production cost, have been identified as major challenges for the furtherance of supercapacitor technologies. To overcome the obstacle of low energy density, active electrode materials with high capacity performance are indispensable [4].

As one of the green supercapacitor electrode materials, MnO_2 shows great potential to replace RuO_2 due to its high specific capacitance, environmental compatibility, low cost, and abundance in nature [5,6]. It is known that, for an electrode to perform effectively in a supercapacitor cell, access of the electrolyte to as much of the internal and external electrode surface as possible is desirable. Attempts have often been made to tailor MnO_2 synthesis to give the highest specific surface area and pore volume [7–9]. Lately, the birnessite-type MnO_2 nanostructures, in which exhibit specific capacitances of over 110 F g^{-1} with surface areas of only 17 m^2 g^{-1}, are attracting great interest due to the small thickness of birnessite platelets allows the access of the electrolyte to almost all of the MnO_2 [6,10]. However, the birnessite MnO_2 nanomaterials are suffered from some disadvantages, such as poor electronic conductivity, easy aggregation and partial dissolution, thus less utilization of MnO_2 in most cases [11]. To improve the electrochemical performance, the combination of birnessite MnO_2 nanostructures with other materials such as graphene, carbon nanotubes, carbon fibers and mesoporous carbons has been investigated extensively [4,5].

On the other hand, GO has tremendous attraction, because of its unique structure, amazing electrical and mechanical properties. It has applications in wide areas including catalysts, solar cell, gas sensor, fuel cell, battery, supercapacitor, antibacterial study, and so on [12–14]. Recently, GO has been investigated as a suitable support for manganese oxide/oxyhydroxide loadings in electroactive materials for supercapacitors [11]. Chen et al. reported needle-like MnO_2-GO nanocomposite achieved the excellent capacitive behavior with the specific capacitance of 197.2 F g^{-1} at 0.2 A g^{-1} current density [15]. Wang et al. investigated MnOOH nanowire-GO and MnO_2 nanowire-GO hybrids for supercapacitors, maximum specific capacitances of 76 F g^{-1} and 155 F g^{-1} at current density of 0.1 A g^{-1} were obtained, respectively [16]. Gund et al. studied

---

* Corresponding author. School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, People's Republic of China. Tel.: +86 931 8912719; fax: +86 931 8913554.
E-mail address: yand@lzu.edu.cn (D. Yan).

0013-4686/$ – see front matter. Crown Copyright © 2013 Published by Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.11.121

the capacitive performance of hybrid Mn_3O_4/GO composite and shown the specific capacitance up to 180 F g^{-1} at scan rate of 20 mV s^{-1} [17]. However, research on the syntheses and supercapacitive behaviors of materials combining the GO with birnessite MnO_2 nanostructures is merely carried. Seredych et al. fabricated MnO_2/GO composites containing GO of different oxidation levels and low crystallization birnessite type MnO_2, and they showed specific capacitances of 125 F g^{-1} and 63 F g^{-1} at current density of 0.1 A g^{-1}, respectively [13]. Nevertheless, the structure of these composites had not been rationally designed to ensure making the best use of each ingredient's advantages and the synergetic effect between them.

Herein, we present a MnO_2-GO hybrid with birnessite-type MnO_2 nanosheet arrays on GO substrate which serves as an electroactive material for supercapacitors. Structurally, the MnO_2 nanosheet arrays work effectively as a pseudosupercapacitor material for energy storage, whereas the GO is selected as a substrate because (i) GO can possess a high surface area for the deposition of MnO_2, accordingly inhibits the aggregation of MnO_2 nanosheets; (ii) the oxygen-containing functionalities (epoxide, hydroxyl, carbonyl and carboxyl groups), acting as anchor sites, enable the subsequent in situ formation of MnO_2 nanostructures attaching on the surfaces of GO sheets [12]; (iii) the high hydrophilicity of GO makes MnO^{4-} ions react with every graphite layer, leading to simultaneous MnO_2 precipitation on each GO sheets in aqueous solution [15]. Here, the hybrid has been synthesized by a simple hydrothermal approach. The structure, morphology, electrochemical performances of the hybrid are fully investigated and discussed. In addition, the electrochemical properties of the pristine GO and birnessite MnO_2 nanosheet have also been investigated for comparison.

2. Methods

2.1. Synthesis of materials

All the reagents were analytical grade and used without further purification, and GO was prepared from powdered flake graphite (400 mesh) by a modified Hummers method as described previously [18,19]. In the typical synthesis procedure of the MnO_2-GO hybrid, GO powder (10 mg) was dispersed in deionized (DI) water (30 mL) by ultrasonic vibration for 2 h, then $KMnO_4$ powder (30 mg) was added into above GO suspension and stirred by magnetic bar for 15 min. Subsequently, the total solution was transferred into a stainless-steel autoclave with a capacity of 40 mL, sealed and heated at 100 °C for 12 h. Finally, the autoclave was cooled to room temperature naturally. The resultant product was collected by centrifugation and repeatedly washed with deionized water. The final product was dried in a vacuum at 60 °C overnight. For comparison, MnO_2-GO hybrids were similarly prepared by hydrothermal reaction for 4 h and 8 h, respectively, and the birnessite MnO_2 nanosheet was synthesized in the absence of GO sheets at 120 °C for 48 h (see supporting information I).

2.2. Characterizations

The crystallographic information of the products was investigated by X-ray diffraction (XRD, Shimadzu X-ray diffractometer 6000, Cu Ka radiation) with a scan rate of 10°/min. Raman spectra were measured on a Laser Raman spectroscopy (HORIBA Jobin Yvon LabRAM HR800) with 532 nm line of an Ar ion laser as an excitation source. Morphologies of as-obtained materials were observed on a field emission scanning electron microscopy (FESEM, Hitachi S4800) at an accelerating voltage of 20 kV and transmission electron microscope (TEM, Tecnai-G2-F30) with an accelerating applied potential of 20 kV, respectively.

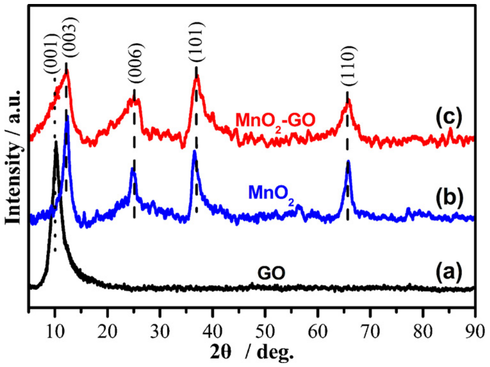

Fig. 1. XRD patterns of the (a) GO, (b) MnO_2 and (c) MnO_2-GO hybrid.

2.3. Electrochemical Measurements

The electrochemical properties of the materials were investigated by the CV, GCD and EIS techniques on a CHI 660E electrochemical workstation (Shanghai CH Instrument Company, China) at room temperature. The working electrode was fabricated by mixing the as-synthesized material (the MnO_2-GO hybrids, GO or MnO_2) with 15 wt% acetylene black and 5 wt% polytetrafluoreneethylene (PTFE) binder. A small amount of ethanol was added to the mixture to produce a homogeneous paste. Then the mixture was pressed onto nickel foam current-collectors (1 cm × 1 cm) and dried at 80 °C for 12 h. The mass of the active material was about 6 mg. Before the electrochemical tests, the prepared electrode was soaked overnight in a 1 M Na_2SO_4 solution. Electrochemical measurements were carried out in a conventional three-electrode cell with 1 M Na_2SO_4 aqueous solution as the electrolyte. Platinum foil and a saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively.

3. Results and discussion

3.1. Microstructure characterizations

Fig. 1 shows the powder X-ray diffraction (XRD) patterns of GO, MnO_2 and MnO_2-GO hybrid. As shown in Fig. 1a, the most intensive peak of GO at around 2θ=10.2° corresponds to the (001) reflection, and the interlayer spacing (0.86 nm) is much larger than that of pristine graphite (0.34 nm) due to the introduction of oxygen-containing functional groups on the graphite sheets [16,19]. The MnO_2 obtained by self-limiting deposition of $KMnO_4$ in hydrothermal treatment shows four peaks at 12.32°, 24.78°, 36.63°, and 65.47° (Fig. 1b), which can be indexed to (003), (006), (101), and (110) reflections of K-birnessite MnO_2 (JCPDS NO. 86-0666) [20,21]. In contrast, the diffraction peaks of the MnO_2-GO hybrid (Fig. 1c) are similar to those of the as-synthesized birnessite MnO_2 but the (001) reflection peak of layered GO has disappeared, indicating the GO sheets are covered by MnO_2 layer.

Raman spectroscopy can be used to gain more information about the structure of MnO_2 and GO sheets in MnO_2-GO hybrid. Raman spectra of the GO, MnO_2 and MnO_2-GO hybrid are shown in Fig. 2. It can be seen from Fig. 2a that there are two diagnostic peaks of GO centered around 1367 and 1590 cm^{-1}, which correspond to the breathing mode of κ-point phonons of A_{1g} symmetry and the first-order scattering of the E_{2g} phonons, respectively [16,22]. For the Raman spectrum of MnO_2 (Fig. 2b), three peaks at 638, 571, and 491 cm^{-1} are observed and can be assigned to the presence of birnessite-type MnO_2 phase [23]. These Raman bands are