Journal of Materials Science & Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org

High-performance asymmetric supercapacitors based on reduced graphene oxide/polyaniline composite electrodes with sandwich-like structure

Jun Ma[a,b], Shaochun Tang[a], Junaid Ali Syed[a], Dongyun Su[c], Xiangkang Meng[a,*]

[a] Institute of Materials Engineering, National Laboratory of Solid State Microstructures, and College of Engineering and Applied Sciences, Nanjing University, Nanjing 210093, China
[b] School of Mechatronics & Traffic Engineering, Nantong College of Science and Technology, Nantong 226007, China
[c] College of Mechanical Engineering, Nantong Vocational University, Nantong 226007, China

ARTICLE INFO

Article history:
Received 29 October 2017
Received in revised form
22 November 2017
Accepted 29 November 2017
Available online xxx

Keywords:
Hybrid electrode
Asymmetric supercapacitor
Sandwich-like
Electrochemical reduced graphene oxide

ABSTRACT

The sandwich-like structure of reduced graphene oxide/polyaniline (RGO/PANI) hybrid electrode was prepared by electrochemical deposition. Both the voltage windows and electrolytes for electrochemical deposition of PANI and RGO were optimized. In the composites, PANI nanofibers were anchored on the surface of the RGO sheets, which avoids the re-stacking of neighboring sheets. The RGO/PANI composite electrode shows a high specific capacitance of 466 F/g at 2 mA/cm^2 than that of previously reported RGO/PANI composites. Asymmetric flexible supercapacitors applying RGO/PANI as positive electrode and carbon fiber cloth as negative electrode can be cycled reversibly in the high-voltage region of 0–1.6 V and displays intriguing performance with a maximum specific capacitance of 35.5 mF cm^{-2}. Also, it delivers a high energy density of 45.5 mW h cm^{-2} at power density of 1250 mW cm^{-2}. Furthermore, the asymmetric device exhibits an excellent long cycle life with 97.6% initial capacitance retention after 5000 cycles. Such composite electrode has a great potential for applications in flexible electronics, roll-up display, and wearable devices.

© 2017 Published by Elsevier Ltd on behalf of The editorial office of Journal of Materials Science & Technology.

1. Introduction

With the more and more widely application of flexible electronics in our daily lives, the demand for high-performance supercapacitors is increasing [1–3]. Because of its high power density, fast charge and discharge, and long cycle life, flexible supercapacitors have become the research focus of safe, portable and all solid state energy storage devices. As a flexbile electrode, one common method is to coat redox-active materials on carbonaceous materials, such as polyaniline (PANI) coated on carbon fiber cloth [4–14]. Polyaniline is a promising electrode material because of its conductivity, thermal and acid-base doping/dedoping properties [15–19]. However, PANI may cause swelling and shrinkage in the processes of doping/dedoping [20–25]. Polymer/carbon composites provide the solution for the insulating nature of conducting polymers at dedoping state by using carbon materials as substrate to grow nanostructured polymer [26,27]. As a unique carbon material, graphene has great potential in supercapacitor electrodes, mainly due to its high conductivity, large theoretical specific surface area (≈2630 m^2 g^{-1}) and excellent mechanical flexibility [28–30]. There are many reports about composite electrode materials composed of graphene and PANI. Graphene-conducting polymer materials are usually prepared by in situ polymerization monomers in graphene suspensions [31–35]. Other methods include polymerizing the monomers in graphene oxide (GO) dispersions followed by chemical reduction of GO, (electro) polymerizing the monomers, and direct mixing of conducting polymers with graphene [36–38]. Li and co-workers have synthesized PANI nanofibers and chemically conversion graphene under acid conditions [39]. Zhou and coworkers reported in situ anodic electro-polymerization of aniline monomers on the graphene paper [40]. Cong et al. fabricated conducting polymers-coated graphene oxide/carbon nanotubes composite films via one-step electrochemical deposition [41]. Feng and coworkers described a convenient one-step method to fabricate large-scale graphene/polyaniline composite films using graphite oxide and

* Corresponding author.
E-mail address: mengxk@nju.edu.cn (X. Meng).

https://doi.org/10.1016/j.jmst.2017.12.006
1005-0302/© 2017 Published by Elsevier Ltd on behalf of The editorial office of Journal of Materials Science & Technology.

Please cite this article in press as: J. Ma, et al., J. Mater. Sci. Technol. (2017), https://doi.org/10.1016/j.jmst.2017.12.006

aniline as the starting materials [42]. Although one-step method was simple, however, the conductivity of the reported PANI-based composites was still unsatisfying.

Sandwich-like polyaniline nanofiber/RGO composite electrode was introduced in this paper. This work describes the fabrication of PANI nanofibers/RGO composite electrodes with a sandwich-like structure. The best electrodeposition parameters, including the potential window, the pH value of reaction solution and the scanning rate, can form this unique sandwich structure. This work opens up a new way to prepare graphene based nanocomposite films with various functions. Asymmetric supercapacitor (ASC) was assembled with polyaniline/graphene as positive electrode and carbon fiber cloth as negative electrode. The ASC achieves a maximum energy density of 45.5 mWh/cm^2 which is higher comparable to the most reported FSCs [18,20,26,51]. The power density of the device could achieve up to 1250 mW/cm^2, showing excellent power output capability and excellent cycle stability (97.6% for 5000 cycles).

2. Experimental

2.1. Materials

The 360 μm thick carbon fiber cloths (CC, WOS1002, 12.5 mg/cm^2) were purchased from CeTech CO., Ltd., China. Carbon cloth sheets with dimensions of 10 mm × 20 mm were treated in 5% potassium permanganate for 60 min, cleaned in alcohol and DI water several times successively, and dried at 70 °C for 6 h [43,44].

The graphene oxide (GO) was prepared using a modified Hummer's method [45], then the GO sample was exfoliated in a 0.1 M pH 8.0 phosphate buffer by ultrasonication for 3 h to obtain a homogeneous 3 mg/mL GO dispersion [46].

2.2. Preparation of sandwich-like PANI/RGO films

PANI-RGO composite films prepared by electrochemical reduction and electrodeposition of polyaniline. Fig. 1 schematically illustrates the preparation of Polyaniline/RGO composite electrode by experiment. The CC was first deposited on polyaniline by five cycles as shown in step a. Then, the PANI/CC composite electrode was electrochemical reduced graphene oxide in pH 8.0 GO solution (GNS), as shown in step b. Finally, PANI/RGO composite electrode was completed by electrochemical polymerization five cycles PANI in step c. Then the as-prepared sandwich-like PANI-RGO electrode was dried at 70 °C for 6 h.

A preliminary carbon fiber cloth sheet, silver/silver chloride (Ag/AgCl), and 20 mm × 20 mm platinum sheet were used as working electrode, reference electrode, and counter electrode, independently. Electro-polymerization of polyaniline by using an electrolyte composed of 0.15 M aniline water solution and 0.1 M sulfuric acid.

The PANI films were electro-polymerized by sweeping the potential between −0.4 V and +1.3 V versus Ag/AgCl reference for five numbers of scans (scan rate: 20 mV/s) [47]. High quality graphene was synthesized by sweeping the potential between −1.4 V and +0.9 V versus Ag/AgCl reference (scan rate: 50 mV/s) [48]. This method is environmentally friendly and fast, and will not cause pollution of the reduction material.

All experiments were carried out at room temperature. Then distilled water and ethanol were washed for three times, vacuum drying 6 h for 70 h, and its properties were studied. Cyclic voltammetry was carried out by using potentiostat/galvanost at AUTOLAB, PGSTA30 (Metrohm, USA).

2.3. Characterization

The morphology Characterizations of PANI-RGO composite electrode was investigated by transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) at an acceleration voltage of 200 kV and a scanning electron microscopy (SEM, JSM-6510, JEOL, Japan). X-ray diffraction (XRD) was performed with an Ultima-III X-ray diffractometer.

2.4. Electrochemical measurements

A three electrode system was used in electrochemical experiments with an AUTOLAB electrochemical workstation, the PANI/RGO (1.0 cm × 1.0 cm) as working electrode, Ag/AgCl as reference electrode and a platinum sheet as counter electrode, 1 M H_2SO_4 was used as electrolyte. Cyclic voltammetry (CV) was performed at varying scan rates of 5, 10, 20, 50, and 100 mV/s, with potential ranging from −0.2 to 0.8 V (vs. SCE). Galvanostatic charge/discharge (CD) properties were measured at step increasing current densities. The electrochemical impedance spectroscopy (EIS) was recorded in a frequency range from 0.1 Hz to 100 kHz, and the AC voltage amplitude was 5 mV. Battery test system test for cycling performance of supercapacitor (Land Co., Ltd., Wuhan, China).

3. Results

Fig. 2 shows the CV of step a-c from schematic diagram. Fig. 2(a) shows the CV of electro-deposition polyaniline for five cycles at 20 mV/s. Fig. 2(b) shows the CV of electrochemical RGO for ten cycles at 50 mV/s. In the first cycle, there was a cathodic current peak at −0.18 V, this reduction current resulted in the reduction of the surface oxygen groups of GO. In the second cycle, the reduction current at negative potentials decreased considerably and disappeared after four potential scans. Fig. 2(c) shows the CV of electrochemical deposition polyaniline for five cycles at 20 mV/s. PANI could be absorbed on the surface of RGO through a strong electrostatic effect between amino group and oxygen functionalities. By simply controlling CV cycles of step b, we precisely assemble PANI-RGO film on the CC.

3.1. Morphology and structure

The morphologies of CC, $PANI_{(5)}$/CC, PANI-$RGO_{(10)}$-PANI/CC, PANI-$RGO_{(20)}$-PANI/CC, PANI-$RGO_{(30)}$-PANI/CC and PANI-$RGO_{(40)}$-PANI/CC were examined by a scanning electron microscopy (SEM, Fig. 3 (a–f)). The SEM image of CC in Fig. 3(a) shows the carbon fibers are smooth. The deposition of polyaniline was carried out at a potential of −0.4 V and 1.3 V, with a scan rate of 20 mV/s for five cycles, and the SEM image is shown in Fig. 3(b). By comparing Fig. 3(a) and (b), we can find some polyaniline attached to the carbon fibers. To investigate the effect of electrochemical reduced graphene oxide on the morphologies and electrochemical performance of RGO/PANI electrode materials, we tested different electrochemical reduced graphene oxide cycles of 10, 20, 30 and 40, the SEM of varied cycles of 10, 20, 30 and 40 were showing in Fig. 3(c–f). One can observe that RGO sheets were tightly wrapped on the surface of carbon fibers (Fig. 3(c) and (d)). In Fig. 3(e) and (f), the morphology is very different from the morphology of 3(c) and 3(d), the graphene mainly exited in two-dimensional sheets form with PANI fibers. Although the resistance of RGO-coated CC can be further reduced by more cycles, some of the pores on CC were filled and covered by compacted RGO layer. As a result, the accessible surface area of RGO sheets in CC was lost.

The magnifying SEM image of PANI-$RGO_{(30)}$-PANI/CC is shown in Fig. 4(a). It can be found that the PANI fibers were anchored on

Please cite this article in press as: J. Ma, et al., J. Mater. Sci. Technol. (2017), https://doi.org/10.1016/j.jmst.2017.12.006

Download English Version:

https://daneshyari.com/en/article/7951945

Download Persian Version:

https://daneshyari.com/article/7951945

Daneshyari.com