Journal of Power Sources 302 (2016) 39–45

Contents lists available at ScienceDirect

Journal of Power Sources

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

Reduced graphene oxide/polypyrrole nanotube papers for flexible all-solid-state supercapacitors with excellent rate capability and high energy density

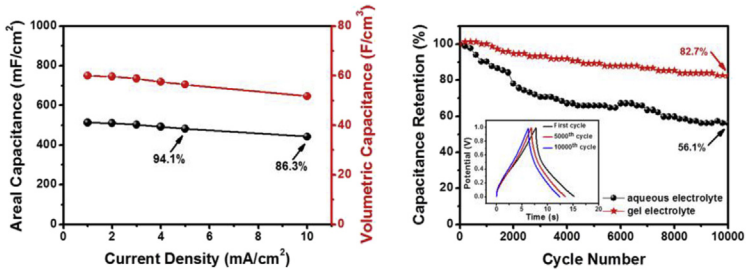
Chao Yang, Liling Zhang, Nantao Hu*, Zhi Yang, Hao Wei, Yafei Zhang**

Key Laboratory for Thin Film and Microfabrication Technology of the Ministry of Education, School of Electronics, Information and Electrical Engineering, Shanghai Jiao Tong University, Dong Chuan Road No.800, Shanghai, 200240, PR China

HIGHLIGHTS

- The structure of the rGO/PPy NT paper is incompact and hierarchical.
- The addition of rGO can improve the cycling stability of PPy NT paper electrode.
- The ASSSC device exhibits 86.3% capacitance retention from 1 to 10 mA/cm^2.
- The device has an areal energy density of 61.4 μWh/cm^2 at 10 mW/cm^2.
- The device provides a volumetric energy density of 7.18 mWh/cm^3 at 1.17 W/cm^3.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 May 2015
Received in revised form
2 October 2015
Accepted 10 October 2015
Available online xxx

Keywords:
Graphene
Polypyrrole nanotube
Rate capability
All-solid-state
Supercapacitor

ABSTRACT

Pseudocapacitive materials are known to suffer from severe capacitance loss during charging/discharging cycling. Here we report flexible all-solid-state supercapacitors (ASSSCs) based on reduced graphene oxide (rGO)/polypyrrole nanotube (PPy NT) papers prepared by a facile vacuum filtration method. It is revealed that the incorporation of rGO nanosheets can improve the electrochemical stability of PPy NT paper electrodes for pseudocapacitors. The hybrid paper electrode shows a high areal specific capacitance of 807 mF/cm^2 at 1 mA/cm^2 and a large volumetric specific capacitance of 94.3 F/cm^3 at 0.1 A/cm^3. The assembled ASSSC possesses a maximum areal specific capacitance of 512 mF/cm^2 at 1 mA/cm^2 and a maximum volumetric specific capacitance of 59.9 F/cm^3 at 0.1 A/cm^3. Moreover, it also exhibits excellent rate capability (86.3% capacitance retention from 1 to 10 mA/cm^2) and cycling stability, little capacitance deviation under different bending states, a small leakage current and a low self-discharge characteristic. The device can provide an areal energy density of 61.4 μWh/cm^2 at 10 mW/cm^2 and a volumetric energy density of 7.18 mWh/cm^3 at 1.17 W/cm^3, indicating this high-performance ASSSC is a promising candidate for flexible high-power supply devices.

1. Introduction

Graphene has aroused increasing interest and brought up a wide range of applications, such as field-effect transistors [1], selective hydrogen separation [2], transparent electrodes for electrochromic

* Corresponding author.
** Corresponding author.
E-mail addresses: hunantao@sjtu.edu.cn (N. Hu), yfzhang@sjtu.edu.cn (Y. Zhang).

http://dx.doi.org/10.1016/j.jpowsour.2015.10.035
0378-7753/

devices [3] and supercapacitors [4,5]. Graphene's flexibility, large surface area and chemical stability, combined with its excellent electrical conductivity [6], make it promising as excellent electrode materials for flexible all-solid-state supercapacitors (ASSSCs), which can address the emerging needs of portable and wearable energy conversion and storage devices. Compared with common supercapacitors (SCs) based on aqueous electrolyte, ASSSCs generally use solid-state electrolyte such as polyvinyl alcohol (PVA)-based gel electrolyte, taking the advantages of avoiding possible electrolyte leakage and reducing cost of packaging materials [7]. The employment of solid-state electrolyte has been reported to improve the electrochemical stability of pseudocapacitor electrodes [8] and the rate capability of electrochemical capacitors [9]. The electrode materials for flexible ASSSCs need to possess not only high electrochemical performances, but also high mechanical integrity upon bending or folding [10]. The emerging 3D graphene hydrogel films have been designed as ASSSC electrodes, but with a low bending angle of only 30°−40° under bending states [11,12]. Graphene papers, obtained by a vacuum filtration method [10,13,14], have shown better flexibility than graphene hydrogels but usually exhibit a rather low capacitance due to the parallel restacking of graphene sheets, which greatly reduces accessible surface area and diffusion rate of solid-state electrolytes [4]. In order to destroy the strong π−π interaction between graphene sheets, pseudocapacitive transition metal oxides and conducting polymers have been incorporated into graphene papers, such as RuO_2 [14], MnO_2 [15,16], polyaniline [16] and polypyrrole [17]. In addition, pseudocapacitive materials hold the promise of achieving battery-level energy density combined with extremely high power density [18]. However, pseudocapacitors usually suffer from bad cycle life and a low retention rate of specific capacitance at a high current density, which are unsatisfactory for practical applications.

Herein, we fabricate a flexible ASSSC based on reduced graphene oxide (rGO)/polypyrrole nanotube (PPy NT) hybrid paper, using PVA-H_2SO_4 gel as the solid-state electrolyte. Compared with the pure PPy NT paper electrode, the hybrid paper electrode shows a better cycling stability, without sacrificing the pseudocapacitance of PPy NTs. The obtained ASSSC possesses high rate capability, accompanied with other excellent electrochemical performances, such as high areal and volumetric specific capacitance, a small leakage current and a low self-discharge characteristic. With a high energy density at a large power density, this ASSSC device is greatly promising for flexible energy storage devices.

2. Experimental

2.1. Materials

Graphite powder (500 meshes) was purchased from Shangdong Jinrilai Co. Ltd (China). Sodium dodecyl benzene sulfonate (SDBS), hydrazine hydrate aqueous solution (85%), Triton X-100, methyl orange (MO), pyrrole, $FeCl_3 \cdot 6H_2O$ and polyvinyl alcohol (PVA) with analytic grades were purchased from Shanghai Chemical Reagents Co. Ltd (China) and used without further purification.

2.2. rGO/PPy NT paper

GO was prepared by the modified Hummers' method [19], which had been mentioned in our previous report [20]. The reduction of GO was performed as follows: 600 mg GO and 1.5 g SDBS were dispersed in 600 mL deionized water. 3 mL hydrazine hydrate aqueous solution (85%) was added, while keeping stirring and refluxing at 100 °C for 14 h. After cooling down, the product was filtered and washed with deionized water. Finally, the as-prepared rGO was dispersed in 1 vol.% Triton X-100 solution for further use. PPy NTs were chemically polymerized as follows [21]: 0.676 g $FeCl_3 \cdot 6H_2O$ was dissolved in 50 mL 5 mM MO solution. Then 0.1677 g pyrrole monomer was added and stirred at room temperature for 24 h. The PPy precipitate was washed with deionized water and ethanol several times, and finally dried at 60 °C for 12 h. Then the obtained PPy NTs were added into the rGO suspension with a concentration of 0.6 mg/mL. After sonication, the rGO/PPy NT suspension was vacuum filtered through nitrocellulose membrane. By adjusting the volume of the rGO suspension and the amount of PPy NTs, the final rGO/PPy NT papers with different PPy NT contents were obtained after drying at room temperature.

2.3. Flexible ASSSCs

1 g H_2SO_4 and 1 g PVA were added into 10 mL deionized water, and then heated to 85 °C under stirring until the mixture became clear. The as-prepared rGO/PPy NT paper was cut into rectangular strips and pressed on carbon paper with PET substrate to form ASSSC electrodes. Then PVA-H_2SO_4 gel electrolyte was slowly poured on two ASSSC electrodes and air-dried at room temperature to evaporate excess water. The two electrodes were pressed together to form an integrated ASSSC device.

2.4. Characterization

The morphologies of the samples were observed by field-emission scanning electron microscope (FE-SEM, Carl Zeiss Ultra 55). Transmission electron microscopy (TEM) was carried out on JEM-2100 (JEOL Ltd., Japan). Fourier Transform Infrared Spectroscopy (FTIR) was recorded on a Bruker (Germany) VERTEX 70 spectrometer (KBr pellets). Raman scattering was performed on a Renishaw inVia Reflex Raman spectrometer using a 532 nm laser source. X-ray photoelectron spectrometry (XPS) was carried out on a Kratos Axis Ultra DLD using monochromated Al Kα X-ray beams as the excitation source (1486.6 eV). Conductivity was recorded using RTS-8 four-point probes resistivity measurement system. Thermal Gravity Analysis (TGA, PerkinElmer Pyris 1) was carried out by heating the samples from 30 °C to 900 °C. All of the electrochemical experiments were carried out on an electrochemical workstation (CHI 760E). Cyclic voltammetry (CV) and galvanostatic charge/discharge measurements were conducted from −0.2 V to 0.8 V in 1 M H_2SO_4. The electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range from 10^5 to 10^{-2} Hz. For three-electrode tests, the areal specific capacitance (C_a) and volumetric specific capacitance (C_v) were calculated as follows: $C_a = (I\Delta t)/(S\Delta V)$ and $C_v = C_a/d$, where I is the discharge current, Δt is the discharge time, S is the area of one electrode, ΔV represents the voltage window and d is the film thickness. For the ASSSCs, the gravimetric specific capacitance (C_{sm}), areal specific capacitance (C_{sa}) and volumetric specific capacitance (C_{sv}) of single electrode were calculated according to the following equations [11,22]: $C_{sm} = 2(I\Delta t)/(m\Delta V)$, $C_{sa} = C_{sm}m/S$ and $C_{sv} = C_{sa}/d$, where m is the mass of one electrode. The areal energy density (E_a) and areal power density (P_a) were calculated by using the equations [22]: $P_a = (I\Delta V)/S$ and $E_a = P_a\Delta t$. The volumetric energy density (E_v) and volumetric power density (P_v) were calculated by using the equations: $P_v = P_a/d$ and $E_v = E_a/d$.

3. Results and discussion

PPy NTs were fabricated though a facile self-degraded template polymerization method. In Fig. 1a, the obtained PPy NT had a closed end with the inner diameter of ~62 nm and the wall thickness of ~38 nm. Then the micro-scale length nanotubes were combined with rGO nanosheets to form freestanding papers. Compared with