



High rate integrated quasi-solid state supercapacitors based on nitrogen-enriched active carbon fiber/reduced graphene oxide nanocomposite



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ABSTRACT

A nitrogen-enriched active carbon fiber/reduced graphene oxide nanocomposite was synthesized by electrospinning, calcination, self-assembled reduction, and post treatment nitrogen doping. The nitrogen content and C/O ratio of nitrogen-enriched active carbon fiber/reduced graphene oxide nanocomposite was up to 12 at.% and 28 after post process N-doping, respectively. High specific capacitance of 208 F g^{-1} at 20 A g^{-1} and excellent rate performance was shown in 6 mol L^{-1} KOH. Meanwhile, a specific capacitance of 212 F g^{-1} was obtained at 3 A g^{-1} and along with 99% capacitance retention after 10 000 cycles for quasi solid state supercapacitors. The excellent electrochemical performance is attributed to unique line-plane structure between the one dimensional active carbon fiber and the two dimensional reduced graphene oxide, and incorporation of nitrogen functional groups.

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1. Introduction

Carbonaceous material has been identified as the building block of almost all new energy devices owing to low cost, abundance, nontoxicity, and environmentally friendly nature, as well as high electronic conductivity and outstanding mechanical stability [1,2]. Among various carbon-based materials, carbon fiber play multi-functional roles as active electrode materials, conductive additives and substrates for supporting active metal in supercapacitors because of low weight, tiny volume, high flexibility, and wearability [3]. Therefore, increasing interest is attracted to explore advanced functional carbon fiber and their hybrids with enhanced electrochemical characteristics for high capacity supercapacitors [4,5]. For instance, a flexible nanocomposite based on a cellulose-derived nanofiber-carbon sheet framework coated with polyaniline was obtained via vacuum filtration and freeze-drying, showing specific areal capacitance of $1838.5 \text{ mF cm}^{-2}$ at 1 mA cm^{-2} [6]. A hollow graphene/conducting polymer fiber composite was tied into knots, rolled up and woven into textiles, and exhibiting specific areal capacitance up to 304.5 mF cm^{-2} at 0.08 mA cm^{-2} [7]. A meso-porous carbon fiber was developed through oxidative exfoliation,

annealing, and reduction, with the specific volumetric capacitance up to 14.2 F cm^{-3} in aqueous H_2SO_4 electrolyte [8]. These carbon fiber as electrode materials of the electrochemical capacitors with a tunable porous structure and a large surface area are desired attributes in tailoring electrode properties to achieve optimum performance. Recently, heteroatom-especially nitrogen containing carbon materials have become a hotspot for research in materials science owing to their unique electronic and mechanical, facilitating better adsorption of ions by making them hydrophilic in nature [9,10]. It is expected that the presence of functional groups on carbon materials endows Faradaic charge-transfer reactions, generating a crowd of exciting performance in energy storage realms [11,12]. For example, a porous nitrogen-doping carbon nanofiber was achieved using electrospinning of polyacrylonitrile/polyvinylpyrrolidone, and with a specific capacitance of 198 F g^{-1} at a current density of 1 A g^{-1} in 6 mol L^{-1} KOH solution [13]. A ferric citrate-derived N-doped hierarchical porous carbon was prepared via carbonization of a mixture containing ferric citrate and ammonium chloride, showing the specific capacitance of 242 F g^{-1} in 6 mol L^{-1} KOH at a current density of 1 A g^{-1} for electrochemical supercapacitors [14]. Although the capacitance and energy density of the supercapacitor derived from the fiber hybrid have been largely improved, it is still too low to meet the requirements of practical applications in electronics. Further investigations are

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needed to develop general and effective strategies to further enhance them. Increasing available electrode surface area for ion adsorption and the conductivity and pore structure of electrodes, which affects the transport of electrons and ions, will greatly promote the electrochemical performance of electric double-layer capacitor. Therefore, tremendous efforts have been devoted to exploration of carbon–carbon composite electrodes containing two different types of carbon materials and introduction heteroatom into carbon electrode materials, in order to satisfy the requirements arising from different applications.

Herein, a nitrogen-enriched active carbon fiber/reduced graphene oxide (ACF-rGO-N) nanocomposite was developed, starting with introduction of reduced graphene oxide not only increases the electrical conductivity of the active carbon fiber (ACF), but also influences their architecture. Meanwhile, nitrogen atom is incorporated into the carbon framework active carbon fiber/graphene composites (ACF-rGO) without introducing impurity, and offering abundant active sites for electrochemical reactions. The ACF decorated by layered graphene are less aggregated, which is favorable for electrolyte penetration into the line-plane structure composites owing to the good electron transfer and easy diffusion of the hydrated ions, improving the electrochemical performance of composite. The ACF-rGO-N electrode delivers a high capacitance value of 208 F g^{-1} at current densities of 20 A g^{-1} in aqueous KOH solution. In particular, the quasi-solid state supercapacitor based on ACF-rGO-N nanocomposite presents a specific capacitance of 212 F g^{-1} was obtained at a current density of 3 A g^{-1} and along with 99% capacitance retention after 10 000 cycles in polyvinyl alcohol/potassium hydroxide (PVA/KOH) gel electrolyte. These results of the symmetric supercapacitor indicate that ACF-rGO-N has great potential in the energy storage industry.

2. Experimental

2.1. Chemicals

Polyacrylonitrile (PAN, 150 000) and polytetrafluoroethylene (PTFE) from Alfa Aesar. N, N-Dimethylformamide (DMF), potassium hydroxide (KOH), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), urea, graphite were supplied from Sinopharm Chemical Reagent Co., Ltd. These reagents were used as received without any further purification process.

2.2. Synthesis of the ACF-rGO-N nanocomposites

PAN-based precursor film was prepared by electrospinning. Firstly, 0.2 g PAN was first dissolved in 10 mL DMF at room temperature under magnetic stirring, and then moved into syringe. The rate of solution was 0.15 mL min^{-1} controlled by a syringe pump. A voltage of 18 kV was applied between the needle and the drum collector to initiate the electrospinning. The distance between the needle and the drum collector was fixed at 18 cm. The spun fiber films were heated to 270°C in air at 5°C min^{-1} heating rate and kept for 1 h. The resulting pre-oxidative films were mixed with KOH (mass ratio of 1:3), and then activated and carbonated at 800°C for 2 h in N_2 flow, after which ACF was obtained. The control sample carbon fiber (CF) was prepared without activation was prepared via the same carbonation procedure.

Aqueous GO dispersion was prepared from graphite following a modified Hummer's method [15]. The dispersion was diluted to 2 mg mL^{-1} with predetermined amount of HCl (0.1 mol mL^{-1}). Zn foil and the above ACF film were immersed into the acidified GO dispersion for 6 h, forming interfacial gelation. Interfacial gel grown at ACF film surface was immersed in dilute HCl solution (20 min) to remove Zn impurities, and then washed with deionized water to

remove acidic impurities. As a result, ACF-rGO was generated. Finally, the ACF-rGO was soaked into urea-saturated solution for 24 h at room temperature. After vacuum freeze drying, the resulting sample was carbonated at 700°C , 800°C , 900°C for 2 h in N_2 gas atmosphere, respectively. The resulting samples were labeled as ACF-rGO-N-700, ACF-rGO-N, ACF-rGO-N-900, respectively. Moreover, the pure rGO was obtained by repeating the experiment above without the ACF and heat treatment.

2.3. Structure characterization

Field emission scanning electron microscopy (FE-SEM) analysis was conducted on a JEOL JSM-6330. Transmission electron microscopy (TEM) experiments were carried out on JEM-2100. Raman spectra were collected on a DXR Microscope Raman Spectrometer, using a 532 nm line of KIMMON laser. The electrical characteristics were implemented by a semiconductor analysis system (Keithley 4200). Nitrogen sorption isotherms were measured with a Micro-Active for ASAP 2460 adsorption analyzer. XPS analysis (EscaLab 250Xi) was conducted using a monochromatic Al K α X-ray at 14 kV.

2.4. Electrochemical measurements

The electrochemical performance of the resulting samples was determined in a three-electrode system and a two-electrode device, respectively. Working electrodes were prepared by coating homogeneous mixtures of the as-prepared active material, carbon black and PTFE (weight ratio of 85:10:5) on the surface of nickel foam. The typical mass loading of each working electrode was about 7 mg cm^{-2} . The electrochemical performance was firstly measured with a three-electrode system, where a platinum rod was the counter electrode, and the Hg/HgO and Ag/AgCl reference electrode were used within KOH and H_2SO_4 aqueous solution, respectively. The quasi-solid state two electrode system was prepared via two working electrodes were pressed together with a PVA/KOH as separator and electrolyte. To prepare PVA/KOH gel electrolyte, 2 g PVA powder was dispersed into 20 mL deionized water, and then heated to 85°C under vigorous stirring until it became clear, followed by the addition of excessive 6 mol L^{-1} KOH aqueous solution. Galvanostatic charge/discharge was tested at various current densities by LAND-CT2001A (Wuhan Jinnuo Electronics. Ltd.). Cyclic voltammetry (CV) at different scanning rate and electrochemical impedance spectroscopy (EIS) with the frequency range from 100 kHz to 0.01 Hz at the amplitude of 5 mV were carried out using a solartron electrochemical workstation (1260 + 1287).

3. Results and discussion

3.1. Synthesis and physical characterization of hybrid composites

The preparation of an ACF-rGO-N is schematically shown in Fig. 1. Firstly, PAN-based precursor film was prepared by electrospinning, which is a facile and scalable method to produce the carbon fiber with large specific surface area, strong mechanical stability. The PAN precursor was further undergone thermal stabilization in air to obtain the pre-oxidative film. After that, the molecular structure of film changed to the conjugated ladder ring structure. Therefore, the pre-oxidative films were mixed with KOH, and followed by activation and carbonation in N_2 gas atmosphere to form ACF with large surface area. Secondly, the ACF-rGO composite was formed during reduction of GO sheets. The GO was reduced via electrons, which were released from Zn foil under acidic condition. The resulting rGO sheets and ACF can readily be assembled into

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