Journal of Power Sources 384 (2018) 270–277

Contents lists available at ScienceDirect

Journal of Power Sources

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

Three-dimensional interconnected porous graphitic carbon derived from rice straw for high performance supercapacitors

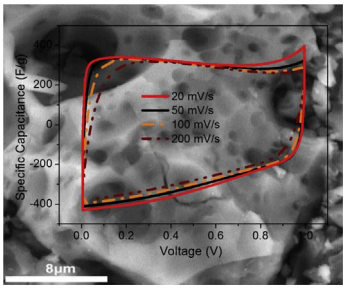
Hong Jin[a,c,*], Jingpeng Hu[a,b,c], Shichao Wu[a,b,c], Xiaolan Wang[a,b,c], Hui Zhang[a,b,c], Hui Xu[a,c,*], Kun Lian[a,c,*]

[a] Suzhou Research Institute, Xi'an Jiaotong University, Suzhou 215123, People's Republic of China
[b] Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China
[c] School of Nano-science and Nano-engineering, Xi'an Jiaotong University, Suzhou 215123, People's Republic of China

HIGHLIGHTS

- Graphitized porous carbon obtained from rice straw.
- The specific surface area of graphitized porous carbon is as high as 3333 $m^2 g^{-1}$.
- The gravimetric capacitance performance is 400 F g^{-1} in aqueous electrolytes.
- Supercapacitor shows good rate performance and excellent cycling stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Supercapacitors
Electrode
Rice straw
Sustainable

ABSTRACT

Three-dimensional interconnected porous graphitic carbon materials are synthesized via a combination of graphitization and activation process with rice straw as the carbon source. The physicochemical properties of the three-dimensional interconnected porous graphitic carbon materials are characterized by Nitrogen adsorption/desorption, Fourier-transform infrared spectroscopy, X-ray diffraction, Raman spectroscopy, Scanning electron microscopy and Transmission electron microscopy. The results demonstrate that the as-prepared carbon is a high surface area carbon material (a specific surface area of 3333 $m^2 g^{-1}$ with abundant mesoporous and microporous structures). And it exhibits superb performance in symmetric double layer capacitors with a high specific capacitance of 400 F g^{-1} at a current density of 0.1 A g^{-1}, good rate performance with 312 F g^{-1} under a current density of 5 A g^{-1} and favorable cycle stability with 6.4% loss after 10000 cycles at a current density of 5 A g^{-1} in the aqueous electrolyte of 6M KOH. Thus, rice straw is a promising carbon source for fabricating inexpensive, sustainable and high performance supercapacitors' electrode materials.

1. Introduction

Supercapacitors (SCs) have attracted great attention due to the ever-increasing application potentials in electronic devices, electric vehicles and other power applications [1–4]. There are two types of SCs, which are classified by the mechanism of the ions storage at the interface between an electrode and an electrolyte [5,6]. First, the electrochemical double layer capacitors (EDLCs), the energy storage of EDLCs is based on the adsorption/desorption of charged ions on the electrode/electrolyte interface, and the electrode materials are various types of carbons [7]. Second, the pseudocapacitors, the energy is achieved by fast and reversible faradaic reactions, while the electrode materials are

* Corresponding authors. Suzhou Research Institute, Xi'an Jiaotong University, Suzhou 215123, People's Republic of China.
E-mail addresses: jhjinhong@xjtu.edu.cn (H. Jin), xhxuhui@xjtu.edu.cn (H. Xu), klian@xjtu.edu.cn (K. Lian).

https://doi.org/10.1016/j.jpowsour.2018.02.089
Received 22 November 2017; Received in revised form 21 February 2018; Accepted 28 February 2018

transitional metal oxides or conductive polymers [5,8,9]. Carbon based electrochemical double layer capacitors are superior to pseudocapacitors in terms of cycle life, power density and temperature sensitivity [10]. Nevertheless, the low energy density (less than 10 Wh Kg^{-1}) of commercial activated carbon materials are hard to meet the ever-increasing requirements [11,12]. Therefore, advanced carbon materials are necessary to be developed to satisfy the high demand of the energy storage market.

Many efforts have been made to boost the properties of carbonaceous materials [13–17]. On the one hand, in view of the three dimensional (3D) nanostructure can not only shorten the diffusion pathway, but also smoothen the electron transport across the carbon skeleton [18]. 3D porous carbon materials have been developed to facilitate the performances of EDLCs [1,19,20]. On the other hand, new carbon materials such as carbon nanotubes and graphene have been utilized as electrode materials on account of their unique intrinsic electrical conductivity [21–23]. Recently, researchers attempt to combine these strategies. Thus, 3D graphene and porous carbon nanotubes have been designed as electrode materials for EDLCs [24,25]. The properties of these carbon materials are superior to commercial activated carbons; however, the high cost and low yield of the synthesizing methods are still retarding the commercialization of 3D graphene and 3D carbon nanotubes. In order to reduce the cost of the 3D graphitized carbon materials, renewable precursors such as biomass or bio-wastes are highly expected to be explored as the carbon sources for generating three-dimensional interconnected porous graphitic carbon materials [26–28].

Rice straw, an agricultural residue, which is normally left on the field and burned after rice harvest [29,30]. It is made up with cellulose, hemicellulose and lignin as other biomass, and also contains some amount of silica [31,32]. The silica is located on the epidermal cells of the rice straw, and combined with lignocellulose to form a chemical and thermal stable matrix [33]. Recently, researchers tried to develop high quality carbon materials from rice straw. For instance, Sudhan et al. prepared an activated carbon from rice straw with a surface area of 1007 $m^2 g^{-1}$ at the temperature of 600 °C for 4 h. However, the symmetric supercapacitor device in inorganic electrolyte can just deliver a specific capacitance of 156 F g^{-1} at 0.5 A g^{-1}, which is even lower than commercial activated carbon materials [34]. Zhu et al. prepared black liquor-derived porous carbon from rice straw and N-doped porous carbon by melamine as additive. The porous carbon and N-doped porous carbon have specific capacitance of 242 F g^{-1} and 337 F g^{-1} at 0.5 A g^{-1}. Nevertheless, the procedure is time-consuming in view of the multiple steps such as milling, drying, sealed stainless steel heating (4 h), 2 °C min^{-1} to 400 °C for 1 h, 5 °C min^{-1} to 800 °C for 2 h, cooling, soaking in KOH for 12 h and washing. Besides, the separation of the liquid portion needs a high speed centrifugation of 14000 r min^{-1}, which is energy-consuming and hard to scale-up.

Herein, we focus on promoting the performance of rice-straw-derived carbon by creating a three-dimensional interconnected porous graphitic carbon (3D-IPGC) with a cost effective method. The route of our strategy is shown in Fig. 1.

The procedure of our approach is made up of two steps. The first step is denoted as carbonization. It is the same as traditional carbonization process, except the catalyst precursor (nickel nitrate) is introduced. During the process, Hemicelluloses decompose as the temperature is higher than 220 °C [35]. Celluloses surmount the small interactions of hydrogen bonds and van der Waals bonds between the bundled cellulose, and then break up into small pieces [35]. Further, nickel nanoparticles are generated by the reduction effect of the organic structures and the syngas in the system. The second step is denoted as a synergistic effect of graphitization and activation. In this step, lignocelluloses are graphitized by nickel nanoparticles, and the disordered carbons are corroded by potassium hydroxide. The silica matrix here in rice straw is favorable for maintaining the three-dimensional structures [36]. The three-dimensional interconnected porous graphitic carbon (3D-IPGC) is created at a moderate temperature of 700 °C by the synergistic effect of nickel graphitization and potassium hydroxide activation. The as-obtained 3D-IPGC delivers a high surface area of 3333 $m^2 g^{-1}$. Moreover, the fabricated EDLC in an aqueous electrolyte of 6 M KOH displays a high specific capacitance of 400 F g^{-1} at a current density of 0.1 A g^{-1}. Further, a good rate performance (312 F g^{-1} at a current density of 5 A g^{-1}) and long cycle performance (with 6.4% loss after 10000 cycles at a current density of 5 A g^{-1}) are also achieved.

2. Experimental

2.1. Preparation of 3D-IPGCs

The dried rice straw was collected from a field near Lake Taihu, Suzhou, China. The other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd and Membrane separators were donated by Celgard Co., Ltd. The rice straw was firstly chopped into small fragments (about 5 millimeters), and washed with hydrochloride acid. The small fragments were then rinsed by deionized water until pH 7, and dried at 80 °C for 12 h. In a typical procedure, 8.0 g rice straw was immersed into nickel nitrate solution (120 ml, 0.055 M) for 12 h. The dried mixture was then introduced into a tube furnace at 400 °C for 1 h, at a heating rate of 5 °C min^{-1} with the nitrogen (100 mL min^{-1}) as the protection gas. The as obtained intermediate product was washed by 1 M nitric acid and dried. Subsequently 3.0 g of the dried intermediate product was soaked into 50 ml aqueous KOH solution (4.3 M). The mixture was dried at 60 °C and then transferred into a tube furnace at 600, 700, and 800 °C separately for 1 h, at a heating rate of 10 °C min^{-1} with the nitrogen (100 mL min^{-1}) as the inert gas. The as obtained samples were washed by deionized water and nitric acid, and dried for utilization.

2.2. Characterization of the as-prepared materials

The morphology, nano- and microstructure were characterized by scanning electron microscopy (Phenom ProX) and the transmission electron microscopy (Tecnai G2 F20 S-TWIN). The BET and pore size distribution analysis were carried out at 77 K on the Autosorb IQ (Quantachrome Instruments). X-ray diffraction (XRD) were tested via D8 Advance of Bruker. Raman spectrum was characterized by DXR 2xi (Thermo Fisher) with a 455 nm laser, and FTIR spectra were obtained by using iS50 from Thermo Fisher.

2.3. Assembly the supercapacitors

The electrodes were firstly fabricated by pressing a slurry containing 80% 3D-IPGC, 10% carbon black and 10% PTFE binder onto a nickel foam. The as-prepared electrodes were then dried in an oven at 80 °C. Two electrodes coin 2032-type supercapacitors were fabricated with celgard-3501 as the film separator and 6M KOH as the electrolyte, respectively.

2.4. Electrochemical measurement of 3D-IPGC

Galvanostatic charge/discharge data were collected by using Neware-CT-4008 (Neware, Shenzhen). The specific capacitance of a single electrode can be calculated through charge/discharge curves by using the equation $C_s = 2It/m\Delta V$, where C_s (F g^{-1}) is the specific capacitance of one electrode, I is the charge or discharge current, t is the charge or discharge time, m is the mass of the active material in one electrode, and ΔV is the voltage range during charge or discharge process, and here in aqueous solution the potential window is 1.0 V. The energy density and the power density of the double layer capacitors can be obtained by using the equations $E = 0.5\ C_t V^2$ and $P = E/\Delta t$, respectively, where E is the energy density, C_t is the total specific