Electrochimica Acta 220 (2016) 331–339

Contents lists available at ScienceDirect

Electrochimica Acta

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

Microporous carbon from a biological waste-stiff silkworm for capacitive energy storage

Chengcheng Gong[a], Xinzhu Wang[a], Danhua Ma[b], Huifeng Chen[a], Shanshan Zhang[a], Zhixin Liao[a,*]

[a] School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, PR China
[b] School of Chemical Science and Technology, Yunnan University, Kunming 650091, PR China

ARTICLE INFO

Article history:
Received 16 May 2016
Received in revised form 14 October 2016
Accepted 17 October 2016
Available online 18 October 2016

Keywords:
carbon
biomass
stiff silkworm
Bombyx Batryticatus
supercapacitor

ABSTRACT

In general, carbon materials with high specific surface area (SSA), well-balanced pore size distributions, and appropriate content of heteroatom functionalities are essential to enhance the performance of electric double layer capacitors (EDLCs) for capacitive energy storage. In this study, a low-cost biological waste-stiff silkworm was first used as precursor for the synthesis of well-developed microporous carbon (SSMC) material by simple steps of carbonization and further activation. The SSMC was endowed with ultra-high SSA ($2523\,m^2\,g^{-1}$), large pore volume ($1.37\,m^3\,g^{-1}$), and high content of heteroatom functionalities ($\sim$3.5 at% N and $\sim$5.1 at% O). EDLCs employed SSMC as active material showed high specific capacitance of $304\,F\,g^{-1}$ and $256\,F\,g^{-1}$ at current densities of $1\,A\,g^{-1}$ and $20\,A\,g^{-1}$, respectively, suggesting the good rate capability. Symmetric-two-electrode test in aqueous electrolyte also delivered the specific capacitance of $235\,F\,g^{-1}$ with the energy density of $\sim$$7.9\,W\,h\,kg^{-1}$. The findings confirmed the feasible way that using the eco-friendly biomass raw material to construct high performance capacitive energy storage device.

1. Introduction

Supercapacitors, as a new type of energy storage device, have attracted tremendous attention because of their outstanding features, such as high power density, fast storage/release charge capability and outstanding cycle life. Supercapacitors can be categorized as electrical double layer capacitors (EDLCs), pseudo-capacitors or hybrid supercapacitors according to the charge storage mechanism [1]. Generally, ideal EDLCs provide capacitance through purely physical storage and release of electrostatic charges at the interface between inert carbonaceous-based electrode and electrolyte [2]. Pseudo-capacitors store charge Faradaically through transfer of charge between electrode (e.g. metal oxides/nitrides or conducting polymers) and electrolyte accomplished through electrosorption, redox reaction, and intercalation processes [2,3]. The hybrid capacitance arises from the combination of both processes [1]. The positive electrode obeys non-Faradaic mechanism and the other component comprising energy source material which utilizes reversible Faradaic reaction [3–5]. Compared with EDLCs, although pseudo-capacitors showed high specific capacitance in aqueous electrolytes, low electrical conductance, narrow potential window [1], poor compatibility with organic electrolytes, and the short cycle life have limited the practical application [6]. In addition, the lower abundance of pseudo-capacitive materials (e.g. nickel, cobalt or ruthenium) in the earth's crust means the high cost for commercial applications [1,7]. As the energy density is strongly dependent on the maximum voltage applied to the EDLCs, the choice of electrolyte may significantly affect the energy density [8]. Aqueous electrolytes typically withstand lower potential (0.6–1.4 V) in comparison with organic electrolytes (2.2–3.0 V) and ionic liquids (2.6–4.0 V) [8], meaning that electrodes in aqueous electrolytes deliver lower energy density [2–9]. Nevertheless, the advantages of using aqueous electrolytes include their very low cost, safety and high ionic conductivity [8].

Carbon based materials are preferred as EDLC electrodes owing to their high surface area (SSA), well-developed pore size distribution (PSD), relatively low cost, physical and chemical stability and its amphoteric nature that allows rich electrochemical properties from donor to acceptor state, and wide range of operating temperatures [2,8]. The appropriate heteroatom doping also plays a noticeable role, it not only can enhance the

---

[*] Corresponding author.
E-mail address: zxliao@seu.edu.cn (Z. Liao).

http://dx.doi.org/10.1016/j.electacta.2016.10.120

conductivity and wettability of carbon-based electrodes, but also extra capacitance that derived from the pseudo-capacitive effect of heteroatom functionalities will be gained [9]. Nano-porous carbon materials, such as activated carbon (AC) [9–12], carbon nanotubes [13], templated carbon [14,15], carbide-derived carbon [16] and graphene [6,17], etc., have been extensively studied employing as electrode materials for EDLCs [8]. Generally, a kind of electrode material only with a competitive ratio of performance to price, it could be able to bring the potential commercial value. Among these porous carbons, comparing with AC, other carbon materials inevitably suffer from the challenge [8,18]. As a matter of fact, AC has been commercially used as the EDLCs electrode material. Unfortunately, commercial AC-based supercapacitors usually had specific capacitance less than 200 F g^{-1} (in aqueous electrolyte) and low energy density values of 4∼6 W h/kg (in organic electrolyte) [6,8], which limits their more widespread applications in fields of electric and hybrid-electric vehicles, energy-efficient industrial equipment and smart-grid, etc.

By using nitrogen-containing biological raw materials as precursors without sophisticated chemical procedures for the formation of nitrogen-doped activated porous carbon has drawn extensive attention [9–12,18]. Among these raw materials, silkworm cocoon or natural silk based nitrogen-doped activated porous carbon have showed impressively electrochemical performance for various energy storage devices, such as supercapacitors, lithium-ion batteries, sodium-ion batteries, lithium-sulfur batteries and lithium-selenium batteries, etc. [9,19–22].

Stiff silkworm (*Bombyx batryticatus*) derives from silkworm (*Bombyx mori* L.) larva, which is infected by Beauveria bassiana before spinning silk and then resulting in stiffness and death [23]. Normally, as a forerunner of silk or silk protein, the silkworm cocoon is expensive, while the stiff silkworm is usually discarded as a uselessly biological waste. Therefore, using stiff silkworm as the precursor for the preparation of efficient AC undoubtedly will bring a low cost competitive advantage in comparison with using silk or silkworm cocoon as raw materials.

In this work, we first employed stiff silkworm as a low-cost precursor for the fabrication of high nitrogen-doping (∼3.5 at%) porous carbon. The carbon had well-developed microporosity, large pore volume and ultrahigh SSA. Accordingly, EDLCs involved the obtained carbon showed enhanced specific capacitance of 304 F g^{-1} and 273 F g^{-1} at current density of 1 A g^{-1} in three-electrode test within the mass loading of activate material of ∼4 mg and ∼7 mg, respectively. Single electrode in the two-symmetric electrode system delivered the specific capacitance of 253 F g^{-1}, and the entire device yielded a maximum energy density of ∼7.9 W h kg^{-1}. The electrochemical measurement results suggested that the synthesized porous carbon was a promising candidate electrode martial for high performance capacitive energy storage device.

2. Experimental

The stiff silkworm was purchased from Simcere Kang Pharmaceutical, Nanjing. All reagents were used as-received without further purification. Distilled water was used throughout the experiment.

2.1. Material synthesis

The stiff silkworm was preliminary dried at 80 °C for 2 hours and then carbonized at 500 °C for 1 h under N_2 atmosphere with a heating rate of 5 °C min^{-1}. The obtained residue was then thoroughly washed with 5% HCl solution and distilled water until neutral pH and then dried at 80 °C to obtain non-activated carbon material, named as SSC. SSC was mixed with KOH (weight $_{\mathbf{KOH}}$/weight $_{\mathbf{Carbon}}$ = 3) and then activated at 750 °C for 1 h under argon gas with a ramp rate of 5 °C min^{-1}. The resulting product was washed with 5% HCl solution and distilled water until the neutral pH and then dried at 80 °C to obtain the activated microporous carbon, named as SSMC.

2.2. Material characterizations

The powder X-ray diffraction data from 0.5°–80° was measured on a Thermo ARL X'TRA instrument with Cu-Kα radiation generated at 40 kV. The microscopic morphology and structure were observed by FEI Nova NanoSEM 450 scanning electron microscope working at 15 kV and JEOL JEM-200CX transmission electron microscope measurements operating at 200 kV. Raman spectra were carried out on Renishaw in Via 2000 Raman spectrometer with Ar laser wavelength of 458 nm. X-ray photoelectron spectroscopy analysis was taken on a Thermo Scientific Escalab 250Xi K-Alpha spectrometer with Al Kα (1486.6 eV) as an X-ray source. The acquisition of high resolution spectrums were carried out on XPS PEAK41 software. Nitrogen sorption isotherm was measured on a Tristar II 3020 surface area analyzer (Micrometritics) at 77 K. Brunauer-Emmett-Teller model was performed to determine the specific surface area. The pore size distribution of micropore and mesopore was analyzed based on Horvath-Kawazoe and Barrett-Joyner-Halenda models, respectively.

2.3. Electrochemical measurements

A viscous slurry containing 85 wt% SSMC, 10 wt% acetylene black and 5 wt% polytetrafluoroethylene binder was uniformly mixed and then pressed onto the nickel foam (10 mm × 10 mm) to fabricate the working electrode. The electrode was then dried at 100 °C. In three-electrode test, a platinum electrode and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Cyclic voltammetry curves were obtained at sweep rates from 5 mV s^{-1} to 150 mV s^{-1}. Galvanostatic charge-discharge profiles were obtained at current densities from 1 A g^{-1} to 30 A g^{-1}. Electrochemical impedance spectroscopy was measured with alternate current amplitude of 5 mV at the frequency from 10 mHz to 10 kHz. For two symmetrical-electrode system, the preparation of working electrodes followed the described procedures. All electrochemical studies were performed on a CHI660E electrochemical workstation (CH Instruments, US) using 6.0 M KOH aqueous as electrolyte. The specific capacitance (C, F g^{-1}) was calculated based on the galvanostatic charge-discharge records by using following equations:

$$C = \frac{I\Delta t}{m\Delta V}(\text{For } 3-\text{electrode test})$$

$$C = \frac{4I\Delta t}{m\Delta V}(\text{For } 2-\text{electrode test})$$

Where I is the constant discharge current (A), ΔV refers the potential window excluding the IR drop (V) within the discharge time Δt (s), and m is the total mass of active material in both electrodes (g).

The energy density (E, W h kg^{-1}) and power density (P, W kg^{-1}) of the two symmetrical-electrode test were calculated according to [14]:

$$E = \frac{1}{4}\times\frac{1}{2}C\Delta V^2\frac{1}{3.6}$$