Electrochimica Acta 136 (2014) 504–512

Contents lists available at ScienceDirect

Electrochimica Acta

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

Meso- and micro- porous composite carbons derived from humic acid for supercapacitors

Jiao Yin[a,c], Duanyi Zhang[d], Jiquan Zhao[d], Xiaolei Wang[b], Hui Zhu[b,*], Chuanyi Wang[a,c,**]

[a] Key Laboratory of Functional Materials and Devices for Special Environments, Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, 40-1 South Beijing Road, Urumqi, Xinjiang 830011, China
[b] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China
[c] Laboratory of Eco-Materials and Sustainable Technology (LEMST), Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, 40-1 South Beijing Road, Urumqi, Xinjiang 830011, China
[d] School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, China

ARTICLE INFO

Article history:
Received 22 April 2014
Received in revised form 16 May 2014
Accepted 25 May 2014
Available online 2 June 2014

Keywords:
composite
porous carbons
humic acid
supercapacitors

ABSTRACT

Herein, humic acid (HA), a kind of biomass (natural polymer), is firstly adopted as a raw material for synthesis of activated carbons (ACs) via a high-temperature activation procedure with KOH. Their porous textures as well as surface groups are fully characterized by N_2 sorption isothermal analysis, SEM, TEM, XPS and IR, respectively. The HA-derived ACs show very high specific surface areas (up to 2990.32 $m^2 g^{-1}$). Furthermore, electrochemical studies such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge (GCD) are carried out to evaluate their specific capacitance and rate capability. It reveals that HA-derived ACs possess high specific capacitance (350 $F g^{-1}$) at a scan rate of 5 $mV s^{-1}$ in 1 M H_2SO_4. Moreover, supercapacitors based on HA-derived ACs demonstrate good cycling stability in which the 92% initial capacitance has been retained even after 9000 cycle numbers at a high current density of 1 $A g^{-1}$.

1. Introduction

Supercapacitors (SCs), also known as electrochemical capacitors, have recently received more and more attention because of their merits of high power density, desirable coulombic efficiency and excellent cycling life [1,2]. On the basis of their charge storage mechanisms, supercapacitors can be divided into two groups: electrical double layer capacitor (EDLC) and pseudocapacitor [2–6]. The capacitance for EDLC originates from pure electrostatic charge collection at interface (electrode/electrolytes), which requires electrode materials with large specific surface area and well-developed pores [7–10]. Up to now, a variety of carbon-based materials such as activated carbons (ACs), carbon aerogels, carbon nanotubes, carbon nanofibers, and graphenes have been utilized as electrode materials for SCs because of their accessibility, easy processability, non-toxicity, and high chemical stability [10–19]. Among them, ACs are considered as one of the most attractive candidates for EDLC because of its high porosity, large surface area that favors good charge accumulation at the interface [20]. More recently, to improve AC's capacitive performance, great efforts have been made to prepare ACs from designing procedure to selecting precursors. Most interestingly, benefiting from the low cost and environmental abundance, various kinds of biomasses have been chosen as the precursors for the ACs' preparation [2,21,22]. For example, a wide variety of biomass materials, including animal's bones [23], animal's feather [24], bacteria [4], fungi [2], biopolymer [21], tea leaves [25], coffee beans [26], cocoon [27], various pollens [28], dead leaves [29], walnut and coconut shells [30,31], pitch coke [32], firewood [33], rice husk [34], banana peel [35], bamboo [36], have been used as the raw materials for the preparation of ACs. Most of them are originated from the living-things above soil, little attention has been paid to the bio-decomposited products under soil. Whether the bacterial decompositions can be used as precursors for ACs is still a concern.

Humic acid (HA) is a kind of natural polymer and also a biomass material. It is a major composition of humic substances, which are the principal organic components of soil (humus), peat, coal, and et al. [37–41]. It derives from biodegradation of dead organic substance. Considering their carbon-enriched chemical composition, it is wondering whether such biomass might act as a new type of carbonaceous precursor for supercapacitor electrodes. The merits

---

* Corresponding author. Tel.: +86 431 85262063; fax: +86 431 85262063.
** Corresponding author. Tel.: +86 991 3835879; fax: +86 991 3835879.
E-mail addresses: huizhu@ciac.ac.cn (H. Zhu), cywang@ms.xjb.ac.cn (C. Wang).

http://dx.doi.org/10.1016/j.electacta.2014.05.115
0013-4686/

of HA as carbon precursor can be summarized as follows. Firstly, the earth abundance and low cost of HA promises large scale production of carbon. Especially, HA, as the major organic composition of peat, brown coal and weathered coal, it conversely provides good chance to deeply explore the coal resources. Furthermore, the high content of carbon in HA promises high yield of resultant carbon. In addition, HA is very stable, which promises the reproduction of carbon. Finally, HA is environmental friendly. In conclusion, HA can be considered as a satisfactory carbonaceous precursor to synthesize high-quality ACs. However, the preparation method is another important factor that influence the performance of resultant ACs such as pore structure parameters and cost of ACs. Traditionally, the highly ordered porous carbons are mainly synthesized by the template methods. The template methods mainly contain hard and soft templates. The hard templates are mainly silica or zeolite, the soft template is surfactant [42–44]. The hard-template method involves in multi-step preparation of the porous carbon and further removal of template. This method is difficult for practical application due to tedious manipulation and high cost of template. Sometimes, the hard-templated carbons also need to be further activated by KOH to enhance its surface area [45]. More important, the porous structure is easy to be destroyed accompanying with removal of hard template. As for the soft-templated method, the porous carbon is produced by self-assembly of surfactant and further removal of template by heat treatment. Most of carbons obtained by this method are also micro-porous structure due to the limited molecule size of surfactant [46]. The expensiveness of the template and the low yield of resultant carbon also confine the large scale production. Moreover, the activation methods also play the same important role in influencing the performance of resultant ACs. Both physical and chemical activation methods are commonly employed to synthesize ACs [47]. The physical activation relies on the utilization of gasifying agents such as CO_2, air or steam at high temperatures (usually from 700 to 1200 °C) to produce porosity in carbonaceous precursors [48]. However, the specific surface area of carbon is too small to meet the critical requirement of capacitors by physical activation. The chemical activation is generally implemented at relatively low temperatures (usually from 600 to 900 °C) with the aid of a chemical activating agent, such as KOH, $ZnCl_2$, H_3PO_4 [47,48]. This activation method is more commonly adopted because of low energy consumption, high yield, well-developed pores, and low cost. Among the various chemical activating agents, KOH is the most wildly used one since it can allow one to control micro- or meso-porosity with extremely large experimental surface area (up to 3000 $m^2\ g^{-1}$) [48,49].

Based on above-mentioned facts, herein, HA was used as the precursor for preparation of ACs under the activating procedure with KOH. The advantages of this facile method lie in easy manipulation, good reproduction, high yield and large scale production. Various measurements including N_2 sorption isothermal analysis, transmission electron microscopy (TEM) and Scanning electron microscopy (SEM) were utilized to investigate the porous properties of these HA-derived ACs. In addition, Fourier transform-infrared (FT-IR) spectra and X-Ray photoelectron spectroscopy (XPS) were employed to analyze the elements and surface groups of HA-derived ACs. Furthermore, electrochemical studies such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge (GCD) were conducted to evaluate their capacitive behaviors in the electrolytes of acid (H_2SO_4), basic (KOH) and neutral (Na_2SO_4) aqueous solutions. The electrochemical investigations indicated that the resultant ACs possessed high specific capacitance (350 Fg^{-1}) at a scan rate of 5 $mV\ s^{-1}$ in 1 M H_2SO_4. Furthermore, supercapacitors based on these ACs demonstrated good cycling stability in which the 92% initial capacitance have been retained even after 9000 cycle numbers at a high current density of 1 $A\ g^{-1}$.

2. Experiments

2.1. Preparation of HA-derived ACs

As a facile synthesis method, HA (Tianjing guangfu chemical Co. Ltd.) was fully mixed with activating agent KOH. After sufficient grinding, the mixed powder was treated in a tubular furnace under nitrogen protection with a heating rate of 5 °C/min from room temperature to 800 °C. Then the activation process took place at 800 °C for 1 hour. Finally, the obtained product was washed with 2 M HCl and distilled water in sequence to eliminate any metal residuals completely. According to the mixing weight ratios (KOH/HA), the samples were referred as HAC_0 (0/1), HAC_1 (1/1), HAC_2 (2/1), HAC_3 (3/1), HAC_4 (4/1) and HAC_5 (5/1).

2.2. Characterization of HA-derived ACs

TEM images were taken on FEI Tecnai G2 F20 transmission electron microscope with an acceleration voltage of 200 kV. SEM images were recorded using a Philips XL 30 instrument and a JEOL JSM-6700F microscope. XPS was measured with an ESCALAB 250 (Thermo Electron). The X-ray excitation was provided by a monochromatic Al Kα (1486.6 eV) source. Data quantification was performed on the Avantage program. The surface atomic concentrations were determined from photoelectron peaks areas using the atomic sensitivity factors reported by Scofield [50]. Binding energies of all core levels were referred to the C-C bond of C1s at 284.6 eV. FT-IR spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer. In addition, elemental analysis was performed on a Vario EL cube (Elementar Analysensysteme GmbH) to determine the carbon, nitrogen and hydrogen contents of the samples. Nitrogen sorption isotherms were measured at 77 K with a Quadrachrome adsorption instrument. Before analysis, the samples were degassed at 200 °C for 24 h. The surface area was calculated according to the Brunauer-Emmett-Teller (BET) method.

Table 1

Textural properties of HACs.

Textural property	S_{BET} a) [m^2g^{-1}]	S_{micro} b) [m^2g^{-1}]	S_{meso} c) [m^2g^{-1}]	V_{total} d) [cm^3g^{-1}]	V_{micro} e) [cm^3g^{-1}]	V_{meso} f) [cm^3g^{-1}]	Average pore diameter (nm)
HAC_0	9.32	-----	9.32	0.00367	-----	0.00367	15.762
HAC_1	1087.04	723.68	363.36	1.149	0.372	0.777	1.845
HAC_2	2148.40	1789.89	358.51	1.413	0.900	0.513	2.632
HAC_3	2990.23	743.66	2246.57	2.113	0.314	1.799	2.827
HAC_4	2442.81	20.46	2422.35	1.807	0.0560	1.751	2.959
HAC_5	1286.99	141.51	1145.48	1.468	0.0580	1.368	4.562
Maxsorb	1333.73	1080.35	236.38	0.666	0.551	0.115	2.016

a) Specific surface area from multiple BET method (calculated in the linear P/P_0 range from 0.05 to 0.3); b) Micropore surface area from t-plot method; c) t-method external surface area ($S_{meso} = S_{BET} - S_{micro}$); d) Total pore volume at $P/P_0 = 0.99$; e) Micropore pore volume from t-plot method micropore analysis; f) $V_{meso} = V_{total} - V_{micro}$.