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Research article

Preparation of porous carbons from waste sugar residue for high performance electric double-layer capacitor

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ABSTRACT

Waste sugar solution is harmful to the environment and abundant in organic waste, and waste sugar residue (WSR) was obtained by drying waste sugar solution. In order to efficiently solve this issue and created values, activated carbon was prepared by WSR with KOH as activation agent. Carbonization temperature, activation temperature, activation ratio and activation time were investigated, based on the effects of preparation conditions on the electrochemical performance of activated carbon. The electrode material shows superior electrochemical performance, especially when the activated carbon was prepared at the carbonization temperature of 600 °C, activation temperature of 700 °C, activation ratio of 3:1 (KOH:char) and activation time of 2.5 h. It possesses the optimal electrochemical performance with a specific capacitance of 273.31 F g^{-1} and a specific surface area of 1953 m^2 g^{-1}. In order to determine the electrochemical stability of activated carbon electrodes, the cycle lifetime was performed at a current density of 1.5 A g^{-1}. After 5000 cycles, the capacitance retention rate of 90.1% could be obtained. Additionally, the energy density was relatively high at 1.5 A g^{-1} (up to 5.09 Wh kg^{-1}). This study provides a value-added approach for WSR treatment and a potential feedstock for low cost-high performance activated carbons for electric double-layer capacitor.

1. Introduction

In modern society, limited fossil fuel energy and serious greenhouse effect have prompted researchers to develop a kind of efficient, economical and green energy storage device [1–3]. Electric double-layer capacitor (EDLC) is considered to be one of the most potential energy storage devices. Taking advantage of the charge separation in a Helmholtz double layer at the interface between the electrolyte and electrode, EDLC possesses the advantages of superior electrochemical performance, environmentally-friendly products and long cycle life [4–6]. It is well known that the electrochemical performances of EDLC are basically determined by the kind of electrode active materials which include activated carbon (AC) [7], carbon nanotube [8], carbon aerogel [9] and graphene [10]. AC is a relatively inexpensive and high-performance electrode material and also has porous structure, large specific surface area (SSA), variable characteristics of surface chemistry and excellent surface reactivity [11]. Meanwhile, it can be prepared by various raw materials, such as coal, coconut shell, fruit shell and biomass [12–15]. AC as the most successful electrode material in the commercialization, many electrochemical workers have focused on the exploration of new precursors via adopting different activation agents (KOH, H_2SO_4 and $ZnCl_2$) to prepare AC with extraordinary performance for EDLC [16–18]. Zhai et al. [19,20] used mesophase pitch to prepare ACs with KOH as activation agent and found the AC with SSA of 2258 m^2 g^{-1}. When AC was applied in the supercapacitors, it had the largest specific capacitance of 145 F g^{-1} in organic electrolytes as well as high energy density of 31 Wh kg^{-1} and power density of 12 kW kg^{-1}. Wu et al. [21] used enteromorpha overrunning in China Sea as precursor to prepare porous carbons with the activation agent of $ZnCl_2$. The specific capacitance reached 206 F g^{-1}, and 93% of the initial specific capacitance was retained even after 5000 cycles. Furthermore, the carbon precursor was activated by KOH, which is more efficient in activating precursor with higher SSA and more controllable pore size distribution, compared with H_2SO_4, $ZnCl_2$ and NaOH [22].

Recycling waste material not only can ease the energy crisis, can also adjust the energy resource structure and environment protection. Moreover, the process of manufacturing vitamin C resulted in the production of high concentrations of waste sugar solution (WSS), which contains various waste materials, such as waste acids and organics, and it will pollute the environment and waste the recyclable resource

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if discharged directly. In addition, WSS is generally used for the production of low value-added products, such as oxalate and detergent. Waste sugar residue (WSR) obtained by drying WSS can be used to prepare porous carbon, which has not been reported until now. Hence, it is significant and necessary to prepare high value-added item like porous AC based electrodes by recycling WSR. It is feasible for WSR to prepare ACs because of its low ash content and abundant elemental contents of C and O which are conducive to increase the electrochemical performance of ACs [23]. Besides, relatively high alkali metal content in WSR is beneficial to activation by the reduce of the application amount of activation agent to some extent [24].

In this study, WSR was favorable to be the precursor for the preparation of ACs with KOH as activation agent applied in EDLC. The prepared ACs were characterized by Fourier transform infrared (FTIR) spectrometer, scanning electron microscopy (SEM), X-ray diffraction (XRD) and N_2 adsorption-desorption. Subsequently, the electrochemical performances of AC based electrodes were investigated by galvanostatic charge-discharge (GCD), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. This paper focuses on the effects of carbonization temperature, activation temperature, activation ratio and activation time on the electrochemical performance of ACs prepared by WSR.

2. Experimental

2.1. Material

The WSS, collected from vitamin C pharmaceutical company in Shandong, China, was dried at 105 °C in the oven for 12 h and the dried WSR was pulverized to pass through a 200-mesh sieve followed by drying at 105 °C for 12 h. Ultimate analysis was carried out by an Elementar vario MACRO cube CHNS elemental determinator [25]. The main characteristics of the WSR are shown in Table 1. Thermodynamic property of WSR was investigated and the thermogravimetry (TG) and derivative thermogravimetry (DTG) are listed in Supplementary material.

2.2. Preparation and characterization of ACs

The AC was prepared by two-step carbonization/KOH-activation method under Ar flow at a fixed heating rate of 10 °C min^{-1} via WSR as the precursor.

Step 1 (carbonization), WSR was carbonized for 2 h at various carbonization temperatures for the preparation of char. Step 2 (KOH-activation), char was activated at various activation temperatures, activation ratios (KOH: char) and activation times. Then, the samples were rinsed with 2 M HCl solution and sufficient deionized water until neutral. Finally, the washed samples were dried at 150 °C for 3 h in a vacuum drying oven. The prepared ACs were designated on the basis of the naming rule: AC-*w*-*x*-*y*-*z* (w = 500, 600, 650 and 700, referring to the carbonization temperature of 500, 600, 650 and 700 °C, respectively; x = 500, 600, 700 and 800, referring to the activation temperature of 500, 600, 700 and 800 °C, respectively; y = 1, 2, 3 and 4, referring to the activation ratio of 1:1, 2:1, 3:1 and 4:1, respectively; z = 1.5, 2, 2.5 and 3, referring to the activation time of 1.5, 2, 2.5 and 3 h, respectively). The schematic illustration of the preparation process of ACs is shown in Fig. 1, and all the experimental data have been carried out in parallel.

Table 1
Proximate and ultimate analyses of WSR.

Proximate analysis (wt%)[a]			Ultimate analysis (daf, wt%)				
A_d	VM_d	FC_d[b]	C	H	N	O[b]	S
6.56	76.26	17.18	48.94	4.46	1.28	42.91	2.41

[a] A: ash; VM: volatile matter; FC: fixed carbon; d: dry basis; daf: dried and ash-free basis.
[b] Calculated by difference.

The functional groups on the surface of ACs were characterized by a Nicolet Corporation IR-560 FTIR spectrometer. A FEI Quanta TM 250 SEM was used to observe the surface morphology of the prepared samples. XRD analysis was performed on the Bruker D8 Advance X-ray diffractometer using Cu Kα radiation (λ = 0.15418 nm). The textural properties of the prepared ACs were tested by N_2 adsorption-desorption experiments at 77 K with a Quantachrome Autosorb-1 apparatus. Moreover, the Brunauer-Emmett-Teller (BET) method and Density Functional Theory (DFT) method were applied to reckon the SSA and the pore size distribution, respectively.

2.3. Fabrication of ACs electrodes and EDLCs

For the fabrication of AC electrodes, the AC (87 wt%) was homogeneously mixed with acetylene black (10 wt%) and polytetrafluoroethylene (PTFE, 3 wt%) in agate mortar [26]. Secondly, the mixture was grinded to half dry state and then was pressed onto the nickel foam which was used as a current collector with 13 mm diameter under a certain pressure for the preparation of electrode. Subsequently, electrodes were immersed in a 6 M KOH solution (24 h) which was used as electrolyte.

EDLC was assembled by two electrodes and a polymer separator in a MTI Corporation EQ-STC split test cell, and two electrodes were separated by polymer separator wetted with the 6 M KOH solution.

2.4. Electrochemical measurements

GCD, CV and EIS measurements are needed to be tested for the investigation of the electrochemical performance of EDLCs. GCD curves were recorded at current densities between 40 and 200 mA g^{-1} within the potential window of 0 to 0.9 V by a NEWARE CT-3008-5V50mA-164 battery testing system. The mass specific capacitance (C_S, F g^{-1}) of a single electrode is calculated by the slope of discharge curves, as the following equation [27]:

$$C_S = \frac{2I\Delta t}{m\Delta V} \quad (1)$$

where I (A) represents current, Δt (s) represents the time of discharge, m (g) represents the mass of single electrode, and ΔV (V) represents the drop of potential in Δt. An Iviumstat Vertex electrochemical workstation was used to assess CV and EIS. CV profiles were recorded between 0 and 1 V at different potential sweep rates. EIS was accomplished by a frequency range from 10 kHz to 10 mHz at open circuit voltage with amplitude of 10 mV.

3. Results and discussion

3.1. Characterization of ACs

The proximate analysis of WSR and the yields of carbonization and activation are listed in the Tables 1 and 2. WSR has relatively low ash content, and its carbonization and activation yields are comparable to the carbonization and activation yields of rice husk and peanut shell [28,29]. Besides, the computational equations of the yields of carbonization and activation are listed in the Supplementary material.

In order to figure out the changes of the surface functional groups, we characterized the WSR, char and AC-600-700-3-2.5 by FTIR spectrometer. As shown in Fig. 2, the peak at 3434 cm^{-1} is assigned to the stretching vibration of –OH stem from adsorbed water molecules and structural hydroxyl groups [30,31]. The weak peaks at 2920 and 1410 cm^{-1} of AC-600-700-2.5 can represent C-H stretching and -COO- symmetrical stretching vibration, respectively. The peaks around 1061–948 cm^{-1} represent hydroxyl stretching vibration in olefin and