Facile one-step synthesis of three-dimensional freestanding hierarchical porous carbon for high energy density supercapacitors in organic electrolyte

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ABSTRACT

Three-dimensional freestanding hierarchical porous carbon materials with high specific surface areas (up to $1688\,m^2\,g^{-1}$) were prepared by the one-step carbonization of sucrose and zinc chloride ($ZnCl_2$), defined as SCs for simplicity. Herein, ZnO particles served as the etchant and template to produce micropores and mesopores. The formation mechanism, morphology and structure were investigated by a series of techniques. The SCs exhibited highly enhanced electrochemical performances as supercapacitors, and the one synthesized at 800 °C (SC-800) showed high specific capacitances of $130\,F\,g^{-1}$ and $124\,F\,g^{-1}$ at the current densities of 1 and $20\,A\,g^{-1}$ in 1 M $TEABF_4/AN$, respectively. This device delivered the high energy density of $55\,Wh\,kg^{-1}$ to afford the power density of $2.5\,kW\,kg^{-1}$ (voltage range of 3 V) and good cycling stability (85% capacitance retention after 10,000 cycles).

1. Introduction

Recently, supercapacitors have attracted wide-spread attention as an important energy storage owing to their unique merits of fast charging/discharging, high power density and long cycle life [1]. Commonly, supercapacitors contain electrical double layer capacitors (EDLCs) and pseudo-capacitors based on the energy storage mechanism and structure [2]. The former stores the charges by electrostatic interactions using the reversible adsorption of ions from the electrolyte onto the activated carbon materials with high specific surface area (SSA) and good electrochemical stability [3]. Unlike EDLCs, the capacitance of pseudo-capacitors is originated from the fast and reversible redox reactions in the charge transfer procedures [4,5]. However, they seriously suffer from limited energy density when compared with batteries. According to the energy density equation [6]: $E = CV^2/2$ (*C*: cell capacitance; *V*: cell voltage), it is feasible to enhance the energy density by enlarging the durable cell voltage and capacitance, which highly depend on electrode materials in supercapacitor when the electrolyte and membrane material are identical [7].

Porous carbon materials are widely researched as advanced electrode materials in supercapacitors due to their large specific surface area, high chemical stability, good electronic conductivity and low-cost [8]. Among them, activated carbons are usually regarded as wide-spread active materials for constructing supercapacitors, thanks to the cost-effectiveness and wide availability of the carbon precursors, coupled with the renewable production [9]. Moreover, a variety of biological precursors were used as carbon resources, such as waste coffee beans [10], sugarcane bagasse [11], rice husk [12], and coconut shell [13].

As it is known, the electrochemical performances of the activated carbons mainly depend on the SSA and pore-size distribution [14]. Generally, it is highly rational to enlarge the specific surface area by chemical activation, physical activation, combined physical and chemical activation, and microwave-induced activation [15]. The specific surface areas are dramatically increased from 500 up to $3000\,m^2\,g^{-1}$ by the introduction of activating agents (*e.g.* KOH, NaOH, carbon dioxide and steam) [16–18]. Nevertheless, their conventional synthesis mainly suffers from the low yield, multi-stepped procedures and time-consuming operation [19,20]. For example, highly porous activated carbons were synthesized by a two-step approach combined the hydrothermal carbonization of sucrose and chemical activation with KOH [21].

Herein, a simple one-step sucrose-derived and zinc chloride ($ZnCl_2$)-assisted carbonization approach was developed to prepare hierarchical porous carbon materials at high temperature, defined as SCs for clarity. The synthesized SCs were examined as electrode materials for supercapacitor. Scheme 1 shows the preparation of symmetric supercapacitor.
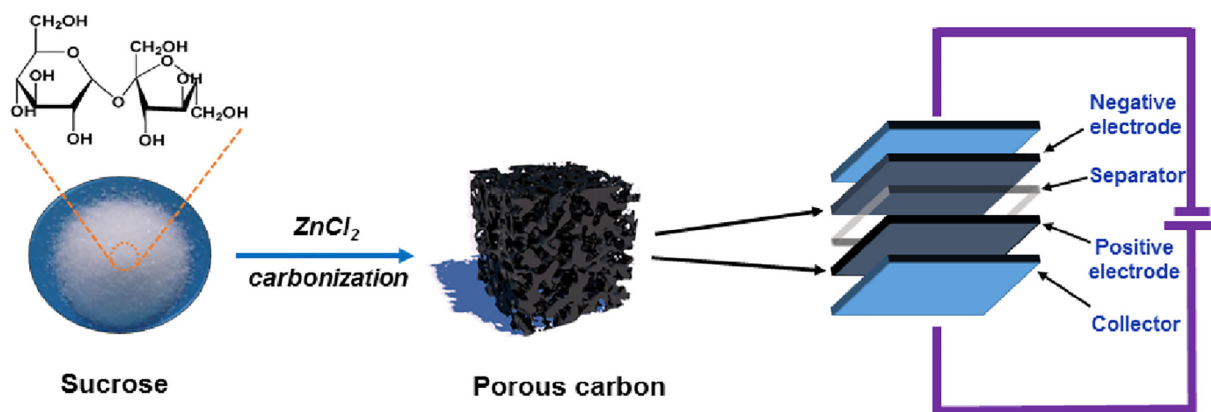
2. Experimental

2.1. Synthesis of the SCs

In a typical procedure, 1 g of sucrose and 3 g of $ZnCl_2$ were ground to form a homogeneous mixture, followed by heating the mixture up to

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Scheme 1. Schematic illustration of the preparation of the symmetric supercapacitor.

120 °C and remained for 1 h. Afterwards, the mixture was put into a tube furnace, and then heated to 750–900 °C at a rate of 5 °C min^{-1} for 2 h in the flowing N_2 atmosphere. After cooling down to room temperature naturally, the resultants were completely washed with a 2 M HCl solution, and thoroughly washed by distilled water until the neutral pH was obtained. Finally, the product was dried at 120 °C in a vacuum for 8 h. The obtained carbon samples were denoted as the SC-T for simplicity and clarity, where T is the carbonization temperature.

2.2. Physical characterization

The morphologies of the samples were recorded by scanning electron microscopy (SEM, Model S-4800) and transmission electron microscopy (TEM, JEM-2100F). The correlative X-ray diffraction (XRD) spectra were acquired on a Smart APex II (Bruker) instrument with a Cu-Kα radiation source. Raman spectra were obtained by using a Ranishaw RM1000 spectrometer with a laser operated at 514 nm. The surface chemical compositions were measured by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) with the Al-Kα radiation source. The nitrogen adsorption isotherms experiments were conducted by a Micromeritics ASAP 2020 analyzer at −196 °C. The surface area was measured by the BET method. The pore size distribution was calculated using the Non-local Density Functional Theory (NLDFT). Thermogravimetric analysis (TGA) was measured on a STA 449C (NETZSCH) instrument.

2.3. Electrochemical characterization

For the typical preparation of the electrode, 90 wt% of the obtained sample, 5 wt% of polyvinylidene fluoride (PVDF) as the binder, and 5 wt% of acetylene black were mixed together to obtain the homogeneous slurry. The slurry was uniformly casted onto an aluminum foil current collector and dried at 80 °C for 12 h in vacuum, and the fabricated electrode was punched into discs (14 mm in diameter). The mass of active materials loading on each electrode was controlled in ∼2 mg. Meanwhile, CR2025 type coin cells were fabricated in a glove box with nitrogen atmosphere, in which the contents of O_2 and H_2O were below 0.1 ppm. Herein, 1 M tetraethylammonium tetrafluoroborate salt (TEABF$_4$) was dissolved in acetonitrile (AN) as the organic electrolyte.

All the cyclic voltammetry (CV) and electrochemical impedance spectroscopy measurements were carried out on a CHI 660E electrochemical workstation with the conventional two-electrode system. The electrochemical impedance spectrum (EIS) was acquired in the frequency range from 100 kHz to 10 mHz with a 10 mV AC amplitude. The galvanostatic charge-discharge (GCD) and the cycling stability tests were conducted at a NEWARE Battery Test System. The specific capacitance (F g^{-1}), energy density (Wh kg^{-1}) and power density (kW kg^{-1}) were calculated by the following formulas:

$$C = 2I\Delta t/m\Delta V \tag{1}$$

$$E = 1/2C(\Delta V)^2 \tag{2}$$

$$P = E/\Delta t \tag{3}$$

where I (A) is the discharge current, m is the mass (g) of the active materials in the single electrode, ΔV (V) is the discharge voltage, and Δt (s) is the discharge time.

3. Results and discussion

3.1. Preparation and structural characteristics of the carbon materials

The hierarchical porous carbon materials (*i.e.* SCs) were formed by the direct pyrolysis of sucrose and $ZnCl_2$ under an inert atmosphere. In this context, $ZnCl_2$ is a Lewis acid, which promotes the dehydration of the carbon precursor and catalyzes the aromatic condensation reactions [22]. Besides, $ZnCl_2$ can react with oxygen donor (*e.g.* water), accompanied by hydrolysis to form ZnO ($ZnCl_2 + H_2O = ZnO + 2HCl$) [23], which plays an important role in the carbonization process, owing to its etching reaction of the carbon atoms to generate micropores at high temperature [24].

Thermogravimetric analysis (TGA) was conducted to investigate the pyrolysis behaviors of the sucrose/$ZnCl_2$ composites (Fig. 1A), using pure sucrose as the standard. As shown, the weight loss of pure sucrose mainly occurs in the two stages. Specifically, sucrose dehydrated and condensed to caramel in the temperature range of 190–220 °C. With the temperature increasing, sucrose was further carbonized, forming gaseous products (CO_2, CO, *etc.*) and furfural compounds [25]. On the contrary, the TGA curve of the sucrose/$ZnCl_2$ composites (Fig. 1B) clearly exhibits two weight losses from room temperature to 250 °C and 420–600 °C. The former is originated from the dehydration of the carbon precursor with the promotion of $ZnCl_2$ and the simultaneous formation of ZnO from the hydrolysis of $ZnCl_2$. The latter is associated with the volatilization of $ZnCl_2$ and aromatic condensation reactions [22,26].

The morphology and structure characteristics of the obtained SCs were firstly characterized by the SEM and TEM measurements. Fig. 2 exhibits the SEM and TEM images of the SC-800. The sample displays the typical amorphous porous structures with abundant macropores (Fig. 2A–B). And there are plentiful meso/macropores observed (Fig. 2C). Furthermore, a variety of randomly distributed micropores are observed from the HRTEM image (Fig. 2D), which are critical for charge accommodation [27]. The carbon materials become more porous due to the increased gaseous products (CO_2, CO, HCl, *etc.*) in carbonization process and the ZnO particles serve as an etchant at high temperature. In addition, the plicate edges are the typical characteristics of carbon materials, suggesting the formation of numerous tiny graphitization regions by the pyrolysis [28].