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Hierarchical porous carbon derived from sulfonated pitch for electrical double layer capacitors

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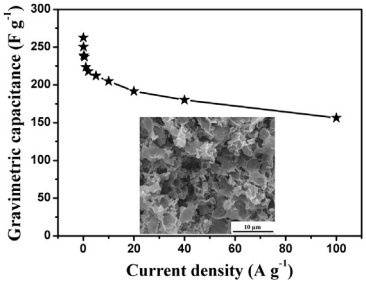
HIGHLIGHTS

- Sulfonated pitch was utilized to synthesize hierarchical porous carbon.
- High BET specific surface area of 2602 m^2 g^{-1} was obtained with an activation agent to precursor ration of 1.5.
- The specific capacitance could be maintained at 157 F g^{-1} even at 100 A g^{-1}.
- Outstanding cyclic stability with a super high capacitance retention ratio of 98.4% after 10,000 cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

Hierarchical porous carbon (HPC) has been synthesized using sulfonated pitch as a precursor with a simple KOH activation process. Sulfonated pitch has a high content of oxygen-containing groups which enable it to be easily wetted in KOH solution and facilitate the activation process. The effect of the activation agent to precursor ratio on the porosity and the specific surface area is studied by nitrogen adsorption–desorption. A maximum specific surface area of 3548 m^2 g^{-1} is achieved with a KOH to sulfonated pitch ratio of 3 and this produces a structure with micro-, meso- and macropores. Among the various HPC samples, the sample prepared with an activation agent to precursor ratio of 1.5 exhibits the best electrochemical performance as an electrode in an electrical double layer capacitor (EDLC) in 6 M KOH electrolyte. Its gravimetric specific capacitance is 157 F g^{-1} at a current density of 100 A g^{-1} and it has a capacitance retention ratio of 98.4% even after 10,000 cycles. The sample also presents outstanding electrochemical performance in 1 M Li_2SO_4 and 1 M TEA BF_4/PC electrolytes. Thus, HPC derived from sulfonated pitch is a promising electrode material for EDLCs.

1. Introduction

Electrical double layer capacitors (EDLCs) have stimulated extensive interest due to their advantages of high power capability, superior reversibility and long cycle life, which are required for new energy storage devices [1,2]. Charge storage in EDLCs utilizes electrostatic adsorption of the electrolyte ions at the electrode–electrolyte interface [3]. An ideal electrode material is expected to

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possess a large surface area, an optimal pore size distribution and excellent conductivity for fast transport of the electrolyte ions and charges [4].

Microporous activated carbons are the most common electrode material because of their high surface area, good conductivity, and chemical inertness [5]. Microporous activated carbon electrodes exhibit high specific capacitances at low current densities. However, the capacitance decreases dramatically with increasing current density. This is mainly caused by many small micropores and irregularly curved pores which slow down the ion transport rate and thus limit power storage. To solve this problem, activated carbons with controllable pore sizes and high surface areas are required.

Currently, hierarchical porous carbons (HPCs) with micro-, meso- and macropore structures have attracted much attention. In these materials the micropores provide abundant adsorption sites which are the primary contributors to the large specific capacitances [6]; the mesopores facilitate the diffusion of the electrolyte ions so they reach the available surface area and the macropores act as ion-buffering reservoirs to ensure adequate penetration of the electrolyte into the electrode materials [7]. In fact, the use of HPCs as electrode materials has been demonstrated to simultaneously achieve high energy and power densities.

The most common method to synthesize HPCs is the template method which has three steps: template replication, carbonization and removal of the template [8]. Various templates such as hierarchical porous silica monoliths [9] and powdery silica [10] have been used. For example, Kim et al. [11] used a beta zeolite as a hard template to synthesize HPC with micropores of 1 nm diameter and mesopores of 10–30 nm. Ma et al. [12] reported the synthesis of micro- and mesoporous carbons spheres by colloidal silica as template. Yamada et al. [13] used colloidal crystals as templates to synthesize 3D ordered porous carbons. Oschatz et al. [14] prepared the carbide-derived carbon materials (CDCs) containing micro-, meso-, and macropores through combining a soft-template approach with subsequent chlorine etching. This new synthesis route avoids the use of hard templates, thus the corresponding template removal process is avoided. Liang and Dai [15] reported the synthesis of highly ordered porous carbon by using self-assembled block copolymers as soft templates. In this method, the extra step of generating a template was unnecessary. Adelhelm et al. [16] used an organic polymer as the template to prepare a meso- and macroporous carbon using spinodal decomposition of the templates and a carbon precursor. Liu and co-workers [17] developed a new way to prepare nanoporous carbon using metal-organic frameworks as the template. The obtained nanoporous carbon with micro-, meso- and macropore structures exhibited remarkable electrochemical performance as an electrode of EDLC. However, all of the above methods contain complicated multistep procedures, which are tedious, cost and low yields, limiting their practical applications. Thus, new template-free methods are needed to synthesize HPCs. Lv et al. [18] reported the synthesis of hierarchical porous carbon foams from the bioresource banana peel through a self-template approach by utilizing its natural pore and zinc ions as the self-template.

In present work, sulfonated pitch (SP) is employed as the raw materials to prepare the HPCs. The SP contains a high concentration of oxygen-containing groups, providing many reactive sites for activation. More importantly, the presence of heteroatoms, e.g. S, O and N enhances the polarity of the carbon surface and increases the affinity of the surface for aqueous electrolytes. It is believed that sulfonated pitch is partly dissolved and partly dispersed in hydrosols [19]. This occurs through nano-scale contact between the reagents and the precursor, which should make it possible to prepare HPCs with large surface areas and well-developed porous structures. Moreover, the oxygen-containing groups in the sulfonated pitch are unstable and can decompose to CO_2 and CO during heat treatment, which can assist in creating additional pores [20]. These properties should enable sulfonated pitch a promising candidate for producing HPCs with the characteristics of preparation simplicity and easy scalability. Combing the advantage of commercially availability, sulfonated pitch precursor shows great potential in the energy storage field.

2. Experimental

2.1. Material preparation

Sulfonated pitch, purchased from Originchem Co., Ltd, was used as the raw material to prepare HPCs. Sulfonated pitch was added to KOH solutions with different KOH to precursor mass ratios and stirred for 1 h. The mixtures were dried at 80 °C for 12 h, and then transferred into a tube furnace and heat-treated at 800 °C for 2 h under a flow of nitrogen. After activation, the samples were washed three times with 1 M HCl solution. Then they were repeatedly rinsed by deionized water for three to five times until the pH of the washing solution was 7. Finally, the samples were dried at 120 °C for 12 h. The obtained samples were named HPC-*x* where *x* represents the weight ratio of solid KOH to sulfonated pitch.

2.2. Characterization

The surface of the samples was characterized by X-ray photoelectron spectroscopy (XPS) using a PHI-1600ESCA electron system (America PE Company) with Al Kα (1486.6 eV) radiation. Fourier transform infrared spectrometry (FT-IR) was carried out with a Nicolet Magna-IR 560 FTIR spectrometer over the wavenumber range of 4000–400 cm^{-1}. Thermogravimetric analysis (TGA) was performed using a TA-50 instrument in a nitrogen atmosphere. Raman spectra were measured by a Renishaw MKI-2000 Raman microscope using an Ar ion laser (488 nm) as the excitation source. The specific surface areas and the pore structures of the samples were examined by nitrogen adsorption measurements at 77 K (ASAP 2020, Micromeritics, USA). Before the measurements, the samples were degassed at 300 °C for 5 h under vacuum. The specific surface area and the total pore volume were calculated using the Brunauer–Emmett–Teller (BET) theory over a relative pressure (P/P_0) range from 0.1 to 0.3 and the volume of nitrogen adsorbed at a relative pressure of 0.99, respectively. The micropore volume was calculated using the t-plot method, and the surface areas and pore volumes of the mesoporous were analyzed according to the Barrett–Joyner–Halenda (BJH) method. The pore size distributions were studied using the nonlocal density function theory (NLDFT) model assuming slit-shaped pores. The microstructures of the HPCs were investigated using field emission scanning electron microscopy (FESEM, Nano430) and high-resolution transmission electron microscopy (HRTEM, Philips Tecnai G2 F20). The samples were deposited on the conductive paste, subsequently coated with gold using a gold sputtering device for field emission scanning electron microscopy and dispersed in absolute ethanol with ultrasonication for 30 min, then dropped onto copper mesh for high-resolution transmission electron microscopy.

2.3. EDLC construction and electrochemical measurements

The obtained HPC material (80 wt%), acetylene black (10 wt%) and poly(tetrafluoroethylene) (10 wt%) were homogenized in a mortar, rolled into an electrode membrane (13 mm in diameter, 100 μm thick). The characterization of the electrode material was performed using a symmetric EDLC cell composed of two HPC-