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RESEARCH PAPER

Efficient preparation of porous carbons from coal tar pitch for high performance supercapacitors

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Abstract: Porous carbons (PCs) for supercapacitors were prepared from coal tar pitch by a one-step microwave-assisted KOH activation with low KOH consumption. The surface area of the PC (PC_{2-M}) made at a KOH/pitch mass ratio of 2 with microwave heating for 30 min reaches 1786 m^2/g. The electrochemical performance of the PC electrode for supercapacitors was evaluated in different electrolytes including KOH, K_2SO_4, Na_2SO_4, Li_2SO_4 in water, and tetraethylammoniatetra fluoroborate in propylene carbonate. The supercapacitors have a high specific capacitance of 267 F/g in 6 mol/L KOH aqueous electrolyte at 0.1 A/g and a high energy density of 12.0 Wh/kg at 1318 W/kg in a 0.5 mol/L K_2SO_4 neutral electrolyte. The one-step microwave-assisted KOH activation is a simple, efficient and low energy-consumption approach for the preparation of high performance PCs for supercapacitors.

Key Words: Coal tar pitch; Porous carbon; Microwave-assisted KOH activation; Supercapacitor

1 Introduction

Supercapacitors with a high power density and an excellent cycling stability are the crucial alternatives in energy storage devices that can meet the fast-growing energy demands and ever-increasing environmental concerns[1,2]. Porous carbons (PCs) have been used as electrode materials of supercapacitors owing to their high surface area and good conductivity[3,4]. Usually, PCs with high surface areas are made by potassium hydroxide (KOH) activation through an external heating source such as electric furnace[5,6]. However, in the external heating mode, thermal energy is firstly supplied to the surface of granular raw material and then transferred to the inside part by heat conduction. Therefore, it is difficult to achieve a uniform temperature within granular reactant by the conventional heating method. Besides, the preparation of PCs with an extremely high surface area by KOH activation usually involves a high KOH consumption and a long activation time, which results in a high energy consumption and a high production cost of PCs. Moreover, the excess surface area of PCs may be profitless for supercapacitors [7]. Consequently, it is urgent to develop an effective technique to produce PCs at both low energy and KOH consumptions from the viewpoint of economic, environmental and societal issues.

Microwave-assisted activation has many advantages over the conventional activation in terms of the quick and uniform heating feature, and the low energy consumption [8], of which energy is supplied to the whole granular materials by producing a high-frequency energy at molecular level based on the intermolecular friction, resulting in a uniform and rapid temperature rise of the bulk granular raw materials. Previously, we found that PCs with a high surface area could be made from petroleum coke by microwave-assisted KOH activation at KOH/coke mass ratio of 5/1, in which KOH consumption was high and needed to be further reduced [9]. As such, one of the key challenges is how to efficiently produce PCs with a desired pore structure for supercapacitors at both a low KOH consumption and energy consumption. As a by-product of the coking process in coal industry, coal tar pitch with a high content of carbonaceous polycyclic aromatics but a low ash content becomes an attractive carbon precursor for the preparation of PCs with a high carbon yield[10].

The capacitance of PC electrodes in supercapacitors depends on the specific surface area, pore size distribution, surface functional groups, conductive properties of PCs, and the properties of the electrolyte. Aqueous (basic and neutral) electrolyte[11−13] and organic electrolyte[14] as well as ionic liquids[15,16] are the main electrolytes used for supercapacitors. Basic and neutral electrolytes are often used owing to their high conductivities and low corrosivities. As for organic electrolytes, they are also welcome because they enable supercapacitors to be operated even at a high voltage of 2.7 V. The electrochemical properties of PC electrodes are decided not only by the exposed surface area, but also by the matching degree between the pore size of PCs and the size of electrolyte ions. The pores in PCs need to be optimized because the pores that are too large or too small would either reduce the density of electrode materials or keep out the electrolyte ions. Besides,

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different electrolytes endow PC electrodes different capacitances and energy densities. Based on above considerations, it is necessary to seek the most favorable electrolyte for selected PC electrode to obtain a high energy density for supercapacitors.

Herein, we report a simple yet efficient method to make PCs with well-developed micropores and mesopores from coal tar pitch by a one-step microwave-assisted KOH activation. The reductions in activation time and KOH dose due to a selective heating of granular raw materials by the microwave-assisted activation lead to an obvious decrease of energy consumption and an increase of the ratio of performance to cost of PCs. The effects of KOH/pitch mass ratio, activation method and electrolyte types including 6 mol/L KOH, 0.5 mol/L K_2SO_4, 0.5 mol/L Na_2SO_4, 0.5 mol/L Li_2SO_4 aqueous solutions and 1 mol/L tetraethylammonia tetrafluoroborate (Et_4NBF_4) in propylene carbonate on the electrochemical performance of PCs for supercapacitors have been addressed in details.

2 Experimental

A commercial coal tar pitch with a softening point of 383 K (Maanshan Ion & Steel Co. Ltd.) was used as carbon precursor, and its proximate analysis and elemental analysis could be found elsewhere [17].

For a typical run, the mixture of coal tar pitch with particle size smaller than 100 μm and KOH at different mass ratios was ground and physically mixed in solid state. The pulverized mixture was transferred to a corundum crucible placed in a quartz protector and then heated for 30 min in a nitrogen flow of 80 mL/min at a continuous microwave output power of 600 W in a microwave reactor (LWMC-205, Nanjing Robiot Co., Ltd, China). The temperature of the reactants in corundum crucible was measured by an armor type thermocouple. The obtained samples in the crucible were washed with 0.5 mol/L HCl solution and distilled water, and dried at 383 K for 24 h to obtain the PCs. As-made PCs are nominated as PC_{x-M}, where x stands for the mass ratio of KOH to pitch, and M stands for the microwave-assisted activation.

For comparison, PC was made from the same mixture of KOH and coal tar pitch by a conventional activation in a nitrogen flow of 80 mL/min at 5 K/min to 1183 K, i.e. the same temperature as that of PC_{2-M}. The PC made by the conventional activation is nominated as PC_{x-C}, where the subscript C stands for the conventional activation. In addition, PC_{x-p-C} was also made from the mixture of KOH and coal tar pitch at 5 K/min to 1183 K and then held for 1 h in the nitrogen flow by the conventional activation, where the subscript p stands for the sample being pressed into a monolith (20 mm in diameter, 5 mm in height) under 15.0 MPa for 10 s. There was no difference between the morphology of PC_{x-C} and PC_{x-p-C} before and after KOH activation. The PC_{x-p-C} is not monolith.

The pore structure of PCs was studied by nitrogen adsorption-desorption isotherms using ASAP2010. The surface area (S_{BET}) was calculated by Brunauer−Emmett−Teller (BET) equation in a relative pressure range from 0.05 to 0.24. The pore size distribution was calculated via the density functional theory (DFT) model assuming a slit pore geometry. The total pore volume (V_t) was obtained at a relative pressure of 0.99. The micropore volume (V_{mic}) was estimated by the t-plot method. The mesopore volume (V_{meso}) was calculated from the difference between V_t and V_{mic}. The average pore size (D_{ap}) was obtained according to $D_{ap} = 4V_t/S_{BET}$. The chemical states and the surface chemical composition of carbon, oxygen and nitrogen elements in PCs were characterized by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB250, USA) [18]. The binding energy was calibrated according to the main C1s peak at 284.6 eV. The binding energy of oxygen around 531.3, 532.9, and 535.2 eV represents the C=O quinine type groups, the C−OH phenol groups and C−O−C ether groups, and the chemisorbed oxygen (COOH carboxylic groups) and water, respectively. The peaks were deconvoluted by means of a standard Casa XPS software (product of Casa XPS Software Ltd., U.S.A) after background subtraction. The contents of oxygen-containing functional groups in PCs were also determined via Boehm titration[19].

The electrodes were made by mixing PCs (87%), carbon black (5%) with a BET surface area of 550 m^2/g and polytetrafluoroethylene (8%), and then pressed at 15.0 MPa for 10 s followed by drying at 383 K for 1 h under vacuum condition. A button-type supercapacitor was assembled with two similar carbon electrodes separated by a separator. The mass loading of the electrode material was about 9 mg/cm^2. For 6 mol/L KOH, 0.5 mol/L K_2SO_4, 0.5 mol/L Na_2SO_4 and 0.5 mol/L Li_2SO_4 electrolytes, the separator was polypropylene membrane and the current collector was nickel foam. For 1 mol/L Et_4NBF_4 organic electrolyte, the separator was TF4050 and the current collector was aluminum foil. The electrochemical performance of supercapacitors in a two-electrode configuration was evaluated by cyclic voltammetry at scan rates from 2 to 50 mV/s at a voltage window ranging from 1 to 1.6 V in neutral electrolytes. The electrochemical impedance spectra were obtained on a CHI760C electrochemical workstation (CH Instrument, Shanghai, China). The charge/discharge performance of supercapacitors was carried out on a CT2001A cell tester (Wuhan, Land Electronic Co. Ltd.) and a supercapacitor test system (SCTs, Arbin Instruments, USA). The maximum voltages for supercapacitors in 6 mol/L KOH, 0.5 mol/L neutral electrolytes, and 1 mol/L Et_4NBF_4 organic electrolyte were 1.0, 1.6, and 2.7 V, respectively. The specific capacitance of the PC electrodes (C, in F/g) was calculated from the slope of the discharge curve according to Eq. (1).

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

Where I is the discharge current (A), $\dfrac{\Delta V}{\Delta t}$ (V/s) is the slope