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Preparation of nitrogen-doped pitch-based carbon materials for supercapacitors

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ABSTRACT

Coal tar pitches (CTP) are used as precursor of electrode material because of their low cost and high carbon yield. In this study, CTP-based activated carbon materials (CACs) with high capacitance for supercapacitors were prepared by doping elemental N with co-carbonization of CTP and melamine. The electrochemical performance and textural characterization of CACs were investigated by constructing a single electrode capacitor in a 6 M KOH electrolyte, N_2 adsorption, scanning electron microscopy, and XPS. Results show that CACs with mass proportion of melamine and CTP being 1:5 possess a surface area of 2573 $m^2\ g^{-1}$, with mesopore volume accounting for 56% of the total volume. After co-carbonization, N content on the surface of the CACs increased by 134% compared to that of undoped activated carbons. Their capacitance reached up to 228 $F\ g^{-1}$ at a current density of 1 $A\ g^{-1}$. The high electrochemical performance of the CACs is attributed to its additional pseudo-capacitance and high surface area. The specific capacitance still possessed 94.2% retention after 1000 cycles, indicating good cycle stability.

1. Introduction

Electric double-layer capacitors (EDLCs), which are also known as electrochemical supercapacitors, are recognized as new promising energy storage devices that have attracted considerable attention because of their advantageous characteristics such as high power density, rapid charging/discharging ability, and long cycle life [1–3]. The study of EDLCs has become a globally popular research topic in recent years. In the literature, electrode materials play key roles in developing the specific capacitance of EDLCs [4]. Activated carbons (ACs), which possess high surface area, good chemical stability, low cost, and large porosity [5–7], can be prepared from various carbonaceous source materials, such as synthetic polymers [8,9], agricultural wastes [10], and fossil fuels [11].

Recent studies have revealed that the heteroatom species of nitrogen in carbon materials, such as carbon fibers and carbon nanotubes, could induce additional pseudo-capacitance via wettability and revisable redox reaction, consequently improving the total specific capacitance of the supercapacitor [12–15]. Electrochemical characterization studies have stated that nitrogen content is responsible for high surface area and pseudo capacitance in improving specific capacitance by enhanced electric double layer formation [16]. Candelaria et al. [17] reported on the modification of resorcinol-furfural porous carbon with hexamine. Surface modification increased the amount of nitrogen four times when compared to unmodified carbon. The increment of surface polarity dramatically improved the wetting behavior of the porous carbon and produced specific capacitance that was nearly twice that of the unmodified carbon.

As an N-enriched carbon precursor, melamine has high nitrogen content, and unlike other polymer precursors, it can maintain the high nitrogen content (>10 wt%) at high temperatures (over 800 °C) [18]. Zhang et al. [19] described the preparation of N-enriched activated carbons for electrochemical capacitors from carbonized coal with melamine acting as an activating agent. The results showed that the activated carbon had a capacitance of 188 $F\ g^{-1}$ at a current density of 50 mA g^{-1} when the mass ratio of carbonized coal and melamine was 3:2. The process involves the removal of ash, which increases the cost. More importantly, the reaction between carbonized coal and melamine is a heterogeneous reaction, which is not beneficial to the introduction of N to carbonized coal.

From the perspective of applications, coal tar pitch (CTP) is regarded as a very suitable precursor for preparing ACs [20,21] because of its low price, low ash content ($\sim$0.2 wt%), and high carbon yield. The prepared ACs, which possessed good thermal stability, high mesopore content, and large superficial area, are particularly suited for applications in supercapacitors [22]. However, limited studies on electrochemical capacitors have explored the preparation of carbon materials with CTP as carbon precursor.

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A previous study [24] has prepared porous carbons from CTP with MgO [23] and Fe_2O_3 as templates for supercapacitors with specific capacitance of 100 and 194 F g^{-1}, respectively. These materials either possess low capacitance or have expensive fabricating cost with the utilization of nano materials. In fact, CTP can be far easily modified than coal because the former has a lower softening point and contains a significant amount of active unsaturated aromatic species. Thus, melamine with 66.7 wt% elemental N acting as nitrogen source is added into the CTP for co-carbonization to enhance the surface polarity of the prepared material and to improve the specific capacitance. As the temperature is increased, the mixture of CTP and melamine with inhomogeneous system gradually resulted in homogeneous reactions. In this environment, CTP and melamine can fully access each other. This stage facilitated the occurrence of two reactants. That is, N content of the co-carbonization material would be greatly enhanced after the reaction. To our knowledge, the preparation of melamine-doped pitch-based carbon materials for supercapacitors has not been reported in the literature so far. The surface structure of the N-doped CTP-based carbon material was characterized by scanning electron microscopy (SEM) and nitrogen adsorption instrument. Their electrochemical performance was investigated by constructing a single electrode capacitor by electrochemical work station in a 6 M KOH electrolyte.

Experimental

Materials: Melamine was obtained from Aladdin Industrial Corporation. Potassium hydroxide was purchased from a commercial chemical reagent company.

Commercially available CTP was used as carbon precursor (softening point of 120 °C, ash content of 0.2 wt%, and the contents of elements C, H, O, N, and S were 93.48%, 4.59%, 0.16%, 1.01%, and 0.56 wt%, respectively). CTP was ground and screened by a sieve of 100 mesh (149 μm) before being used.

Preparation of N-doped pitch-based carbon materials: Melamine and CTP of different mass proportions (0:1,1:7, 1:5, 1:3 and 1:1) were mixed and heated at a heating rate of 5 °C min^{-1} to 250 °C and then rinsed at a rate of 3 °C min^{-1} to 500 °C under N_2 flow rate of 50 mL min^{-1}, followed by maintaining for 2 h. After that, carbonization products were ground to powder and mixed with KOH powder with a weight proportion of 1:3, followed by heating until the temperature of 800 °C and standing for 2 h. After cooling, the carbon materials were washed repeatedly with 1 mol L^{-1} hydrochloric acid solution and distilled water until the pH of the filtrating solution was 6–7. Finally, the cleaned sample was dried at 110 °C for 4 h. The resultant carbon materials are referred to as CAC-N-*x*, where *x* is percentage value of melamine in the mixture of CTP and melamine.

Characterization: Iodine adsorption value was determined by the method published by the state standard of the People's Republic of China of GB/T 12496.8-1999. Thermogravimetric analysis (TG) was conducted with a BOIF WCD-2D analyzer. Approximately 10 mg of sample placed in a platinum crucible was heated to the designed temperature with a carrier gas (N_2) flow rate of 80 mL min^{-1} and heating rate of 10 °C min^{-1}. The pore structures of the resultant N-doped pitched carbon materials were obtained using a Micrometrics ASAP 2020 adsorption instrument at a temperature of 77 K. The specific surface area was calculated from the Brunauer–Emmett–Teller (BET) plot of the nitrogen adsorption isotherm. The micro-pore volume (V_{mic}) and total volume (V_t) were estimated by using the *t*-plot method. The morphologies for the material were observed by SEM (TESCAN MIRA 3).

Electrochemical analysis was performed on a CHI660D electrochemical work station in 6 M KOH electrolyte. A typical three-electrode experimental cell equipped with a working electrode, a platinum plate as a counter electrode, and a saturated calomel electrode as reference electrode were used for measuring the electrochemical properties of the working electrode. To prepare the working electrode, the carbon material powders were mixed with polytetrafluoroetylene and acetylene black at a mass ratio of 8:1:1. The mixture was pressed on a nickel foam current collector disks with a diameter of 12 mm. The electrode test consisted of cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS) measurements. The CV and galvanostatic charge/discharge measurements were obtained at a scan rate of 10, 20, and 40 mV s^{-1} in the potential range of 0 to −1 V. The EIS measurements were carried out with an amplitude of 5 mV over the frequency range of 0.01 Hz to 100 kHz.

The specific capacitance (C) of a single electrode was calculated from the charge–discharge curve using Eq. (1):

$$C = i \cdot t/(m \cdot v) \tag{1}$$

where *i*, *t*, *m*, and *v* refer to the discharge current, discharging time, the mass of active materials in the working electrode and the voltage drop upon discharge, respectively.

2. Results and discussion

Preparation of materials: Iodine adsorption is relatively easy. The surface area of carbon materials can be preliminary reflected by the adsorption value. For this reason, iodine adsorption values and specific capacitance from as-prepared carbon materials at different mass proportion of CTP to melamine were investigated, as shown in Fig. 1(a). The results indicated that CACs from CTP and melamine have higher iodine adsorption value and specific capacitance than that from CTP. The addition of melamine in CTP greatly increased the iodine adsorption and specific capacitance of

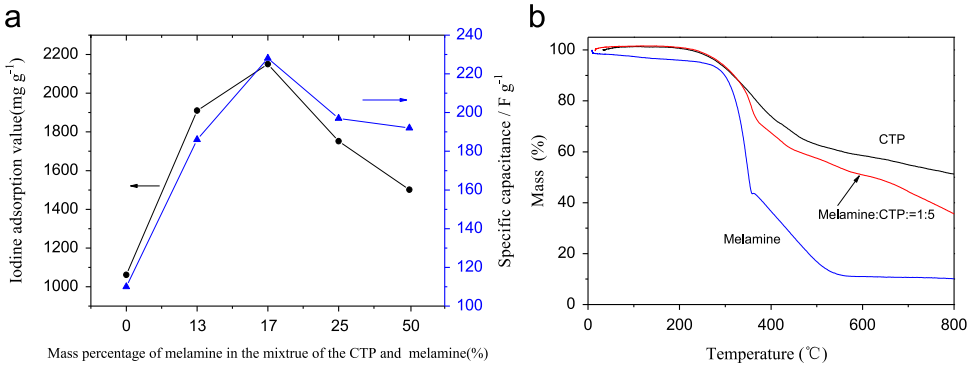

Fig. 1. (a) Iodine adsorption value and specific capacitance at current density of 1 A g^{-1} from CACs with different mass proportion of melamine; (b) TG curves of CTP and melamine.