



Influence of nitric acid activation on structure and capacitive performances of ordered mesoporous carbon



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ABSTRACT

Ordered mesoporous carbon CMK-3 was successfully prepared by a hard template nanocasting method followed by carbonization at temperatures from 700 to 900 °C. The values of specific surface area, pore diameter and pore volume were found to increase with the rise of carbonization temperatures. After chemical activation by 6M HNO₃, the specific surface areas decreased significantly, but the specific capacitances increased remarkably in both alkaline (3 M KOH) and neutral (0.5 M Na₂SO₄) electrolytes. Analysis of the surface structure and composition showed that the chemical activation introduced oxygen-containing functional groups on carbon surface, which are responsible for the enhancement of supercapacitive performances revealed by electrochemical tests. The best achieved specific capacitance is 182.1 F/g in 0.5 M Na₂SO₄, and 223.5 F/g in 3 M KOH, both at the current density of 0.5 A/g. The specific capacitance retentions after 500 cycles are 95.6% and 86.3% in 0.5 M Na₂SO₄ and 3 M KOH, respectively. The higher specific capacitance in KOH electrolyte is due to the lower faradic charge transfer resistance and better electrochemical surface area utilization than in Na₂SO₄ electrolyte.

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1. Introduction

Due to the depleting energy resources and increasing environmental concerns, one of the biggest challenges for researchers is to design high-performance energy storage and conversion devices, such as batteries, fuel cells and supercapacitors, to meet the present day power demands [1,2]. Supercapacitors are one of rechargeable electrochemical energy-storage device, in that charge carriers migrate reciprocally between electrolytes and electrodes in the processes of charging and discharging. Supercapacitors have high power density, excellent reversibility, and long cycle life so that they are particularly suitable for large-scale applications of portable electronic systems and automotives. However, one of the major barriers of supercapacitors is the relatively low energy density so that efforts are being made in this respect by designing and optimizing the materials for electrodes, which are one of the key components of supercapacitors.

Porous carbons are widely used as supercapacitor electrode materials because of their relatively low cost, high specific areas, large pore volumes, chemical inertness, and good mechanical stability [3]. It is well known that the pore structures (micro-, meso- and macro-pore) critically affect the physical and chemical

properties of porous carbon materials [4,5]. An abundance of micropores can certainly lead to a large specific surface area, but the exposed surface in micropores cannot be fully utilized for charge storage due to the low ionic mobility in such small pores [6]. In order to enhance both specific capacitance and rate performance of carbon electrodes, much attention has been paid towards fabrication of mesoporous carbon, where pore size distribution was concentrated at the desired region using nano-template materials [7–9]. The presence of mesopores could shorten the path length of micropores for ion transportation, and could alleviate pore blockage in micropores due to the aggregation of ions [10]. The first example of mesoporous carbon obtained by the nanocasting method was synthesized by using siliceous molecular sieve MCM-48 as a hard template in 1999 [11].

Up to now, ordered mesoporous carbons with different porous structure are prepared by various methods such as hard template nanocasting, soft template replicating and self-assembly. Several reports have exhibited promising electrochemical capacitive properties of the mesoporous carbons as supercapacitor electrode materials [6,12–14]. For instance, Zhou *et al.* [12] synthesized the self-ordered mesoporous carbons (CMK-3), from a template of hexagonal self-ordered mesoporous SiO₂ (SBA-15) using sucrose as the carbon source, and exhibited a capacitance of 60–90 F/g in scan rates from 50 to 0.5 mV/s in 1 M LiPF₆. Li *et al.* [13] synthesized mesoporous carbons by converting triblock copolymers (P123) and sucrose in the channels of SBA-15 into carbon and achieved the

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highest specific capacitance of 170 F/g at a scan rate of 100 mV/s in 30% KOH. Xia *et al.* [14] synthesized ordered mesoporous carbons CMK-3 from mesoporous silica SBA-15, and reported a maximum specific capacitance of 115 F/g at 2 mV/s in 6 M KOH.

In order to further improve the capacitive performance, several studies have found that functional groups containing foreign atoms such as O, N, B, and P, introduced using methods of dry or wet chemical oxidation, plasma treatment, and electrochemical modifications, are favorable to enhance the capacitance [14–16]. Generally, wet chemical oxidation which involves the use of nitric acid, sulfuric acid, potassium hydroxide, *etc.* can provide high energy and power densities, and is compatible with the processing of supercapacitors in industry [17]. The ordered mesoporous carbons CMK-3 by CO₂ activation synthesized by Xia *et al.* [14] reached a specific capacitance of 223 F/g at a scan rate of 2 mV/s, and a retention ratio of 73% at 50 mV/s. Li *et al.* [15] synthesized ordered mesoporous carbon materials by an facile oxidation method in nitric acid aqueous solution and the specific capacitance reached ~250 F/g at a scan rate of 1 mV/s. Recently, Lang *et al.* [16] synthesized ordered mesoporous carbon CMK-3 by a hard template nanocasting method, and after nitric acid modification, the capacitive performance was improved in KOH electrolyte, but showed no change in Na₂SO₄ electrolyte. However, it remains unclear of the mechanisms for this electrolyte-dependence of the enhancements by chemical activations of carbon materials.

In this study, orderly mesoporous carbon CMK-3 was synthesized through the hard template nanocasting method followed by carbonization at temperatures from 700 to 900 °C. Afterwards, the samples were chemically activated by 6 M HNO₃. The present work is mainly focused on the supercapacitive properties of CMK-3 before and after chemical activation in both Na₂SO₄ and KOH electrolytes. In such a way, it can be possible to understand the redox reaction of functional groups on carbon surface, which could affect the capacitance of electrodes in an electrolyte solution. Finally, a detailed electrochemical study in a three-electrode cell was performed to investigate the effects of nitric acid modification, the capacitive performances of the electrodes are obviously improved in both Na₂SO₄ and KOH electrolytes.

2. Experimental

2.1. Materials and agents

The main materials used in this work were sucrose (AR), concentrated H₂SO₄ (98 wt%), HF (35 wt%) and HNO₃ (68 wt%) from Shanghai Sinopharm Chemical Reagent Company, China. Mesoporous silica SBA-15 was purchased from Nanjing XF Nano Materials Technology Company. Nickel foams were purchased from Jiangsu Kunshan Desso Electronic Company. Acetylene black and polytetrafluoroethylene (PTFE) were of reagent quality. All the chemicals were used as received without any further purification.

2.2. Synthesis of mesoporous carbon CMK-3

The mesoporous carbon CMK-3, which is the carbon replica of the SBA-15 silica template, was prepared using sucrose as the carbon source. The synthesis procedure of CMK-3 was similar to that reported by Ryoo *et al.* [11] except for the process of carbonization. In a typical experiment procedure, 1.0 g of SBA-15 was impregnated in a solution which was obtained by dissolving 1.25 g of sucrose and 0.14 g of H₂SO₄ in 5.0 g of deionized water. Then, the mixture was dried in an oven at 100 °C for 6 h, and subsequently maintained at 160 °C for 6 h, to produce a silica sample with partially polymerized and carbonized sucrose. Afterwards, the silica sample was impregnated again in a fresh aqueous solution of 0.8 g of sucrose, 0.09 g of H₂SO₄ and 5.0 g of

deionized water, and was treated again at 100 °C and 160 °C for 6 h, respectively. In order to analyze the influence of carbonization temperature on the CMK-3, the carbon/silica composite was placed in the tube furnace and heated (1 °C/min) under nitrogen at three different temperatures (*i.e.* 700 °C, 800 °C and 900 °C, respectively) for 4 h to complete the carbonization. The carbon/silica composite after pyrolysis was washed by 10% HF solution at room temperature (approximately 25 °C) for 24 h under magnetic stirring, to remove completely the silica template. Finally, the template-free carbon products were filtrated, washed with deionized water until the pH value of the filtrate was around 7 and further dried at 80 °C for 12 h in air. Accordingly, the obtained samples of CMK-3 were denoted as CMK-3-700, CMK-3-800 and CMK-3-900, respectively, where the numbers stands for the heat-treatment temperatures.

2.3. Chemical activation of mesoporous carbon CMK-3

The chemical activation of HNO₃ was performed to introduce oxygen-containing functional groups on the carbon CMK-3 surface. Briefly, 0.2 g of the samples (CMK-3-700, CMK-3-800 and CMK-3-900) was suspended in 25 ml of 6 M HNO₃ for 24 h at 70 °C under refluxing. After the chemical activation, the samples were filtered and washed thoroughly with the deionized water until the pH was close to 7, and further dried at 80 °C for 12 h in air. The nitric-acid-activated CMK-3 carbons were denoted as A-CMK-3-700, A-CMK-3-800 and A-CMK-3-900, respectively.

2.4. Characterization of samples

Both of the mesoporous silica and its carbon replica materials were characterized by powder X-ray diffraction (D/max-RC) using Cu- α radiation source ($\lambda = 0.154056$ nm). Their hexagonally ordered structures and carbonization structures were evaluated in the 2θ range of 0.5–5° (40 kV and 40 mA) and 10–80° (40 kV and 250 mA), respectively. The scanning rate was 0.5 °/min for the low-angle XRD measurements, and 8 °/min for the wide-angle XRD measurements. Transmission electron microscopy (TEM) images were conducted on a JEOL JEM-200CX microscope operated at an accelerating voltage of 120 kV. The chemical compositions of the samples were analyzed by a Nicolet 380 FT-IR spectrophotometer over the wave number range of 1000–4000 cm⁻¹ by making pellets with KBr. The porous textures of the prepared carbons were characterized by N₂ adsorption and desorption experiments using a mode 3H-2000PS2 instrument from Beishide Instrument Company. The samples were degassed in vacuum at 200 °C for at least 1 h. The specific surface area was calculated according to the Brunauer-Emmet-Teller (BET) method. The total pore volume was calculated from the adsorption amount of N₂ at a relative pressure of 0.99. The pore size distribution was obtained from the adsorption branch of the isotherms by using the Barrett-Joyner-Halenda (BJH) method.

2.5. Fabrication and electrochemical measurements of electrodes

The working electrodes were prepared as follows: nickel foams (1 × 2 cm²) were first etched in a 5 M HCl solution for 30 min to remove the oxide layer before washing thoroughly by deionized water and ethanol. Then, the mesoporous carbon samples, acetylene black conductor and polytetrafluoroethylene binder with a weight ratio of 70:15:15 were mixed in absolute ethanol to form slurry. After being mixed thoroughly, the black mixture was coated onto the foamed nickel with an area of 1 × 1 cm², and was dried at 80 °C for 12 h. After the solvent evaporated, the sample was pressed at approximately 10 MPa. The mass of electroactive material on each electrode was approximately 10 mg. In this

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