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Effect of the pore length and orientation upon the electrochemical capacitive performance of ordered mesoporous carbons

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ABSTRACT

By utilizing hard template method to adjust the mesopore length, and alkali activation to generate micropores, two hierarchical porous carbons (HPCs) were prepared. With controlling of their mesopore length and the activation conditions, the complex system composed by HPCs and electrolyte was simplified and the effect of mesopore length on the performance of HPCs as electrodes in supercapacitors was investigated. It is found that with the mesopore length getting smaller, the ordered area gets smaller and the aggregation occurs, which is caused by the high surface energy of small grains. HPC with long pores (HPCL) exhibits a donut-like morphology with well-defined ordered mesopores and a regular orientation while in HPC with short pores (HPCS), short mesopores are only orderly distributed in small regions. Longer ordered channels form unobstructed ways for ions transport in the particles while shorter channels, only orderly distributed in small areas, results in blocked paths, which may hinder the electrolyte ions transport. Due to the unobstructed structure, HPCL exhibits good rate capability with a capacitance retention rate over 86% as current density increasing from 50 mA/g to 1000 mA/g. The specific capacitance of HPCL derived from the cyclic voltammetry test at 10 mV/s is up to 201.72 F/g, while the specific capacitance of HPCS is only 193.65 F/g.

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1. Introduction

Nowadays, with decline of the traditional environment-unfriendly energy demand and development of the novel clean energy market, energy storage technologies get a good chance to fulfill their applications [1]. Supercapacitors, one of these promising energy storage technologies, also known as electrochemical capacitors (ECs), are well known for their high power density and good cycle ability [2,3]. They are widely used in consumer electronics, memory back-up systems, industrial power and energy management [2–4]. Various materials have been investigated as electrodes for supercapacitors, including carbonaceous materials, conducting polymers and transition-metal oxides [5–7]. Among these materials, carbon materials are the most promising candidates for supercapacitors and have been extensively studied because of their high electrical conductivity, high stability, easy processability and carbon materials can be made into a variety of forms such as pow-

ders, fibers, tubes and composites [8,9]. Carbon materials include activated carbons (ACs), ordered mesoporous carbons (OMCs), hierarchical porous carbons (HPCs), graphene and carbon nanotubes, etc. [8–14]. AC has been widely used due to its advantages such as scalable manufacturing, reasonable cost, and high specific surface area [15]. The specific capacitance of AC is high at low current density [16], but it decreases rapidly with increasing the current density. OMC exhibits superior capacitive behavior and power output due to its controllable pore size distribution and highly interconnected mesoporous structure [16]. However, it was revealed that the specific capacitance isn't simply proportional to the specific surface area of carbon materials [9], and an anomalous increase in specific capacitance will be resulted in when the pore size of carbons was smaller than the size of solvated electrolyte ions [17]. On the other hand, the rate capability of electrochemical capacitors is related to the ionic conductivity of electrode materials which is determined by the mobility of ions inside the pores. Mesopores and macropores can provide faster mass-transport of electrolyte ions than micropores [12]. Considering these aspects, HPCs can be the optimal choice and allow both high power density and energy density to be achieved when used as electrodes in ECs. However, there are still so many factors that affect the

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performances of HPCs as electrode materials in ECs. The kinetics of the electrolyte ions transporting within HPCs electrodes is still a challenging problem [18–20]. The system composed by HPCs and electrolyte is complex due to the factors such as the parameters of the pores, the nature of the electrolyte and the solid–liquid interface [20].

In this work, two HPCs with different mesopore length were prepared by utilizing hard template method to adjust the mesopore length of HPCs, and alkali activation to generate micropores in HPCs [21–24]. The templates employed to prepare the HPCs were two kinds of SBA-15 which were only different in pore length so that the mesopore length of the obtained HPCs was different, as well. For two kinds of HPCs, alkali activations were conducted under the same conditions to make sure the parameters of the micropores in the HPCs are close. With controlling of the mesopore length and the activation conditions, the complex system composed by HPCs and electrolyte was simplified. And by characterizing the structural parameters of the HPCs and the performances of the electrodes, the effect of mesopore length on their electrochemical capacitive properties was investigated.

2. Experimental

2.1. Material preparation

2.1.1. Fabrication of the templates

There were two kinds of SBA-15 used as templates which were different in pore length. For HPC with long mesopores (HPCL), template SBA-15 was prepared by Zhao's method [25,26]. And according to Choi [27], SBA-15 with different wall thicknesses were fabricated by adjusting the weight ratio of P123 to TEOS. For HPC with short mesopores (HPCS), SBA-15 was prepared by Zhang's method [28]. By adjusting the weight ratio of decane to P123, SBA-15 with different wall thicknesses and pore lengths were obtained.

2.1.2. Fabrication method for SBA-15 with long pores

4.9 g of EO₂₀PO₇₀EO₂₀ (Pluronic P123) was dissolved in 30 g of water and 120 g of 2 M HCl solution with stirring at 313 K until the solution became clear. Then 8.50 g of TEOS was added into that solution with stirring at 313 K for 24 h. The mixture was transferred into an autoclave for further reaction at 373 K for 24 h and the product was then filtered, washed, and air-dried at room temperature. The obtained precursor was calcined at 823 K in air for 5 h.

2.1.3. Fabrication method for SBA-15 with short pores

2.4 g of P123 was dissolved in 84 mL of HCl solution (1.07 M) and then stirred at 313 K until the solution became clear. 18.24 g of decane (C₁₀H₂₂) (with weight ratios of decane:P123 = 7.6:1) were then added into the solution. The mixture was stirred at 313 K for at least 1 h. Finally, 0.027 g of NH₄F was added under stirring as a hydrolysis catalyst, followed by adding 5.1 g of TEOS. The above mixture was stirred at 313 K for 20 h and then transferred into an autoclave for further reaction at 373 K for 48 h. The products were collected by filtration, dried in air, and calcined at 813 K for 5 h and SBA-15 with short pores was obtained.

2.1.4. Preparation of HPCs

The HPCs were prepared by combining hard template method and alkali activation to build the mesopores and the micropores in the HPCs, respectively. First the OMCs were fabricated by hard template method. After alkali activation micropores were introduced and the target HPCs were obtained.

The OMCs with different pore sizes, no matter with long-pore-length or short mesopores, were prepared by the following impregnation method. 1 g SBA-15 powder was added into a solution prepared by dissolving 0.5 g sucrose (mass ratio of SBA-15:sucrose=2:1) in 25 mL of H₂O. After stirring for 30 min, the

mixture was sonicated for 2 h. Then it was dried at 373 K in an electric oven for 8 h. The aforementioned operation was then repeated twice more. After that the mass ratio of SBA-15:sucrose was adjusted to 3:1 and the impregnation procedure was repeated twice. The resulting products were then carbonized at 973 K for 2 h under N₂ flow. The template was removed by dispersing the carbon-silica composite into 25 mL 2 M KOH solution at room temperature. The mixture was stirred for 8 h. After washing with deionized water and filtration, the as-prepared OMCs were activated with alkali to generate micropores. The OMCs were homogeneously mixed with KOH (mass ratio of carbon:KOH=1:4) and then the mixture was calcined at 1073 K for 2 h under N₂ flow. Finally HPCs with mesopores of different length were obtained. Then HPCL and HPCS with similar surface area and close mesopore diameter were picked out for further study.

2.2. Physical characterization

Small angle X-ray powder diffraction (SAXD) patterns were taken on an X'pert Pro-1 operated at 40 kV and 40 mA. Cu-K_α radiation ($\lambda=0.154$ nm) was used for crystal structure analysis and the SAXD dates were collected from 0.5° to 10° in 2θ at a scanning rate of 0.05 °/s.

A field emission scanning electron microscope (FESEM, JEOL, JSM-7800F) and a transmission electron microscope (TEM, JEOL, JEM-2100) were used to observe the morphology of the samples. An Accelerated Surface Area and Porosimetry System (Micromeritics, ASPS 2020) were employed to measure the specific surface area and pore size distribution of the samples.

2.3. Electrochemical characterization

To fabricate the electrodes, 85 wt% HPC (or OMC) powder, 10 wt% acetylene black and 5 wt% polytetrafluoroethylene (PTFE) binder were thoroughly mixed with a mortar and pestle. Then the mixture was pressed to form a uniform membrane and dried at 393 K for 10 h under vacuum.

The membrane was punched into round pellets of 10 mm in diameter. A pellet was mounted onto a round current collector of nickel foam. To build symmetric supercapacitor, two as-prepared electrodes separated by a cellulose acetate separator were parked into a CR2016 coin cell with 6 M KOH aqueous solution as electrolyte. Galvanostatic charge–discharge (GCD) tests were performed with a battery testing system (BTS50V50mA, Neware Electronic Co. Ltd., China) with voltages arranged from 0 V to 1 V under ambient conditions.

And to build a three-electrode system, an as-prepared round pellet was sandwiched between two pieces of nickel foam to form a working electrode. 6 M KOH aqueous solution was applied as electrolyte. A Pt sheet and a Ag/AgCl (Saturated KCl) electrode were used as counter and reference electrode, respectively. Cyclic voltammetry (CV) and Electrochemical impedance spectroscopy (EIS) measurements were carried out with an Advanced Electrochemical System (PARSTAT 2273, Princeton Applied Research, USA) to evaluate the electrochemical performance of OMCs and HPCs. EIS measurements were carried out at 0 V vs. open circuit voltage with an amplitude of 5 mV, from 10 MHz to 15 kHz.

3. Results and discussion

3.1. Structure and morphology

The SAXD patterns of both the SBA-15 templates with long and short ordered mesopores are shown in Fig. 1. The pattern of SBA-15 with long mesopores gives about three well-resolved diffraction peaks, indicating the orderliness of its structures in the long range,

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