

Electrochemical performance of rod-type ordered mesoporous carbons with different rod lengths for electric double-layer capacitors

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Abstract: Rod-type ordered mesoporous carbons were synthesized by the direct carbonization of sulfuric-acid-treated silica/triblock copolymer composites, followed by etching the silica with a HF solution. The morphologies, microstructures and pore structures of the mesoporous carbons were investigated by scanning electron microscopy, high resolution transmission electron microscopy, X-ray diffraction and nitrogen sorption. Their electrochemical performance as electrodes for supercapacitors was investigated by impedance spectroscopy and charge/discharge tests. It was found that the rod length of the mesoporous carbons can be changed from one to tens of micrometers by changing the synthesis parameters. The sample with the longest rod length has the highest specific capacitance. The sample with two pore sizes has the highest capacitance retention ratio of 92% at a high current density of 2 A/g.

Key Words: Ordered mesoporous carbon; Rod-type; Template; Triblock copolymer; Supercapacitor

1 Introduction

Electric double-layer capacitor (EDLC) is a next-generation energy storage device, which can be applied to an auxiliary power supply and space flight technology. The double layer is formed at electrode/electrolyte interface, where electric charges are accumulated on the electrode surfaces^[1,2]. Compared with conventional capacitors, EDLCs can store much more energy because there is a very small charge separation distance at the interface between electrode and electrolyte and a large amount of charges on electrode of the large surface area^[3]. On the basis of the double-layer energy-storage mechanism, the key to enhance the specific capacitance is to enlarge the specific surface area^[4] and to control the pore size and its distribution of the electrode materials^[5].

Since the first report in 1999^[6], ordered mesoporous carbons (OMCs) have been widely studied as the electrode materials for EDLC owing to their well-ordered pore channels, high specific surface areas and narrow pore size distributions^[7-10]. Recently, Tang et al^[11] synthesized an OMC through a facile way without any templates and the carbon showed a high specific capacitance (259 F·g⁻¹) and high rate capability (189 F·g⁻¹ at 100 A·g⁻¹). Jurewicz et al^[12] investigated the electrochemical performance of carbon materials with a highly ordered mesoporous structure. The highest capacitance values

are obtained for the carbons with the highest total surface area, the highest total pore volume and the most marked microporous character. It is obvious that the presence of interconnected mesopores and micropores makes the active surface more available for charge accumulation on EDLC than in a strictly microporous material. Xing et al^[13] presented the EDLC performance of the OMCs with 3-D cubic and 2-D hexagonal mesopore structures. It was found that the 2-D hexagonal OMC exhibited better high-rate capability than the 3-D cubic OMC. This is attributed to the favorable ion transport in mesopores of the 2-D hexagonal OMC. Gao^[14] synthesized a 3-D cubic OMC with a high energy density of 6.53 Wh·kg⁻¹ at a power density of 5 000 W·kg⁻¹, indicating a promising application for the high performance supercapacitors. Wang et al^[15] studied the ion transport behavior in hexagonal OMC rods with diverse mesopore diameters and lengths by evaluating the dynamic process of inner-pore electric double layer formation. They considered that the ion transport behavior was affected by the ratio between mesopore length and diameter, and the behavior can be enhanced by minimizing the aspect ratio of the mesopores. Xiao^[16] studied the fiber-like and rod-like OMC performance in EDLC and the latter showed a better property because the short rod-like morphology and the well-defined pore size distribution favor the ions penetration into their pores. Liang et al^[17] compared the EDLC performance of the OMC with an

interconnected channel structure to the OMC with an unconnected channel structure, and found that the former has better performance than the latter owing to rapid mass transport in the former.

Our group^[5] have compared the EDLC behavior of three types of OMCs with different pore characteristics and found that the OMC with a high surface area and appropriate pore size distribution (centered at 3.6 nm) exhibits the lowest resistance and highest specific capacitance. In this work, we fabricated four types of OMC rods from the carbonization of silica/triblock copolymer composites. By changing the synthesis parameters, the rod length of the carbons can be controlled from one to tens of micrometers. The electrochemical performance of the capacitor electrodes prepared from the OMC rods have been investigated and are tentatively correlated with their structures and pore characteristics.

2 Experimental

2.1 Preparation of OMCs

Rod-type OMCs were synthesized using a triblock copolymer P123 as the carbon source and tetraethoxysilicon (TEOS) as the silica source. The P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_{\text{av}} = 5800$) was purchased from Sigma. All commercial chemicals were used without further purification. The typical experiment^[18-20] procedure is shown in the Fig.1.

The micelle was formed after the P123 was dissolved in water. The P123/SiO₂ composite was formed in the presence of the inorganic precursor and sulfuric acid. OMCs were obtained after carbonization of the composites and etching of the SiO₂ with a HF solution. In a typical run, 5.0 g P123 was dissolved in 130 mL distilled water at 38 °C, then 6.4 mL sulfuric acid (98 wt%) and 9.2 mL TEOS were added to the solution under vigorous stirring. After the stirring for 5 min, the mixture was kept statically at 38 °C for 24 h, followed by aging at 100 °C for 24 h. The solid product was filtered and dried at 100 °C for 6 h and 160 °C for 6 h, respectively to get the P123/silica composite. The dark powder was carbonized under N₂ flow at 850 °C for 2 h. The obtained silica/carbon composite was treated by a diluted HF solution to remove the silica to get the OMC. By changing the adding order of sulfuric acid and P123, we obtained two samples, C1 (sulfuric acid added at the same time with P123) and C2 (sulfuric acid added after P123 dissolved). By varying the amount of TEOS with the same adding order as C1 but stop stirring 5 min after the addition of TEOS, two samples were synthesized, C3 (9.2 mL TEOS) and C4 (13.8 mL TEOS).

2.2 Characterization

The OMCs were characterized by X-ray diffraction scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM) and nitrogen adsorption. XRD patterns were recorded on a Rigaku D/max-2500B2+/PCX system operating at 40 kV and 20 mA

using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The interplanar spacings of the OMCs are calculated from the Bragg's equation: $\lambda = 2d(hkl) \sin\theta$. SEM images were obtained using a Zeiss Supra 55 electron microscope operating at 20 kV. Nitrogen adsorption were performed with an ASAP 2020 Micromeritics Instrument at 77 K. The pore size distributions were calculated from the desorption branch of the isotherms using the BJH (Barrett–Joyner–Halenda) method. The specific surface areas were calculated from the adsorption data in the relative pressure interval from 0.04 to 0.2 using the Brunauer–Emmett–Teller (BET) method. The total pore volumes were estimated at a relative pressure of 0.98. HR-TEM images were obtained using a JEOL JEM-2100 electron microscope operating at 200 kV. The samples were prepared by dispersing the products in ethanol with an ultrasonic bath for 20 min and then a few drops of the resulting suspension were spread on a copper grid.

The EDLC electrodes were obtained by pressing a mixture of the OMC (80 wt%), graphite (10 wt%), and polytetrafluoroethylene (10 wt%) to the nickel foam as a current collector. The electrodes had a surface of 100 mm² and thickness of 0.4 mm. A platinum wire and the Hg/HgO electrode were used as the counter and reference electrodes, respectively. The electrolyte was a 30 wt% KOH aqueous solution. The galvanostatic charge/discharge capacitance (C) of the electrode was measured using a Program Testing System (produced by Wuhan LAND Co. Ltd., China). Charge and discharge were carried out between 0.9 and 0.01 V. The C in Farad was calculated on the basis of the equation: $C = (I \Delta t)/(m \Delta V)$ ^[21], where C is the capacitance, I the constant discharge current, Δt the discharge time, m is the mass of active material within the electrode and ΔV is the potential range.

The cyclic voltammetry and AC impedance were carried out with a CHI 660B electrochemical working station. For the cyclic voltammetric measurements, the sweep rate ranged from 1 to 10 mV·s⁻¹ within a potential range of -0.3 to 0.2 V. For the AC impedance measurements, the potential amplitude of AC was kept as 30 mV and the frequency range was from 10 kHz to 1 Hz. The impedance spectra were fitted to an equivalent circuit model^[22] by ZView software.

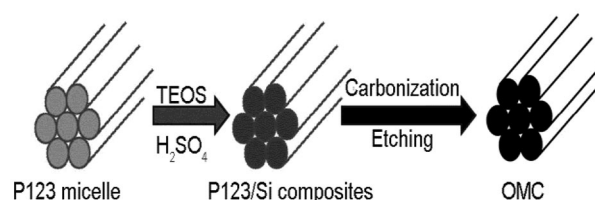


Fig. 1 Synthesis of OMCs.

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