PREPARATION OF GRAPHITIZABLE ORDERED MESOPOROUS CARBON FROM ASPHALTENE AND THEIR ELECTROCHEMICAL PERFORMANCE

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Introduction

Ordered mesoporous carbon (OMC) has attracted great attention recently as electrode materials in electrochemical double layer capacitors (EDLC) for the good electrical conductivity and ordered porous textures [1]. In the present work, OMC materials with different graphitization degree were synthesized from asphaltene obtained from coal liquefaction residue (CLR) via template technique. The effects of high temperature treatment on the characteristics of OMC materials such as surface area, pore size distribution, graphitization degree, and on their electrochemical properties in EDLC were investigated systematically.

Experimental

Asphaltene was separated from CLR following a procedure reported by Li et al. [2]. The OMC was synthesized by a template method with SBA-15 [3] as template and asphaltene as carbon precursor. The typical procedure was similar to our previous report [4]. OMC carbonized in flowing argon atmosphere at 900 ^{o}C was denoted as OMC-A-900. To make OMC materials with different graphitization degree, carbonization step was conducted at different temperatures, of which the corresponding products were denoted as OMC-A-T, where T stands for the heat treatment temperature.

Physical characterizations of the as-made OMCs were obtained from XRD, TEM and N_2 adsorption techniques. Electrochemical performances were evaluated using a three-electrode system consisting of working electrode, a platinum counter electrode and a Hg/HgO reference electrode. Working electrodes were fabricated by mixing the OMC and polytetrafluoroethylene in a weight ratio of 95:5. The mixture with small amount of ethanol was rolled into a thin sheet and cut into round disk of 10 mm in diameter, after which the carbon sheet was pressed between two nickel foam that functions as current collectors. All electrochemical tests were carried out in 6 M KOH aqueous solution. Before the electrochemical measurements, the electrodes were soaked in electrolyte and evacuated for 24 h to ensure the active material contact with the electrolyte completely and thoroughly.

Results and Discussion

Asphaltene was filled into the channel-like pores of SBA-15 and converted to OMC after heat treatment, which is evidenced by the XRD results in Fig.1. It is noticed that as the heat treatment temperature increases, resolved small angle diffraction peaks of the as-made OMCs in Fig 1a become weaker and shift to higher angle slightly, implying structure shrinkage occurs during the heat treatment step. At the same time, the wide angle diffraction peaks of carbon shift to higher angle gradually, and become sharper and stronger, suggesting OMC samples with varying graphitization degree have been obtained.

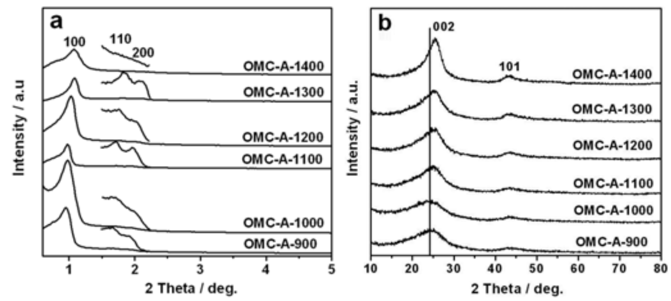

Fig. 1 Small (a) and wide (b) angle XRD patterns of OMCs.

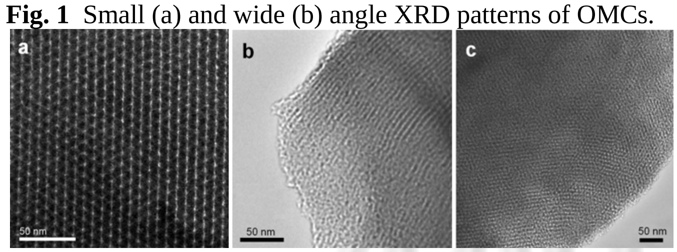

Fig. 2 TEM images of OMC-A-900 (a), OMC-A-1200 (b) and OMC-A-1400 (c).

Typical TEM images for OMC-A-900, OMC-A-1200 and OMC-A-1400 are shown in Fig. 2. It can be seen that the primary structure of ordered pore arrangement can be retained after high temperature treatment though the regular pore channels become obscure and disappear partly for OMC-A-1200. In the case of OMC-A-1400, the ordered mesoporous domain can be hardly seen, and worm-like pores are formed instead. The XRD and TEM results have revealed that high temperature treatment can be employed to tune the graphitization degree and the structure of the as-made OMCs to some degree. As the heat temperature increases, the long-range ordering in the as-made OMC samples is lost, but the interconnectivity of pores is still preserved.

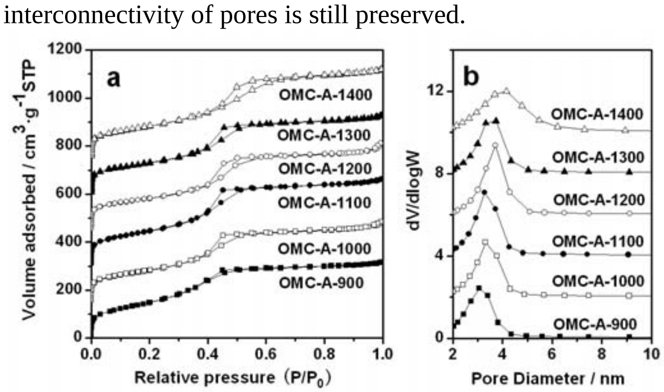

Fig. 3 N_2 adsorption-desorption isotherms (a) and BJH pore size distributions (b) of OMCs. (N_2 adsorption-desorption isotherms and pore size distributions are offset vertically for 150 $cm^3 \cdot g^{-1}$ STP and in a step of 2 starting from OMC-A-1000)

All N_2 sorption isotherms of the as-made OMCs exhibit typical type IV isotherms with distinct capillary condensation steps occurring at P/P_0 of 0.4-0.7 (Fig. 3a), indicative of narrow mesopore size distributions. The condensation step for OMC-A-1400 is higher than that other OMCs, indicative of larger mesopore volume and bigger pore diameter, which is further confirmed by the BJH mesopore size distributions shown in Fig. 3b. The mesoporosity is listed in Table 1. It can be seen that the total pore volume, BJH pore diameter and mesoporosity increase gradually with the increment of heat treatment temperature.

Table 1. Textual structure properties of OMCs.

samples	V_t ($cm^3 \cdot g^{-1}$)	S_{BET} ($m^2 \cdot g^{-1}$)	V_{meso} ($cm^3 \cdot g^{-1}$)	D (nm)	V_{meso}/V_t (%)
OMC-A-900	0.49	542	0.36	3.1	73.4
OMC-A-1000	0.51	485	0.38	3.3	74.5
OMC-A-1100	0.56	534	0.42	3.3	75.0
OMC-A-1200	0.56	469	0.42	3.7	75.0
OMC-A-1300	0.51	471	0.38	3.7	74.5
OMC-A-1400	0.57	487	0.45	4.1	78.9

The electrochemical characteristics of asphaltene-based OMCs with different heat treatment temperatures were evaluated using cyclic voltammetry (CV), galvanotactic charge-discharge and electrochemical impedance spectroscopy (EIS). In Fig. 4, all OMC samples have a quasi-rectangular CV curves and linear charge-discharge curves without obvious ohmic drop, indicative of excellent candidates as electrode materials for EDLC and good capacitive behavior. Fig. 5a shows the variation trend of the specific capacitances calculated from the discharge curves [5] of OMCs with current densities, showing that all the OMCs exhibit high-rate performance, which leads one to believe that these asphaltene-derived OMCs may be of potential in EDLC. The lower specific capacitance of asphaltene-based OMCs, which may results from the lower specific surface area, can be further improved by optimizing the pore textures. There is a tendency that C_g decreases slightly with the increase of heat treatment temperature at same current density, which may be ascribed to the removal of heteroatoms and functional groups composed in asphaltene at high temperature treatment.

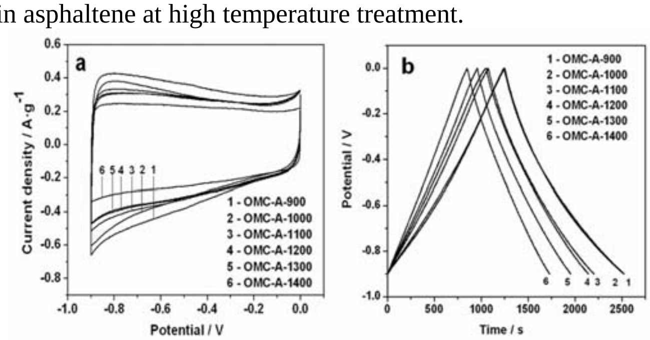

Fig. 4 (a) CV curves of OMCs at a scanning rate of $5 mV \cdot s^{-1}$ and (b) charge-discharge curves of OMCs at a current density of $50 mA \cdot g^{-1}$.

EIS of OMCs are shown in Fig.8. Nearly 90° capacitive spike starting from the mid-high frequency indicates the suitability of the OMC samples as electrode materials for supercapacitors. OMC-A-1400 has lower contact resistance and better conductivity, which can be ascribed to the graphite-like structures with larger pore size caused by high temperature treatment. The graphite-like structure, on one hand, decrease the equivalent series resistance, on the other hand, results in the lower specific capacitance because the electrolyte ion migration occurs in a direction of low conductivity in graphite-like structures [6].

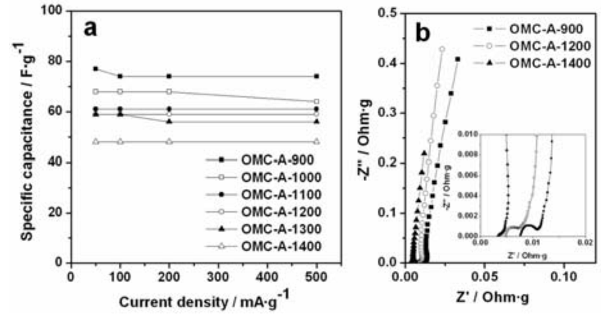

Fig. 5 (a) Specific capacitance of OMCs at different current densities and (b) Nyquist plots (inset: the enlargement of high frequency region).

Conclusions

OMC materials are synthesized from asphaltene derived from CLR by template method, which may pave a new way for the effective utilization of CLR. The textural structure and the graphitization degree of OMC can be tuned by changing the heat treatment temperature. When used as electrode materials of EDLC, all the asphaltene-based OMCs present ideal electric double behavior. High temperature treatment of OMCs caused higher mesoporosity, bigger pore volume and graphite-like structure, which could improve the electrical conductivity and decrease the impedance of capacitor to some degree.

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References

[1] Lee J, Yoon S, Hyeon T, Oh SM, Kim KB. Synthesis of a new mesoporous carbon and its application to electrochemical double-layer capacitors. Chem Commun 1999;(21):2177-2178.
[2] Li X, Hu HQ, Zhu SW, Hu SX, Wu B, Meng M. Kinetics of coal liquefaction during heating-up and isothermal stages. Fuel 2008;87:508-513.
[3] Zhao DY, Feng JL, Huo QS, Melosh N, Fredrickson GH, Chmelka BF, et al. Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. Science 1998;279(5350):548-552.
[4] Zhou Y, Yu GH, Zhang Y, Li JN, Qiu JS. Template synthesis and characterization of ordered mesoporous carbons from asphaltene. New Carbon Materials 2008;23(1):63-68.
[5] Chmiola J, Yushin G, Gogotsi Y, Portet C, Simon P, Taberna PL. Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer. Science 2006;313(5794):1760-1763.
[6] Yang HF, Yan Y, Liu Y, Zhang FQ, Zhang RY, Meng Y, et al. A simple melt impregnation method to synthesize ordered mesoporous carbon and carbon nanofiber bundles with graphitized structure from pitches. J Phys Chem B 2004;108(45):17320-17328.