Facile preparation of mesoporous carbons for supercapacitors by one-step microwave-assisted ZnCl2 activation

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Abstract
Mesoporous carbons (MCs) with high surface area of 1409–1552 m² g⁻¹ for supercapacitors were prepared from peanut shell by one-step microwave-assisted ZnCl2 activation. The MC made at the ZnCl2/peanut shell mass ratio of 4 in 20 min at 600 W microwave power (nominated as MC4-M) retains a high specific capacitance of 184 F g⁻¹ at 0.05 A g⁻¹ current density after 1000 cycles, showing perfect cycle stability. At 1.6 A g⁻¹ current density, the energy density of the supercapacitor made from MC4-M reaches 4.94 Wh kg⁻¹ at 740 W kg⁻¹, exhibiting excellent rate performance. The findings clearly indicate that the one-step microwave-assisted ZnCl2 activation technique is a facile approach to the preparation of high performance MCs for supercapacitors.

1. Introduction
Supercapacitors are drawing much more attention as a promising energy storage device. Porous carbons (PCs) including mesoporous carbons (MCs) are the commonly used electrode materials for supercapacitors [1,2]. The specific capacitance of microporous carbons dropped obviously while MCs had high capacitance retention at high current density [3,4]. The template methods are often used to make MCs [5,6], however, the template has to be synthesized before use and removed by strong acids after carbonization. The high production cost of templated MCs is a major obstacle to their commercial use. Bear in mind that microwave heating has remarkable advantages over the conventional heating including the rapid temperature rise and saving of energy; we recently reported the synthesis of MCs for supercapacitors from coal tar pitch by coupling microwave-assisted KOH activation with an MgO template [7]. Compared with fossil raw materials, peanut shells with low ash content are friendly environmental biomass wastes for the preparation of MCs [8]. Zinc chloride (ZnCl2) is used as the activation agent because it can produce a well-developed porosity besides high carbon yield, since ZnCl2 acts as a dehydrating agent allowing more carbon to be kept fixed [9]. Here we report a facile technique to prepare MCs with well-developed mesopores for supercapacitors from peanut shell by one-step microwave-assisted ZnCl2 activation.

2. Experimental
Peanut shell with an ash content of 1.44% on a dry basis was obtained from Huai-an in Jiangsu province, China. The dried peanut shell with the particle size of 3–10 mm was impregnated in ZnCl2 solution for 12 h while the total mass of ZnCl2 and peanut shell was kept at 27 g. The ZnCl2 solution was made by dissolving ZnCl2 in 60 ml distilled water. The ZnCl2-impregnated peanut shell was dried at 383 K for 24 h before being activated by microwave heating in a LWMC-205 type microwave oven at 600 W microwave power in 20 min. The resultant MC was made by conventional heating at 5 K min⁻¹ to 1123 K, and held at 1123 K for 1 h in 60 ml min⁻¹ flowing nitrogen [10]. The resultant MC is nominated as MCx–C, where the subscript (x) and (C) refer to the mass ratio of ZnCl2/peanut shell, and the microwave heating. For comparison, MC was made by conventional heating at 5 K min⁻¹ to 1123 K, and held at 1123 K for 1 h in 60 ml min⁻¹ flowing nitrogen [10]. The resultant MC is nominated as MCx–M, where the subscript (x) and (M) refer to the mass ratio of ZnCl2/peanut shell, and the microwave heating. The pore structures of the MCs were characterized using nitrogen adsorption [7]. The electrode of symmetrical supercapacitor was fabricated by mixing MCs, carbon black and poly(tetrafluoroethylene) in a weight ratio of 87:5:8. More details can be found elsewhere [7]. The supercapacitors made from MCs in 6 M KOH aqueous electrolyte were evaluated by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) on an electrochemical workstation (CHI-760C) [7]. The charge–discharge performance of supercapacitors was tested on a land cell tester (CT-2001A).
3. Results and discussion

Fig. 1(a) is the N$_2$ adsorption–desorption isotherms, showing that the isotherm of PC$_{1-M}$ made at 1 of ZnCl$_2$/peanut shell ratio is typical I isotherm corresponding to microporous carbon materials. When the mass ratio of ZnCl$_2$/peanut shell ranges from 2 to 5, the isotherms of MCs have obvious hysteresis loops, evidencing the existence of abundant mesopores. The total pore volume ($V_t$) of MCs rises from 0.95 to 1.83 cm$^3$ g$^{-1}$ with increasing mass ratio of ZnCl$_2$/peanut shell. The specific surface area ($S_{BET}$) of PC$_{1-M}$, MC$_{2-M}$, MC$_{3-M}$, MC$_{4-M}$ and MC$_{5-M}$ is 1307, 1454, 1528, 1552, 1409 m$^2$ g$^{-1}$ while their corresponding mesopore surface area ($S_{meso}$) is 739, 1150, 1462, 1467 and 1291 m$^2$ g$^{-1}$. The micropore surface area ($S_{mic}$) of the mentioned carbons is only 568, 304, 66, 85 and 118 m$^2$ g$^{-1}$. It can be easily seen that the $S_{meso}$ and $S_{BET}$ of MCs increases with increasing ZnCl$_2$/peanut shell ratio from 2 to 4, and then drops to 1409 m$^2$ g$^{-1}$ at ZnCl$_2$/peanut shell ratio of 5, illustrating that the $S_{BET}$ of MCs are tunable by changing ZnCl$_2$/peanut shell ratio. The porosity created by ZnCl$_2$ activation is due to the space activated and left by ZnCl$_2$ after washing, and the widening and collapsing of the pores occur simultaneously with increasing ZnCl$_2$/peanut shell ratio from 4 to 5.

Fig. 1(b) is the pore size distribution curves, showing that the pore of MCs widens with increasing ZnCl$_2$/peanut shell mass ratio, leading to increasing average pore diameter of MCs from 2.61 to 5.20 nm. The macropores in MCs are ignorable, and the mesopore percentage of MC$_{3-M}$, MC$_{4-M}$ and MC$_{5-M}$ ranges from 97.8% to 99.2%. The $S_{BET}$ of MCs produced by microwave heating is found to be larger than that made by conventional heating even at longer activation time [8], which is ascribed to the efficiency of microwave heating at molecular level. The yields of MCs drop from 38.4% to 32.3% with increasing ZnCl$_2$/peanut shell ratio from 2 to 5, showing that the increasing ZnCl$_2$/peanut shell mass ratios aid releasing more gaseous products and thus are responsible for the decreasing yields of MCs. Fig. 1 shows that the MC$_{4-C}$ has obvious mesopores with a $S_{meso}$ of 1212 m$^2$ g$^{-1}$ and a $S_{mic}$ of 422 m$^2$ g$^{-1}$. The average heating rate of MC$_x-M$ ranges from 41.3 to 48.5 K min$^{-1}$, obviously higher than conventional heating, illustrating that microwave heating can save time and energy.

Fig. 2(a) shows the EIS of all the electrodes. At high frequency, the supercapacitor made from MC$_{5-M}$ electrodes has smaller value crossing with the $Z'$ axis than other electrodes, indicating that the low contact resistance of MC$_{5-M}$. At high-medium
frequency, the electrodes exhibit a depressed semicircle [11]. The diameter of the semicircle reflects the ion transfer resistance in the pores of MCs. The inset in Fig. 2(a) shows that the ion transfer resistance of PC$_{1-M}$ is obvious due to the limitation in charge transfer process that possibly results from the narrow micropores. The smaller ion transfer resistances of MC$_{5-M}$, MC$_{4-M}$, MC$_{3-M}$ and MC$_{2-M}$ are ascribed to their higher mesopore percentage, which provides abundant channels for the transport of electrolyte ions. At low frequency, the curves of MC$_{5-M}$, MC$_{4-M}$, MC$_{3-M}$ and MC$_{2-M}$ are nearly vertical to the $Z^2$ axis. In contrast, in the case of MC$_{4-C}$ and PC$_{1-M}$ electrodes, a large slope exists, indicating that the capacitance behaviors of MC$_{5-M}$, MC$_{4-M}$, MC$_{3-M}$ and MC$_{2-M}$ electrodes are better than those of MC$_{4-C}$ and PC$_{1-M}$.

Fig. 2(b) shows the CV curves of different electrodes at a scan rate of 100 mV s$^{-1}$. In comparison to those of MC$_{4-M}$, MC$_{3-M}$ and MC$_{5-M}$ electrodes, the CV curves of MC$_{2-M}$ and PC$_{1-M}$ electrodes become distorted, indicative of a poor rate performance owing to that the narrow micropores (0.12–0.25 cm$^3$ g$^{-1}$) in MC$_{2-M}$ and PC$_{1-M}$ limit the fast transport of electrolyte ions. This indicates the quick ion propagation and the small motion resistance in MC$_{4-M}$, MC$_{3-M}$ and MC$_{5-M}$ electrodes. The high rate performance favors the delivery of both high energy density and high power density.

The variation of the specific capacitance with the cycle number at 0.05 A g$^{-1}$ current density is shown in Fig. 3(a). After 1000 cycles, the retention of the specific capacitance of all the electrodes ranges from 92.1% to 94.8%, showing perfect cycle stability. The specific capacitance of MC$_{4-M}$ retains 184 F g$^{-1}$ after 1000 cycles. The specific capacitances drop in the order of MC$_{4-M}$ > MC$_{3-M}$ > MC$_{2-M}$ > PC$_{1-M}$ > MC$_{5-M}$. The biggest capacitance of MC$_{4-M}$ is mainly ascribed to its biggest $S_{BET}$. Xu et al. [12] reported that the specific capacitance of MC with a $S_{BET}$ of 892 m$^2$ g$^{-1}$ reached 155 F g$^{-1}$ at a current density of 0.05 A g$^{-1}$ in 6 M KOH aqueous electrolyte. Fig. 3(b) is the variation of the energy density of supercapacitors with the average power density. The energy densities of MC$_{4-M}$, MC$_{3-M}$ and MC$_{2-M}$ are apparently bigger than those of MC$_{5-M}$ and PC$_{1-M}$. At low discharge current density of 0.05, 0.1 and 0.2 A g$^{-1}$, the energy densities of PC$_{1-M}$ are bigger than those of MC$_{5-M}$. However, at higher current density, the energy density of PC$_{1-M}$ drops obviously, and is smaller than MC$_{5-M}$. The bigger pore size, mesopore percentage and $S_{BET}$ of MC$_{5-M}$ are responsible for its bigger energy density at higher current density due to the fast ion transport channels in mesopores, which enable MC$_{5-M}$ supercapacitor to possess excellent rate performance. Fuertes et al. [13] reported the synthesis of bimodal MCs using mesostructured silica materials as template, and the energy density of MC supercapacitor reached 3 Wh kg$^{-1}$ at 300 W kg$^{-1}$. In our case, the energy density of MC$_{4-M}$ reaches 6.68 Wh kg$^{-1}$ at 0.05 A g$^{-1}$ current density, and remains 4.94 Wh kg$^{-1}$ at 740 W kg$^{-1}$ at 1.6 A g$^{-1}$ current density with 74.0% of the energy density retention. The retention of the energy density of MC$_{5-M}$, MC$_{3-M}$ and MC$_{2-M}$ ranges from 72.5% to 75.0% while that of PC$_{1-M}$ is only 63.8%. The smallest retention of the energy density of PC$_{1-M}$ limit the fast transport of electrolyte ions. This indicates the quick ion propagation and the small motion resistance in MC$_{4-M}$, MC$_{3-M}$ and MC$_{5-M}$ electrodes. The smaller ion transfer resistances of MC$_{5-M}$, MC$_{4-M}$, MC$_{3-M}$ and MC$_{2-M}$ are ascribed to their higher mesopore percentage, which provides abundant channels for the transport of electrolyte ions. At low frequency, the curves of MC$_{5-M}$, MC$_{4-M}$, MC$_{3-M}$ and MC$_{2-M}$ are nearly vertical to the $Z^2$ axis. In contrast, in the case of MC$_{4-C}$ and PC$_{1-M}$ electrodes, a large slope exists, indicating that the capacitance behaviors of MC$_{5-M}$, MC$_{4-M}$, MC$_{3-M}$ and MC$_{2-M}$ electrodes are better than those of MC$_{4-C}$ and PC$_{1-M}$.

**References**