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Facile preparation of mesoporous carbons for supercapacitors by one-step microwave-assisted $ZnCl_2$ activation ☆

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ABSTRACT

Mesoporous carbons (MCs) with high surface area of 1409–1552 $m^2 g^{-1}$ for supercapacitors were prepared from peanut shell by one-step microwave-assisted $ZnCl_2$ activation. The MC made at the $ZnCl_2$/peanut shell mass ratio of 4 in 20 min at 600 W microwave power (nominated as $MC_{4\text{-}M}$) 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 $MC_{4\text{-}M}$ 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 $ZnCl_2$ 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 ($ZnCl_2$) is used as the activation agent because it can produce a well-developed porosity besides high carbon yield, since $ZnCl_2$ 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 $ZnCl_2$ 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 $ZnCl_2$ solution for 12 h while the total mass of $ZnCl_2$ and peanut shell was kept at 27 g. The $ZnCl_2$ solution was made by dissolving $ZnCl_2$ in 60 ml distilled water. The $ZnCl_2$-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 or PC is nominated as $MC_{x\text{–}M}$ or $PC_{x\text{–}M}$, where the subscript (x) and (M) refer to the mass ratio of $ZnCl_2$/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 $MC_{x\text{–}C}$, where the subscript (C) refers to the conventional 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).

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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 mesopore percentage of MC_{4-C} is 82.0%. 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^1 axis than other electrodes, indicating that the low contact resistance of MC_{5-M}. At high-medium

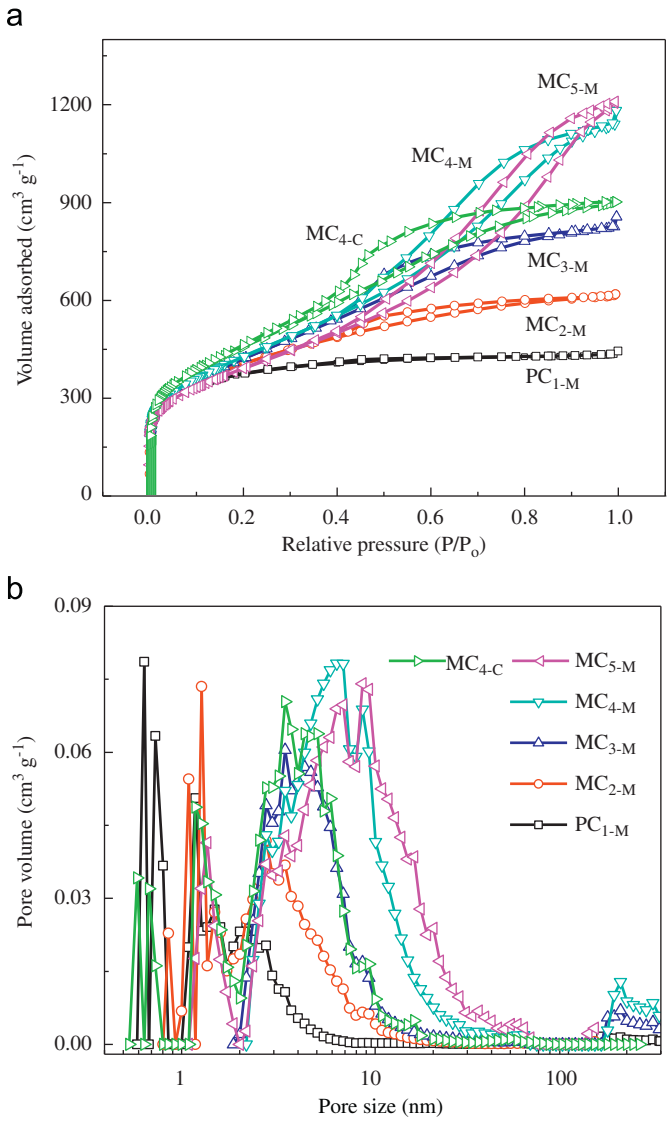

Fig. 1. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution curves of MCs and PC.

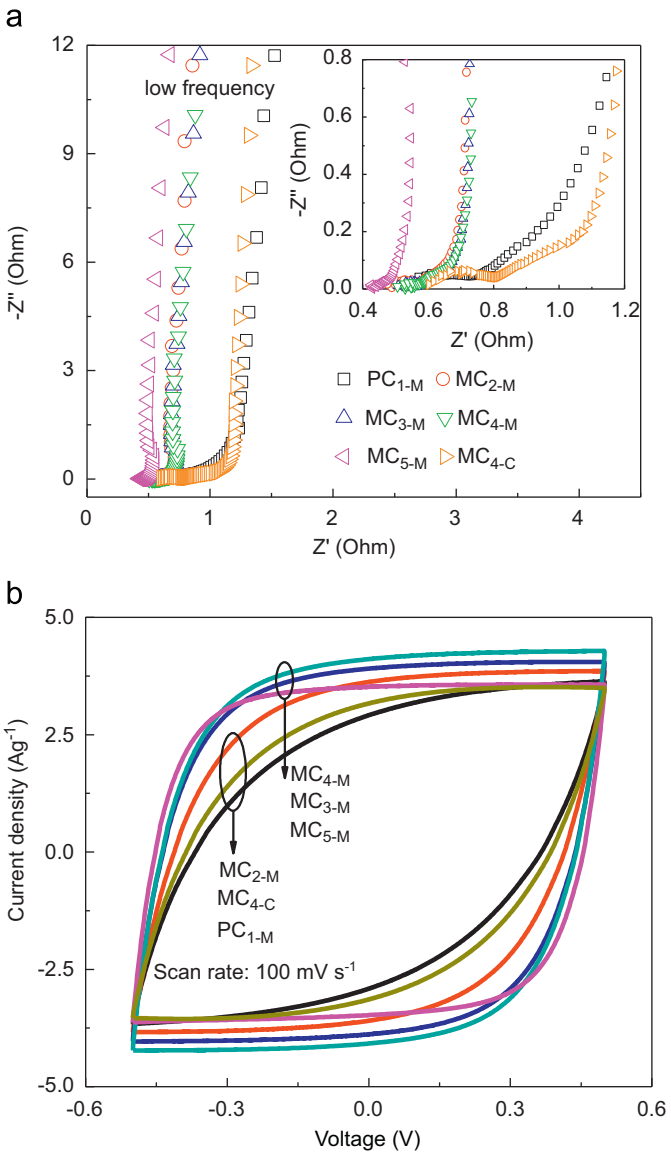

Fig. 2. (a) EIS of different electrodes and (b) CV curves of different electrodes.

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^1 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 obviously 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 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} supercapacitor is ascribed to its bigger S_{mic}, indicating that some micropores in PCs are inaccessible in the formation of electric double-layer at high rate charge-discharge process. In summary, these novel MCs for supercapacitors with a high capacitance and an excellent rate performance are close to the requirements of practical applications due to their abundant mesopores.

4. Conclusions

MCs with high surface area of 1409–1552 $m^2\,g^{-1}$ for supercapacitors can be prepared from peanut shell by a simple one-step microwave-assisted $ZnCl_2$ activation. The MC_{4-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 supercapacitor made from MC_{4-M} shows excellent rate performance, indicating that the one-step microwave-assisted $ZnCl_2$ activation is a simple technique for the preparation of high performance MCs for supercapacitors.

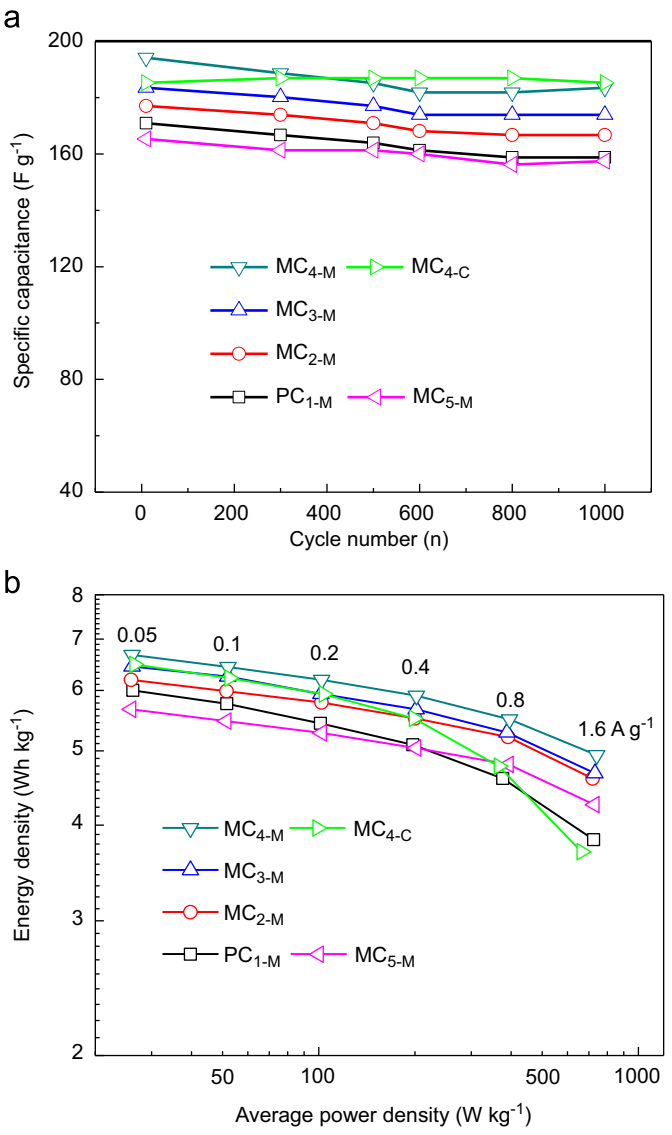

Fig. 3. (a) Specific capacitance of the electrodes vs. cycle number and (b) energy density of supercapacitors vs. average power density.

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