



Preparation of high-performance activated carbons for electric double layer capacitors by KOH activation of mesophase pitches

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Abstract: Two kinds of mesophase pitches with different softening points were prepared at different soaking times and directly activated with KOH to study the effects of the softening point on the textural characteristics of the resulting activated carbons and their behavior as electrodes in capacitors. Results show that the softening points of the two mesophase pitches are 280 and 330 °C, and the specific surface areas of the activated carbons are 1337 and 1300 m²·g⁻¹, respectively. The specific capacitance of the higher softening point mesophase pitch-derived carbon is higher (255.6 F·g⁻¹) than that of the lower softening point mesophase pitch-derived carbon (190.8 F·g⁻¹) at the same current density. Cyclic voltammograms show that the lower softening point mesophase pitch-derived carbon exhibits better rectangular-shaped I-V curves. The softening points of the mesophase pitches prepared from even the same precursor can significantly affect the electrochemical performance of the resulting activated carbons.

Key Words: Capacitors; Activated carbons; Mesophase pitch; Electrochemical properties

1 Introduction

Electric double-layer capacitors (EDLCs) have been widely used as energy devices in many fields of modern technology, such as memory back-up systems, electric devices, and hybrid electric vehicles^[1-3]. EDLCs can supply high power for several seconds and are very quickly rechargeable. High power density, reversibility, a low temperature coefficient for power, and energy densities make EDLCs receive considerable attention^[4-5].

Porous carbon materials have been widely studied for electrode materials of EDLCs, including activated carbons, carbon aerogels, templated carbons, carbide-derived carbon, etc^[2,6-7]. Specifically, porous graphitic carbon shows advantages over amorphous carbon because of the well-developed crystalline structure, high electronic conductivity and thermal stability, and satisfactory oxidation resistance at low temperature^[9]. Mesophase pitch is composed of lamellar macromolecules in parallel stack and has a dense structure, is a suitable precursor for the preparation of graphitic porous carbon, and may have the potential application in producing high-specific capacity electrodes for EDLCs. Weng et al.^[8] prepared activated carbons from a mesophase pitch powder generated by

heat treatment of a coal-tar pitch having 3-6% quinoline insolubles and found that the highest specific capacitance of 130 F·g⁻¹ was achieved with a specific surface area of 2860 m²·g⁻¹. Mora et al.^[9] developed activated carbons with a specific surface area of 2173 m²·g⁻¹ from mesophase pitch AR24 and found that the specific capacitance values obtained were very high, reaching 400 and 200 F·g⁻¹ at low and high current densities, respectively. However, to our best knowledge, little work has been devoted to the understanding of the effects of softening points of mesophase pitches prepared from the same precursor on the performance of the EDLC.

In this study, two mesophase pitches with different softening points were prepared from a kind of isotropic petroleum pitch. The mesophase pitches were chemically activated with KOH to produce porous carbons that were then used as electrodes in EDLC. Cyclic voltammograms (CVs) and constant current charge/discharge have been used to study the electrochemical performance of the activated carbons.

2 Experimental

2.1 Preparation of the mesophase pitches and the activated carbons

The isotropic petroleum pitch was heat-treated in a

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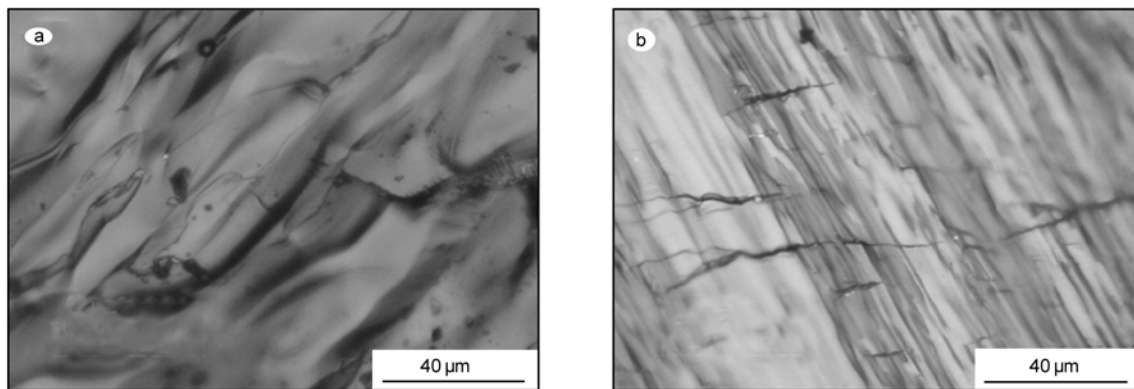


Fig.1 Optical microscope micrographs of the two mesophase pitches

cylindrical stainless steel reactor, fitted with an anchor-type stirrer and a thermocouple connected to a temperature controller and programmer. It was heated by means of a cylindrical furnace. The reactor also incorporates a gas inlet and an exit for the distilled material. In the experiment, the reactor was loaded with the precursor pitch and heated at $3\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ up to the final temperature $420\text{ }^{\circ}\text{C}$. Two mesophase pitches were obtained at 7 and 9 h of soaking time. During the heat treatment, an agitation of $70\text{ r}\cdot\text{min}^{-1}$ was maintained and nitrogen with a flow rate $0.5\text{ m}^3\cdot\text{h}^{-1}$ was applied for the removal of volatile materials, which was collected in the cooled trap. The as-obtained mesophase pitches were named as MP1 and MP2 for the soaking times 7 and 9 h, respectively.

For the activated carbon production, the powders of the as-received mesophase pitches were mixed with an activating agent (4:1 KOH to carbon mass ratio) by grinding in a mortar and then carbonized at a temperature of $800\text{ }^{\circ}\text{C}$ for 1 h under a nitrogen flow. After completion of the heat treatment, the sample was allowed to cool to room temperature. The resultant material was neutralized with HCl and then washed with distilled water until pH 7. Finally, the carbon was dried at $110\text{ }^{\circ}\text{C}$ in a vacuum oven for 24 h.

2.2 Preparation of electrode and cell capacitor

The powders of the as-obtained activated carbons were used as active materials for EDLC. The electrodes were composed of activated carbon, carbon black as an electronic conductor, and polytetrafluoroethylene as a binder in a weight ratio of 85:10:5. Electrodes were punched out of the carbon sheet, and the discs were then mounted onto a Ni-current collector. For the cell capacitor construction, two disc electrodes of the same size were mounted face-to-face into the holder with a separator in between. After the electrolyte solution of $6\text{ mol}\cdot\text{L}^{-1}$ KOH was introduced, the capacitors were sealed. The cell capacitors were kept at room temperature for 24 h before electrochemical measurements in order for the electrolyte to reach and distribute within pores effectively.

2.3 Structural and electrochemical analyses

The mesophase pitches were also characterized by optical microscopy to evaluate the amount and the characteristics of the anisotropic material formed. Surface area and pore volume of the activated carbon were measured according to the BET method by physical adsorption of nitrogen at 77 K, using an automatic absorption system. Crystal structure analysis was carried out using X-ray wide angle diffraction (XRD). For the electrochemical analysis, charge–discharge was performed at a constant current from $50\text{ mA}\cdot\text{g}^{-1}$ to $1000\text{ mA}\cdot\text{g}^{-1}$ between 0V and 1V, CV measurement was performed from 0V to 1V with scanning rate from $1\text{ mV}\cdot\text{s}^{-1}$ to $20\text{ mV}\cdot\text{s}^{-1}$. All the electrochemical measurements were conducted at ambient temperature.

3 Results and discussion

3.1 Characteristics of the mesophase pitches and the activated carbons

The soaking time of the raw petroleum pitches determines the properties of the as-obtained mesophase pitches (Table 1 and Fig.1). Thus, the MP1 obtained by the short-soaking time heat treatment exhibits a low softening point compared with the MP2. In the process for preparing the mesophase pitch, origin of the raw materials, temperature, soaking time, and the amount of volatile matter released are the most important factors that effect the formation of the mesophase^[10–11]. In this study, we increase the soaking time of the raw pitches in the preparation process of the mesophase pitch, and the softening points of the as-obtained mesophase products were increased. The high pyridine-insoluble material content of the MP2 reveals a high degree of polyaromatic condensation compared with MP1. Fig.2 shows the optical micrographs of the mesophase pitches, revealing that the mesophase content of the two pitches is 100%, and the morphology of the MP1 is domain-like and MP2 is fiber-like.

Table 1 Properties of the two mesophase pitches

Sample	Reaction temperature	Reaction time	Softening point	Mesophase content	TS ^a TI-PS ^b PI ^c			Mesophase texture
	<i>t</i> /	<i>t</i> /h	<i>t</i> /°C	ϕ /%	w/%	w /%	w/%	
MP1	420	7	280	100	3.4	10.7	85.9	domain-like
MP2	420	9	330	100	2.7	6.2	91.1	fiber-like

Note: a, toluene-soluble; b, toluene-insoluble but pyridine-soluble; c, pyridine-insoluble

Table 2 Surface characteristics of the activated carbons from mesophase pitch with KOH etching

Material	BET surface area	Micropore volume	Mesopore volume	Total pore volume	Average pore diameter
	$A/m^2 \cdot g^{-1}$	$v_{mi}/cm^3 \cdot g^{-1}$	$v_{me}/cm^3 \cdot g^{-1}$	$v_{tot}/cm^3 \cdot g^{-1}$	D/nm
Activated MP1	1 337	0.45	0.23	0.68	2.1
Activated MP2	1 300	0.51	0.12	0.63	1.9

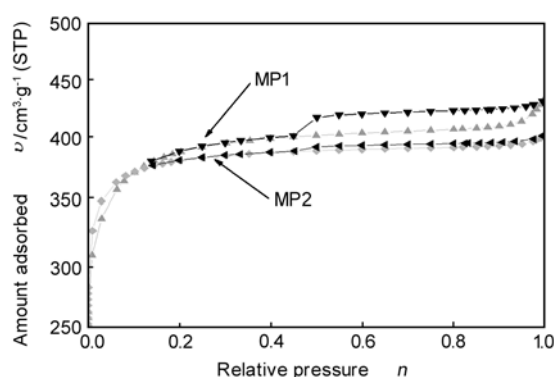


Fig.2 N₂ adsorption/desorption isotherms at 77 K of the activated carbons

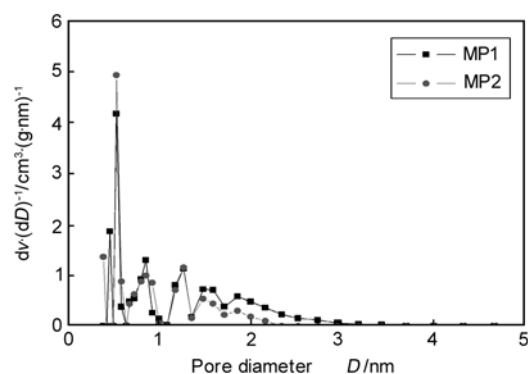


Fig.3 Pore size distributions of the activated carbons by KOH

Heat treatment of petroleum pitch through a long residence time results in the formation of large condensed and more planar molecules. The viscosity and softening point are thus increased. In addition, heat treatment also increases the stability of the pitch and decreases the weight loss in the activation process. The activation yield of the MP1 and MP2 is 70% and 79%, respectively. The nitrogen sorption of the activated mesophase pitches is shown in Fig.2, and the textural parameters are compiled in Table 2. The isotherms of acti-

vated MP1 at temperature 800 °C for 1h show type IV character with a clear hysteresis loop in the relative pressure range 0.4-0.9, indicating the presence of mesopores. It is noteworthy that MP2 activated at the same conditions with MP1 did not result in the formation of many mesopores as the activated MP1, and the isotherms are typical of microporous carbons. In fact, the contribution of micropores in this sample is 0.51 cm³·g⁻¹. The textural parameters calculated from the isotherm data in Table 2 show that higher BET surface area and pore volumes are obtained for KOH activation of mesophase pitch with lower softening point, and the ratio of micropore volume to mesopore volume is significantly high in the high-softening point meophase pitch. The calculated pore size distributions of the activated carbons are shown in Fig.3.

3.2 Electrochemical performance of activated carbons

The electrochemical performance of the two activated mesophase pitch powders as the electrodes for EDLCs were studied by charge-discharge cycles of a two-electrode cell at different current densities. Examples of the charge-discharge profiles were shown in Fig.4. All the samples show triangular chronopotentiograms, indicating a typical behavior of capacitive electrodes. In general, the initial voltage rise or voltage drop observed in the charge-discharge profiles, which correspond to the electrochemical impedance, is relatively small.

The specific capacitance of the single electrode was calculated from $C = (2 I \cdot \Delta t)/(m \cdot \Delta V)$, where Δt is the discharge time, ΔV is the voltage change during discharge, I is the discharge current, and m is the mass of active material on one electrode. The measured specific capacitances of the cell capacitors at different discharge current densities are shown in Fig.5. It can be seen that the specific capacitance of MP2-derived activated carbons is significantly larger than that of MP1-derived activated carbons at the same current densities. In general, carbon is good electrode material in which the capacitance and the energy come from the carbon-electrolyte interface. The specific capacitance of carbon material is linked to (1) the electrical conductivity, the surface area, the ratio of edge-to-basal orientation, and the porosity of the carbon; (2)

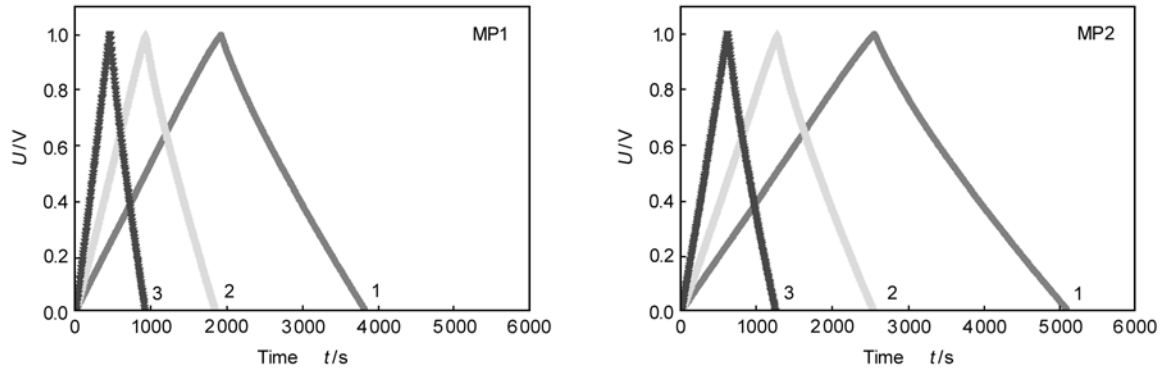


Fig.4 Constant current charge-discharge curves of the two activated carbons. Current loading: (1) $50 \text{ mA} \cdot \text{g}^{-1}$, (2) $100 \text{ mA} \cdot \text{g}^{-1}$, (3) $200 \text{ mA} \cdot \text{g}^{-1}$

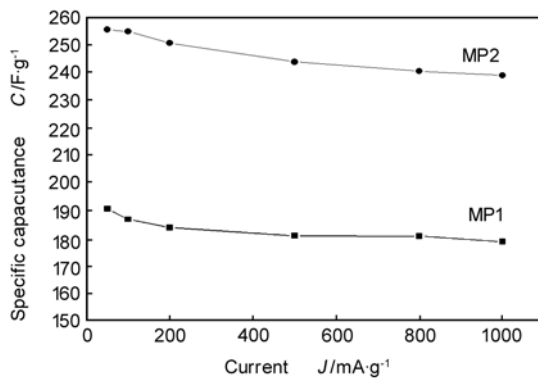


Fig.5 Variation of the specific capacitance with the current densities of activated carbons

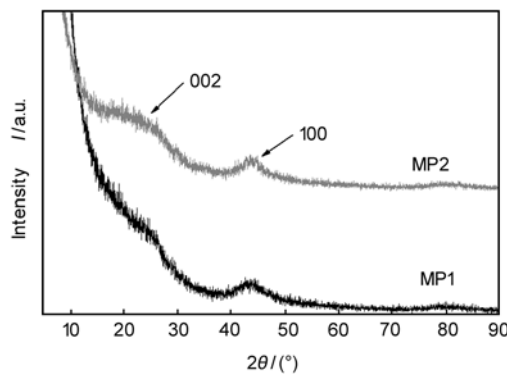


Fig.6 XRD patterns of the three mesophase pitches after activation

the accessibility of the electrolyte for penetrating into the carbon pores; and (3) the electrolyte properties^[12-13]. In this study, the electrolyte for all capacitors is the same, and it is worth noting that the surface area of the two activated carbons is almost the same. The total pore volume of MP2-derived carbons is slightly smaller than that of MP1-derived carbons, and the mesopore content of MP2-derived carbons is also smaller than that of MP1. So the higher specific capacitance of the activated carbons prepared from MP2 may be due to the higher ratio of edge-to-basal orientation. To measure the crys-

talline structure of the activated carbons, XRD was performed. Fig.6 shows the XRD patterns of the activated carbons. The 100 peaks of the two porous carbon appeared, but the 002 peaks of MP1 derived carbons disappeared after activation.

Activated carbons are high-surface area, high-porosity carbons that produced by either thermal activation or chemical activation. The carbons are made of small hexagonal carbon rings called graphene sheets. The crystal parameters are determined by carbon precursor and the preparation method. Generally, there is very little order and no long three-dimensional order. The XRD patterns of this work are very similar to the work of Liu et al.^[14]; according to the results of Liu's, the in-plane structure of the graphene sheets is more or less the same (L_a) for the two samples while the stacking arrangement of the sheets (L_c) is different. The peak height of XRD can be considered proportional to crystal size, e.g. 002 peak height is proportional to L_c and 100 peak height is proportional to L_a ^[13]. L_a for the two samples are similar, whereas L_c size for MP2-derived carbons is higher than that of MP1-derived carbons. It can also be seen from the 002 peaks of MP2-based carbons. So the ratio of edge-to-basal orientation (L_c/L_a) of MP2-derived carbons is higher.

Fig.5 shows the specific capacitance obtained at various discharge rates for MP1- and MP2-derived carbons. From Fig.5, it is clear that with increasing discharge rate, the specific capacitance decreases for the two carbons, which is attributable to the decreased sites for the electronic double layer formation. Slower decrease in the capacitance with increasing discharge rate was observed for the MP1-derived carbons, suggesting the transport of more rapid ions due to the higher content of the mesopores.

The typical CV curves of the two activated carbon electrodes in 6 mol/L KOH are shown in Fig.7. The voltage sweep range was from 0 to 1V and the sweep rates were 1, 5, 10, and 20 $\text{mV} \cdot \text{s}^{-1}$. Achieving rectangular-shaped CV curves over a wide range of scan rates is the ultimate goal in EDLC. This behavior is important for practical applications involving high energy and power density. Interestingly, the CV curves show typical capacitor-like characteristics in the form of almost rectangular cyclic behavior. These results indicate that the

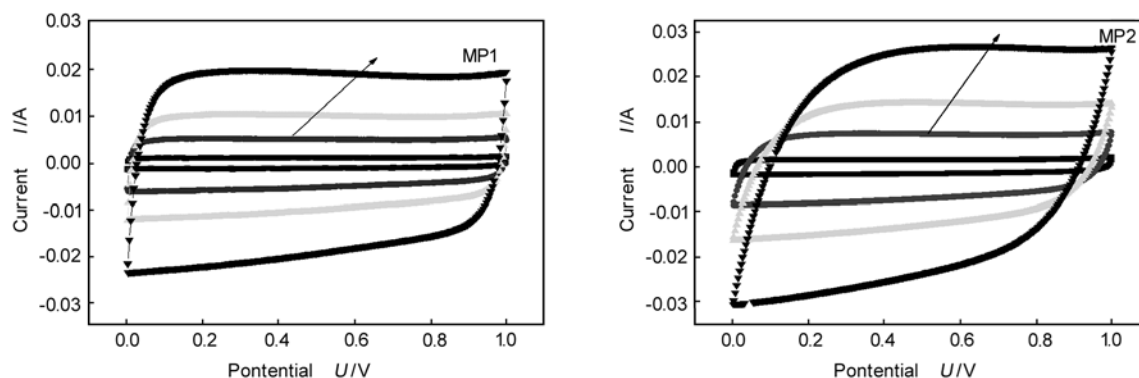


Fig.7 CV curves at various scan rates for the capacitors using different activated carbons. Arrow indicating increasing scan rates

charge-discharge responses of the electric double layer are highly reversible. At the same scan rate, more ideal capacitive behavior was observed for MP1-derived carbons with a steeper current change at the switching potential, resulting in better rectangular-shaped I-V curves. The slower changes at the switching potentials in the CV measurement of MP2-derived carbons stem from the slower reorganization of the double layer owing to slower ionic motions in the micropores.

4 Conclusion

Two kinds of mesophase pitches with different softening points were prepared through different soaking time during the preparation process, and activated carbons with high surface area have been developed from the direct activation of mesophase pitches using KOH. Activated carbons from lower softening point mesophase pitch have mesopore volume higher than that from higher softening point mesophase pitch, and the latter are microporous carbons.

Activated carbons with higher surface area and larger pore volume were obtained from the lower softening point mesophase pitch. In the discharge current density range, specific capacitance of the higher softening point mesophase pitch-derived carbons is higher ($255.6 \text{ F} \cdot \text{g}^{-1}$) than that of lower softening point mesophase pitch-derived carbons ($190.8 \text{ F} \cdot \text{g}^{-1}$) at the same current densities. At the same activation conditions, higher softening point mesophase pitch-derived carbons exhibit higher micropore content and lower mesopore content. CV curves show that lower softening point mesophase pitch-derived carbons exhibit the better rectangular-shaped I-V curves. The results obtained in this study indicate that activated carbons from mesophase pitches prepared from even the same precursor, the softening points can significantly affect the structural properties of the resultant activated carbons and the electrochemical performance of the as-prepared capacitors.

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