Preparation of mesoporous MgO-templated carbons from phenolic resin and their applications for electric double-layer capacitors

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Mesoporous carbons were synthesized using thermoplastic phenolic resin (PF) as carbonaceous precursor and magnesium citrate as template precursor. Pore structure was determined as ink-bottle-like geometry through TEM, N_2 adsorption analysis combined with TG curves. The porous carbons prepared were then applied as electrode material for electric double-layer capacitors. The capacitor performance was examined in 30 wt% KOH aqueous solution by cyclic voltammetry and galvanostatic charge/discharge measurements. The carbon prepared with MgO/PF mass ratio of 8/2 had a BET surface area of $1920 \text{ m}^2 \text{ g}^{-1}$ and exhibited a capacitance of 220 F g^{-1} at a current density of 50 mA g^{-1} . Besides, the carbon with the ratio of 4/6 had the optimize proportion of mesopores, which ensures its good rate performance that up to 98.3%, expressed as the ratio of the capacitance measured at 1000 mA g^{-1} against that at 50 mA g^{-1} .

mesoporous, EDLC, MgO-templated carbon

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Porous carbons have attracted great attention because of their hydrophobic surface nature, high surface area, large pore volumes, chemical inertness, as well as good thermal and mechanical stability [1]. For the excellent physical and chemical property, porous carbons have been used in various fields, the nature of which depends on the pore size of carbon materials. For application as electrode of electric double-layer capacitor (EDLC), carbons should have mesopores for transferring electrolyte ions and micropores for adsorbing electrolyte ions to form electric double layer [2]. Thus, the preparation of carbons containing both mesopores and micropores has sparked enormous interest.

Ordered mesoporous carbons with different pore sizes and morphologies have been prepared by casting carbon frameworks with mesoporous silica templates [3–5]. However, template removal for this preparation method requires the employment of corrosive acids, making large-scale production difficult. A promising preparation method was

recently reported that involves coating ceramic substrates with thermoplastic precursors [6–8]. Among various substrates, MgO and organic magnesium salt, such as magnesium citrate, magnesium acetate, magnesium gluconate, were proved to be ideal because the pyrolysis product, MgO, exhibit perfect performance: chemical and thermal stability, no structural and compositional changes, no reaction with carbon up to carbonization temperature of carbon precursors, and easily dissolving into a diluted acidic solution [9,10]. What's more, this preparation method was proved to be energy-saving because nanoporous carbons were prepared without any stabilization and activation processes starting from thermoplastic precursors in this method [11–15].

Although many carbon precursors have been selected to investigate various kinds of MgO-templated carbons, the interaction between carbon precursors and magnesium precursors during carbonization has not been properly discussed and the pore morphology of resultant carbons has not formed final conclusion. In the present work, we selected thermoplastic phenolic resin as carbon precursor, for

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its purity, low cost and high carbon yield, and magnesium citrate as MgO template because the abundant carbonaceous formed during carbonization can prevent the cohesion of MgO particles effectively.

1 Experimental

1.1 Carbon preparation

Magnesium citrate (MgCi, reagent grade, Tianjin Guangfu Fine Chemical Research Institute, China) with phenol formaldehyde resin (PF, novolac-type, Tianjin Daying Resin Co., Tianjin, China) was mixed in anhydrous ethanol, with mass ratios varying from 2/8 to 8/2, which were calculated on the basis of the mass of MgO, which was expected to be formed from MgCi, against PF itself.

After drying, the mixture of MgCi and PF was heat-treated in a horizontal furnace with a heating rate of 5°C/min up to 900°C in a nitrogen atmosphere and maintained at this temperature for 1 h. The carbonized products were washed by stirring with 500 mL of 1 mol L⁻¹ hydrochloric acid solution at 100°C for 2 h and then leached with distilled water for several times until they were free of chloride ion. The leached products were then dried in vacuum at 120°C for 12 h. The products were ground to a size of less than 48 μm before being subjected to characterization and electrode preparation. The carbons prepared are called phenolic-resin-based MgO-templated carbons and coded MCPFab, where ab is the MgO/PF mass ratio used. For example, the carbon prepared from the mixture with MgO/PF mass ratio of 2/8 is denoted MCPF28.

1.2 Structural characterization

Pore characteristics of the resultant carbons were measured with a gas adsorption analyzer (Micromeritics Instrument Corporation Tristar 3000) using N₂ at 77 K. BET surface area S_{BET} was calculated from the isotherm in the relative pressure range 0.05–0.30. The micropore volume V_{micro} and the total pore volume V_{total} were calculated from the amount of N₂ adsorbed at a relative pressure (P/P_0) of 0.1 and 0.95, respectively, using t-plot method. Besides, total pore area S_{total} and micropore area S_{micro} were also determined by t-plot method, and mesopore area S_{meso} was calculated as a balance between S_{total} and S_{micro} . Pore size distributions were determined by the Barrett Joyner Halenda (BJH) model. Nanostructure of carbons was examined with a transmission electron microscope (TEM, Philips Tecnai G2F-20). Thermogravimetric (TG) analysis was performed on MgCi, PF and their mixtures by using a thermogravimetric analyzer (TA Instruments TA-50) under N₂ atmosphere.

1.3 Electrochemical characterization

EDLC electrodes were prepared by mixing the carbon sample

with acetylene black as an electrical conductor and polytetrafluoroethylene (PTFE) as a binder in a mass ratio of 80:10:10, using nickel foam as a current collector. The electrolyte was 30 mass% KOH. Cyclic voltammetry (CV) measurement was performed on a potentiostat/galvanostat (Princeton Applied Research PARSTAT 2273) with a potential scan rate of 2–50 mV s⁻¹. The capacitance was determined by constructing symmetric coin-type cell with a charge/discharge battery-measurement system (Land CT2001A, Wuhan, China) with a potential window of 0–1 V. Based on the results of charge-discharge cycling, the specific discharge capacitance of a single electrode in the capacitors can be calculated according to the following equation:

$$C = (I \cdot \Delta t) / (\Delta V \cdot m),$$

where I refers to the discharge current, Δt to the discharge time, ΔV to the change of voltage, and m to the mass of resultant carbon on the single electrode. Performance rating of the capacitors was evaluated by the ratio of the capacitance measured at 1000 mA g⁻¹ against that at 50 mA g⁻¹, C_{1000}/C_{50} . All electrochemical measurements were carried out at room temperature.

2 Results

2.1 Characteristics of the porous carbons used in electrodes

Figure 1 shows TEM images of a pristine mixture of MgCi and PF with MgO/PF mass ratio of 8/2 (a), after carbonization (b) and after dissolution of MgO (c and d). The particles emphasized by a white circle in Figure 1 (a) and (b) correspond to MgCi and MgO, respectively. Dispersion of the particles seemed to be more uniform in the carbonized sample than in the pristine mixture. Although the crystalline particles of MgCi has sharp edges (Figure 1(a)), its decomposition product MgO is changed to be round particles (Figure 1(b)). This process can be illustrated by TG curves shown in Figure 2, along with the probable pyrolysis reaction of MgCi shown in formula (1) [16]. Three weight loss peaks for MgCi pyrolysis are evident, between 100–200°C, 300–400°C, and 400–600°C, respectively: the first peak indicates the removal of crystal water, the second one the decomposition of MgCi to Mg carbonate, and the third one the formation of MgO. On phenolic resin, its decomposition occur gradual up to around 800°C to become carbonaceous solids. The mixture of MgCi with phenol also shows three weight loss peaks, similar to MgCi, but each peak is shifted to lower temperature side by about 50°C. These peaks are reasonably supposed to be formed due to the decomposition of MgCi and the shift happened as a result of the influence of phenolic resin.

Figure 1 TEM images of the mixture of phenolic resin and magnesium citrate with MgO/PF ratio of 8/2. (a) Before carbonization, (b) after carbonization at 900°C, (c) and (d) after dissolving MgO (MgO-templated carbon).

Figure 2 Thermogravimetric curves for Mg citrate (MgCi), phenolic resin (PF) and their mixture with MgO/PF ratio of 8/2 (MCPF82).

Figure 3(a) presents the nitrogen adsorption/desorption isotherms of the resultant carbons measured at 77 K and the pore parameters determined from these isotherms are listed

Figure 3 (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution in the region of mesopores for the MgO-templated carbons.

up in Table 1. As shown in Figure 3(a), all the samples exhibit type-IV isotherms with hysteresis loops caused by capillary condensation in mesoporous structure, revealing that the pores in all the samples are structured mainly by mesopores. Figure 3(b) shows that the size distribution of mesopores is very sharp in these carbons, in other words, the carbons have uniform mesopore size of about 4 nm. In addition, all the isotherms reveal a considerable adsorption at relative low pressure, which is an indication of certain amount of microporosity.

As can be seen from Table 1, all pore parameters determined, S_{BET} , S_{total} , S_{meso} , S_{micro} , V_{micro} , and V_{total} , increase with

Table 1 Pore parameters calculated from N_2 adsorption isotherms by the BJH method

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{total} ($\text{m}^2 \text{g}^{-1}$)	S_{meso} ($\text{m}^2 \text{g}^{-1}$)	S_{micro} ($\text{m}^2 \text{g}^{-1}$)	$S_{\text{meso}}/S_{\text{total}}$ (%)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)
MCPF28	1037	1039	894	145	86.04	0.117	0.829
MCPF37	1066	1086	936	150	86.19	0.149	1.219
MCPF46	1393	1386	1228	158	88.60	0.153	1.276
MCPF55	1460	1479	1269	210	85.80	0.244	1.686
MCPF64	1760	1752	1471	281	83.96	0.286	1.863
MCPF73	1874	1852	1552	300	83.80	0.331	2.120
MCPF82	1920	1902	1569	333	82.49	0.384	2.334

increasing mass ratio of MgO/PF and all reach a maximum at the mass ratio of MgO/PF=8/2. As for the ratio of $S_{\text{meso}}/S_{\text{total}}$, it increases at first and then goes down with increasing MgO/PF mass ratio, maximizing at the ratio of 4/6. Moreover, from both the point view of pore area and pore volume, the amount of mesopores is far more abundant than micropores.

2.2 Performance of capacitors

In Figure 4 (a), voltage sweep CV curves with a sweep rate of 2 mV s^{-1} are shown for phenolic resin based MgO-templated carbons, revealing that the present carbons show rectangular-shaped (mirror-imaged) I - V curves. No pronounced reversible redox peaks attributed to pseudocapacitance are evident. These results indicate that the charge-discharge responses of the electric double layer are highly reversible in discharge over the same potential range as that required to store the energy on charging. Figure 4(b) presents the CV curves for the sample MCPF82 with various sweep rates changing from 2 to 50 mV s^{-1} . As the scan rate increases, the CV curves become gradually depressed but still maintain rectangular-shaped characteristics, suggesting that a good accessibility of the electrolyte ions to the carbon surface used in two electrodes and an excellent capacitive behavior of the present carbons even in quick charge-discharge operations.

As expected from rectangular CV curves, I - V relations on charge-discharge experiment could be approximated to be linear and no potential drop was observed for all carbons tested. In Figure 4(c), the dependence of EDLC capacitance on current density during discharging is shown for the carbons. The decrease in capacitance with increasing current density is rather small for all carbons, and capacitance keeps a constant at current density of more than 250 mA g^{-1} .

In Table 2, EDLC capacitances (current density=50 or 1000 mA g^{-1}) together with the performance rating defined by C_{1000}/C_{50} are listed for the resultant carbons. With growing S_{BET} , both C_{50} and C_{1000} increase and reach a maximum at MgO/PF=8/2, fitting with the general understanding that high surface area is preferable to high capacitance. Capacitance retentions are all above 92%. Moreover, comparing two sets of data, $S_{\text{meso}}/S_{\text{total}}$ in Table 1 and C_{1000}/C_{50} in Table 2, the performance rating C_{1000}/C_{50} follows the same trend with the $S_{\text{meso}}/S_{\text{total}}$ ratio, maximizing at mass ratio of MgO/PF=4/6 with the value of 98.3%, although S_{BET} of the sample MCPF46 was merely $1393 \text{ m}^2 \text{ g}^{-1}$.

3 Discussion

3.1 Formation of mesoporous carbons

It is known that the surface of MgCi particles is covered by plasticized resin during dehydration process (step I in formula (1)). The coating of MgCi particles by resinous materials is reasonably supposed to inhibit the grain growth of MgCO_3

Figure 4 (a) CV curves obtained from the MgO-templated carbons at a scan rate of 2 mV s^{-1} , (b) those on the sample MCPF82 at different scan rates, and (c) the rate performance of MgO-templated carbons.

and MgO particles during further decomposition (step II and III in formula (1)). In addition, MgCO_3 yielded from MgCi prevents further agglomeration of MgO particles. This was the reason why the decomposition product MgO could keep geometric identity, uniform size of ca.4 nm and uniform morphology, as shown in Figure 1 (b). A comparison of Figure 1 (a) and (b) shows that the edges of crystal decrease from (a) to (b), which reveals that a crystal transfer happened during the decomposition process of MgCi. This

Table 2 EDLC capacitances at different charging rates and rate performance for the carbons obtained

Sample	C_{50} (F g ⁻¹)	C_{1000} (F g ⁻¹)	C_{1000}/C_{50} (%)
MCPF28	133	125	94.1
MCPF37	150	145	96.7
MCPF46	172	169	98.3
MCPF55	177	171	96.6
MCPF64	184	175	95.1
MCPF73	194	184	94.8
MCPF82	221	204	92.2

result is in accordance with formula (1), which exhibits the decomposition process of MgCi into MgO. Removal of the MgO particles left mesopores of homogeneous size and morphology afterwards, as shown by TEM image in Figure 1(c) and by pore size distribution in Figure 3(b).

Since mesopores are formed as the heritages of MgO nanoparticles, the amount of mesopores grows with the increasing amount of MgCi mixed. However, it has to be pointed out that some amount of micropores is formed, particularly in the carbon prepared from the mixtures with high MgO/PF ratios (Table 1). Micropores, which existed principally on the wall of mesopores, however, are supposed to have two resources, citric acid in MgCi and the starting resin PF. As illustrated by the TG curves in Figure 2, the generation of MgO occurs at about 470°C followed by the final generation of carbonaceous residues from PF, resulting in the complete coating of MgO nanoparticles by carbonaceous residues formed from citric acid and PF. Therefore, the shrinkage of carbon is supposed to be hindered in the carbonaceous film coated the MgO nanoparticles up to 800°C and the movement of carbonaceous residues during their carbonization above 800°C is strongly limited. Accompanying the formation of residues, evolution and liberation of gases like CO₂, H₂O from both MgCi and PF occurred, and thus micropores were created. This is supposed to follow the mechanism of physical activation by these gases.

Because all adsorption/desorption isotherms of N₂ show marked hysteresis loops, they belong to physisorption isotherms type IV and the hysteresis loops belong to type-H2 according to IUPAC [17] and related to the capillary condensation associated with ink-bottle-type pores, the simplest image of which is a spheroidal cavity fitted with one or several narrow cylindrical necks. Pore structure model deducted from hysteresis loops is also found to be in accordance with pore formation process: micropores, which existed in the carbonaceous residues formed from two precursors, MgCi and phenolic resin, are supposed to be connected to the MgO crystal after the completion of whole decomposition process of two precursors, and consequently they were directly connected to mesopores after the removal of MgO, forming a pore network structure, just like necks of ink

bottle connect to the cavity.

3.2 Capacitor performance of mesoporous carbons

With the mesoporous carbons prepared using as electrode material, electric double-layers were formed even with a sweep rate of 50 mV s⁻¹ and no evidence for pseudocapacitance is observed on CV curves (Figure 4(b)). Moreover, good rate performance of more than 92.2% by using performance rating C_{1000}/C_{50} is got. This result might be due to the short ion transport paths through the ink-bottle mesopores to the micropores.

The capacitance of the capacitors, however, does not have a linear relationship with their specific surface area S_{BET} . A probably explanation is the fact that the solvated electrolyte ions are too big to adsorb into some micropores, which lead to low utilization rate of surface area. Thus, the surface area of these non-accessible micropores will not contribute to the total EDLC capacitance of the electrode materials [18,19]. The carbon MCPF46, which got the highest ratio of $S_{\text{meso}}/S_{\text{total}}$, shows the highest retention in capacitance, performance rating C_{1000}/C_{50} reaching 98.3%, even though the capacitance is not the highest. This may suggest a successful match of mesopores and micropores, namely a best balance between double-layer contributor and ion-channel contributor, the former increasing capacitance, and the latter enhancing rate performance of capacitors.

Considering that MgCi and PF are both cheap industrial product, the preparation of carbons was carried out without any stabilization and activation process, and the template MgO was experimentally demonstrated to be recycled [10]. Thus this method is a promising way to prepare electrode material of EDLC for its price advantage.

4 Conclusions

Templated mesoporous carbons with surface area around 1400 m² g⁻¹ were prepared from mixtures of thermoplastic phenolic resin and MgCi only through carbonization. MgO, the pyrolysis product of MgCi, dispersed uniformly in the carbonized samples and ensured the uniform size of mesopores. According to the pore formation process and N₂ adsorption isotherms, pore morphology is supposed to be ink-bottle, whose cavities correspond to mesopores, and the necks to micropores. The performance of the samples in electrochemical capacitors is essentially based on electric double-layer mechanism. The pore structure facilitates the ion transport and enhances the rate performance of capacitors. The values of performance rating reach a maximum of 98.3%, expressed in the form of C_{1000}/C_{50} . As far as the correlation between the cost and the specific capacitance is concerned, the carbons obtained by the carbonization of mixtures of phenolic resin with magnesium citrate seem to be promising material for electrode of EDLC.

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