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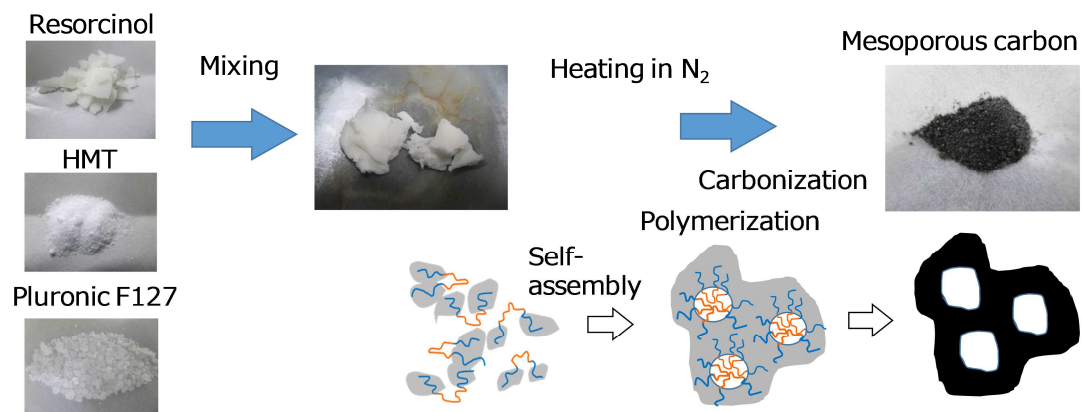
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Graphical Abstract

Solvent-free synthesis and KOH activation of mesoporous carbons using resorcinol/Pluronic F127/hexamethylenetetramine mixture and their application to EDLC

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Abstract

Ordered mesoporous carbons were synthesized through a solvent-free route. The synthesis process involves mixing and grinding of solid raw materials of resorcinol, hexamethylenetetramine and Pluronic F127, followed by a thermal treatment of the composite. An ordered mesostructure seemed to be formed after melting of resorcinol at 100°C. And then, Pluronic F127 was decomposed at 350-400°C to form straight pore channels with a diameter of 6.2 nm. The mesoporous carbons were activated by a solvent-free method using KOH to obtain a microporous/mesoporous carbon with a high surface area of 1520 m²/g. The KOH-activated carbon showed a superior EDLC characteristics due to its high mesoporosity and high surface area.

Keywords: ordered mesoporous carbon, solvent-free method, soft-templating method, KOH activation, EDLC

1. Introduction

Ordered mesoporous carbon materials are used in various applications, such as electrodes, adsorbent agents, separation membranes and catalyst supports due to their high surface area, large pore volume, chemical inertness, and electrical conducting property [1-5]. In these applications, the functionality of activated carbon is mainly attributed to the nanosized pores, which are further classified into micro- (<2 nm), meso- (2-50 nm) and macropores (>50 nm) by the International Union of Pure and Applied Chemistry (IUPAC)

The templating method is one of the most important approaches to achieve mesoporous carbons with unique morphology that could not be easily obtained through other methods. Ordered mesoporous carbons have been first reported by Ryoo's [6-9] and Hyeon's [10] groups who synthesized mesoporous carbons through an inorganic hard templating method. This process includes a synthesis of ordered mesoporous silica, pore-filling of sucrose into the mesopores of silica and carbonization with subsequent removal of the silica frameworks by HF or NaOH. However, the

drawbacks of the hard templating method are the extra steps required to prepare the silica scaffolds and to remove the silica. Since the hard templating process is a multi-step and of a high cost, another simple process is required for practical applications.

A soft-templating method has been developed by several groups [11-18]. The soft-templating method is based on the self-assembly of block copolymers or surfactants. So far, a triblock copolymer (Pluronic F127) has been used as a soft templating for the preparation of the mesoporous carbons [13-18]. The ordered mesoporous carbon, designated as COU-1, has straight channels aligned with a hexagonal symmetry [17]. Another mesoporous carbon with a 3D wormhole-like structure (COU-2) was also synthesized by changing the molar ratio of Pluronic F127/carbon source [18].

Recently, an advanced soft-templating method without a solvent has been reported [19-21]. This process consists of a mixing solid carbon sources with a triblock copolymer, followed by a heating under N₂ atmosphere. Since a solvent is not used in this method, a treatment for waste liquid is not necessary. Furthermore, this process enable us to omit a polymerization step in a solution which often takes for several hours ~ a few days.

However, a major problem of the solvent-free method is low reproducibility and ordered/disordered structure ratio in the products. In the conventional solvent method, a mesostructured composite with an optimized composition, which is often different from that in a starting solution, are deposited from a liquid phase. For example, the molar ratio of resorcinol/triblock copolymer (Pluronic F127) for the formation of the ordered mesostructures (COU-1 and COU-2) is ranged from 90 to 200 [15]. While, in the solvent-free method, the composition of starting solid materials including carbon sources and triblock copolymer should be adjusted more carefully compared to the solvent method to form an ordered mesostructure with a high yield ratio.

Another problem is a stability of the ordered mesostructure under heating. Even though a mesostructured composite is formed, structural shrinkage occurs during polymerization and carbonization processes to form dense carbon pore walls, which causes deterioration of the ordered structure. So far, in the conventional solvent method, formaldehyde has been often used as a cross-linking agent and as a second carbon source. The polymerization in the presence of a cross-linking agent seems to be effective to form stable mesostructures under heating.

In this study, we have developed a facile and reproducible solvent-free synthesis route for mesoporous carbons using hexamethylenetetramine (HMT) as a solid cross-linking agent. The synthetic procedure is (1) mixing of carbon precursors (resorcinol and HMT) with triblock copolymer (Pluronic F127), (2) grinding, and (3) heating. During the heating process, self-assembly, polymerization and carbonization occur with a rise in temperature.

Meanwhile, coexistence of micropores in addition to mesopores is effective to increase the surface area, which improve functions when the carbons are utilized as catalysts, adsorbents and electrodes

such as electric double layer capacitors (EDLC) and so on. An alkaline activation using a KOH solution is one of the most effective methods to increase micropore surface area [16, 22, 23]. But, in accordance with the objective of this study, we have tried a solvent-free KOH activation method, which is (1) mixing KOH powder with mesoporous carbons and (2) heating under N₂ atmosphere.

In this study, the pore size and pore structure have been studied with the mesoporous carbons synthesized by the solvent-free self-assembly method. The effect of the solvent-free KOH activation treatment on the pore size and surface area has been examined. For their application to EDLC, discharge capacity was measured using an organic electrolyte.

2. Experimental

2.1 Synthesis of mesoporous carbons

A solvent-free synthesis of carbon was performed using solid raw materials of resorcinol (2.2 g), HMT(1.4 g), and triblock copolymer (Pluronic F127, 2.0 g). All raw materials were smashed into pieces (less than 100 μm). After the raw materials are mixed and ground, the obtained composite was heated under N₂ atmosphere at 400 °C for 3h and 800°C for 3 h with a heating rate of 1.3 °C/min up to 400 °C and 1.6 °C/min up to 800 °C. The sample obtained after carbonization is named MPC (mesoporous carbon).

In order to increase micropore volume and surface area, an alkaline activation is performed. The MPC sample was mixed with KOH powder with a mass ratio of KOH: MPC = 3: 1 (g/g) and ground. The KOH/MPC composite was heated under N₂ atmosphere at 800°C for 1 h with a heating rate of 13 °C/min. The activated carbon was washed using HCl and deionized water, and then dried at 90°C. The KOH-activated MPC carbons is named MPC-K.

2.2 Characterization

The nitrogen adsorption/desorption isotherms were measured at 77 K using BELSORP-Max (Microtrac BEL). The total surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The pore volume and pore size distribution were calculated by the Barrett-Joyner-Halenda (BJH) method. The transmission electron microscope (TEM) images were recorded on a Hitachi H800 electron microscope at an acceleration voltage of 200 kV. Thermogravimetric analysis (TGA) was performed using DTG-60 (Shimadzu). Elemental analysis was performed with PerkinElmer 2400II.

2.3 Electrochemical Measurement

The EDLC characteristics was examined by charge-discharge measurements. The composite electrode was also prepared by obtained carbons, acetylene black, and PTFE binder (90: 5: 5 in mass). The test capacitor cell (two-electrode system) was fabricated by the test electrodes, paper-type separator (TF40-30), and organic electrolyte (1.5M-SBP-BF₄/PC). The capacitance was measured by the galvanostatic method (0.4 mAcm⁻², 0~2.5 V) at room temperature. Commercial

microporous carbon (YP-50F) was also used as a reference.

3. Results and discussion

3.1 Synthesis of mesoporous carbon

The N_2 adsorption/desorption isotherms collected at 77 K reveals that the obtained carbons exhibit a hysteresis loop, indicating a presence of mesopores as shown in Fig. 1(a). Pore size distributions of the carbons were shown in Fig. 1(b). A pore size distribution is calculated from the adsorption branch based on the BJH model. The pore size distribution in Fig. 1(b) shows that the MPC carbon has mesopores of 6.2 nm. The data of textual properties are summarized in Table 1. Even after activation, the mesopore size did not change. The increase of mesopore volume after the activation can be explained by the reduction of the mass density of carbon pore wall. The mass of the MPC carbon reduced by 30% after the activation, which is consistent with the increase in mesopore volume per unit mass of the carbons. These results indicate that the KOH activation hardly affected on the mesopores of MPC. Instead, the micropore volume increased from $0.14 \text{ cm}^3 \text{ g}^{-1}$ for the MPC carbon to $0.62 \text{ cm}^3 \text{ g}^{-1}$ for the MPC-K carbon. The MPC-K carbon possesses a micro/meso bimodal porous structure. The BET surface area (S_{BET}) is $396 \text{ m}^2 \text{ g}^{-1}$ for the MPC carbon and $1520 \text{ m}^2 \text{ g}^{-1}$ for the MPC-K. The increase of the BET surface area can be mainly contributed by the increase of micropores in the carbon pore wall. During the KOH activation, micropores were formed in the carbon pore wall due to the generation of gases such as CO_2 and CO . In this study, we performed the KOH activation by only mixing KOH powder with carbon without solvent. The successful micropore formation suggests that KOH and K species can penetrate into carbon pore walls and activate the internal carbon pore wall.

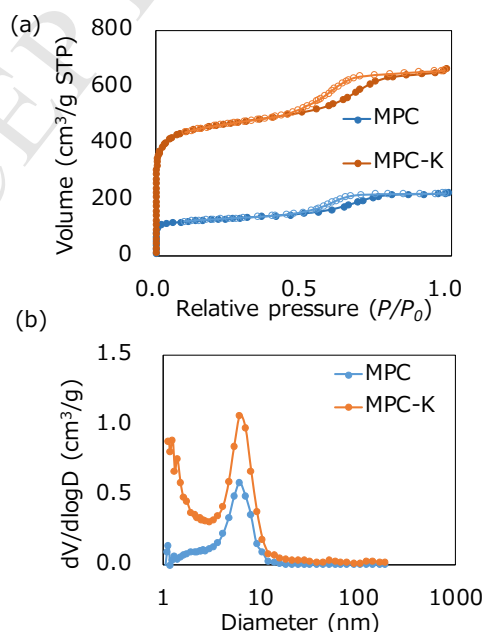


Fig. 1 (a) N_2 adsorption-desorption isotherms and (b) corresponding pore size distributions of the carbons.

Table 1 Textual properties of the porous carbons.

Sample	S_{BET} [m ² /g]	$V_{\text{micro}}(<2 \text{ nm})$ [cm ³ /g]	$V_{\text{meso}}(2-50 \text{ nm})$ [cm ³ /g]	$V_{\text{macro}}(>50 \text{ nm})$ [cm ³ /g]	V_{total} [cm ³ /g]
MPC	396	0.137	0.201	0.00439	0.342
MPC-K	1520	0.616	0.454	0.0174	1.09
YP-50F (Ref)	1600	0.608	0.675	0.101	0.777

Transmission electron microscope (TEM) images for MPC and MPC-K were shown in Fig. 2. Both the MPC and MPC-K carbons have a similar pore channel structure. For the MPC-K carbon, the micropores can be observed in pore walls (Fig. 3(b)), indicating that KOH penetrates into the pore wall and micropores ($< 1 \text{ nm}$) are formed in the pore walls by gasification, which is consistent with the results of the N₂ adsorption.

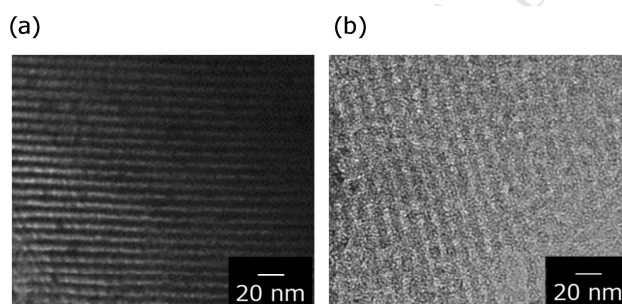


Fig. 2 TEM images of (a) MPC carbon and (b) MPC-K carbon.

The mesopore volume of the MPC-K carbon is smaller than the K-COU-2 carbon [16] possibly because the pore structure of MPC-K (1D channel-like pore structure) is different from the K-COU-2 (3D wormhole-like pore structure). The 1D mesopore structure has less porosity than the 3D mesopore structure.

While, the micropore volume and surface area of the MPC-K carbon is comparable to that of the K-COU-2 carbons activated by a conventional solvent method [16]. Fig. 3 shows the TGA curve of the MPC/KOH composite. Activation (gasification) occurs over 740 °C according to the TG result. The penetration of KOH into carbon pore wall seems to be possible after melting of KOH over 360 °C. Once the activation started, adsorption of H₂O which is produced by the reaction KOH and CO₂ may accelerate the penetration of KOH into the pore wall. Our results show that the solvent-free activation is an alternative activation method for increasing micropore surface area.

By the solvent-free method, the pore size and pore structure of the mesoporous carbons are similar to the COU-1 carbon [17-18] synthesized by the solvent method. This fact suggests that the self-assembly of resorcinol/triblock copolymer is not much affected by the presence of solvent such as water and alcohol. It is noteworthy that the ordered structure was observed in almost all powders in the TEM sample, indicating that the yield ratio of the ordered structure is quite high (> 90%), which seems to be hardly attained by other soft-templating methods including both solvent and solvent-free methods. In addition, reproducibility of the properties of the products such as pore size and pore volume is quite high in this method, indicating that a mixing at a molecular level followed by self-assembly readily occurs after melting of resorcinol as described below.

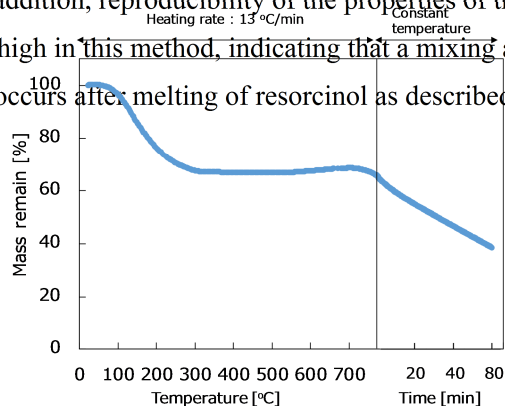


Fig. 3 The TGA curve of the MPC/KOH composite.

TG analysis of the resorcinol/HMT/F127 composite was performed in a nitrogen flow. The TG curve is shown in Fig. 4. The TG curve is similar to the one for the resorcinol/formaldehyde/F127 composite which was obtained by the solvent method [15]. Triblock copolymer (Pluronic F127) decomposes at 350-400 °C resulting in the formation of uniform mesopores. This result suggests that self-assembly of the triblock copolymer in an ordered mesostructured occurs below 350 °C. When we assume that Pluronic 127 is completely decomposed, the carbon yield of the carbon source materials (mass of carbon/(mass of resorcinol + HMT)) is calculated to be 45 %.

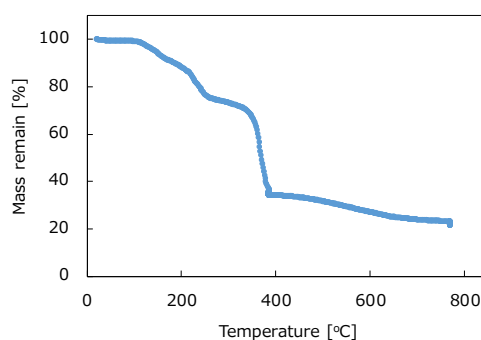


Fig. 4 TGA curve of the resorcinol/HMT/F127 composite in a nitrogen flow (heating rate: 1.3 °C/min up to 400 °C and 1.6 °C/min up to 800 °C). The temperature was kept constant at 400 °C for 3h and 800°C for 3 h.

Fig. 5 shows a photo of resorcinol-HMT-Pluronic F127 composite heated at different temperatures. We found that the resorcinol/HMT/F127 composite powder was melt at 90-100 °C. Then, the color of the composite started to change from red to black over 110 °C. These facts suggest that polymerization occurs slowly at 110-400 °C. Once polymerization proceeds to some extent, self-assembly is expected to be difficult to occur anymore. Thus, we can conclude that self-assembly of the triblock copolymer occurs at 90-110 °C because a mixing at a molecular level is possible only in the molten phase.

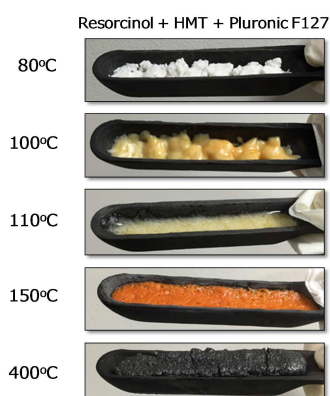


Fig. 5 The resorcinol-HMT-F127 composite heated under N₂ atmosphere.

The nitrogen content of the MPC carbon is 2.3 wt%. Apparently, HMT in the raw materials acts as a cross-linking agent. As for the conventional solvent methods using resorcinol/ formaldehyde (RF) resin, polymerization undergoes by an addition reaction of formaldehyde to form RF polymer. Meanwhile, thermal decomposition of HMT is reported to produce ammonia and formaldehyde at 200-300 °C [24]. However, ammonia was not contained in the outlet gas during the heating in this synthesis. This result implies that the formation of formaldehyde and its addition reaction is not a main pathway for the polymerization in this method. An intermediate in the Duff reaction seems to be formed by the reaction of HMT and resorcinol which is the early stage of the Duff reaction. But, a detailed reaction mechanism is still not elucidated.

3.2 Electrochemical measurements

Table 2 listed discharge capacity of the MPC and MPC-K carbons together with a commercial microporous carbon (YP-50F). The specific discharge capacity per unit mass significantly increased after the KOH activation due to an increase of surface area. The comparison of the mesoporous carbons with the microporous carbon (YP-50F) also shows an advantageous effect of the mesopores.

The ion size of SBP-BF₄ is reported to be 0.4 nm for cation and 0.46 nm for anion, respectively [25,26]. But, the size of their solvate seems to be larger than 1 nm. The mesopores are more favorable for the diffusion of electrolyte ions.

The specific discharge capacity per unit surface area for MPC is comparable to that of YP-50F and lower than MPC-K. These results suggest that the 1D channel structure is not always suitable for ion diffusion, which depends on the orientation of pore channels. The high capacity of MPC-K suggests that the presence of micropores formed by the KOH activation effectively enhances an inter-channel ion diffusion. The diffusion resistance for ions can be negligible because of thin pore walls (short diffusion path).

Table 2 EDLC performance of the MPC carbons

Sample	Discharge capacity	
	[mAh/g]	[mAh/m ²]
MPC	11.1	28.0
MPC-K	55.2	36.3
YP-50F (Ref.)	39.2	28.1

4. Conclusion

An ordered mesoporous carbon was synthesized by the solvent-free method using HMT as a cross-linking agent as well as resorcinol and Pluronic F127. The KOH activation without a solvent was also effective to increase micropore volume and surface area. The MPC-K carbon with both micropores and mesopores showed a superior EDCL capacitance in the organic electrolyte.

Acknowledgement

TEM measurements were carried out using a facility at the Research Center for Ultrahigh Voltage Electron Microscopy, Osaka University.

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Figure Captions

Fig. 1 (a) N_2 adsorption-desorption isotherms and (b) corresponding pore size distributions of the carbons.

Fig. 2 TEM images of (a) MPC carbon and (b) MPC-K carbon.

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Fig. 5 The resorcinol-HMT-F127 composite heated under N_2 atmosphere.

Highlights

1. An Ordered mesoporous carbon was synthesized by the solvent-free method using hexamethylenetetramine as a cross-linking agent as well as resorcinol and Pluronic F127.
2. KOH activation was performed by a solvent-free method.
3. The ordered mesoporous carbon with micropores showed a superior EDCL capacitance in the organic electrolyte.