KOH activation of ordered mesoporous carbons prepared by a soft-templating method and their enhanced electrochemical properties

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ABSTRACT

Ordered mesoporous carbon (COU-2) was synthesized by a soft-templating method. The COU-2 mesoporous carbon was activated by using KOH to improve its porosity. The mesopore size of COU-2 was 5.5 nm and did not change by the KOH activation. But, the BET surface area of COU-2 largely increased from 694 to 1685 m^2/g and total pore volume was increased from 0.54 to 0.94 cm^3/g after the KOH activation. The large increase of micropore volume is due to the increase of the surface area. Electrochemical cyclic voltammetry measurements were conducted in aqueous (1 M sulfuric acid) and organic (1 M tetraethyl ammonium tetrafluoroborate/polypropylene carbonate) electrolyte solutions. The KOH-activated COU-2 carbon shows superior capacitances over the COU-2 carbon and a commercial microporous carbon both in aqueous and organic electrolyte solutions. These results suggest that the carbons having regularly-interconnected uniform mesopores and micropores in thin pore walls are desirable for the electrodes in electrochemical double-layer capacitors.

1. Introduction

Electrochemical double-layer capacitors (EDLCs) or supercapacitors store energy by electrostatic accumulation of charge at electrode surface. The electrochemical double-layer phenomena in EDLCs have the potential to achieve rapid electrical charge and discharge compared to modern secondary batteries. In addition, EDLCs have much longer life cycle life than batteries because no or negligibly small chemical charge transfer reactions are involved. However, the specific energy of EDLCs is a fraction of a conventional battery.

The specific energy of EDLCs is influenced strongly by the surface area of the electrodes. Pore size distribution and the size of the electrolyte ions could also influence electrochemical performance significantly [1,2]. It has been reported that a high–surface–area mesoporous carbon could be potentially more advantageous than microporous carbons to transport the large organic salt ions such as tetraethyl ammonium tetrafluoroborate (Et_4NBF_4) ions at a fast charge–discharge rate [3–5]. On the other hand, Kyotani's group demonstrated that ordered carbons with uniform micropores (pore size: 1.2 nm) exhibited excellent rate characteristics in the organic electrolyte solution [6]. In any case, it is important to design carbon electrode materials with pores that are small enough to ensure a large surface area, but large enough for the organic ions to easily penetrate.

Activated carbons with high–surface–areas, typically from petroleum coke or coal, are the most common electrode materials used in EDLCs [7,8]. However, conventional activated carbons have drawbacks such as irregular pore structure and wide pore size distributions. To realize the benefits

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of EDLCs in high-power-demand applications, development of new electrode materials with high energy density is required.

In recent years, ordered mesoporous carbons have been proposed as novel high performance electrode materials for EDLCs [3,4,9–11] since they have both micropores and mesopores with narrow pore size distributions and a large specific surface area. In addition, mesopore size and pore structure can be precisely controlled by using various templating agents.

Several researchers have first synthesized ordered mesoporous carbons by using mesoporous silicas as hard templates [11–14]. The EDLC performances for the ordered mesoporous carbons have been measured by Hyeon's group who prepared mesoporous carbons using mesoporous silica (MCM-48) and showed its high EDLC performance [14]. However, the drawbacks of the hard template method are the extra steps required to prepare the silica scaffolds and remove the silica. Therefore, the production process is a multi-step and of a high cost, which may cause a barrier to industrial applications.

On the other hand, a direct synthesis of ordered mesoporous carbons using a soft-templating method has been developed by several groups [15–18]. We have first used a triblock copolymer (Pluronic F127) as a soft template for the preparation of the mesoporous carbons. 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].

In this study, the mesoporous carbon COU-2 was activated by using KOH to improve its porosity. The KOH activation was reported to be effective for increasing micropore volume [19–20]. The effect of the pore size distribution on the capacitance was studied using the ordered mesoporous carbons and commercial microporous carbons.

2. Experimental

2.1. Preparation of COU-2

Pluronic F127 was dissolved in ethanol solution, and then resorcinol (R) was added and stirred for 30 min. After complete dissolution of F127 and resorcinol, formaldehyde (37 wt.%) (F) was added to the above solution and stirred for 30 min. Finally, HCl (5 N) was added as a catalyst to the solution. The molar ratios of the solutions were 0.0074 F127:15 EtOH:5.6 water:1.0 R:2.5 F:0.05 HCl. After stirring for 72 h, the precursor solution separated into two phases. The transparent upper phase was ethanol–water rich and the yellow lower phase was polymer-rich. Then the upper phase was discarded while the lower phase was preheated in an oven at 90 °C for 24 h. Subsequently, the resultant brown sample was carbonized under a nitrogen atmosphere by stepwise heating at 800 °C for 3 h, respectively. The heating rate was 1 °C min^{-1}.

A commercial carbon (SX-II, Norit Co.) was also used as a reference. The sample name is called AC hereafter.

2.2. Preparation of K-COU-2, K-AC

The post-synthesis activation was performed by impregnating COU-2 (0.3 g) with KOH solution (1 M 15 ml) followed by water evaporation at 120 °C. This process was carried out at 800 °C for 1 h in a tube furnace under flowing nitrogen. A heating rate was 10 °C min^{-1}. To assure a complete removal of KOH, the resulting sample after carbonization was washed consecutively with 0.1 M HCl solution followed by deionized water until the pH of the filtrate water became 7.

The same post-synthesis activation was also carried out for the commercial activated carbon (AC). The AC carbon activated with KOH is called K-AC.

2.3. Characterization

The ordered structure of the mesoporous carbons were investigated by X-ray diffraction (XRD) with a Phillips X'Pert-MPD diffractometer using Cu-Kα radiation with $\lambda = 1.5418$ Å. The copper anode was operated at 40 kV and 30 mA. The peak evolution was followed in the $\theta/2\theta$ Bragg–Brentano scattering geometry with a step size of 0.02° and a time per step of 0.5 s. The nitrogen adsorption/desorption isotherms of the carbons were measured at −196 °C using an AUTOSORB-1 instrument (Quantachrome Co.). The pore size distributions were calculated by the Brunauer–Joyner–Halenda (BJH) method using adsorption branches for the mesopore analysis. Micropore/mesopore surface areas and total surface area were calculated by the t-plot and Brunauer–Emmett–Teller (BET) methods. Pore volume was calculated by the t-plot and BJH methods.

2.4. Electrochemical measurements

Electrochemical measurements consisted of cyclic voltammetry (CV) experiments using Solartron 1287. The electrodes were prepared by mixing porous carbon materials with 10 wt.% of polytetrafluroethylene (Dupont–Mitsui Fluorochemicals Co.) as binder and 10 wt.% of carbon black (Tokai carbon Co.). The electrode mass was pressed into 15–20 mg pellets. The electrochemical behavior of the carbon electrode was analyzed with a three-electrode configuration in aqueous 1 M H_2SO_4 and organic 1 M Et_4NBF_4/polypropylene carbonate electrolyte solutions. A Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The assembling was carried out under a nitrogen atmosphere in a glove box.

3. Results and discussion

Fig. 1 shows XRD patterns of COU-2 and K-COU-2. An ordered mesostructure was observed for both COU-2 and K-COU-2, suggesting that the ordered mesostructure was still retained after activation. However, the reflection peak became weaker after activation, indicating activation deteriorated ordered mesostructure to some extent. A decrease in the density of pore wall also may contribute to the reduction of the peak intensity. The peak position ($d(1\,0\,0) = 10.0$ nm), did not shift after the KOH activation, indicating that a structural shrink-
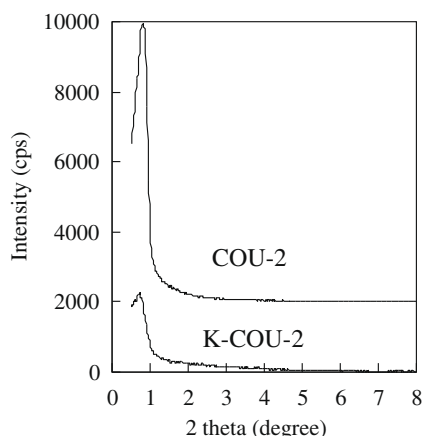
Fig. 1 – XRD patterns of COU-2 and K-COU-2.

age did not occur during activation. The pore structure of COU-2 was described elsewhere [18].

The mass of COU-2 and AC was similarly decreased by about 20 wt.% by the KOH activation. N_2 adsorption isotherms of COU-2, K-COU-2, AC and K-AC were shown in Fig. 2(a). Their textural properties are summarized in Table 1. Pore size distributions of COU-2, K-COU-2, AC and K-AC calculated by the BJH method using the adsorption branches were shown in Fig. 2(b). The narrow pore size distributions of COU-2 and K-COU-2 indicate that both the COU-2 and K-COU-2 have a well-ordered mesostructure with uniform mesopores.

The BET surface area of COU-2 largely increased from 694 to 1685 m^2/g by the KOH activation. Total pore volume of COU-2 was also increased from 0.54 to 0.94 cm^3/g. Micropore volume was largely increased for COU-2. Consequently, the ratio of S_{me}/S_t was decreased by the KOH activation. The increase of micropore volume mainly contributes to the increase of the surface area after the KOH activation.

As shown in Fig. 2(b), the mesopore size of K-COU-2 was 5.5 nm and similar to that of COU-2. The XRD results suggest that there is no structural shrinkage by the KOH activation. The XRD and N_2 adsorption results suggest that the thickness of carbon pore wall did not change and new micropores were generated in carbon pore walls.

From Fig. 2(b), the commercial carbon (AC) has little mesopores but a large pore volume of micropores and macropores compared to COU-2. The micropores, mesopores and macropores increased by 0.16, 0.08 and 0.11 cm^3/g, respectively after the KOH activation. Namely, all pores almost uniformly increased in volume, possibly because the pore size distribution of AC is broad. The high–surface–area for AC (1047 m^2/g) and K-AC (1464 m^2/g) is due to their large micropore volumes.

Fig. 3(a) exhibited a set of cyclic voltammogram (CV) measured at scan rates of 2 and 10 mV s^{-1} for COU-2 and K-COU-2 in 1 M sulfuric acid aqueous solution. The CV profiles show rectangular voltammograms without any redox peaks in the chosen potential range. The capacitance was plotted as a function of the voltage scan rate in Fig. 4(a). The COU-2 carbon shows higher capacitance than the K-AC carbon although the surface area of COU-2 was much smaller than that of K-AC, which indicates that the existence of mesopores benefits the penetration of ions. Comparing with K-AC and COU-2, K-COU-2 shows a superior capacitance at all scan rates. The appropriate pore size distribution without useless macropores and the 3D-interconnected pore system might effectively reduce the diffusion resistance of ions in the porous electrode. Figs. 3(b) and 4(b) show a set of cyclic voltammogram (CV) and capacitance measured at scan rates of 2–10 mV s^{-1} for K-AC, COU-2 and K-COU-2 in Et$_4$NBF$_4$ solution. The K-COU-2 carbon shows much higher capacitance than K-AC. The size of ions Et$_4$N$^+$ is reported to be about 0.7 nm [2]. The diffusivity of the Et$_4$N$^+$ ions in micropores seems to be much smaller than that of H$^+$. Therefore, the existence of interconnected mesopores in microporous carbon could reduce an overall resistance of penetration of ions into the carbon, which is much more effective when the organic electrolyte is used. Instead, the K-COU-2 carbon has few macropores which do not contribute to the enhancement of capacitance.

As well as mesopores, the large micropores volume of K-COU-2 apparently contributes to the superior capacitance ability in organic electrolyte solutions by increasing the surface area. For ordered mesoporous carbons, the micropores are present in very thin carbon mesopore walls. The thickness of the pore wall is about 6 nm [17]. Thus, the diffusion path length in pore walls is very short and uniform
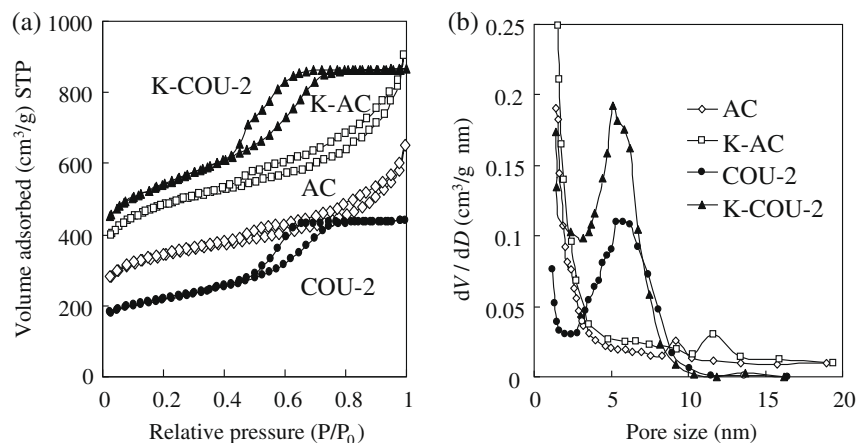

Fig. 2 – (a) Nitrogen adsorption isotherms and (b) pore size distributions calculated by the BJH method.

Table 1 – Textual properties of the porous carbons.

Sample	S_t^a (m^2/g)	S_{mi}^b (m^2/g)	S_{me}^c (m^2/g)	S_{me}/S_t (%)	d_{me}^d (nm)	V_{mi}^e (cm^3/g)	V_{me}^f (cm^3/g)	V_{ma}^f (cm^3/g)	V_t^g (cm^3/g)
AC	1047	787	260	25		0.43	0.24	0.34	1.01
K-AC	1464	1085	379	26		0.59	0.32	0.45	1.36
COU-2	694	264	430	62	5.5	0.16	0.48	0.02	0.66
K-COU-2	1685	847	849	50	5.5	0.47	0.75	0.03	1.25

[a] Total surface area calculated using the BET method.
[b] Micropore surface area ($S_{mi} = S_t - S_{me}$).
[c] Mesopore surface area calculated using the t-plot method.
[d] Mesopore diameter calculated using the BJH method.
[e] Micropore volume calculated using the t-plot method.
[f] Mesopore (2 nm < d < 10 nm) and macropore (d > 10 nm) volume calculated using the BJH method.
[g] $V_t = V_{mi} + V_{me} + V_{ma}$.
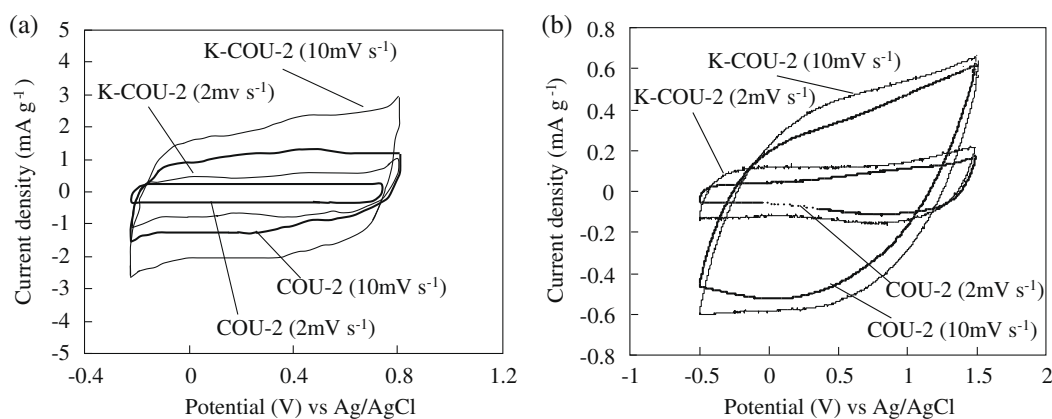
Fig. 3 – Cyclic voltammograms of COU-2, K-COU-2, AC and K-AC in (a) 1 M sulfuric acid aqueous solution and (b) in 1 M Et$_4$NBF$_4$/polypropylene carbonate solution (scan rate is 2 and 10 mV/s).
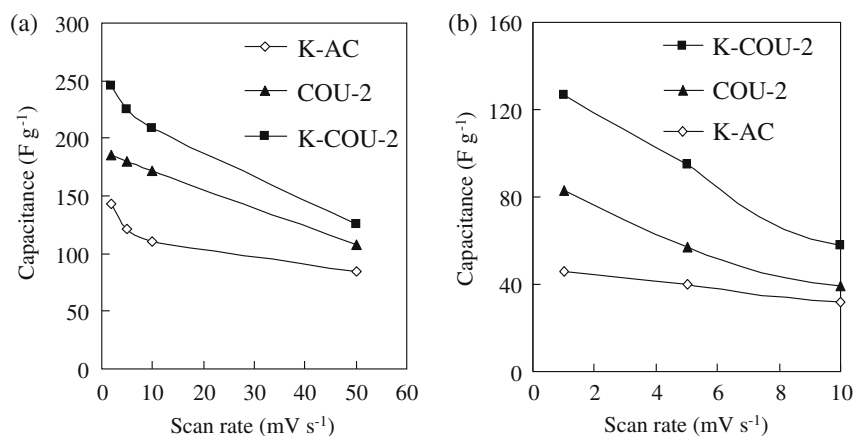
Fig. 4 – Capacitance of COU-2, K-COU-2, AC and K-AC in (a) 1 M sulfuric acid aqueous solution and (b) in 1 M Et$_4$NBF$_4$/ polypropylene carbonate solution.

compared to that of conventional microporous carbons and disordered mesoporous carbons, which provide a fast penetration of ions. In addition, these micropores are surrounded by 3D-interconnected uniform mesopores. These results suggest that the carbons having regularly-interconnected mesopores and thin pore walls made of high–surface–area microporous carbons are desirable for EDLCs electrode.

4. Conclusions

Ordered mesoporous carbons (COU-2) were synthesized by the soft-templating method using a triblock copolymer (Pluronic F127). The COU-2 carbon activated with KOH (K-COU-2) showed a high–surface–area of 1685 m^2/g because of an increase in micropore volume. The size of the wormhole-like mesopores was about 5.5 nm and did not change by the acti-

vation. These results suggest that carbon structure did not shrink and new micropores were generated in carbon pore walls. Electrochemical characterizations demonstrate that K-COU-2 showed superior capacitances both in aqueous (1 M sulfuric acid) and organic (1 M Et_4NBF_4/polypropylene carbonate) electrolyte solutions. The possible reasons for the high EDLC performance are (1) the K-COU-2 carbon has few macropores which do not contribute to the enhancement of capacitance. (2) Diffusion path length in microporous carbon wall is very short (<6 nm) and uniform. (3) The K-COU-2 carbon has regularly-interconnected uniform mesopores around the microporous carbon walls.

Acknowledgements

REFERENCES

[1] Wang L, Toyoda M, Inagaki M. Dependence of electric double layer capacitance on pore surface areas of activated carbons. New Carbon Mater 2008;23:111–5.
[2] Mysyk R, Raymundo-Pinero E, Pernak J, Beguin F. Confinement of symmetric tetraalkylammonium ions in nanoporous carbon electrodes of electric double-layer capacitors. J Phys Chem C 2009;113:13443–9.
[3] Jurewicz K, Vix-Guterl C, Frackowiak E, Saadallah S, Reda M, Parmentier J, et al. Capacitance properties of ordered porous carbon materials prepared by a templating procedure. J Phys Chem Solids 2004;65(2–3):287–93.
[4] Fuertes AB, Pico F, Rojo JM. Influence of pore structure on electric double-layer capacitance of template mesoporous carbons. J Power Sources 2004;133(2):329–36.
[5] Fernandez JA, Tennison S, Kozynchenko O, Rubiera F. Effect of mesoporosity on specific capacitance of carbons. Carbon 2009;47:1598–604.
[6] Nishihara H, Itoi H, Kogure T, Hou P, Touhata H, Okino F, et al. Investigation of the ion storage/transfer behavior in an electrical double-layer capacitor by using ordered microporous carbons as model materials. Chem Eur J 2009;15:5355–63.
[7] Shi H. Activated carbons and double layer capacitance. Electrochim Acta 1996;41(10):1633–9.
[8] Balathanigaimani MS, Shim WG, Lee MJ, Kim C, Lee JW, Moon H. Highly porous electrodes from novel corn grains-based activated carbons for electrical double layer capacitors. Electrochem Commun 2008;10:868–71.
[9] Sheng ZM, Wang JN, Ye JC. Synthesis of nanoporous carbon with controlled pore size distribution and examination of its accessibility for electric double layer formation. Mesopor Mater 2008;111:307–13.
[10] Liang Y, Feng X, Zhi L, Kolb U, Müllen K. A simple approach towards one-dimensional mesoporous carbon with superior electrochemical capacitive activity. Chem Commun 2009:809–11.
[11] Inagaki S, Oikawa K, Kubota Y. Effect of carbon source on the textural and electrochemical properties of novel cage-type mesoporous carbon as a replica of KIT-5 mesoporous silica. Chem Lett 2009;38:918–9.
[12] Ryoo R, Joo SH, Jun S. Synthesis of highly ordered carbon molecular sieves via template-mediated structural transformation. J Phys Chem B 1999;103:7745–6.
[13] Jun S, Joo SH, Ryoo R, Kruk M, Jaroniec M, Liu Z, et al. Synthesis of new nanoporous carbon with hexagonally ordered mesostructure. J Am Chem Soc 2000;122(43):10712–3.
[14] Lee J, Yoon S, Hyeon T, Oh SM, Kim KB. Synthesis of a new mesoporous carbon and its application to electrochemical double-layer capacitors. Chem Commun 1999:2177–8.
[15] Liang C, Hong K, Guiochon GA, Mays JW, Dai S. Synthesis of a large-scale highly ordered porous carbon film by self-assembly of block copolymers. Angew Chem Int Ed 2004;43:5785–9.
[16] Zhang F, Meng Y, Gu D, Yan Y, Yu C, Tu B, et al. A facile aqueous route to synthesize highly ordered mesoporous polymers and carbon frameworks with Ia3d bicontinuous cubic structure. J Am Chem Soc 2005;127:13508–9.
[17] Tanaka S, Nishiyama N, Egashira Y, Ueyama K. Synthesis of ordered mesoporous carbons with channel structure from an organic–organic nanocomposite. Chem Commun 2005;16:2125–7.
[18] Jin J, Nishiyama N, Egashira Y, Ueyama K. Pore structure and pore size controls of ordered mesoporous carbons prepared from resorcinol/formaldehyde/triblock polymers. Micropor Mesopor Mater 2009;118:218–23.
[19] Gorka J, Zawislak A, Choma J, Jaroniec M. KOH activation of mesoporous carbons obtained by soft-templating. Carbon 2008;46:1159–74.
[20] Tian HY, Buckley CE, Wang SB, Zhou MF. Enhanced hydrogen storage capacity in carbon aerogels treated with KOH. Carbon 2009;47:2112–42.