Synthesis of Mesoporous Carbon-Containing Ferrocene Derivative and Its Electrochemical Property

Hiroyasu Furukawa, Mitsuhiro Hibino, Hao-Shen Zhou, and Itaru Honma*
Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology (AIST),
1-1-1 Umezono, Tsukuba, Ibaraki 305-8568

(Received November 5, 2002; CL-020934)

Ordered mesoporous carbon-containing ferrocene derivative (Fc-MC) with a hexagonal framework structure has been prepared using a SBA-15 silica template. The electric double-layer capacitance of Fc-MC increases in comparison with that of pure mesoporous carbon.

Ordered mesoporous carbons prepared from silica templates are of general interests because these materials are useful for hydrogen storage, catalysts, catalyst supports, and adsorbents for relatively large molecules.[1–4] In recent years, research on the electric double-layer capacitors (EDLCs) using such mesoporous carbons has been paid much attention for their use in high energy power sources,[5–7] because these materials possess both high specific surface area and electrical conductivity. However, the electrical conductivity depends on starting materials or procedures in preparation.[8] This encourages us to improve the electrical conductivity of mesoporous carbons in terms of the EDLC materials.

This is the first report on the synthesis of mesoporous carbon containing ferrocene derivative (ferrocenecarboxaldehyde, Fc) with a hexagonal structure using SBA-15 as the hard template. The advantages of Fc-containing mesoporous carbon in comparison with conventional carbons can be as follows: (i) increase in electrical conductivity,[9] (ii) catalytic growth of carbon framework,[10] and (iii) possibility of appearance of the pseudocapacitance originated from iron species.[8]

The mesoporous SBA-15 was prepared using Pluronic P123 (non-ionic triblock copolymer, $EO_{20}PO_{70}EO_{20}$) as a surfactant and tetraethoxysilane as a silica source, according to Zhao et al.[11] With a view to introducing Fc into the SBA-15 mesopores, Fc was dissolved in furfuryl alcohol (FA) as the main carbon source. The calcined SBA-15 was impregnated with aqueous solution of FA, sucrose, 0.5 mol dm^{-3} H_2SO_4, and Fc (H_2O : FA : sucrose : H_2SO_4 : Fc = 9 : 6 : 1 : 1 : 0.2 (w : w)). About 10 wt% of sucrose was added to support formation of ordered array of carbonic nanorods. The mixture was placed in a drying oven for 6 h at 80 °C, and kept for 6 h at 160 °C. Two steps of thermal treatment is due to incorporation and polymerization of carbon sources, respectively. Similar process was repeated again; the recovered SBA-15 complex was impregnated with aqueous solution (H_2O : FA : sucrose : H_2SO_4 : Fc = 9 : 4.5 : 0.65 : 1 : 0.13 (w : w)), and heated at 80 and 160 °C in the same procedure as above. An obtained dark brown powders were carbonized at 800 °C for 3 h in the N_2 flow, and etched with 1 mol dm^{-3} NaOH solution (H_2O : ethanol = 1 : 1 (v : v)) to remove silica template. Hereafter this sample is labeled as Fc-MC. The amount of iron resided in the mesoporous carbon was estimated to be 1.5 wt% by thermogravimetry (TG).[12] As a reference, mesoporous carbon without Fc (denote by MC) was also synthesized. The removal of silica for both MCs was confirmed by TG.

The observed X-ray diffraction (XRD) peaks of MCs are assigned to 100, 110, and 200 of hexagonal structure (Figure 1), indicating that well-ordered mesostructure could be constructed using FA and sucrose as the carbon source. The fact that 110 and 200 peaks for Fc-MC are observed more clearly than that for MC, indicating that the addition of Fc facilitates the formation of carbon frameworks to some degree. However, ordered hexagonal array of carbon nanorods are hardly obtained if carbonization is performed after the first impregnation of carbon source. This means that one time impregnation is insufficient for development of carbon frameworks in the SBA-15 mesopores.[4] In the higher angle region, two broad peaks originated from graphite appeared in Fc-MC (Figure 1 (inset)). The *d*-spacing value of 002 is ca. 0.38 nm, which is much larger than that of ideal graphite (0.33 nm), indicating low crystallinity of Fc-MC. Similar phenomenon was observed in MC (d_{002} = 0.38 nm). It is noted that no diffraction peak originated from iron was observed.

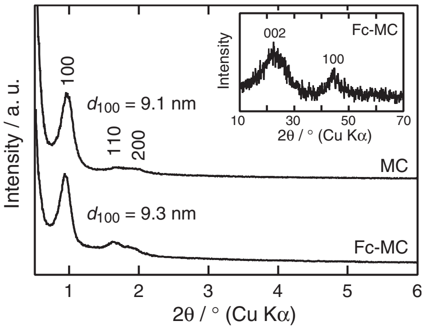

Figure 1. XRD patterns for mesoporous carbons. (Inset) High-angle XRD pattern of Fc-MC.

All the N_2 isotherms at 77 K are of type IV, and the adsorption and desorption ones of MCs overlap each other in almost all region (data not shown). The capillary condensations originating from adsorption in mesopores was observed in the relative pressure from 0.4 to 0.6. These trends confirm the presence of ordered mesopores after the etching. This is also supported by the fact that the full widths at half maximum of the pore size distribution based on the BJH method were also narrow in both samples.[13] From the average pore size (4.1 nm for MC; 4.3 nm for Fc-MC), the diameter of carbon nanorod was also estimated to be ca. 3.4 nm. Therefore we can see that the distance between carbon nanorods would be sufficiently large and allow electrolyte to access the surface of each carbon nanorods in electrochemical use. Nevertheless, the specific surface areas of MCs (630 m^2 g^{-1} for MC; 700 m^2 g^{-1} for Fc-MC) were not so high as that of CMK-

3 (ca. 1500 $m^2 g^{-1}$).[2] This may be attributed to partial collapse of carbonic mesostructures.

The formation of carbon mesostructure was also confirmed by transmission electron microscopy (TEM) observations. As shown in the Figures 2a and 2b, well-ordered hexagonal arrays of carbon nanorods were observed in both MCs. From high-dark contrast in the TEM images, the distance between nanorods are estimated to be ca. 9 nm, in agreement with the result of XRD. It should be noted that the small amounts of iron compounds were observed in the carbon nanorods for Fc-MC (Figure 2c arrows).[14] The diameter of these particles was equal to that of carbon nanorods. Taking into account the XRD results, the incorporated iron species may have poor crystallinity.

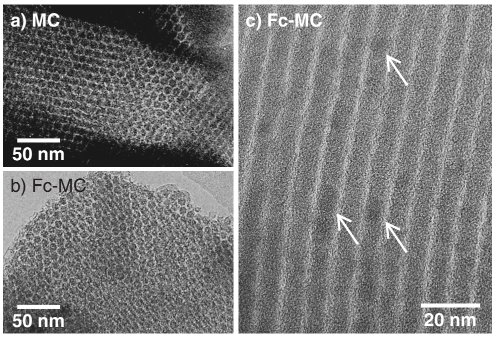

Figure 2. Typical TEM images of the ordered mesoporous carbon.

Finally, the preliminary EDLC behaviors of MCs were investigated in a 0.5 mol dm^{-3} KCl solution. For the electrochemical measurements, carbon powders were spread on a Ti mesh with polytetrafluoroethylene binder. A Ti mesh and saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The capacitance obtained from cyclic voltammetry was shown as a function of potential in Figure 3, and was calculated by dividing current both by scan rate and specific surface area. The rectangular-shaped voltammograms were recorded at lower scan rate. The value of double-layer capacitance of Fc-MC (ca. 20 $\mu F cm^{-2}$) is about half of commercial activated carbons.[8] The distortion of the voltammogram grew with the scan rate. The degree of distortion was greatly suppressed by the addition of Fc. This is because the difference in the resistance-capacitance (*RC*) time constant between these MCs. Actually the *RC* time constant of Fc-MC, roughly estimated to be 8 s, was about half that of MC. This difference is caused mainly by a lower internal resistance of Fc-MC, because a difference in surface area between MCs is at most 10%. Thus it is found that the incorporation of Fc can improve capacitor performance through an increase of conductivity. Additionally, for Fc-MC, no faradaic current was observed in this potential range. These results indicate that incorporated Fc molecules act as a catalyst to form carbon frameworks rather than redox species for appearance of pseudo-capacitance.[15] Much amount of iron-species may be necessary for higher energy densities due to pseudo-capacitance.

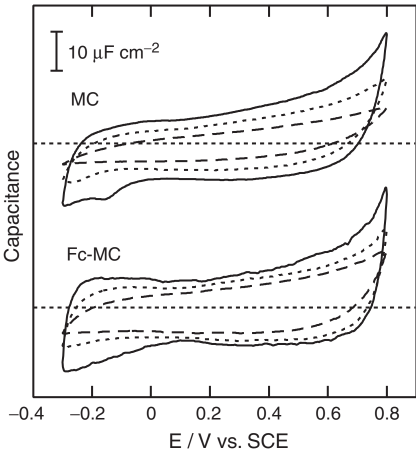

Figure 3. Capacitance vs voltage profiles obtained with MC and Fc-MC electrodes. Broken curve: 20 mV s^{-1}; dotted curve: 5 mV s^{-1}; solid curve: 1 mV s^{-1}.

References and Notes

1 R. Ryoo, S. H. Joo, and S. Jun, *J. Phys. Chem. B*, **103**, 7743 (1999).
2 S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, and O. Terasaki, *J. Am. Chem. Soc.*, **122**, 10712 (2000).
3 S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, and R. Ryoo, *Nature*, **412**, 169 (2001).
4 S. H. Joo, S. Jun, and R. Ryoo, *Microporous Mesoporous Mater.*, **44–45**, 153 (2001).
5 J. Lee, S. Yoon, T. Hyeon, S. M. Oh, and K. B. Kim, *Chem. Commun.*, **1999**, 2177.
6 J. Lee, S. Yoon, S. M. Oh, C.-H. Shin, and T. Hyeon, *Adv. Mater.*, **12**, 359 (2000).
7 S. Yoon, J. Lee, T. Hyeon, and S. M. Oh, *J. Electrochem. Soc.*, **147**, 2507 (2000).
8 E. Frackowiak and F. Béguin, *Carbon*, **39**, 937 (2001).
9 J. Ozaki, M. Mitsui, Y. Nishiyama, J. D. Cashion, and L. J. Brown, *Chem. Mater.*, **10**, 3386 (1998).
10 H. Hou, A. K. Schaper, F. Weller, and A. Greiner, *Chem. Mater.*, **14**, 3990 (2002).
11 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, and G. D. Stucky, *Science*, **279**, 548 (1998).
12 As judged from the color of Fc-MC residue obtained after TG, the residue is probably an iron(III) oxide. The weight change pattern of Fc-MC was generally similar to that of mesoporous carbon without Fc.
13 E. P. Barrett, L. G. Joyner, and P. P. Halenda, *J. Am. Chem. Soc.*, **73**, 373 (1951).
14 Ozaki et al. reported that there were three species (α-Fe, γ-Fe, and cementite) in the carbons prepared by the mixtures of ferrocene and poly(furfuryl alcohol).[9] Although the state of iron compounds in carbon nanorods is not clear, it is thought that the iron compounds are same species as above.
15 There is no evidence that the incorporated Fc acts simply as a catalyst. However, this assumption should be supported by the fact that C/H ratio of Fc-MC is higher than that of MC. Moreover, when nickel phthalocyanine was used instead of Fc, similar structural and electrochemical property was essentially observed. This does not conflict with the previous report that Fe, Ni, and Co atoms catalyze the formation of carbon nanotubes.[16]
16 M. Yasuda, R. Kikuchi, Y. Ohki, and S. Yoshimura, *Carbon*, **35**, 195 (1997).