Structure and Electrochemical Capacitance of Nitrogen-enriched Mesoporous Carbon

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Nitrogen-enriched mesoporous carbon which has been successfully prepared from quinoline-polymerized pitch using mesoporous silica as a template denoted ordered hexagonal assembly of fibrous carbon having ca. 6–7 nm in diameter and higher capacitance amounting to 200–300 F·g^{-1} in H_2SO_4 electrolyte than ordinary mesoporous carbons prepared using divinylbenzene as a carbon precursor (<180 F·g^{-1}).

Template carbonization method has been regarded as a unique and versatile technique for providing well-designed nanostructure to a carbon body. Besides, most of these nanostructures introduced by the template method may be infeasible using other approaches for a figuration. One of recent noticeable outcome is undoubtedly preparation of highly ordered mesoporous carbons using mesoporous silica templates (such as MCM-48 and SBA-15). Pioneer study on this field was simultaneously done by two Korean groups, viz., Ryoo et al. (designated CMK series)[1] and Hyeon et al. (designated SNU series).[2] Their intensive and comprehensive works enabled us to recognize the great potential of the mesoporous carbons as an innovative carbon material.

From the viewpoint of electrochemical usage of the mesoporous carbons, Hyeon et al. have already considered about application of them to the electrode of electric double layer capacitors (EDLC) in their early articles.[2,3] Subsequent to them, similar works have been followed up by other groups.[4–6] This situation proves the mesoporous carbons to be promising candidate for the electrode of supercapacitors.

Meanwhile, we have already reported that nitrogen-enriched mica template carbons exhibit high double layer capacitance in H_2SO_4 electrolyte.[7] Because of nonporous characteristic of them, specific capacitance per unit surface area could reach 1.2–2.2 F·m^{-2}, which is over 10-times as high as the capacitance of commercially available activated carbons. Because of the above background, we aim at obtaining the synergy effect of mesoporous structure and nitrogen doping on EDLC performance. The present study describes synthesis, structural characterization, and EDLC performance of nitrogen-enriched mesoporous carbons prepared by a template method.

Nitrogen-enriched mesoporous carbon has been prepared from quinoline-polymerized pitch using laboratory-made mesoporous silica as a template. Quinoline pitch was synthesized at 553–573 K using $AlCl_3$ as a catalyst according to the method previously reported by Mochida et al.[8] The obtained pitch was impregnated at 573 K into the pore of mesoporous silica known as SBA-15 (2d-hexagonal, *p*6*mm*). The resulted pitch/silica composite was heat-treated at 1023 K in an inert atmosphere and then washed by HF for removing silica. For comparison, ordinary mesoporous carbon (nitrogen free) was also prepared by a liquid impregnation of divinylbenzene as a carbon precursor using the same template. The structural investigations of obtained carbons were mainly performed by electron microscopy, nitrogen adsorption, and so on. Samples for EDLC experiments were molded from a mixture of template carbon (80 wt %), polytetrafluoroethylene (Teflon®) powder (10 wt %), and acetylene black (10 wt %). After vacuum drying at 373 K, the pellet was assembled into the working electrode for three electrode cell equipment by insertion between Pt-mesh and glass fiber paper and then by fastening with two Teflon® plates. Prepared electrodes were evaluated in 1 M aqueous H_2SO_4 solution by cyclic voltammetry (CV) and galvanostatic charge/discharge measurement (GC). For CV, the potential range was −100 to 900 mV (vs. Ag/AgCl) and scan rate was mainly 1 mV/s. The GC was cycled between −100 and 900 mV (vs. Ag/AgCl) at a constant current of 20–1000 mA/g.

Elemental analysis values of the synthesized quinoline pitch were C, 73.5; H, 5.4; N, 9.4 wt %; hence, $H/C = 0.87$ and $N/C = 0.11$ of atomic ratios. The nitrogen content in the pitch was close to that in quinoline (10.8 wt %). From now on, the carbons originated from quinoline pitch and divinylbenzene will be designated as MC-Q and MC-D, respectively. It is expected that on account of the nitrogen atoms in the starting pitch, a certain amount of nitrogen remained in the resulting MC-Q. In accordance with the elemental analysis, the residual nitrogen content of MC-Q prepared at 1073 K was ascertained to be 5.1 wt %.

Figure 1 shows nitrogen adsorption/desorption isotherms at 77 K onto SBA-15 mesoporous silica and corresponding negative replica carbons derived from the above two carbon sources. SBA-15 indicates a typical isotherm for mesoporous materials having relatively large and uniform mesopores, which is accompanied with steep hysteresis loop in the middle pressure range of the isotherm. The MC-D displays a larger adsorbed amount than template silica does and linearly increasing adsorptive property. This isotherm also exhibits hysteresis loop but inclines more gently. These features appeared on the isotherm can be ascribable to the development of micropores and disordered mesostructure in MC-D. Although the MC-D is certainly mesoporous, its pore size distributes widely. In case of the MC-Q, the shape of isotherm shows a gradual increase in the low pressure range and the following plateau, namely presence of smaller mesopores. A similar isotherm to MC-Q is rather observed in case of MCM-41 and -48. From the calculated pore size distribution (based on DH-method using adsorption branch) of SBA-15 and MC-Q, both of them indicate narrow size distribu-

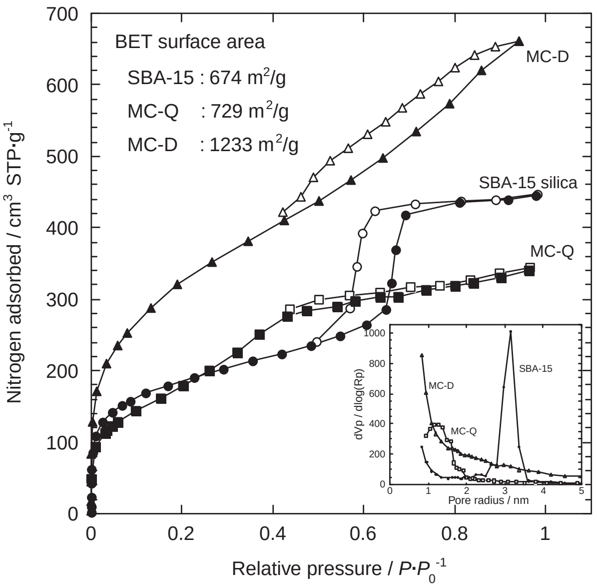

Figure 1. Adsorption isotherms of N_2 at 77 K for SBA-15 silica and template carbons. The inset is pore size distribution plot calculated by DH-method using adsorption branch of the isotherms.

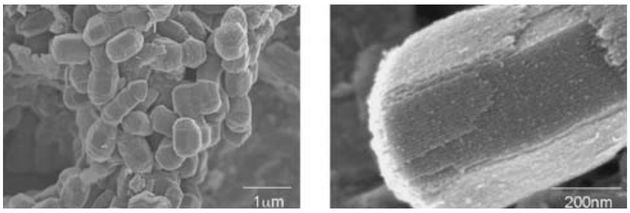

Figure 2. Scanning electron micrographs of MC-Q prepared from quinoline pitch in SBA-15 silica template (left: overall view of the aggregate, right: enlarged single particle).

tion, while the average pore size is markedly different (ca. 3 nm in radius for SBA-15 and ca. 1.5 nm for MC-Q). The estimated BET surface areas are also listed in Figure 1. MC-D has by far higher surface area than the others do, as mentioned above, this is due to the developed microporous structure in it. MC-Q and SBA-15 having less-developed micropores show a similar level of the surface extent except for the aforementioned average size of mesopores.

Figure 2 shows SEM images of MC-Q prepared at 1073 K after elimination of silica network by HF solution. The obtained carbon maintained original particle shape of template silica. Moreover, the enlarged micrograph reveals the mesostructure of MC-Q to be an ordered hexagonal assembly of fibrous carbon having ca. 6–7 nm in diameter. Taking into account the negatively reproduced, fibrous carbon should be attributable to the mesopores of SBA-15. Consequently, interfiber gap originated in the silica wall can act as mesopores. On the other hand, micropores are certainly located on the surface of each nanofiber.

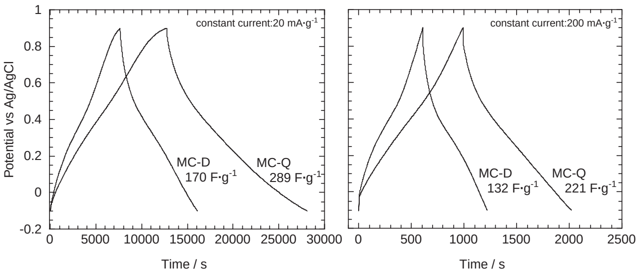

Figure 3. Galvanostatic charge/discharge curves of MC-D and MC-Q in 1 M H_2SO_4 electrolyte (left: at $20\,mA{\cdot}g^{-1}$, right: at $200\,mA{\cdot}g^{-1}$).

Next, to pursue the performance of template carbons for EDLC electrode, CV and GC measurements in aqueous electrolyte (1 M H_2SO_4) have been carried out. From the results on CV measurement, the gravimetric capacitance at 400 mV was found from calculation to be $178\,F{\cdot}g^{-1}$ for MC-D and $228\,F{\cdot}g^{-1}$ for MC-Q. Thus, the capacitance of nitrogen-enriched carbon was about 1.3 times as high as that of DVB carbon. We have empirically known the capacitance of carbon materials in such aqueous electrolytes is practically in proportion to BET surface area up to $2000\,m^2{\cdot}g^{-1}$ Consequently, being considered with lower surface area of MC-Q ($729\,m^2{\cdot}g^{-1}$ vs $1233\,m^2{\cdot}g^{-1}$ of MC-D), the obtained capacitance is notably high. Specific capacitance per unit surface area could reach $0.31\,F{\cdot}m^{-2}$ (vs $0.14\,F{\cdot}m^{-2}$ for MC-D). The results chronopotentiometrically collected at 20 and $200\,mA{\cdot}g^{-1}$ demonstrated reproducible curves as shown in Figure 3. The calculated capacitances were $289\,F{\cdot}g^{-1}$ for MC-Q and $170\,F{\cdot}g^{-1}$ for MC-D at $20\,mA{\cdot}g^{-1}$, and 221 and $132\,F{\cdot}g^{-1}$ at $200\,mA{\cdot}g^{-1}$, respectively. These values correspond to 0.30–$0.40\,F{\cdot}m^{-2}$ for MC-Q and 0.11–$0.14\,F{\cdot}m^{-2}$ for MC-D. Thus, the capacitance per unit surface area of MC-Q is obviously higher than those appeared not only using MC-D but also using ordinary carbon electrode materials ($<0.2\,F{\cdot}m^{-2}$). Such a high capacitance appears to be due to the presence of residual nitrogen in carbon. Although the mechanism of implication of nitrogen for the capacitance is still left uncertain, owing to pseudo capacitive additional effect, the nitrogen-enriched mesoporous carbon holds high promise for EDLC electrode material.

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Published on the web (Advance View) June 5, 2006; doi:10.1246/cl.2006.680