

STRUCTURE AND ELECTRIC DOUBLE LAYER CAPACITANCE OF NITROGEN-ENRICHED MESOPOROUS CARBON

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Introduction

Template carbonization method has been regarded as unique and versatile technique for providing well-designed nanostructure to the 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). Pioneering 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 [4,5]. This situation proves the mesoporous carbons to be promising candidate for the electrode of supercapacitors.

Meanwhile, we have already reported nitrogen-enriched mica template carbons exhibit high double layer capacitance in H₂SO₄ electrolyte [6]. Because of non-porous characteristic of the carbons, specific capacitance per unit surface area could reach 1.2-2.2F·m⁻², which is over ten 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.

Experimental

Nitrogen-enriched mesoporous carbon has been prepared from quinoline polymerized pitch using laboratory made mesoporous silica as a template. Quinoline pitch was

synthesized at 553-573K using AlCl_3 as a catalyst according to previously reported method by Mochida et al. [7]. The obtained pitch was impregnated at 573K into the pore of mesoporous silica known as SBA-15 (2d-hexagonal, $p6mm$). The resulted pitch/silica composite was heat-treated at 1023K in an inert atmosphere and then washed by HF for removing silica. To attempt a comparison, ordinary mesoporous carbon was also prepared using divinylbenzene as a carbon precursor. The structural investigations of obtained carbons were performed by electron microscope, XRD, nitrogen adsorption and so on.

Samples for EDLC experiments were molded from a mixture of template carbon (80wt%), polytetrafluoroethylene (Teflon®) powder (10wt%) and acetylene black (10wt%). After vacuum drying at 373K, 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 1M H_2SO_4 aqueous solution by cyclic voltammetry (CV) and galvanostatic charge/discharge measurement (GC). For CV, the potential range was -100~900mV (vs. Ag/AgCl) and scan rate was mainly 1mV/s. The GC was cycled between -100 and 900mV (vs. Ag/AgCl) at a constant current of 20mA/g.

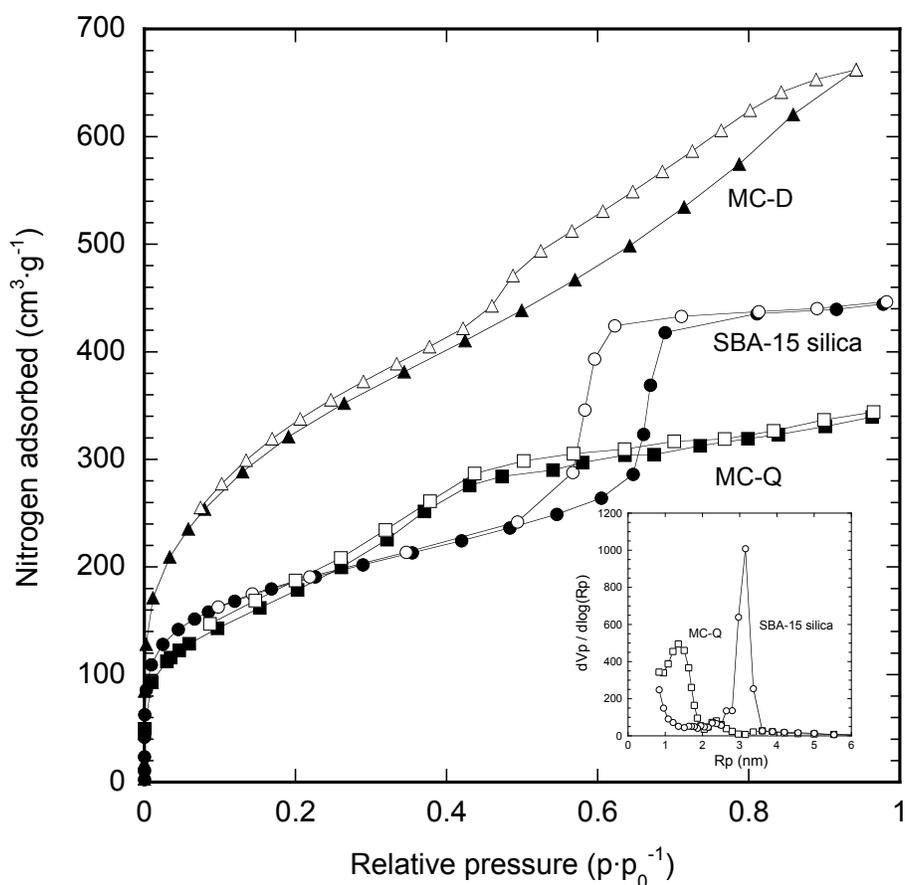


Figure 1. Adsorption isotherms of N_2 at 77K for SBA-15 silica and template carbons. The inset is pore size distribution plot calculated by DH-method using adsorption branch of the isotherms.

Results and Discussion

Elemental analysis values of the synthesized quinoline pitch were C=73.5wt%, H=5.4wt% and N=9.4wt%, and hence H/C=0.87 and N/C=0.11 of atomic ratios. The nitrogen content in the pitch is close to that in quinoline (10.8wt%). Then, mesoporous carbons were prepared using quinoline pitch or divinylbenzene for carbon source. From now on, the carbon 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 1073K was ascertained to be 5.1wt%.

Figure 1 shows nitrogen adsorption/desorption isotherms at 77K onto SBA-15 mesoporous silica and corresponding negative replica carbons derived from above two carbon sources. SBA-15 indicates 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 larger adsorbed amount than template silica does and linearly increasing adsorptive property. This isotherm also exhibits hysteresis loop, however, 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 gradually increase in 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. Pore size distribution (based on DH-method using adsorption branch) of SBA-15 and MC-Q is also shown in the inset graph in Fig.1. Both of them indicate narrow size distribution, while the average pore size is markedly different (ca.3nm in radius for SBA-15 and ca.1.5nm for MC-Q). For further detailed surface characteristics of these materials, Table 1 presents several calculated values. MC-D has by far higher

Table 1. Calculated surface characteristics of SBA-15 and template carbons.

Sample	BET-plot			α_s -plot			
	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	S_{total} ($\text{m}^2\cdot\text{g}^{-1}$)	V_{total} ($\text{cm}^3\cdot\text{g}^{-1}$)	S_{micro} ($\text{m}^2\cdot\text{g}^{-1}$)	V_{micro} ($\text{cm}^3\cdot\text{g}^{-1}$)	S_{meso} ($\text{m}^2\cdot\text{g}^{-1}$)	V_{meso} ($\text{cm}^3\cdot\text{g}^{-1}$)
SBA-15	674	604	0.68	507	0.56	98	0.12
MC-Q (from q-pitch)	729	636	0.53	531	0.40	104	0.13
MC-D (from DVB)	1233	1037	1.02	—	—	—	—

— :couldn't make reliable α_s analysis

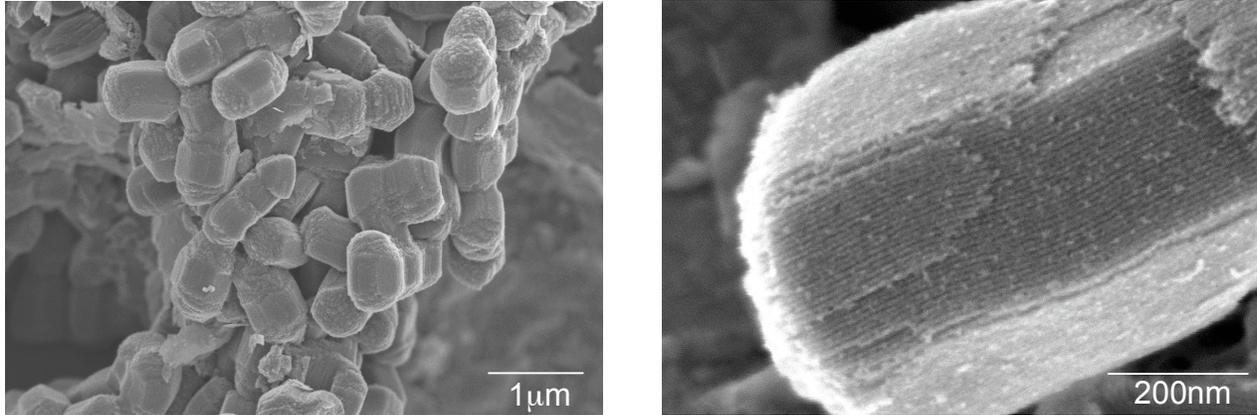


Figure 2. Scanning electron micrographs of MC-Q prepared from quinoline pitch in SBA-15 silica template (left:overall view of the aggregate, right:enlarged single particle).

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 similar level of the surface extent except for aforementioned average size of mesopores.

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

Next, to pursue the performance of template carbons for EDLC electrode, CV and GC measurements in aqueous electrolyte (1M H_2SO_4) have been carried out. As shown in Fig. 3, the gravimetric capacitance at 400mV was found from calculation to be $178F \cdot g^{-1}$ for MC-D and $228F \cdot g^{-1}$ for MC-Q. Thus, the capacitance of nitrogen-

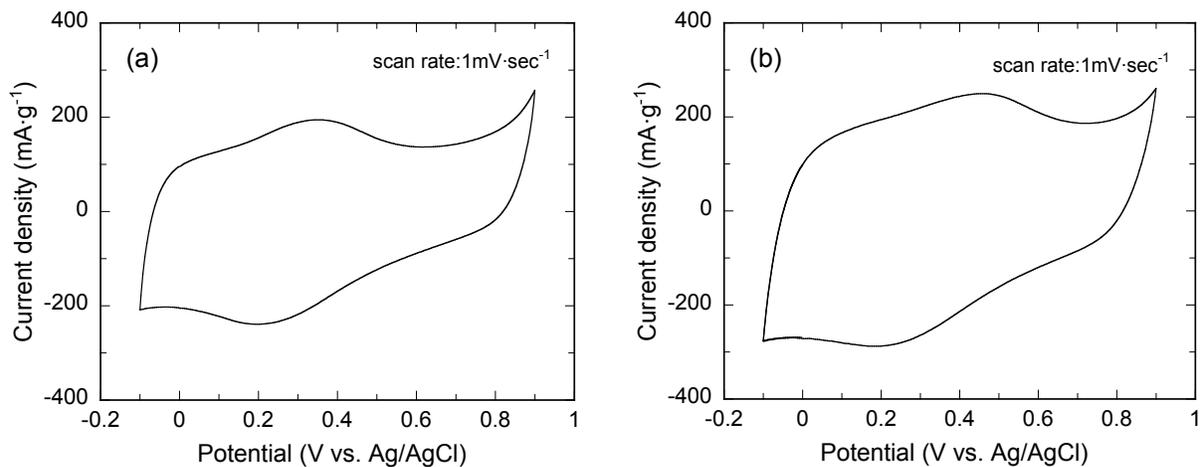


Figure 3. Cyclic voltammograms of (a)MC-D and (b)MC-Q electrodes in 1M H_2SO_4 electrolyte.

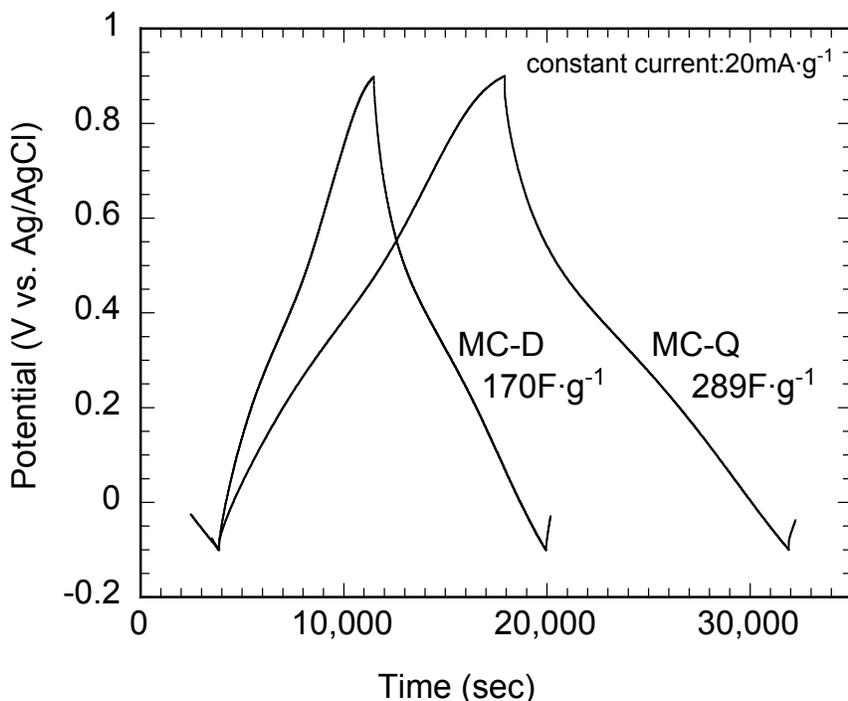


Figure 4. Galvanostatic charge/discharge curves of MC-D and MC-Q in 1M H₂SO₄ electrolyte.

enriched carbon was about 1.3 times as high as that of DVB carbon. Furthermore, being considered with lower surface area (729m²·g⁻¹ vs. 1233m²·g⁻¹ of MC-D) of MC-Q, the obtained capacitance is notably high. Specific capacitance per unit surface area could reach 0.31F·m⁻² (vs. 0.14F·m⁻² for MC-D).

The results chronopotentiometrically collected at 20mA·g⁻¹ demonstrated reproducible curve of a double layer capacitance as shown in Fig.4. The calculated capacitance was 170F·g⁻¹ for MC-D and 289F·g⁻¹ for MC-Q. These values are corresponding to 0.14 and 0.40F·m⁻², respectively.

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 materials (<0.2F·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 can be presumed as a promising electrode material.

Conclusions

Nitrogen-enriched mesoporous carbon has been successfully prepared from quinoline polymerized pitch using mesoporous silica as a template. The structural investigation denoted that the obtained carbon consists of ordered hexagonal assembly of fibrous carbon having ca. 6~7nm in diameter, and mesopores are formed as gaps between each nanofiber.

The capacitance of the nitrogen-enriched mesoporous carbon amounting to $200\sim 300\text{F}\cdot\text{g}^{-1}$ was higher than that obtained using ordinary mesoporous carbons prepared using divinylbenzene as a carbon precursor ($<180\text{F}\cdot\text{g}^{-1}$). In particular, specific capacitance per unit surface area could reach $0.3\sim 0.4\text{F}\cdot\text{m}^{-2}$. We cannot give concrete expression to the effect of nitrogen. Nevertheless, this sort of carbon holds high promise for EDLC electrode material.

Now, detailed electrochemical measurements are still in progress. The additional result will be presented with the result on another type of mesoporous carbon (MCM-48 templated) at the conference.

References

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