CHEMICAL TREATMENT OF MICROPOROUS CARBON WITH A THREE-DIMENSIONAL NANO-ARRAY STRUCTURE

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Introduction

High surface area microporous carbon with a three-dimensional nano-array structure has been synthesized by using zeolite Y as a template in our lab. [1]. This kind of carbon, which has high surface area and large microporous volume, is extremely attractive in a variety of fields, and now is in great demand for the application to the electrodes of electric double-layer capacitors. One of the important factors for such electrodes is the affinity to the solvent in the capacitor. In this context, here we try to introduce more oxygen atoms into the porous carbon by chemical treatment (nitric acid and sulfuric acid) with its high microporosity unchanged as much as possible.

Experimental

The porous carbon was synthesized by the two-step method as is described in the reference [1]. The zeolite/polyfurfuryl alcohol composite was heated to 700 °C under a N_2 flow. As soon as the temperature reached 700 °C, propylene CVD was carried out at that temperature for 1 h. After the CVD, the composite was further heat-treated at 900 °C for 3 h under a N_2 flow. The resultant carbon was liberated from the zeolite framework by HF acid washing. The porous carbon obtained from the above method was then treated by either 30 wt% nitric acid or 95 wt% sulfuric acid. Sulfuric acid treatment was performed at 140°C for 2 h. We mainly investigated the nitric acid treatment at different temperatures and for different times. The as-prepared and the treated porous carbons were examined with elemental analysis, X-ray diffraction, N_2 adsorption at –196 °C and water adsorption at 25 °C. The BET surface area of all the samples was determined using the data in the relative pressure range of 0.01-0.05. The micropore volume was calculated from the Dubinin-Radushkevich (DR) equation. The mesopore volume was determined by subtracting the micropore volume from the volume of N_2 adsorbed at a relative pressure of 0.95.

Results and discussion

The results of the elemental analysis of the as-prepared and those treated carbon are summarized in the upper part of Table 1. The oxygen content of the sulfuric acid treated carbons (S-carbons) is lower than that of the nitric acid treated carbons (N-carbons). Besides oxygen, S was also introduced for the S-carbons. As shown in this table, the oxygen content increased with the increase of temperature and time of the nitric acid treatment. The oxygen content can reach 30 wt% upon the treatment even at low temperature and for a short time like at 45 °C for 15 min. In the case of the most severe condition (80 °C and 120 min), its content becomes as large as 40 wt% and thus the atomic ratio of C to O is about 1.8, which is comparable with that of graphite oxide. In addition to oxygen, some amounts of nitrogen were introduced, but its amount does not change so much with the different conditions.

Table 1 Acid treatment conditions and the analysis results of the porous carbons

Carbon sample	Pristine	S	N1	N2	N3	N4
Treatment temperature (°C)	-	140	45	45	80	80
Treatment time (min)	-	120	5	15	60	120
C (wt%)	90	73	71	65	58	55
N (wt%)	0	0	2	2	2	2
H (wt%)	3	2	2	3	3	3
O (wt%)	7	23	25	30	37	40
S (wt%)	0	2	0	0	0	0
BET surface area (m^2/g)	4100	2600	2500	2200	1200	800
Micropore volume (cm^3/g)	1.93	1.26	1.15	0.92	0.36	0.35
Mesopore volume (cm^3/g)	0.08	007	0.09	0.06	0.03	0.04

Pristine: porous carbon before chemical treatment; S: sulfuric acid treated carbon; N: nitric acid treated carbon.

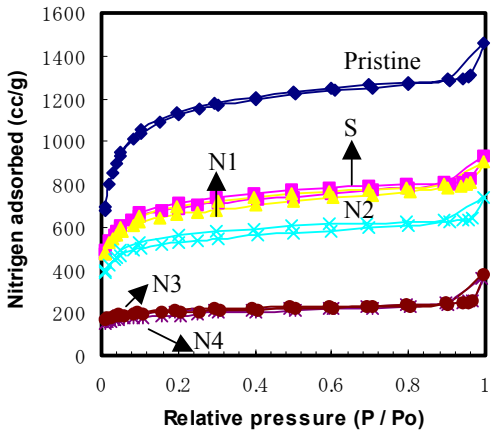

Figure 1. N_2 adsorption isotherms

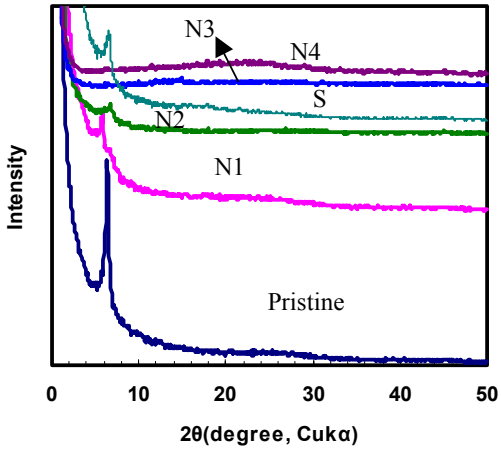

Figure 2. XRD patterns

Although the oxygen content increased as we expected, the pore structure was changed upon the treatment. The N_2 adsorption isotherms are illustrated in Fig. 1 and the BET surface area and the pore volumes calculated from the isotherms are shown in the last half of Table 1. The shape of isotherms for all the samples is that of Type-I, indicating that all the samples are microporous. However, the BET surface area and the micropore volume decreased with the severity of the nitric acid treatment. The BET surface area and micropore volume of S-carbons are higher than those of all the N-carbons.

The XRD patterns of the treated carbons are shown in Fig. 2, which indicates that the intensity of the peak at about 6° corresponding to the three-dimensional regularity decreased with the increase of the treatment temperature and time, and this XRD peak disappeared completely upon the 80°C treatment. In other words, such excessive treatment destroys the ordered pore structure, although the oxygen content is increased very much. According with the elemental analysis and the N_2 adsorption results, the peak intensity at about 6° in S-carbons are higher than that in N-carbons, which indicated that the ordered-structure in S-carbons is better.

Water adsorption isotherms of the treated carbons were plotted in Fig.3. It can be seen that water adsorption isotherms are of type-V, a consequence of the low interaction of the water molecules with the graphitic surface [2,3]. The relative pressure where the water uptake started decreased greatly upon the treatments. Furthermore, the uptake relative pressure decreased with the increase of oxygen content, which indicates that affinity to water for the porous carbon increased with the increase of oxygen content. And total water adsorption amount was decreased with the decrease of the micro-pore volume (Table 1). In order to get the porous carbon that possess lower uptake relative pressure of water and higher water adsorption amount, new chemical treatment method was under investigation.

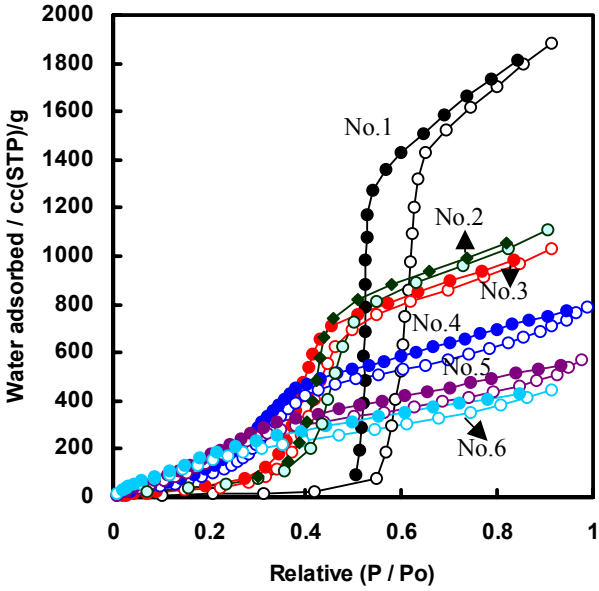

Figure 3. Water adsorption isotherms

Conclusions

The porous carbon with a three-dimensional nano-array structure synthesized by the template carbonization technique was treated by either nitric acid or sulfuric acid. The carbon has not only high surface area (2600 m^2/g), but also high oxygen content (23 wt%). In addition to oxygen, S is also introduced into. The porous carbon is very

reactive with nitric acid and the treatment for 2 h at 80 °C increased the oxygen content to 40 wt%, which is comparable with that of graphite oxide. While the BET surface area still is as high as 800 m^2/g. At a mild treatment condition (45 °C, 15 min), the oxygen content reached about 30 wt%, whereas the BET surface area was more than 2000 m^2/g. So far, this kind of porous carbon possessing so high BET surface area and oxygen content has not been prepared. The results of water adsorption isotherm clearly indicate that the affinity to water for porous carbons considerably increases upon the chemical treatments.

Acknowledgment

This work was partly supported by the Japan Society of Promotion of Science (JSPS) postdoctoral fellowship (P03075) for foreign researchers.

Reference

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