Short communication

Preparation and characterization of carbonaceous materials containing nitrogen as electrochemical capacitor

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Abstract

Carbonaceous materials containing nitrogen (C/N materials) were prepared by a pyrolysis of 2,3,6,7-tetracyano-1,4,5,8-tetraazanaphthalene (CAN). A C/N material prepared by the pyrolysis of CAN at 1070 K (CAN-1070 K) had a C/N atomic ratio of 3.0 and a non-crystalline carbonaceous structure with a BET surface area of $880 \, m^2 \, g^{-1}$. The material CAN-1070 K showed large capacitances of $160–180 \, F \, g^{-1}$ and $110–120 \, F \, cm^{-3}$ in case of current density of $10 \, mA \, cm^{-2}$ ($2 \, A \, g^{-1}$) by using three-electrode cell in $1 \, M \, H_2SO_4$ aqueous solution, in comparison with that of activated carbon ($160 \, F \, g^{-1}$ and $55 \, F \, cm^{-3}$) having BET surface area of $2300 \, m^2 \, g^{-1}$. ESCA study indicated that pyridinic and quarternary nitrogen atoms existed in the C/N materials, which could result in producing a pseudo-capacitance in addition to the electric double layer capacitance. Also introduction of nitrogen into the carbonaceous material could enhance the wettability of material, which might also improve the capacitance.
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Keywords: Carbon/nitrogen material; Electrochemical capacitor; Structure; Chemical bond; Pseudo-capacitance; Adsorption

1. Introduction

A lot of researches about electric double layer capacitor (EDLC) using activated carbon were reported so far [1], since it was first demonstrated by GE group [2]. Conductive polymers such as polypyrole were also proposed as capacitors having pseudo-capacitance [3]. Recently, introduction of heteroatoms into carbonaceous material has been investigated and is expected to modify the structure and properties of material [4–6]. For example, carbonaceous materials containing nitrogen (C/N materials) have been prepared and characterized for some applications such as electrochemical capacitor [7–11]. The materials performed high specific capacity in spite of the small specific surface area. However, the role of nitrogen in the materials for the improvement of capacitance has not been clearly explained yet.

The authors prepared C/N materials with the layered structure [12], and with the tetrahedral (sp^3) structure [13,14] by chemical reactions and investigated the properties as a host material, the mechanical properties and the luminescent properties. In the present study, we have prepared new C/N materials by pyrolysis of a nitrogen-rich starting material (2,3,6,7-tetracyano-1,4,5,8-tetraazanaphthalene, which is called CAN in the present paper) and investigated their adsorption properties and electrochemical properties as a capacitor. The roles of nitrogen in the materials for the improvement of capacitances have been also considered from the results.

2. Experimental

2.1. Preparation of C/N materials

2,3,6,7-Tetracyano-1,4,5,8-tetraazanaphthalene (CAN, Fig. 1) was used as a starting material for the preparation of C/N materials. The CAN was manufactured and supplied by Nippon Soda Co. Ltd., Japan. CAN powders (5.0 g) were set on a vessel made of carbon sheet. The vessel was set at the center of the quartz reaction tube (inner diameter: 30 mm; length: 1 m) and was heated at a temperature between 570 and 1270 K for 1 h under N_2 atmosphere.
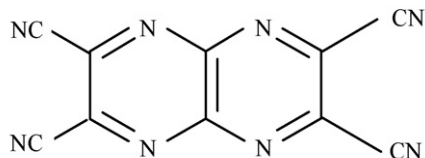
Fig. 1. The starting material 2,3,6,7-tetracyano-1,4,5,8-tetraazanaphthalene (CAN).

2.2. Characterization of C/N materials

The obtained powders were pulverized by using mortar into fine powders with diameters under 45 μm. Elemental analysis for the obtained powders was performed by the usual combustion method, followed by gas chromatography. X-ray diffraction data were obtained by using a diffractometer (Rigaku RINT-Ultima+) with Ni-filtered Cu Kα radiation. FTIR absorption spectra were measured by the KBr method and obtained by an infrared spectrophotometer (Perkin-Elmer PARAGON-1000). ESCA measurements were carried out by using an electron spectrometer (Shimadzu ESCA-3400) with Mg Kα radiation. The binding energies of the elements were corrected by placing the Au $4f_{7/2}$ line at 84.0 eV.

Nitrogen adsorption isotherms were measured at 77 K by gas sorption method with an instrument BELSORP28, Japan BEL Co. Ltd. Specific surface area was estimated by BET method. Pore distribution was analysed by MP method using t-plot. Water vapor adsorption isotherms were measured at 298 K by gas sorption method with an instrument BELSORP18, Japan BEL Co. Ltd. These measurements were performed after drying of the materials at 380 K under vacuum (6.7×10^{-2} Pa).

The electrochemical measurements for C/N powders were performed by using three-electrode cell in 1 M H_2SO_4 aqueous solution. Working and counter electrodes were made of a mixture of the C/N powders, PTFE powders, and acetylene black powders with a ratio of 8:1:1 in weight. The Ag/AgCl electrode was used as a reference electrode. The capacitances of the materials were calculated from the slopes of charge/discharge curves at a current density of 10 mA cm^{-2} (ca. 2 A g^{-1}) by galvanostatic method. The specific capacitances were then calculated from the capacitances and the weight of single electrode. Cyclic voltammograms were also measured by using three-electrode cell. Discharged energy and discharged power were estimated by galvanostatic charge/discharge curves using two-electrode cell in a cell voltage of 0–1 V in the solution same as that used by three-electrode cell.

3. Results and discussion

3.1. Products

The CAN began to sublime at around 570 K and decomposed at the temperatures higher than 670 K with polymerization. About 1.0 g of black powders was obtained on the carbon vessel in the cases of the heat-treatment at 1070–1270 K. The recovery of the powders was about 20% in these cases. Elemen-
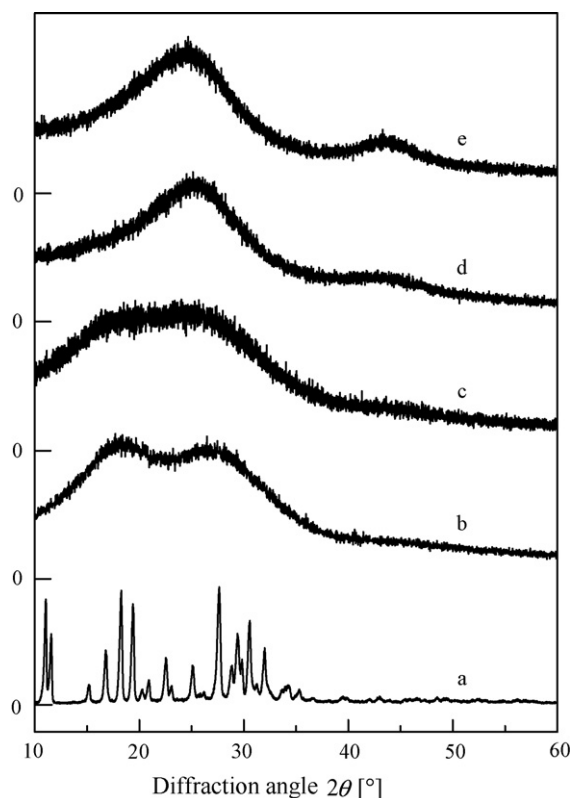

Fig. 2. X-ray diffraction patterns of (a) the starting material CAN, C/N materials prepared by the pyrolysis of CAN at the temperature of (b) 670 K, (c) 870 K, (d) 1070 K, and (e) 1270 K.

tal analyses indicated that the composition of the product was $C_{3.0}N_{1.9}H_{1.8}O_{1.3}$ and $C_{3.0}N_{1.0}H_{0.6}O_{0.2}$ for the material prepared at 970 K (CAN-970 K) and 1070 K (CAN-1070 K), respectively. The oxygen and hydrogen should be mainly due to the water adsorbed by the materials, as is mentioned later in this paper. Therefore, the composition was approximately C_3N_2 and C_3N for each material. The large contents of nitrogen in the materials could be explained by the stable C–N ring structure in the obtained material, which was detected by FTIR.

3.2. Structural change from CAN to carbon-like layered structure

Fig. 2 shows X-ray diffraction patterns of the products obtained at temperatures in the range of 670–1270 K. The starting material CAN is a molecular crystal, which shows sharp X-ray diffractions (Fig. 2a). Two broad diffraction peaks ($2\theta = 18.3°$ and $26.6°$) were observed for the product obtained at 670 K. These peaks might be due to regularity among oligomer-type molecules made by the decomposition of CAN with polymerization at lower temperature. The structural change was again observed at around 870 K (Fig. 2c), and the products obtained at 1070 K showed a diffraction pattern similar to the carbon with a non-crystalline layered structure (Fig. 2d). X-ray diffraction of material obtained at 1270 K indicated broad diffractions at 24.6° ($d = 0.362$ nm) and 43.5° ($d = 0.208$ nm) in 2θ, each of which is at the similar position of (0 0 2) and (1 0)
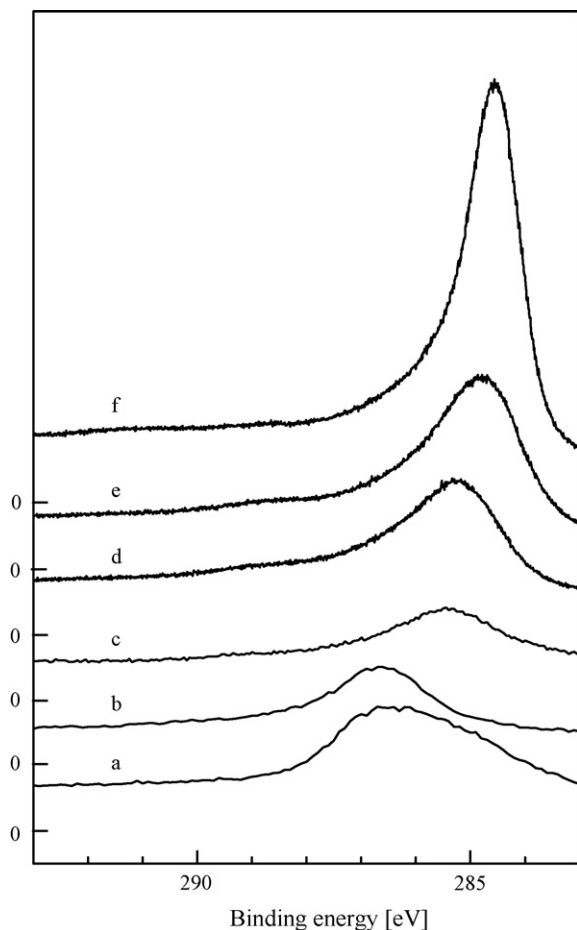
Fig. 3. ESCA C 1s spectra of (a) the starting material CAN, C/N materials prepared by the pyrolysis of CAN at the temperature of (b) 670 K, (c) 870 K, (d) 1070 K, (e) 1270 K, and (f) graphite.
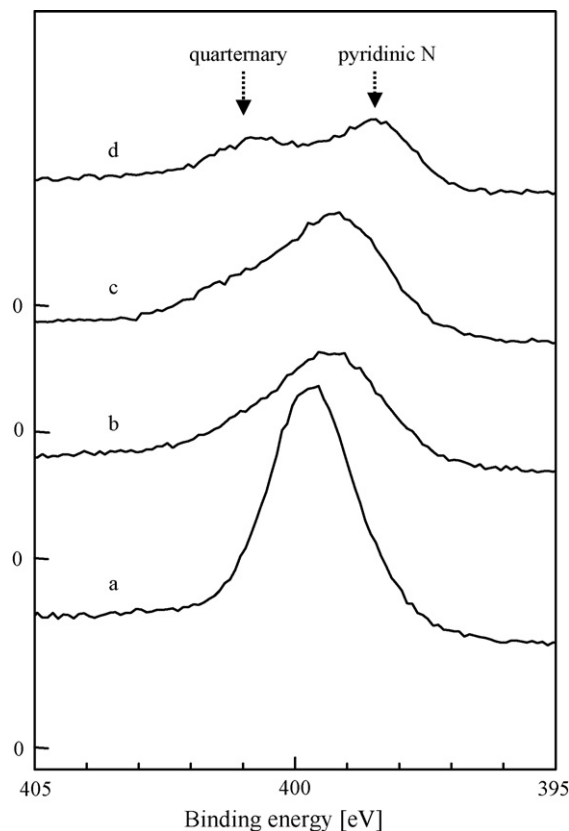

Fig. 4. ESCA N 1s spectra of (a) the starting material CAN, C/N materials prepared by the pyrolysis of CAN at the temperature of (b) 670 K, (c) 870 K, and (d) 1070 K.

diffraction of carbon, respectively. The C/N materials obtained at temperatures higher than 1070 K, therefore, had the layered structure similar to non-crystalline carbon.

Fig. 3 shows ESCA C 1s spectra of the C/N materials obtained at temperatures in the range of 670–1270 K. The starting material CAN shows a broad peak in a range of 284–288 eV, which was due to three kinds of carbons in the structure. The peak shifted to the lower binding energy with increasing the heat-treatment temperature. The peak at higher binding energy decreased, while the peak at lower binding energy increased by the heat-treatment at 870 K (Fig. 3c). This remarkable change is probably due to the elimination of nitrile groups and the structural change from oligomer-type to graphitic structure, which has been mentioned above (X-ray diffraction). The peak position reached to the binding energy near that of graphite by the heat-treatment at 1270 K.

Fig. 4 shows ESCA N 1s spectra of the C/N materials. There are two kinds of nitrogen atoms in the structure of CAN. The peak was broadened by the heat-treatment at 870 K because of the structural change. The peak separated into two major peaks by the heat-treatment at 1070 K (Fig. 4d). Peak identification for N 1s spectra was studied and reported by several researchers [15,16]. One at around 401 eV could be attributed to the quar-

ternary nitrogen, which is surrounded by three carbon atoms in the graphitic-layered structure. The other at around 398.5 eV could be due to pyridinic nitrogen, which exists at the edge part of the graphitic structure. The material CAN-1070 K, therefore, had at least these two kinds of nitrogen in the structure.

Fig. 5 shows FTIR spectra of the C/N materials obtained at temperatures in the range of 670–1070 K. Sharp four bands in the range of 1100–1500 cm^{-1} observed for the starting material CAN should be due to the absorptions of C=C and C=N stretching and ring vibration of the tetraazanaphthalene, while a band at 2200 cm^{-1} is due to the absorption of nitrile C≡N stretching. Broad bands were observed for the material prepared at 870 K probably because of a formation of ring structure caused by the polymerization at around 870 K. A clear spectrum was observed for the material obtained even at higher temperature (CAN-1070 K: Fig. 5d), while almost no distinct spectrum was observed for the non-crystalline carbon. The distinct spectra observed in Fig. 5 should be due to the polarization between carbon and nitrogen in the C/N materials. A broad band in the range from 1000 to 1800 cm^{-1} is attributed to the polymerized C–N aromatic ring structure [12,17], which is thermodynamically stable and hold the nitrogen atoms in the structure. In this case pyridinic nitrogen were made and stabilized at the edge part of the layered structure. In other words, the pyridinic nitrogen produced a lot of edge parts in the structure, creating a large amount of micro-pores in the material.
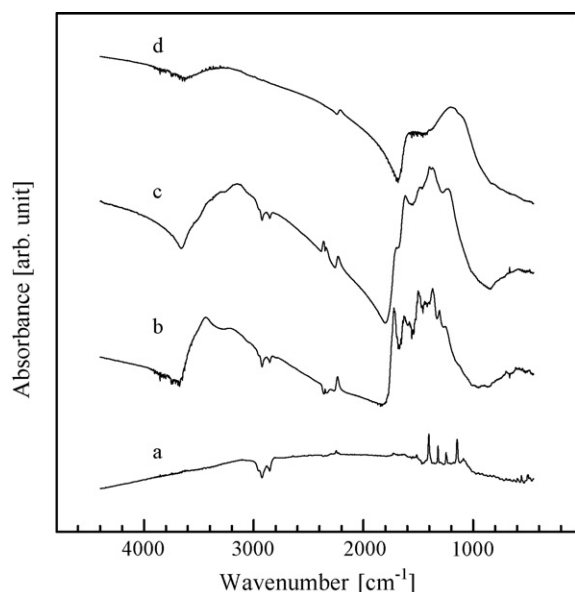
Fig. 5. FTIR spectra of (a) the starting material CAN, C/N materials prepared by the pyrolysis of CAN at the temperature of (b) 670 K, (c) 870 K, and (d) 1070 K.

The formation mechanism of this material is as follows. The starting material CAN decomposed with the elimination of cyano groups (C≡N) and the resulted species C_6N_4 polymerized by themselves to form the layered structure similar to that of the non-crystalline carbon having micro-pores.

3.3. Adsorption characteristics

Fig. 6 shows the nitrogen adsorption isotherm of the material CAN-1070 K. The material indicated I-type of isotherm, which showed large increase of the adsorption in the low-pressure range. The result indicated that CAN-1070 K had micro-pores in the same manner as activated carbon. The isotherms did not show any hysteresis on a cycle of adsorption and desorption, suggesting that cylindrical type micro-pores were produced in
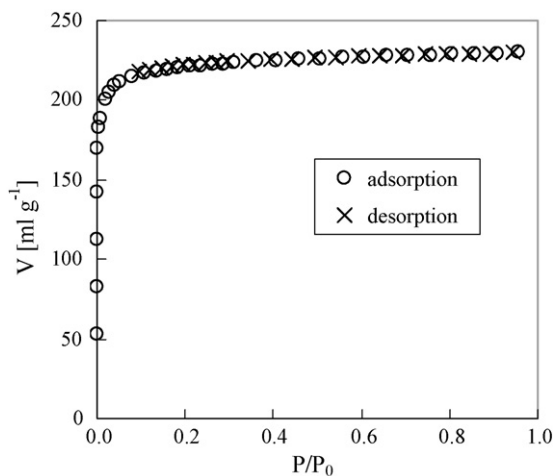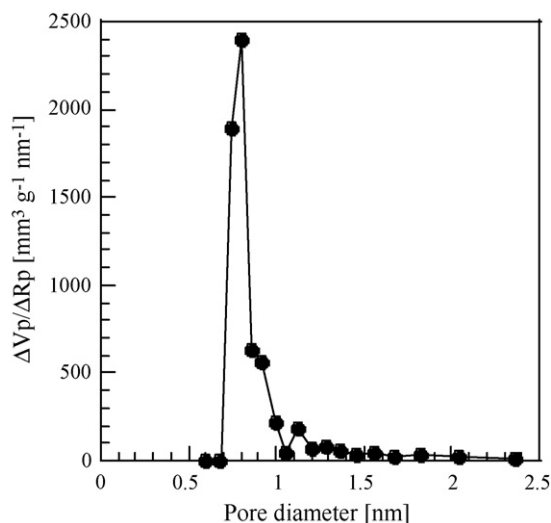

Fig. 7. Pore diameter distribution of C/N material prepared by the pyrolysis of CAN at 1070 K.

the material. The specific surface area calculated by BET equation was $880\,\mathrm{m^2\,g^{-1}}$ for CAN-1070 K, which was the largest value among those of the C/N materials prepared in the present study. Fig. 7 shows the pore size distribution of the material. The material showed average diameter of 0.8 nm, which is slightly smaller than that of activated carbon.

Water adsorption isotherm of the material was different from that of activated carbon. Fig. 8 shows the water adsorption isotherms of CAN-1070 K, compared with that of activated carbon. CAN-1070 K adsorbed water vapor efficiently more than activated carbon particularly in the low pressure range of water vapor. It is considered that the C/N material had wettability better than that of activated carbon, probably because of a stronger interaction of the polar water molecule with a part of C/N material having polarity between carbon and nitrogen in the structure. The adsorption, however, was not so fast that the adsorbed amount for CAN-1070 K proportionally increased, because water vapor could slowly condense into the smaller size of micro-pores.
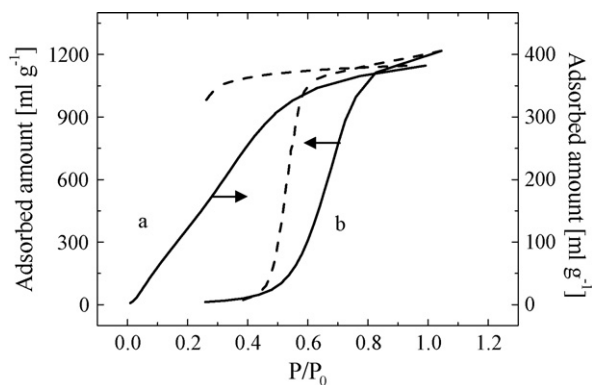

Fig. 6. Nitrogen adsorption isotherm (77 K) of C/N material prepared by the pyrolysis of CAN at 1070 K.

Fig. 8. Water adsorption isotherm (298 K) of (a) C/N material prepared by the pyrolysis of CAN at 1070 K (BET surface area: $880\,\mathrm{m^2\,g^{-1}}$), compared with that of (b) activated carbon ($2300\,\mathrm{m^2\,g^{-1}}$). (—) Adsorption; (– – –) desorption.
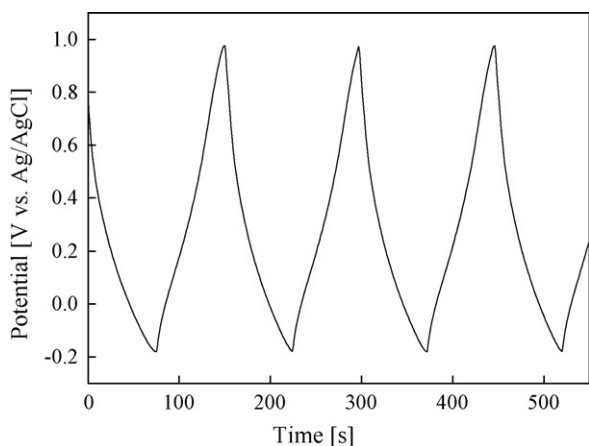
Fig. 9. Charge and discharge curves for C/N material prepared by the pyrolysis of CAN at 1070 K. Electrolyte: 1 M H_2SO_4 aqueous solution; current density: 10 mA cm^{-2} (2 A g^{-1}); three-electrode cell.

Fig. 11. Cyclic voltammograms of C/N material prepared by the pyrolysis of CAN at 1070 K. Electrolyte: 1 M H_2SO_4 aqueous solution; scan speed: 1 mV s^{-1}; three-electrode cell.

3.4. C/N materials as an electrochemical capacitor

Fig. 9 shows galvanostatic charge/discharge curves of CAN-1070 K, which had the specific surface area of 880 m^2 g^{-1}. The capacitance was calculated from the slope of this curve to be 160–180 F g^{-1} (per single electrode of capacitor) in the case of current density of 10 mA cm^{-2} (2 A g^{-1}), which is almost the same capacitance of activated carbon (160 F g^{-1}) having larger specific surface area of 2300 m^2 g^{-1}. Since the apparent density was 0.68 and 0.34 g cm^{-3} for CAN-1070 K and the activated carbon, respectively, the volumetric capacity of CAN-1070 K was 110–120 F cm^{-3}, which is twice larger than that of the activated carbon (55 F cm^{-3}). The large capacitance despite the smaller specific surface area could be explained by a pseudo-capacitance in addition to the electric double layer capacitance. By using a two-electrode cell at a current density of 10 mA cm^{-2} (1 A g^{-1} by using the weight of two electrode), a discharged energy and a discharged power for CAN-1070 K were measured to be 0.494 Wh kg^{-1} and 658 W kg^{-1}, respectively.

The pseudo-capacitance could be caused by the existence of quaternary or pyridinic nitrogen in the material, which was detected by ESCA. The pseudo-capacitance is typically observed for the electrochemical capacitor using conductive polymer [3]. Fig. 10 shows a possible pseudo-faradaic reaction performed during the charge/discharge on a part of the C/N materials. Considering the acid dissociation constant of the pyridine ($pK_a = 5.17$), the pyridinic nitrogen in the material tends to be protonated in 1 M H_2SO_4 [18]. The electrochemical reduction could occur by adding the electron to the protonated nitrogen in the material and the oxidation could occur vice versa, hence the pseudo-faradaic reaction.
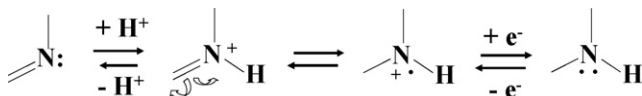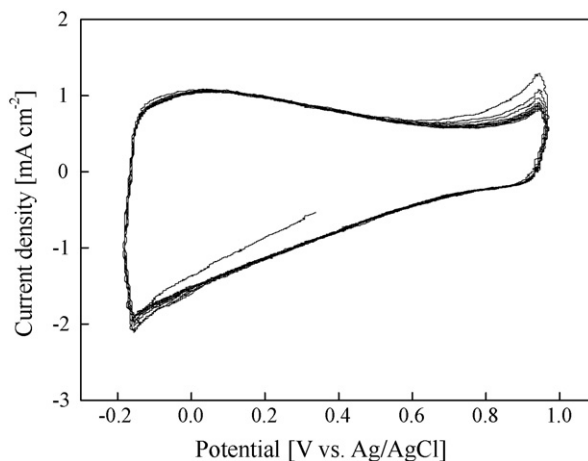
Fig. 11 shows cyclic voltammograms of the material CAN-1070 K. The shape of CV was not the rectangle of typical EDLC but an asymmetrical one. This might be due to the reversible pseudo-faradaic reaction, which is mentioned above and could cause at lower potentials. Another possibility is that the difference of diffusion capability between solvated anions and cations in the electrolyte. In this case, small protons (H^+) diffused faster than anions (HSO_4^-) even they were solvated. Particularly, the pyridinic nitrogen in C/N materials interacts strongly with the protons in a manner of formation of coordinate bond shown in Fig. 10. The asymmetric CV curves observed for CAN-1070 K, therefore, could be due to the diffusion of ions as well as the pseudo-faradaic reaction.

Fig. 12 shows the relation between the heat-treatment temperature and the specific capacity of C/N materials prepared at the temperature in the range of 670–1270 K. CAN-1070 K had the largest specific capacity of 160–180 F g^{-1}, which is described above. The material had the largest surface area (880 m^2 g^{-1}) among the materials prepared in the present study. Also ESCA

Fig. 10. A possible pseudo-faradaic reaction for the protonated nitrogen of C/N material in the acidic aqueous solution.
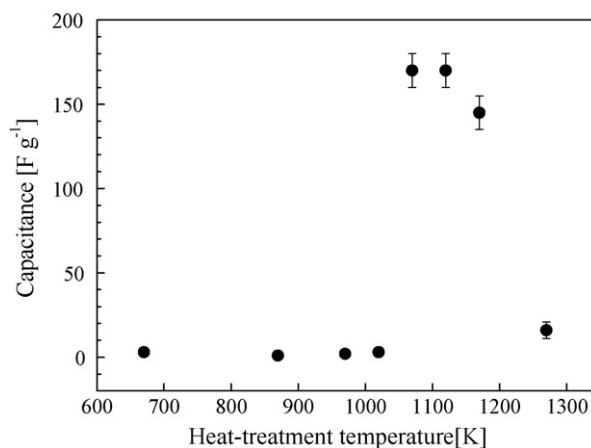

Fig. 12. Heat-treatment temperature vs. capacitance for C/N materials prepared by the pyrolysis of CAN. Capacitances were measured in 1 M H_2SO_4 aqueous solution with the three-electrode cell by using a current density of 10 mA cm^{-2} (2 A g^{-1}).
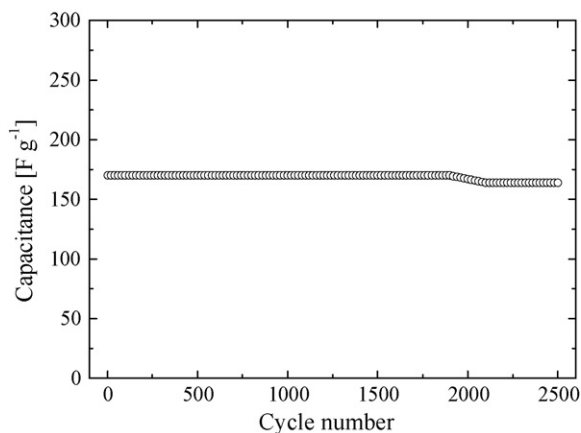
Fig. 13. Cyclability test for electrode made of C/N material prepared by the pyrolysis of CAN at 1070 K. Electrolyte: 1 M H_2SO_4 aqueous solution current density: 10 mA cm^{-2} (2 A g^{-1}); three-electrode cell.

measurements suggested the existence of quaternary or pyridine-type nitrogen in this material. The largest capacitance, therefore, could be explained not only by the specific surface area but also by the pseudo-faradaic reaction caused by the two types of nitrogen in the material. The good wettability of the material against the aqueous solution could also improve the capacitance. Fig. 13 shows a result of cyclability test for the electrode made of CAN-1070 K. Only 3.5% of degradation was observed after 2500 cycles, indicating the good cyclability of the electrode.

4. Conclusions

The carbonaceous materials containing nitrogen with the atomic ratio C/N = 3.0 was obtained by the heat-treatment of 2,3,6,7-tetracyano-1,4,5,8-tetraazanaphthalene (CAN) at 1070 K. The material showed the large capacitance of 160–180 F g^{-1} and 110–120 F cm^{-3} by using three-electrode cell with a current density of 10 mA cm^{-2} (2 A g^{-1}) in 1 M H_2SO_4 aqueous solution, in spite of the relatively small surface area (880 m^2 g^{-1}). The roles of nitrogen in the materials for the improvement of capacitance have been considered as follows: (1) quarternary and pyridinic nitrogen in the material resulted in producing the pseudo-capacitance, which was caused in a

similar manner to that of conductive polymer, in addition to the electric double layer capacitance; (2) the polarization between carbon and nitrogen in the material could cause the better wettability against the aqueous solution, which might also improve the capacitance. From these results, the C/N materials could be a promising material as the electrochemical capacitor.

Acknowledgements

References

[1] B.E. Conway, Electrochemical Capacitors, Kluwer Academic/Plenum Publishers, New York, 1999.
[2] H.E. Becker, U.S. Patent to General Electric Co., No. 2,800,616 (1957).
[3] A. Rudge, J. Davey, I. Raistrick, S. Gottesfeld, J.P. Ferraris, J. Power Sources 47 (1994) 89–107.
[4] Y. Hishiyama, A. Yoshida, K. Kaburagi, M. Inagaki, Carbon 30 (1992) 333–337.
[5] H. Hatori, Y. Yamada, M. Shiraishi, Carbon 30 (1992) 303–304.
[6] T. Nakajima, M. Koh, Carbon 35 (1997) 203–208.
[7] G. Lota, B. Grzyb, H. Machnikowska, J. Machnikowski, E. Frackowiak, Chem. Phys. Lett. 404 (2005) 53–58.
[8] E. Frackowiak, G. Lota, J. Machnikowski, C. Vix-Guterl, F. Béguin, Electrochim. Acta 51 (2006) 2209–2214.
[9] D. Hulicova, M. Kodama, H. Hatori, Chem. Mater. 18 (2006) 2318–2326.
[10] M. Kodama, J. Yamashita, Y. Soneda, H. Hatori, K. Kamegawa, I. Moriguchi, Chem. Lett. 35 (2006) 680–681.
[11] S. Shiraishi, M. Kibe, A. Oya, Carbon, Providence, USA, July 2004 (Abstract E022).
[12] M. Kawaguchi, K. Nozaki, Chem. Mater. 7 (1995) 257–264.
[13] M. Kawaguchi, Y. Tokimatsu, K. Nozaki, Y. Kaburagi, Y. Hishiyama, Chem. Lett. (1997) 1003–1004.
[14] M. Kawaguchi, S. Yagi, H. Enomoto, Carbon 42 (2004) 345–350.
[15] J.R. Pels, F. Kapteijn, J.A. Moulijn, Q. Zhu, K.M. Thomas, Carbon 33 (1995) 1641–1653.
[16] D. Cagniant, R. Gruber, J.P. Boudou, C. Bilem, J. Bimer, P.D. Salbut, Energy Fuels 12 (1998) 672–681.
[17] S. Matsumoto, K.K. Chattopadhyay, M. Mieno, T. Ando, J. Mater. Res. 13 (1998) 180–186.
[18] M.A. Petit, C. Clarisse, F. Templier, J. Electrochem. Soc. 140 (1993) 2498–2500.