

## Preparation and Characterization of Nitrogen-rich C/N Materials as Electrochemical Capacitor

M. Kawaguchi<sup>1)</sup>, A. Itoh<sup>1)</sup>, S. Yagi<sup>1)</sup>, H. Ito<sup>2)</sup>, and H. Oda<sup>3)</sup>  
Osaka Electro-Communication University<sup>1)</sup>,  
Nippon Soda Co. Ltd.<sup>2)</sup>, Kansai University<sup>3)</sup>  
18-8 Hatsu-cho, Neyagawa, Osaka 572-8530, Japan<sup>1)</sup>  
12-54 Goi-Minamikaigan, Ichihara, Chiba 290-0045, Japan<sup>2)</sup>  
3-3-35 Yamate-cho, Suita, Osaka 564-8680, Japan<sup>3)</sup>

### 1. Introduction

Introduction of nitrogen into carbonaceous material could be expected to modify its structure and properties. Recently several kinds of carbon/nitrogen (C/N) materials were prepared and characterized for applications such as electrochemical capacitor [1]. The authors prepared nitrogen-rich C/N materials with the layered structure [2], and with the tetrahedral ( $sp^3$ ) structure [3] by chemical reactions.

In the present study, we have prepared a new nitrogen-rich C/N materials by pyrolysis of a nitrogen-rich starting material (2,3,6,7-tetracyano-1,4,5,8-tetraazaphthalene) and investigated their adsorption properties and electrochemical properties as a capacitor.

### 2. Experimental

The C/N materials were prepared by heat-treatment of the starting material 2,3,6,7-tetracyano-1,4,5,8-tetraazaphthalene (TCNA) at a temperature between 670K and 1270K for 1 hour under  $N_2$  atmosphere. Nitrogen adsorption isotherms were measured at 77K by gas sorption method. Specific surface area was estimated by BET method. The electrochemical measurements for C/N powders were performed by 3 electrode cell with a saturated calomel electrode as a reference in 1M- $H_2SO_4$  aqueous solution. The specific capacitances of the materials were calculated from the charge/discharge curves by galvanostatic method. Cyclic voltammograms were also measured.

### 3. Results and Discussion

The starting material TCNA decomposed above 670K and changed the color from yellow to black. Elemental analyses indicated that the composition of the product was  $C_{3.0}N_{1.9}H_{1.8}O_{1.3}$  and  $C_{3.0}N_{1.0}H_{0.6}O_{1.3}$  for the material prepared at 970K and 1070K, respectively. X-ray diffraction pattern indicated that the material had a non-crystalline carbon-like structure. The material prepared at 1070K had a specific surface area of  $990m^2/g$  with a peak diameter of 0.8nm in the pore size distribution. Figure 1 shows a possible structure of C/N material prepared at 970K, which was estimated on the basis of the pyrolysis process, composition, etc.

Figure 2 shows galvanostatic charge/discharge curves of C/N material prepared at 1070K. Specific capacitance was calculated from this curve to be 160F/g (per single electrode of capacitor), which is larger than that of activated carbon with the same specific surface area. The large capacitance could be explained by the existence of quaternary or pyridine-type nitrogen in the material, which was detected by ESCA. Almost no change in the specific capacitance was observed by using different current densities for galvanostatic method. Figure 3 shows cyclic voltammograms of the same material as that in Fig.2. In addition to a typical faradaic reaction, a reversible pseudo-faradaic reaction was observed at

lower potentials.

### References

- [1] For example: M. Kodama, *et al.*, *Mat. Sci. Eng. B-Solid*, **108**, 156 (2004).
- [2] M. Kawaguchi, and K. Nozaki, *Chem. Mater.*, **7**, 257(1995).
- [3] M. Kawaguchi, *et al.*, *Carbon*, **42**, 345 (2004).

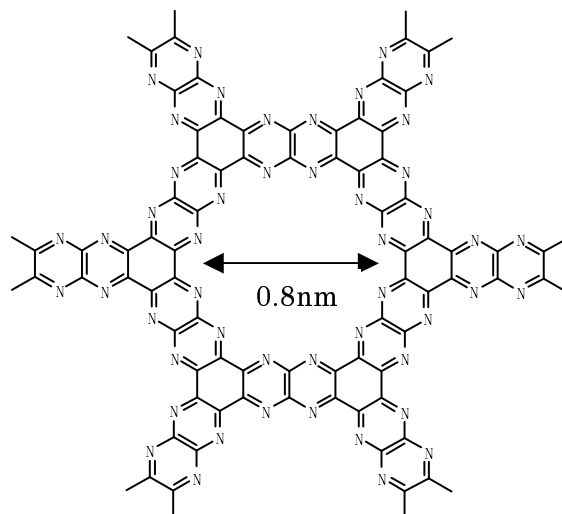


Figure 1 A possible structure of C/N material prepared by the pyrolysis of TCNA at 970K.

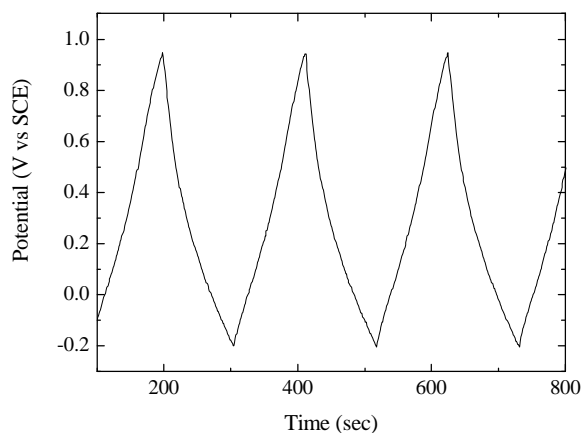


Figure 2 Galvanostatic charge/discharge curves for C/N material prepared by the pyrolysis of TCNA at 1070K. 1M- $H_2SO_4$  aqueous solution. Current density:  $10mA/cm^2$ . Three electrode cell.

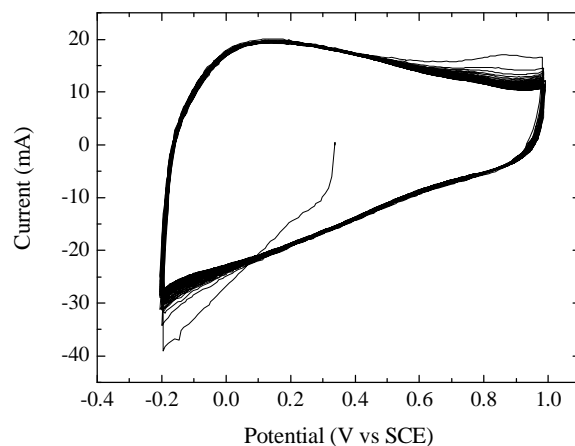


Figure 3 Cyclic voltammograms for C/N material prepared by the pyrolysis of TCNA at 1070K. 1M- $H_2SO_4$  aqueous solution. Scan speed:  $10mV/sec$ . Three electrode cell.