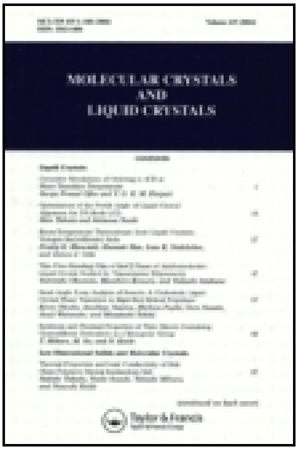

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Electrochemical Intercalation of Lithium or Perchlorate Ion into Graphite-Like Layered Material of BC_6N

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The material of composition BC_6N with high crystallinity has been synthesized by CVD reaction of BCl_3 with acrylonitrile at 1500–2000°C. BC_6N electrode has shown opposite electrochemical behavior to graphite electrode in the several electrolyte. Comparison of the open circuit potentials at the initial stage for the intercalation of lithium suggests that the conduction band of BC_6N could be more antibonding than that of graphite. On the other hand, the electrochemical intercalation of perchlorate suggests that the highest levels of the valence bands are not so different for both BC_6N and graphite The band gap of BC_6N could be estimated to be 1.7eV by this electrochemical method.

Keywords: layered B/C/N material; electronic state; electrochemical intercalation

INTRODUCTION

Boron/Carbon/Nitrogen (B/C/N) materials based on the graphite network have been of particular interest in recent years because of their potential applications as new semiconductors and host materials[1]. So far, B/C/N hybrids[2], stoichiometric compounds BC_2N[3,4], BC_3[4,5] and C_5N[4] were prepared by chemical vapor deposition (CVD) method. We have recently synthesized BC_3N[6,7], BCN[7] and BC_6N_2[8] by CVD reaction of BCl_3 with organic nitriles and pyrolyses of precursors. Their fundamental properties[9,10] and some applications such as electrode matrix of secondary lithium batteries[11-15] have been investigated in these years.

Electrochemical intercalation of lithium into these materials would give important information about the application for anode matrix of secondary lithium batteries as well as fundamental characteristics such as electronic state of the material. For such experiments, we need stoichiometric compounds with high crystallinity which have not been prepared so far. Furthermore, the comparison of these properties with those of graphite will be useful for considering the application of these new materials.

In this paper, we report the preparation of B/C/N materials by high temperature CVD method and the electrochemical intercalation of lithium and perchlorate ions into these materials and discuss about the electronic states of the materials.

EXPERIMENTAL

Preparation of B/C/N Materials[16]

PBN (Pyrolytic boron nitride) plate (30×5×1mm) as a substrate was set on a carbon suscepter. Acrylonitrile (70 cm^3/min) carried by N_2 (410 cm^3/min) and BCl_3 gas (35 cm^3/min) were introduced into the reactor in which the carbon suscepter was heated at 1500-2000℃ by radio-frequency induction. The reaction was carried out under atmospheric pressure.

Electrochemical Intercalation of Lithium and Perchlorate

Electrochemical intercalation of Li^+ and perchlorate (ClO_4^-) ions into BC_6N, BC_3N or artificial graphite (Toyo Tanso Co., LX-001S-60: average particle size 60 μm, La and Lc>100nm) were performed in the solution of 1.0 mol/dm^3 $LiClO_4$/propylene carbonate (PC) or ethylene carbonate and diethyl carbonate mixed solvent (EC/DEC) by using Li reference and counter electrodes.

RESULTS AND DISCUSSION

B/C/N Materials

Black films whose composition was approximately BC_6N[16] were obtained on the carbon suscepter as well as the PBN substrate when the CH_2CHCN:BCl_3 gas molar ratio was 2:1. On the other hand, black films with an approximate composition BC_3N were obtained when the CH_2CHCN:BCl_3 gas molar ratio was 1:1. These results and the analyses of by-products suggest that each reaction proceeded as follows:

$$2CH_2CHCN + BCl_3 \rightarrow BC_6N + 3HCl + NH_3 \cdots\cdots\cdots (1)$$

$$CH_2CHCN + BCl_3 \rightarrow BC_3N + 3HCl \cdots\cdots\cdots (2)$$

X-ray diffraction analysis indicates that BC_6N and BC_3N prepared at 1800℃ have the graphite-like layered structure similar to the artificial carbon heat-treated at the same temperature. The BC_6N films show the electrical conductivity of 175 Scm^{-1} at room temperature and behave as the n-type semiconductor[16].

Electrochemical Intercalation of Lithium

Figure 1 shows closed circuit potential changes for the electrochemical intercalation/deintercalation of lithium into/out of BC_6N electrode in the $LiClO_4$/PC electrolyte. The capacities gradually decreased with the cycles, while the coulomb efficiency (deintercalation capacity/intercalation capacity) increased. On the other hand, BC_3N shows small capacities from the first cycle. Table 1 indicates charge capacities of the first cycle for the materials. Note that BC_6N electrode shows large capacity in the $LiClO_4$/PC electrolyte, while the graphite has large capacity in the $LiClO_4$/(EC/DEC) electrolyte.

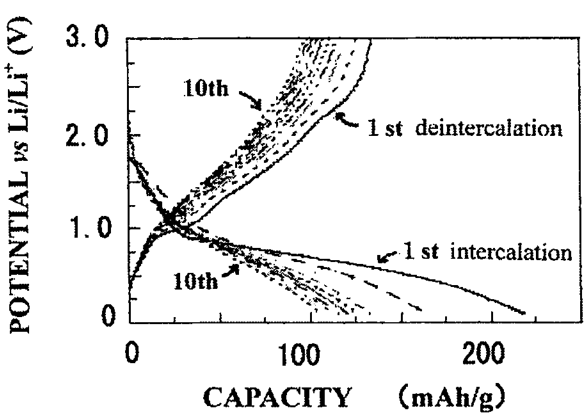

FIGURE 1 Potential changes for the electrochemical intercalation/deintercalation of lithium into/out of BC_6N electrode in 1.0 mol/dm^3 $LiClO_4$/PC solution. Current density: 50 μ A/cm^2.

These results suggest that the electronic states of materials are quite different among BC_6N, BC_3N and graphite and affect the solvents. For example, BC_6N electrode does not interact with the PC solvent but could reduce to decompose the EC/DEC. Reverse phenomenon is observed for the graphite electrode, which has been well known[17].

TABLE 1 Capacities of the first cycles for the electrochemical intercalation of lithium into BC_6N, BC_3N and graphite electrode. Current density: 50 μ A/cm^2.

Solvent	BC_6N electrode	BC_3N electrode	Graphite electrode
PC	218 mAh/g	8 mAh/g	36 mAh/g
EC/DEC	3 mAh/g	8 mAh/g	185 mAh/g

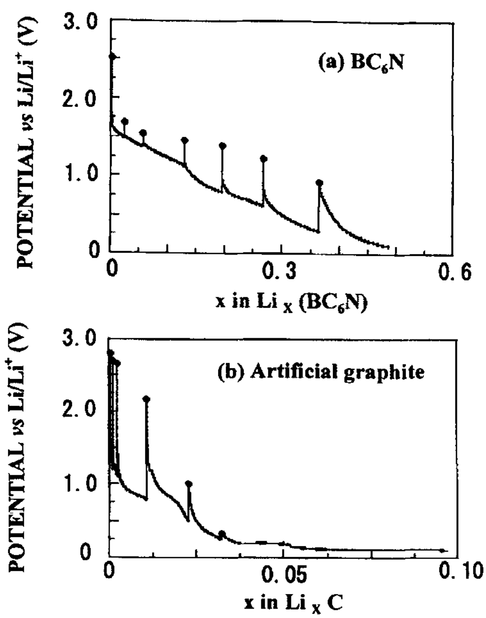

FIGURE 2 Open circuit potentials (dots) of the first cycle for the electrochemical intercalation of lithium into (a)BC_6N in 1.0 mol/dm^3 $LiClO_4$/PC solution and (b)graphite in 1.0 mol/dm^3 $LiClO_4$/ EC+DEC solution. Current density: 50 μ A/cm^2.

Electronic States of Materials

Figure 2 (a) and (b) show the open circuit potentials for the first cycles of BC_6N and artificial graphite. The closed circuit potentials (intercalation of Li) for BC_6N electrode tended to be higher than those for the graphite. However, open circuit potentials for BC_6N electrode were lower than those for the graphite. These results indicate that the overpotentials caused by the diffusion of intercalant (Li) in the interlayer of BC_6N are smaller than those for graphite. Similar results were observed by means of cyclic voltammetry for these materials.

The open circuit potential at the initial stage (<1mol%) of the intercalation of lithium indicates the lowest level of the conduction band (Fig.3). The open circuit potentials for BC_6N and graphite are 1.5V and 2.5V *vs* Li/Li^+, respectively, when 1 at% of lithium was intercalated electrochemically. The comparison of the open circuit potentials suggest that BC_6N can not be reduced easier than graphite. In other word, the conduction band of BC_6N could be more antibonding than that of graphite.

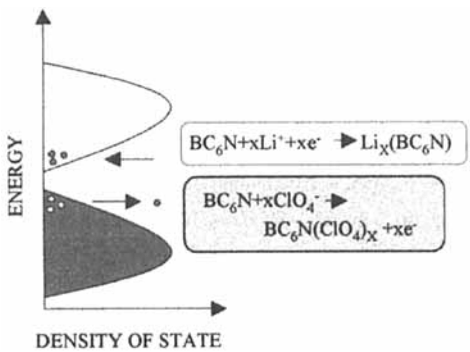

FIGURE 3 Electronic state of BC_6N estimated by electrochemical method.

On the other hand, the electrochemical intercalation of perchlorate ion into BC_6N electrode showed large overpotentials. Irreversible cyclic voltammograms were also observed for both BC_6N and graphite electrodes in the potential range between 3 and 5 V *vs* Li/Li^+. The open circuit potentials of BC_6N and graphite electrodes at the intercalant concentration of 1 at% ClO_4^- were 3.2 and 3.0 V *vs* Li/Li^+, respectively. This result suggests that the highest levels of the valence bands are not so different for both BC_6N and graphite. The shape of the valence band has been observed by means of X-ray emission spectroscopy[18]. From these results, the band gap of BC_6N could be estimated to be 1.7eV (3.2-1.5V).

Acknowledgements

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