The Role of Boron in B/C/N and B/C Materials as an Anode of Sodium Ion Batteries

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ABSTRACT

Graphite-like layered materials composed of boron/carbon/nitrogen (B/C/N) and boron/carbon (B/C) have been prepared by CVD method using BCl_3 and CH_3CN or C_2H_4 as starting materials, respectively. Electrochemical behaviors of B/C/N and B/C materials as anodes of sodium ion batteries have been investigated. Their properties have been compared with those of carbon/nitrogen (C/N) material and carbons prepared by CVD method. B/C/N and B/C materials showed reversible intercalation and de-intercalation on their discharge and charge cycles. The formation of stage structures was observed during the discharge (electrochemical intercalation) in 1M- $\text{NaPF}_6/\text{EC}+\text{DEC}$ (1:1) electrolyte solution, which was not clearly observed in the cases of C/N material and carbon. Potentials at the beginning of discharge (intercalation of Na^+ ion) were higher than those of C/N material and carbons, and depended on the boron content in the material. B/C materials having larger boron content tended to show higher reversible capacity. B/C/N materials showed highest reversible capacity 190 mAh g^{-1} among the materials prepared in this study by using CVD method. These results could be explained by the electronic structure of the material in which electron deficient boron atom lowered the bottom of conduction band, and will provide useful information for designing materials as electrodes.

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Keywords : B/C/N Material, B/C Material, Sodium Ion Battery, Electrochemical Intercalation

1. Introduction

Sodium (Na) ion batteries are one of the candidates for secondary batteries in the next generation, because Na resources are rich on earth and can be industrially transformed to Na metal. Similar to graphite used as an anode matrix of lithium (Li) in Li ion batteries, a host material such as an anode matrix of Na in Na ion batteries will be needed. However, graphite cannot be used as the anode of Na ion batteries because of the difficulties in intercalating Na into graphite.^{1–3} Instead of graphite, hard carbon^{4–6} and other materials have been studied as potential host materials for anodes of Na ion batteries. In the case of hard carbon as the matrix of anode, Na might not be intercalated into the layered structure, but is inserted into nano-pores among the boundaries of carbon crystals.^{4–6} We have recently investigated the intercalation of Na into boron/carbon/nitrogen (B/C/N) materials by using an electrochemical method as well as a chemical reaction method, and found that Na could be intercalated into a material that produces lower stage compounds.^{7,8}

The B/C/N materials with a graphite-like layered structure are types of hetero-atom substituted carbon alloys,⁹ and have been prepared using a chemical vapor deposition (CVD) method or other methods.^{10,11} The materials are expected to be new host materials for secondary batteries and new semi-conductors.^{10,12–15} As is described above, Na^+ ion can be electrochemically intercalated and de-intercalated into and out of a material with a composition BC_2N ,^{7,8} while Na cannot be easily intercalated into graphite. This reversible intercalation/de-intercalation of Na^+ ion can be applied to the anode of Na ion batteries. Also, magnesium (Mg) can be intercalated into BC_2N through a vapor phase reaction of Mg with BC_2N ,¹⁶ while Mg has never been intercalated into graphite. The X-ray absorption spectroscopy indicated that the bottom of the conduction band of BC_2N was at an energy lower than that of graphite;^{7,16} in other words, BC_2N has a large electron affinity

compared with that of graphite. This might be the reason why Na and Mg, which have large ionization potentials among group 1 and 2 metals, can be intercalated into BC_2N . Since the conduction band of BC_2N is made of a hybridization of carbon 2p and boron 2p orbitals, boron atoms in B/C/N materials have an important role in making the electronic structures.¹⁷

From the results described above, we consider that graphite-like layered materials composed of boron and carbon (so-called B/C materials) can be effectively intercalated with Na^+ ion by electrochemical method. The B/C materials have been investigated as the anode matrix of Li ion batteries,^{18–20} and showed good performances. However, the materials have not been investigated as the anode of Na ion batteries.

In order to clarify the hybridization of orbitals and extend the application of carbon alloys into the field of batteries, preparation and characterization of B/C/N and B/C materials for the electrode matrices might be useful. We consider that B/C/N and B/C materials having high electron affinity intercalate alkali metals such as Na easier than graphite or hard carbon, and have high reversible capacities as a result of it. In this paper, preparation of B/C/N and B/C materials using the CVD method and characterization of the materials as the anode matrices of Na ion batteries have been reported. Particularly relations among boron contents in the materials, potentials on the intercalation of Na^+ ion, and reversible capacities have been summarized, compared with the cases of non-crystalline carbon and carbon/nitrogen (C/N) materials. Then we consider roles of boron and nitrogen in B/C/N and B/C materials from the results obtained in the present study.

2. Experimental

B/C/N and B/C materials were prepared using the CVD apparatus reported elsewhere.^{10,11} Based on the research previously made by the present authors, Na was efficiently intercalated into

B/C/N material which was prepared at 1770 K. According to this information, B/C/N materials prepared at 1770 K having two different compositions were used in this study. The B/C/N thick film was prepared at 1770 K using boron trichloride (BCl_3 : 4.0×10^{-5} or $8.0 \times 10^{-5} \text{ m}^3/\text{min}$) and acetonitrile (CH_3CN : $4.0 \times 10^{-5} \text{ m}^3/\text{min}$) as the starting materials under atmospheric pressure. The B/C/N film was deposited on a carbon susceptor which was set in the CVD apparatus and heated through radio frequency induction. The reaction temperature was monitored with a radiation thermometer. The reaction was carried out for 6 hours at 1770 K. The materials prepared at 1770 K using the molar ratios $\text{BCl}_3:\text{CH}_3\text{CN} = 1:1$ and $2:1$ are called B/C/N (1770 K, 1:1) and B/C/N (1770 K, 2:1), respectively, in this paper.

This is the first report that the B/C materials were used as the anode of Na ion batteries. Therefore, B/C materials prepared at several temperatures were used in this study. The B/C thick film was prepared at temperatures in the range of 1270–1770 K using ethylene (C_2H_4 : $3.4 \times 10^{-5} \text{ m}^3/\text{min}$) and boron trichloride (BCl_3 : $4.6 \times 10^{-5} \text{ m}^3/\text{min}$) as the starting materials under atmospheric pressure. The B/C film was deposited on a carbon susceptor in the same way as the B/C/N film. The reaction was carried out for 6 hours at a temperature in the range of 1270–1770 K. The obtained materials are called B/C (1270 K), B/C (1370 K), B/C (1470 K), B/C (1570 K), and B/C (1770 K) in this paper.

In order to compare the results obtained for B/C/N materials, carbon and C/N films were prepared at a temperature of 1770 K using C_2H_4 and CH_3CN ,²¹ respectively. Furthermore, to check the effect of the preparation temperature of the material on the electrochemical performances, the carbon film prepared at 2070 K was also used. These materials were described as C (1770 K), C (2070 K), and C/N (1770 K) in this paper.

The prepared films were scraped from the susceptor after the reaction and pulverized in a mortar into fine powders, followed by collecting powders under $45 \mu\text{m}$ using stainless steel mesh. The X-ray diffraction (XRD) analysis of the powders was performed with a X-ray diffractometer (Rigaku Co., RINT2000 Ultima⁺) using $\text{Cu-K}\alpha$ radiation. Elemental analyses were made using the usual combustion method for carbon, hydrogen, and nitrogen contained in the material, and through the decomposition of the material using acids followed by the ICP emission spectroscopy for boron.

In order to make electrodes for the electrochemical measurements, the active material of B/C/N powder or B/C powder was mixed with acetylene black (AB) as a conductive additive and polyvinylidene difluoride (PVDF) as a binder with a ratio of the active material:AB:PVDF = 20:2:1 in wt% using *N*-methylpyrrolidone (NMP) as a solvent. The mixture was pasted on a copper plate as a current collector, and was dried at 470 K under vacuum for 0.5 hour. Electrochemical measurements were performed using potentiostat/galvanostat (Hokuto Denko Co., HJ-SD8) using a three electrode cell with Na metal as counter and reference electrodes. The electrolyte was sodium hexafluorophosphate (NaPF_6) dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) as a mixed solvent with a 1:1 volume ratio. 1 mol cm^{-3} NaPF_6 dissolved in the mixed solvent is described as $1 \text{ M-NaPF}_6/\text{EC}+\text{DEC}(1:1)$ in this paper. The construction of the cell and the electrochemical measurement were made under Ar atmosphere in a vacuum-type glove box. Galvanostatic discharge (intercalation of Na^+ ion) and charge (de-intercalation of Na^+ ion) cycles were measured with a current density of $100 \mu\text{A cm}^{-2}$. Cyclic voltammetry was performed with a sweep rate of 0.1 mV/sec . A constant current-constant voltage (CCCV) method was used to prepare intercalation compounds. The intercalation compounds were washed with the mixed solvent EC+DEC(1:1) and mounted on a sample holder which was then covered with polyvinylidene chloride (PVDC) film in the glove box. Crystal structures of the compounds were measured using XRD.

Table 1. Composition of B/C/N material.

Preparation temperature/K	B/C/N(1:1)	B/C/N(2:1)
	Composition	
1770	$\text{BC}_{4.7}\text{N}_{0.75}$	$\text{BC}_{2.2}\text{N}_{0.76}$

Table 2. Composition of B/C material.

Preparation temperature/K	Composition
1270	$\text{BC}_{7.9}$
1370	$\text{BC}_{8.0}$
1470	$\text{BC}_{8.3}$
1570	$\text{BC}_{9.6}$
1770	$\text{BC}_{6.9}$

3. Results and Discussion

3.1 Appearance and composition of B/C/N and B/C materials

The B/C/N films whose appearances were shiny black in color were obtained on the carbon susceptor. The films were pulverized into fine powders whose appearances were almost black with particle sizes under $45 \mu\text{m}$. On the other hand, the appearances of B/C films obtained on the susceptor were metallic silver, being different from those of B/C/N films. The pulverized powders were almost black in color.

Tables 1 and 2 indicate the compositions of B/C/N and B/C materials prepared in this study. The boron and nitrogen contents of B/C/N materials increased along with increasing the molar ratio of BCl_3 and CH_3CN . A material with composition $\text{BC}_{2.2}\text{N}_{0.76}$ was obtained when the molar ratio of $\text{BCl}_3:\text{CH}_3\text{CN}$ was 2:1, while a material with composition $\text{BC}_{4.7}\text{N}_{0.75}$ was obtained when the molar ratio of $\text{BCl}_3:\text{CH}_3\text{CN}$ was 1:1. The nitrogen/boron ratios in B/C/N materials were almost the same in the range from 0.75 to 0.80. On the other hand, boron contents in B/C materials increased along with decreasing the reaction temperature in the range from 1270 to 1570 K. The increase of boron content in B/C materials at temperatures lower than 1570 K might be due to an alloying of boron atoms in the layered structure. The boron contents in B/C materials increased over 1570 K because of the formation of boron carbide B_4C as a by-product together with the formation of graphite-like layered material as the main product, which is described below (3.2 Structure of B/C/N and B/C materials). The boron content in the material prepared at 1770 K having layered structure, therefore, should be lower than that indicated in Table 2.

3.2 Structure of B/C/N and B/C materials

Figure 1 shows X-ray powder diffraction patterns of (a) the B/C/N material prepared at 1770 K with the molar ratio of starting material $\text{BCl}_3:\text{CH}_3\text{CN} = 1:1$, (b) the B/C material prepared at 1270 K, and (c) the B/C material prepared at 1770 K, compared with (d) the C/N material prepared at 1770 K, and (e) the carbon prepared at 1770 K. Only 00 l diffraction lines were observed on the XRD patterns for the as-prepared films of all the materials, while other hkl diffraction lines together with the 00 l ones were observed for the pulverized powders. This result suggests that the *a*-axis in the structure of the film was oriented parallel to the surface of substrate.

The XRD pattern of B/C/N material (a) had sharp 00 l diffraction lines, indicating that the material had the layered structure similar to that of graphite in the direction of *c*-axis. However, it also had broad 10 diffraction line, suggesting that the material had the structure

Figure 1. X-ray diffraction patterns of (a) B/C/N powder prepared at 1770 K with the molar ratio $\text{BCl}_3:\text{CH}_3\text{CN} = 1:1$, (b) B/C powder prepared at 1270 K, (c) B/C powder prepared at 1770 K, (d) C/N powder prepared at 1770 K, and (e) carbon powder prepared at 1770 K used in this study as original host materials.

similar to turbostratic one, in which stacking sequences are almost random.²² In the case of turbostratic structure, 100 and 101 diffraction lines are not separated so that only the broad 10 diffraction line is observed. The B/C/N material prepared at 1770 K had the structure similar to the turbostratic one, though it showed high crystallinity in the direction of *c*-axis.

Figures 1-b and 1-c show XRD patterns of the B/C powders obtained at a reaction temperature of 1270 and 1770 K. The sharp 00 ℓ diffraction lines were observed for the materials prepared at the temperature between 1270 and 1770 K, indicating that the materials had high crystallinity in the direction of the *c*-axis. Compared to the carbons obtained by the CVD reaction using only C_2H_4 at 1770 K (Fig. 1-e), the B/C material obtained at the temperature between 1270 and 1570 K had higher crystallinity than the carbon. This comparison is quantitatively described later in this paper. These results suggest that the boron in the B/C material had a role of crystallization of the materials.

One of the roles of boron in B/C materials described above was already suggested in the previous papers.^{18–20,23–28} Lowell indicated that boron atoms dissolved into the graphite lattice with a maximum solid solubility of 2.35 at% and the lattice constant a_0 increased with boron content within the solubility.²⁹ Kouvetakis et al. first prepared BC_3 from the CVD reaction of BCl_3 and benzene,³⁰ and Ottaviani et al. prepared B/C materials through the same CVD reaction and suggested that the boron atoms substituted for carbon atoms in the graphitic planes, with a maximum solid solubility of 17 at%, increased the crystallinity within the solubility.²³ From the results indicated in Fig. 1, we recognized that the boron in the B/C materials showed the role also in the present study.

The broad 10 diffraction line on Fig. 1-b for B/C material prepared at 1270 K indicates that the B/C material had a structure similar to the turbostratic carbon, although the sharp 00 ℓ diffraction

lines indicate high crystallinity in the direction of *c*-axis. The B/C materials prepared at 1770 K (Fig. 1-c) and temperatures higher than 1770 K showed the diffraction lines at similar positions of 100 and 101 as those of graphite and 021 diffraction of boron carbide B_4C . This result indicates that materials obtained at 1770 K and temperatures higher than 1770 K had a graphite-like layered structure whose stacking sequence is regularly ordered as a main component together with B_4C as a by-product.

Figures 1-d and 1-e shows XRD patterns of C/N powder prepared from CH_3CN at 1770 K, and carbon powders prepared from C_2H_4 at 1770 K, respectively. The full width at half maximum (FWHM) of 002 diffraction line of carbon powder prepared at 1770 K (Fig. 1-e: $\text{FWHM} = 1.9^\circ$ in 2θ) was larger than that of $\text{BC}_{6,9}$ prepared at the same temperature (Fig. 1-c: $\text{FWHM} = 0.50^\circ$ in 2θ) or $\text{BC}_{7,9}$ prepared at 1270 K (Fig. 1-b: $\text{FWHM} = 0.72^\circ$ in 2θ) from the same starting material C_2H_4 as the carbon source. This result indicates that the carbon had crystallinity lower than those of $\text{BC}_{6,9}$ and $\text{BC}_{7,9}$, suggesting that boron in B/C materials had an important role in crystallization for the materials. On the other hand, FWHM of 002 diffraction line of C/N prepared at 1770 K (Fig. 1-d: $\text{FWHM} = 4.5^\circ$ in 2θ) was much larger than that of other materials prepared in this study. This result suggests that nitrogen in C/N diminished the crystallite size.

3.3 Discharge/charge curves of B/C/N and B/C materials

Figure 2-a shows first discharge/charge curves of B/C/N materials prepared at 1770 K with the different molar ratios of the starting materials. The terms “discharge” and “charge” mean intercalation (or reduction) and de-intercalation (or oxidation) of Na^+ ion into and out of host material respectively in this study. First discharge curves consist of three parts that have rather small slopes. The potentials at the slopes could not be easily distinguished on Fig. 2-a, but with cyclic voltammograms (Fig. 2-b). Figure 2-b shows first and second cyclic voltammograms for B/C/N material prepared at 1770 K with the molar ratio $\text{BCl}_3:\text{CH}_3\text{CN} = 1:1$. Three peaks at 0.79, 0.51, and almost 0 V vs. Na/Na^+ were observed on the first discharge in Fig. 2-b, which correspond to the three small slopes shown in Fig. 2-a. The peak at 0.79 V in Fig. 2-b was observed also on the second discharge and thereafter, and might be mainly due to a formation of an intercalation compound. An oxidation peak was observed at 0.92 V during the charge, corresponding to the de-intercalation of Na^+ ion out of B/C/N material. The peak at 0.51 V in Fig. 2-b was not observed on the second discharge and thereafter, and might be mainly due to a formation of a solid electrolyte interface (SEI) in a similar manner to the anode of Li ion batteries.^{31,32} The peak at around 0 V in Fig. 2-b was observed every time, and is presumably due to a formation of low stage intercalation compound. An oxidation peak was observed at 0.12 V during the charge, corresponding to the de-intercalation of Na^+ ion out of B/C/N material. These results suggest that the intercalation of Na^+ ion into B/C/N materials mainly proceeds in two levels. One was at a higher potential of 0.79 V and the other was at almost 0 V vs. Na/Na^+ during discharge (intercalation of Na^+ ion). Concerning the former, the intercalation of Na^+ ion into B/C/N materials began to occur at potentials higher than carbon. Usually Na^+ ion can be inserted into non-crystalline carbon at potentials lower than 0.79 V vs. Na/Na^+ , which was reported elsewhere^{4,5,33,34} and also described later in this study.

Figure 2-a indicates that the intercalation of Na^+ ion into the B/C/N material having higher boron content began at a potential higher than that of the other one having lower boron content, suggesting that boron content in the B/C/N material tended to determine the potentials on the discharge/charge cycles. The intercalation of Na^+ ion into reduced B/C/N materials (B/C/N^-) occurred at higher potentials could be due to a coordination of the B/C/N $^-$ layers to Na^+ ion at lower energy on its conduction band,

Figure 2. First discharge/charge curves measured by (a) the galvanostatic method using a current density $100 \mu\text{A cm}^{-2}$ for B/C/N materials prepared at 1770 K ($\text{BCl}_3:\text{CH}_3\text{CN} = 1:1$) and ($\text{BCl}_3:\text{CH}_3\text{CN} = 2:1$), and (b) the cyclic voltammometry using a sweep rate 0.1 mV/sec for B/C/N material prepared at 1770 K ($\text{BCl}_3:\text{CH}_3\text{CN} = 1:1$), in $1 \text{ M-NaPF}_6/\text{EC}+\text{DEC}$.

which is shown in Fig. 3 as an energy scheme. In fact, the X-ray absorption spectroscopy (XAS) indicated that the bottom of the conduction band of BC_2N was at an energy lower than those of non-crystalline carbon and graphite.^{7,35} Molecular orbital calculation suggested that the conduction band of B/C/N material is constructed by the hybridization of carbon 2s and 2p orbitals with boron 2s and 2p orbitals.¹⁷ Based on these experimental and calculated results, we explained that the electron deficiency of boron atom in B/C/N material decreases the energy level in the bottom of conduction band, in comparison with that of graphite.^{7,8,16,35} In other words, B/C/N materials have the electron affinity larger than that of graphite. This might be the reason why Na having a large ionization potential can be intercalated into B/C/N materials easier than that into graphite. This is another important role of boron in B/C/N materials. It is expected that Na^+ ion can be also electrochemically intercalated into the B/C/N⁻ layers during the discharge at potentials over the redox potential of Na (deposition of Na metal), resulting in that the materials showed the high reversible capacities as the anode matrix of Na ion batteries.

Figure 4 shows first discharge/charge curves of B/C materials, which were prepared at the temperatures between 1270 and 1570 K.

Figure 3. Energy scheme of the bottom of conduction band and the electrochemical potential for B/C/N and B/C materials, non-crystalline carbon, and graphite.

Figure 4. First discharge/charge curves of B/C materials by the galvanostatic method using a current density $100 \mu\text{A cm}^{-2}$ in $1 \text{ M-NaPF}_6/\text{EC}+\text{DEC}$.

The interesting thing is that the B/C material prepared at lower temperature showed a potential at the beginning of the discharge (intercalation of Na^+ ion) higher than that of the material prepared at higher temperature. Table 2 indicates that the material prepared at lower temperature in the range 1270 to 1570 K had larger amount of boron in it. Therefore, B/C material containing larger amount of boron showed the higher discharge potential. This result consistent with that observed for the B/C/N materials (Fig. 2-a) and might be explained by the electronic structure shown in Fig. 3.

Figure 5 shows first discharge and charge curves of C/N material prepared at 1770 K (C/N 1770 K) and carbons prepared at 1770 K (C 1770 K) and 2070 K (C 2070 K) as references. Potentials at the beginning of the discharge were low, compared to those of B/C/N and B/C materials, probably because of the lack of boron in C/N material and carbons.

From these results, the boron contents tended to increase the discharge/charge potentials in the intercalation of Na^+ ion into the B/C/N and B/C materials, compared with those into carbon and C/N materials. This tendency would increase the rechargeable capacities which are measured at potentials over the redox potential of Na (deposition of Na metal) during the discharge/charge cycles.

Figure 5. First discharge/charge curves of C/N material (1770 K), C (1770 K), and C (2070 K) by the galvanostatic method using a current density $100 \mu\text{A cm}^{-2}$ in 1 M-NaPF₆/EC+DEC.

3.4 Discharge/charge capacities of B/C/N and B/C materials

Figure 6 indicates the change in discharge (intercalation of Na⁺ ion) and charge (de-intercalation of Na⁺ ion) capacities of B/C/N, B/C, C/N materials and carbon. These capacities were calculated from the time between the potentials of 0.003 and 2.7 V vs. Na/Na⁺. The B/C/N materials having the composition of BC_{4.7}N_{0.75} and BC_{2.2}N_{0.76}, which were prepared at 1770 K with the molar ratio of starting materials BCl₃:CH₃CN = 1:1 and 2:1, showed high charge (de-intercalation of Na⁺ ion) capacity of 190 mAh g^{-1} and 187 mAh g^{-1} , compared with those of B/C and C/N materials and carbon. Charge capacities of B/C materials tended to increase with the boron contents except B/C material prepared at 1770 K. The irreversible capacities observed in the first discharge/charge cycle for all the materials presumably corresponds to mainly the formation of SEI on the electrode in a way similar to the anode of Li ion batteries.

Figure 7 summarizes the results of reversible capacities, which were average values through the second to the fifth charges shown in Fig. 6, in relation to the boron contents of B/C/N and B/C materials. The boron contents affected the reversible capacities particularly for B/C materials. This result can be interpreted by the explanation of the role of boron in B/C/N and B/C materials, as is described in the section “3.3 Discharge/charge curves of B/C/N and B/C materials”. B/C/N materials showed capacities higher than those of B/C materials probably because of the larger boron contents. In the case of B/C/N materials, nitrogen acts as atoms which capture boron atoms in the layered structure. This is one of the roles of nitrogen in the B/C/N materials. However, reversible capacities of two kinds of B/C/N materials were not so different each other even the boron contents were different. This reason is not clear yet. The nitrogen, which is electron rich element in the carbon-based material, might compensate the role of boron in B/C/N materials, because the nitrogen contents proportionally increased with the boron contents in B/C/N materials, which is indicated in Table 1.

On the other hand, discharge and charge capacities of C/N material were higher than B/C materials and carbon prepared in this study, but lower than those of B/C/N materials. Therefore, B/C/N materials showed highest reversible capacities among the materials prepared in this study. It is noted that the mechanism of the electrochemical discharge/charge for B/C/N and B/C materials should be different from that of C/N material and carbon.

Figure 6. (a) Discharge (intercalation) and (b) charge (de-intercalation) capacities of B/C/N (1770 K (BCl₃:CH₃CN = 1:1)), B/C (1270 K), C/N (1770 K) materials and C (1770 K) measured by the galvanostatic method using a current density $100 \mu\text{A cm}^{-2}$ in 1 M-NaPF₆/EC+DEC.

Figure 7. Influence of boron contents on reversible capacities of B/C/N and B/C materials. (a) B/C/N (1770 K (BCl₃:CH₃CN = 1:1)), (b) B/C/N (1770 K (BCl₃:CH₃CN = 2:1)), (c) B/C (1270 K), (d) B/C (1370 K), (e) B/C (1470 K), and (f) B/C (1570 K).

Figure 8. X-ray diffraction patterns of Na-B/C/N material (1770 K ($\text{BCl}_3:\text{CH}_3\text{CN} = 1:1$)) prepared by the CCCV method fixing a potential at (a) 0.003 V and (b) 0.70 V vs. Na/Na^+ in 1 M- $\text{NaPF}_6/\text{EC}+\text{DEC}$.

Electrochemical behavior of B/C/N and B/C materials is based on the intercalation of Na^+ ion into the layered structure. On the other hand, electrochemical behavior of C/N materials and carbon is based on the insertion of Na^+ ion into the nano-pore among the small crystallites.^{4–6} It should be the advantage that B/C/N and B/C materials had the capacity only by the intercalation.

3.5 Stage structure of intercalation compounds Na-B/C/N and Na-B/C

Figure 8 indicates XRD patterns of Na-intercalated B/C/N (Na-B/C/N) obtained using CCCV method with which the potentials were fixed at 0.003 V (Fig. 8-a) and 0.70 V (Fig. 8-b) vs. Na/Na^+ , respectively. The Na-B/C/N showed black in color, which were almost the same as those of the original host materials. It is well known that Li-intercalated graphite intercalation compound (Li-GIC) having the first stage structure Li shows gold or brown in color.³⁶ No color change was observed after the intercalation of Na^+ ion into B/C/N in this study. The difference in color change could be due to the difference in the electronic structure of intercalation compound. When the potential was fixed at 0.003 V during the first discharge, the material with a d -spacing of 0.440 nm (20.16° in 2θ on Fig. 8-a) was obtained. The d -spacing 0.440 nm was close to the d -spacings of the Na intercalated layer of the first stage compound Na-B/C/N (0.430 nm)^{8,35} and the eighth stage compound Na-GIC,^{1–3} indicating that the material having the XRD pattern shown in Fig. 8-a is presumably the first stage compound. The material obtained by fixing the potential at 0.70 V, which was the potential slightly lower than the peak at 0.79 V observed on the cyclic voltammogram (Fig. 2-b), had the d -spacing of 0.403 nm (21.62° in 2θ on Fig. 8-b). The obtained material could be the second stage compound on the basis of the calculation by the following equation:

$$I_c = d_i + (n - 1) \times d_{\text{host}} \quad (1)$$

where I_c is the identity period along the c -axis, d_i is the d -spacing of intercalated layer, n is the stage number, and d_{host} is the d -spacing of the original host material. The I_c is calculated as $d_{00l} \times l$, where d_{00l} is the d -spacing of 00 l diffraction line. Specifically the equation is as follows: $0.403 \times 2 = 0.463 + (2 - 1) \times 0.343$, suggesting that the diffraction line with the d -spacing 0.403 nm could be the 002 diffraction of second stage compound. Although the $d_i = 0.463$ nm

Figure 9. X-ray diffraction patterns of Na-C (1770 K) prepared by the CCCV method fixing a potential at (a) 0.003 V and (b) 0.70 V vs. Na/Na^+ in 1 M- $\text{NaPF}_6/\text{EC}+\text{DEC}$.

is slightly larger than the expected value 0.440 nm, this estimation is most probable among the calculations using various kinds of l - d_i - n combinations. The capacity used until the 0.70 V using CCCV method was 120 mAh g^{-1} , which was larger than half of the reversible capacity 190 mAh g^{-1} , even if it could include a part of the capacity for the formation of SEI. This result also supports the formation of the second stage compound. Similar to the case of B/C/N materials, first stage and second stage Na-intercalated B/C compounds (Na-B/C) were made by fixing the potential at 0.70 V and 0.003 V vs. Na/Na^+ , respectively, using CCCV method. The lower stage compounds were made probably because Na^+ ion could begin to be intercalated into the B/C materials at higher potentials.

Figure 9-a indicates an XRD pattern of a Na inserted carbon (Na-C) prepared by the CCCV method fixing the potential at 0.003 V vs. Na/Na^+ . A broad diffraction line was observed at 23.40° in 2θ ($d = 0.380 \text{ nm}$), which could be calculated by the Eq. (1) to be due to 003 diffraction line of third stage compound. When electrodes made of the C/N material and the carbons were fixed at 0.70 V vs. Na/Na^+ , no intercalation was observed (Fig. 9-b). This result is explained by that the potentials at the beginning of discharge were lower than 0.70 V vs. Na/Na^+ in the cases of C/N material and carbons, being different from the cases of B/C/N and B/C materials.

From these results, B/C/N and B/C materials made the first and the second stage compounds by using CCCV method at the potential 0.003 V and 0.70 V vs. Na/Na^+ . The boron in B/C/N and B/C materials had the role of increase in the electron affinity of the materials so that Na^+ ion could be easily intercalated into the B/C/N and B/C materials. Hence they showed higher reversible capacities.

4. Conclusions

B/C/N and B/C materials with the graphite-like layered structure were made by the CVD method using BCl_3 and CH_3CN or C_2H_4 as starting materials, respectively. The boron and nitrogen contents in B/C/N materials, which were prepared at 1770 K, increased with increasing the molar ratio of starting materials $\text{BCl}_3:\text{CH}_3\text{CN}$. However, the nitrogen/boron ratio in B/C/N materials remained constant in the range from 0.75 to 0.80. The boron contents in B/C materials increased with decreasing the

preparation temperature in the range between 1270 and 1570 K. Electrochemical properties of B/C/N and B/C materials were evaluated as the anodes of Na ion batteries in 1M-NaPF₆/EC+DEC(1:1) electrolyte solution. The potentials at the beginning of discharge (intercalation of Na⁺ ion) were higher than those of C/N material and carbons, and depended on the boron contents in the materials. This result could be explained by the electronic structure of the material in which electron deficient boron atom lowered the bottom of conduction band. Both B/C/N materials having different compositions showed the highest reversible capacity of ca. 190 mA g⁻¹ among the materials prepared in the present study. On the other hand, B/C materials having larger boron content showed higher reversible capacities. The order of reversible capacities was summarized as follows: B/C/N materials > C/N material > B/C materials > carbons. The first stage and the second stage compounds were made from B/C/N and B/C materials by fixing the potential at 0.70 V and 0.003 V vs. Na/Na⁺, respectively, using CCCV method. This behavior was different from that of C/N material and carbons in which Na⁺ ion could be inserted into the nano-pore among the small crystallites. The results obtained in this study will provide useful information for designing materials as electrodes, suggesting that B/C/N materials will be one of the candidates of the anodes of Na ion batteries. Modification of the B/C/N composition, which can be made through the preparation conditions, may increase the reversible capacity of the materials as anode of Na ion batteries.

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