Behavior of BC_2N treated under Various Temperatures as a Negative Electrode Matrix for Rechargeable Lithium Batteries

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Layered-structure compounds, BC_2N have been synthesized by a vapor-phase reaction of acetonitrile (CH_3CN) and borontrichloride (BCl_3). The electrochemical behavior of BC_2N treated under various temperatures (1000, 1500, and 2000 °C) as a negative electrode matrix was investigated in the organic electrolyte systems in connection with rechargeable lithium batteries, focusing on the correlation between the charge/discharge characteristics and physical properties. The influences of the grain size, interlayer spacing and crystallinity of BC_2N , and the Li diffusivity in this matrix upon the charge/discharge properties were discussed. Although BC_2N contains a disordered structure, the diffusivity of Li in BC_2N treated at 1500 °C was found to be comparable to that of a typical carbon electrode with a graphite structure.

1 INTRODUCTION

Negative electrode matrices which can take lithium (Li) in their structure have been extensively studied in connection with rechargeable lithium battery systems to improve a cycleability of the negative electrode¹⁻⁹). Although metallic Li promises high energy density, the application of metallic Li to negative electrode often causes serious problems which lead to the degradation of the rechargeability of the electrode¹⁰). It is widely known that various carbon materials can reversibly take alkali metals in their interlayer to form intercalation compounds¹⁻⁹). Thus, many preliminary and practical battery systems with the carbon electrode have been reported¹¹⁻¹⁴). While considerable interest has so far been focused on the utilization of

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layered "pure" carbon material for the negative electrode matrix, little is known about the application of carbon-based layered material with other light atoms such as boron and nitrogen to this purpose. It seems important to understand the electrochemical properties of such a material from the standpoint of the further development of suitable electrode matrix for Li battery.

We have synthesized a new inorganic compound, BC_2N , which has a graphite like structure, and reported fundamental charge/discharge behavior of the Li negative electrode with a BC_2N matrix in propylene carbonate (PC)-based organic electrolytes^{15,16}). We report herein the behavior of BC_2N treated under various temperatures as a negative electrode matrix, focusing on the correlation between the charge/discharge behavior and physical properties. We have investigated the influences of the grain size, interlayer spacing and crystallinity of BC_2N , and the Li diffusivity in this matrix upon the charge/discharge properties.

2 EXPERIMENTAL

BC₂N was prepared by a chemical vapor deposition (CVD) method proposed by Kouvetakis, *et al.*¹⁷; acetonitrile (CH₃CN) and borontrichloride (BCl₃) were reacted in a vapor phase at 1000 °C [Eq. (1)].

Dark brown or black powder was deposited in a tubular reactor. It was further ground to fine powder and then heated at appropriate temperature between 1000 and 2000 °C in dry nitrogen for 1 h. The resulting BC₂N was characterized by elemental analysis and X-ray diffractometry (XRD).

The electrochemical properties of BC₂N was investigated in organic electrolyte systems. The BC₂N working electrode was prepared by mixing the BC₂N powder (85 mg, 30 mg, or 10 mg) with poly(tetrafluoroethylene) (PTFE, 15 mg, 5 mg, or 1mg, respectively) as a binder followed by molding under a pressure to form a tablet (13 mmφ). A beaker-type three-electrode cell was used for cyclic voltammetry (CV), open circuit potential measurement, and AC impedance analysis. The counter and reference electrodes were a large surface area Li sheet and a Li chip, respectively. A beaker-type two-electrode cell with a Li sheet as a counter electrode was used for the charge/discharge cycling test of BC₂N electrode matrices.

High purity propylene carbonate (PC), ethylene carbonate (EC), and 1,2-dimethoxyethane (DME) (Mitsubishi Petrochemical, Battery Grade) were used as the solvents of electrolyte solutions. LiClO₄ (Ishizu Pharmaceutical, Extra Pure Grade) LiPF₆, LiBF₄ (Morita Chemical Industries) were used for electrolytic salts after drying under reduced pressure at appropriate temperatures (80-170 °C) for 24 h. The electrochemical measurements were carried out under a dry argon atmosphere at room temperature (19-25 °C).

3 RESULTS AND DISCUSSION

Scanning electron microscopic (SEM) images for BC₂N powder heat-treated at various temperatures are shown in Fig. 1. BC₂N treated at 2000 °C [BC₂N (2000 °C)] had high crystallinity as compared with that for BC₂N treated at 1000 °C [BC₂N (1000 °C)] and 1500 °C [BC₂N (1500 °C)]. The grain size was ca. 0.3 μm for BC₂N (1000 °C) and BC₂N (1500 °C), and 1-3 μm for BC₂N (2000 °C). Thus, BC₂N (2000 °C) has the smallest specific surface area among the three types of BC₂N.

As previously reported, BC₂N has a layered structure like graphite with a partly disordered one^{15,16}. Figure 2 shows the variation of the interlayer spacing *d*(002) and the crystallite size of (002) plane as a function of heat-treatment temperature for the preparation of BC₂N. The interlayer spacing *d*(002) of BC₂N, which is larger than that of natural graphite (0.335 nm), decreased gradually with increasing the temperature. On the other hand, the crystallite size of (002) plane increased remarkably over 1750 °C.

In order to obtain preliminary information on the difference in the charge/discharge characteristics of three types of the electrode material, BC₂N heat-treated at 1000, 1500, and 2000 °C, we examined the discharge capacities of these electrode materials by constant-current polarization in PC/LiClO₄ electrolyte as a typical Li salt electrolyte solution (The mass of BC₂N; 85 mg, Current; 15 mA g-BC₂N⁻¹). Cut-off potentials were 0 V for charging and 3 V for discharging. The discharge capacity decreased in the order of BC₂N (1500 °C) > (1000 °C) > (2000 °C) throughout any cycle number as shown in Fig. 3. The high capacities for BC₂N (1500 °C) and BC₂N (1000 °C) may be ascribed to the larger surface area (shown in Fig. 1) and the relatively large interlayer spacing (indicated in Fig. 2), the latter of which facilitates the intercalation/deintercalation of Li. However, the reason why BC₂N (1500 °C) showed the

Fig. 1 SEM photographs of BC_2N treated at various temperature.

Fig. 2 Variations of interlayer spacing $d(002)$ and the crystallite size in the c -axis direction with heat-treatment temperature for the synthesis of BC_2N .

Fig. 3 Cycle dependence of discharge capacities in PC solution containing $1 \text{ mol dm}^{-3} \text{LiClO}_4$.
 ○ : 1000 °C △ : 1500 °C □ : 2000 °C.
 Cut-off potential : 0 ~ 2 V, The amount of $\text{BC}_2\text{N}(1500^\circ\text{C})$ is 85 mg, $i = 15 \text{ mA g}^{-1}$.

maximum discharge capacity cannot be fully explained by such factors as the surface area and the interlayer spacing. In order to clarify this point, we investigated the other electrochemical properties as described below.

First, we examined which electrolytic salt facilitates large current response during the potential sweep of the BC_2N electrode. In this test, BC_2N (1500°C) was applied to the electrode active material on behalf of three types of BC_2N prepared at the different temperatures. Figure 4 shows CV curves for BC_2N (1500°C) in PC containing 1 mol dm^{-3} LiClO_4 , LiPF_6 , and LiBF_4 . The CV curves at

Fig.4 Cyclic voltammograms of BC_2N (1500°C) electrode in PC containing 1 mol dm^{-3} various electrolyte.
Scan rate : 1 mV s^{-1} ,
Dashed line : 1st cycle, Solid line : 10th cycle.

1st cycles were different from those at the subsequent cycles. After the 2nd cycles, the shape of the curves did not change much. The curves at the 10th scans are representatives of the steady-state relations after ca. 5th scans. The cathodic currents, increasing at 1.0 V (vs. Li/Li^+) or below, are mainly based on the electrochemical intercalation of Li into the BC_2N matrix^{14,15}. The anodic currents with broad peak at ca. 1.5

V (vs. Li/Li^+) are accompanied by deintercalation of Li from the matrix^{14,15}. Judging from the response of the intercalation/deintercalation depending on the electrolytic salts, LiClO_4 and LiPF_6 may be suitable for electrolytic salts in the system involving BC_2N electrode. We applied LiClO_4 to the electrolytic salt in all the following measurements.

The open circuit potential of the Li -intercalated BC_2N heat-treated at the different temperatures (1000 , 1500 , and 2000°C) was measured after the polarization under a constant current in PC containing LiClO_4 (The mass of BC_2N ; 30 mg , Current; $40\text{ mA g-BC}_2\text{N}^{-1}$). Figure 5 shows the variations of the potential with the electrode composition, x in $\text{Li}_x(\text{BC}_2\text{N})$, which is calculated from the quantity of electrical charge passed. The electrode potential showed a steady-state value within about 10 min after the electrical circuit was open. As shown in Fig. 5, the steady-state open circuit potentials of BC_2N treated at 1000°C and 1500°C decreased gradually with increasing x in the composition.

Fig.5 Relationship between open circuit potential and lithium content in BC_2N .

Electrolyte solution : 1 mol dm^{-3} LiClO_4/PC ,
The amount of BC_2N is 30 mg , $i = 40\text{ mA g}^{-1}$,
 $\circ$: 1000°C $\triangle$: 1500°C $\square$: 2000°C .

On the other hand, the potential composition curve of BC_2N treated at 2000°C showed a plateau at about 1.2 V vs. Li/Li^+ when $x > 0.1$. It is widely known that the open circuit potentials of Li-intercalated compounds decrease and approach 0 V vs. Li/Li^+ in the process of Li-intercalation into the compounds. Therefore, the variation in the potential of BC_2N (2000°C) suggests that Li-intercalation into BC_2N (2000°C) matrix may not satisfactorily proceed probably because electricity passed would be spent upon the reductive side reaction on the electrode. In fact, it was observed that the cathodic polarization of BC_2N (2000°C) resulted in some covering products. Hence, it is supposed that the real composition of $\text{Li}_x(\text{BC}_2\text{N})$ (2000°C) was deviated from the calculated one represented in Fig. 5,

Focusing on the diffusivity of Li in the electrodes, we measured the AC impedance of the $\text{Li}_x(\text{BC}_2\text{N})$ electrodes in PC containing LiClO_4 under an open circuit condition after different quantities of electrical charge passed. The diffusivity of Li in the electrode can be estimated from Warburg impedance (Z_w) as an impedance component¹⁸⁾. The relation between Warburg impedance (Z_w) and the chemical diffusion coefficient (D) are expressed by Eqs. (2) and (3)¹⁸⁾.

$$Z_w = A\omega^{-1/2} \quad (2)$$

$$A\omega = V_m(dE/dx)/zFAD^{1/2} \quad (3)$$

In the equations, $A\omega$ is Warburg factor, ω the angular frequency of AC, V_m the molar volume of the electrode, (dE/dx) the slope of the open circuit potential with the composition, z the valence of the diffusion species, F the Faraday constant, and A the geometric surface area of the electrode (1.33 cm^2). The slopes of the Z_w vs. $\omega^{-1/2}$ plot and the potential-composition curve (Fig 5) give $A\omega$ and (dE/dx) , respectively. Using Eq. (3), therefore, the D value of Li in $\text{Li}_x(\text{BC}_2\text{N})$ can be determined. Furthermore, the diffusivity of Li, or the

Fig. 6 Variations in the component diffusion coefficients of Li (D_{Li}) in $\text{Li}_x(\text{BC}_2\text{N})$ at 298 K .

Electrolyte solution : $1\text{ mol dm}^{-3}\text{ LiClO}_4/\text{PC}$,
 $\circ$: 1000°C $\triangle$: 1500°C $\square$: 2000°C .

component diffusion coefficient of Li, D_{Li} is derived from the following relation¹⁹⁾.

$$D = -D_{\text{Li}}(F/RT) \times (dE/dx) \quad (4)$$

The diffusivity is generally equivalent to the self diffusion coefficient in a solid that is independent on the concentration of the species in question¹⁹⁾.

Figure 6 shows the component diffusion coefficient of Li (D_{Li}) in the BC_2N electrodes as a function of the electrode composition. The D_{Li} values of BC_2N (1000 and 1500°C) were almost independent of the electrode composition, x . The effect of the heat-treatment temperature on the diffusivity of Li was significant in the present systems. The D_{Li} values of BC_2N (2000°C) were very low in the range between 10^{-12} and $10^{-13}\text{ cm}^2 \text{s}^{-1}$. These values of BC_2N (2000°C) may include uncertainty because the x values are supposed to deviate from the corresponding true values as described in the interpretation of Fig. 5. On the other hand, two types of BC_2N (1000 and 1500°C) showed high D_{Li} values in the range between 10^{-10} and $10^{-11}\text{ cm}^2 \text{s}^{-1}$. Especially, BC_2N (1500°C) showed

Fig.7 XRD patterns of BC_2N electrodes before and after cycle in $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{PC}$.
Cut-off potential : 0 ~ 3 V, The amount of BC_2N is 30 mg , $i = 40 \text{ mA g}^{-1}$.

the highest diffusivities of all (*ca.* $10^{-10} \text{ cm}^2 \text{ s}^{-1}$). These were about 10 times higher than that in the system involving BC_2N (1000°C), and were comparable to those reported for carbon black electrodes (*ca.* $D_{\text{Li}} = 10^{-10}$ - $10^{-9} \text{ cm}^2 \text{ s}^{-1}$)²⁰) and for carbon fiber electrodes with a graphite structure (*ca.* $D_{\text{Li}} = 10^{-11}$ - $10^{-10} \text{ cm}^2 \text{ s}^{-1}$)²¹). Thus, the highest discharge capacity of BC_2N (1500°C) as shown in Fig. 3 may be ascribed to the facile diffusion of Li in BC_2N (1500°C) matrix.

Good charge/discharge behavior of BC_2N (1000°C and particularly 1500°C) were also observed for the XRD measurements which

indicated the variation of interlayer spacing of BC_2N during charge/discharge tests. Figure 7 shows that XRD patterns of the (002) plane corresponding to the interlayer distance of BC_2N (The mass of BC_2N was 30 mg .) before and after charge/discharge cycles. The charge/discharge current density was $40 \text{ mA g-BC}_2\text{N}^{-1}$ and cut-off potentials were 0 and 3.0 V. Although the height of peaks decreased after several charge/discharge cycling somewhat for BC_2N (1500°C) and considerably for BC_2N (1000°C), the cycling essentially kept the original profiles of the peaks. Further, the peak shifted slightly to the

negative direction of 2 θ corresponding to the expansion of the interlayer spacing when BC₂N (1500 °C) was charged to 0 V vs. Li/Li⁺. These results suggest that considerably reversible intercalation/deintercalation of Li caused in BC₂N (1000 °C) and in BC₂N (1500 °C).

On the basis of these results, we found that BC₂N (1500 °C) has favorable properties with respect to the capacity and cycleability during charging and discharging. Then, we tried to improve the capacity and the efficiency of BC₂N (1500 °C) using PC-DME and EC-DME solutions as electrolytes.

Figure 8 shows cycle dependence of charge and discharge capacity for the BC₂N (1500 °C; The mass of BC₂N was 10 mg.) in PC-DME (1:1 mixture by volume) and EC-DME (1:1 mixture by volume) containing 1 mol dm⁻³ LiClO₄. The current density in this experiment was 30 mA g⁻¹. The first charge capacity for the EC-DME system was ca. 300 mAh g⁻¹. The quantity of electricity passed during first charge in EC-DME gave a theoretical intercalation level of $x = 0.55$ for Li_x(BC₂N), which corresponds to $x' = 0.74$ for Li_xC₆ of graphite intercalation compounds with respect to the capacity per weight. The charge and discharge capacities of this BC₂N in EC-DME were higher than those in PC-DME. However, these capacities decreased gradually with an increase in cycle number.

In the present study, we have demonstrated the factors affecting the capacity such as the grain size, the interlayer spacing, the crystallinity, and the Li diffusivity. The high capacities for BC₂N (1500 °C) and BC₂N (1000 °C) would be ascribed to the larger surface area and the relatively large interlayer spacing. The highest discharge capacity of BC₂N (1500 °C) would be due to the high diffusivity (*ca.* 10⁻¹⁰ cm² s⁻¹) which corresponds to the facile diffusion of Li in BC₂N (1500 °C) matrix. Although the reason why BC₂N (1500 °C) has the highest diffusivity has been not fully understood, one of the reasonable explanations is as follows.

Fig.8 Cycle dependence of charge and discharge capacities in various solutions containing 1 mol dm⁻³ LiClO₄.
 ● : Charge in EC-DME, ○ : in PC-DME,
 ▲ : Discharge in EC-DME, △ : in PC-DME,
 Cut-off potential : 0 ~ 2 V, The amount of BC₂N(1500 °C) is 10 mg, $i = 30$ mA g⁻¹.

In general, high temperature treatment leads to the development of high-oriented layer ordering of the crystallite, which facilitates the Li diffusion, even if the crystallite size is independent of the treatment temperature^{22,23}). However, at the same time, the high temperature treatment decreases the interlayer spacing (Fig. 2), resulting in the limitation of the Li diffusion. In this context, moderate temperature treatment (1500 °C) would promise both the relatively high-oriented layer ordering of crystallite and the large interlayer spacing.

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