A new negative electrode matrix, BC$_2$N, for rechargeable lithium batteries

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Abstract

A new layered-structure compound, BC$_2$N, has been synthesized by a vapor-phase reaction of CH$_3$CN and BCl$_3$. The electrochemical behavior of BC$_2$N as a negative electrode matrix of a rechargeable lithium battery was investigated in organic electrolyte solutions containing lithium salts. Cyclic voltammetry and X-ray diffraction analysis showed that the electrochemical intercalation/deintercalation of lithium in the BC$_2$N electrode is applicable to the negative electrode reaction for a rechargeable battery with a high-energy density. A thermal treatment after the BC$_2$N synthesis drastically changed the crystal structure of BC$_2$N and the electrochemical charge/discharge characteristics in propylene carbonate-based electrolytes. A 100% coulombic efficiency was obtained for the BC$_2$N electrode treated at 1500 °C.

Introduction

One of the key issues for rechargeable lithium (Li) batteries with high electric capacities is high coulombic efficiency for charge/discharge cycles of the Li negative electrode in nonaqueous electrolytes. The use of Li alloys instead of metallic Li improves the cycleability of the electrode, but causes decreases in the capacity and energy density. Some carbon materials can take alkali metals in their graphite structure to form graphite-intercalation-compounds (GICs). Such an intercalation process can be utilized for the battery electrode. The light weight of carbon materials is advantageous for high-energy density. Thus, much attention has been directed to the electrochemical Li intercalation/deintercalation of carbon materials in organic media [1–5]. Some prototypes of rechargeable Li batteries with carbon electrodes have so far been demonstrated [6–8].

Graphite interacts with alkali metal so strongly that a part of the intercalated Li tends to be left in the layered structure during the electrochemical discharge. On the other hand, hexagonal boron nitride (h-BN), which has also a graphite-like structure but is an insulator, exhibits little interaction with alkali metals. Thus, it must be very interesting to note how layered-structure compounds consisting of a B–C–N system behave electrochemically in organic solutions. We have synthesized a new inorganic

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compound, BC$_2$N, which has a graphite-like structure with light atoms, and attempted to use it for the negative electrode matrix of a rechargeable Li battery [9]. In this paper, we report fundamental charge/discharge behavior of the Li negative electrode with a BC$_2$N matrix in propylene carbonate (PC)-based organic electrolytes. Also, the effects of crystalization for BC$_2$N on the electrochemical behavior is discussed. Utilization of this material in practical batteries will be demonstrated.

Experimental

BC$_2$N was synthesized by a chemical vapor deposition (CVD) method proposed first by Kouvetakis *et al.* [10]. Acetonitrile (CH$_3$CN) and boron trichloride (BCl$_3$) were reacted in a vapor phase at 1000 °C:

$$CH_3CN + BCl_3 \longrightarrow BC_2N + 3HCl \qquad (1)$$

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 working electrode was prepared by mixing the BC$_2$N powder with poly(tetrafluoroethylene) (PTFE) as a binder followed by molding to form a tablet (diameter: 13 mm or 16 mm). A beaker-type three-electrode cell was used for cyclic voltammetry (CV) — the mass of BC$_2$N used was 85 mg. The counter and the reference electrodes were a large surface area Li sheet and a Li chip, respectively. A bobbin-type (cylindrical) cell with a Li disk counter electrode was used for measuring the basic charge/discharge behavior of Li at the BC$_2$N electrode matrix — the mass of BC$_2$N used was 51.5 mg. Propylene carbonate (PC) and a 1:1 mixture (by volume) of PC and 1,2-dimethoxyethane (DME) were used as the solvents of the electrolyte solutions. Vacuum-dried LiClO$_4$, LiBF$_4$ and LiPF$_6$ were mainly used as the salts. The electrochemical measurements were carried out under a dry argon atmosphere at room temperature (18 to 24 °C).

Results and discussion

The chemical composition of the product obtained by eqn. (1) was determined by elemental analysis and found to be almost consistent with stoichiometric BC$_2$N. The X-ray diffraction (XRD) pattern of the prepared BC$_2$N powder shows broad peaks that are typical of a layered structure like small particle graphite. The average interlayer spacing, Co/2, of BC$_2$N was 0.354 nm, which was slightly larger than that of natural graphite (0.335 nm). The real atomic configuration of B, C and N in a basal plane of the layered structure has not been clear yet. However, a possible arrangement of the atoms in the basal plane is schematically represented as Fig. 1, which is the most symmetric one.

A comparison of the XRD patterns of the BC$_2$N powder heat-treated at different temperatures is shown in Fig. 2. The crystallinity was drastically changed by the heat treatment. The powder treated at higher temperature tended to have higher crystallinity. However, the treatment at 2000 °C led to the formation of another phase, which may be boron carbide. The electrical resistivity of the BC$_2$N tablet pressed with a PTFE binder was ranged from 1 to 10 Ω m. The effect of the heat-treating temperature on the resistivity of the tablet was rather small.
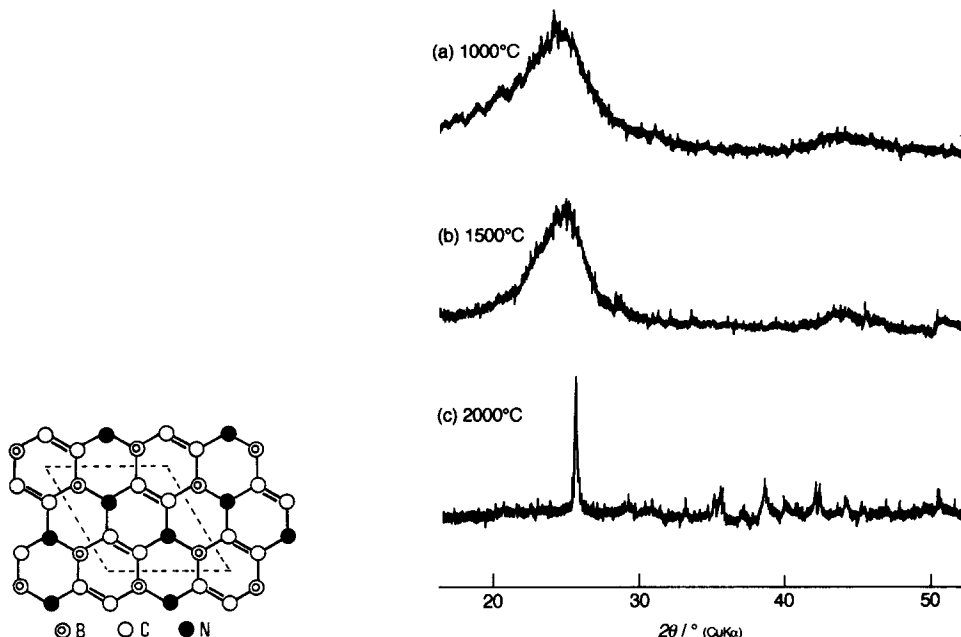
Fig. 1. A possible configuration of atoms in the basal plane of BC_2N.

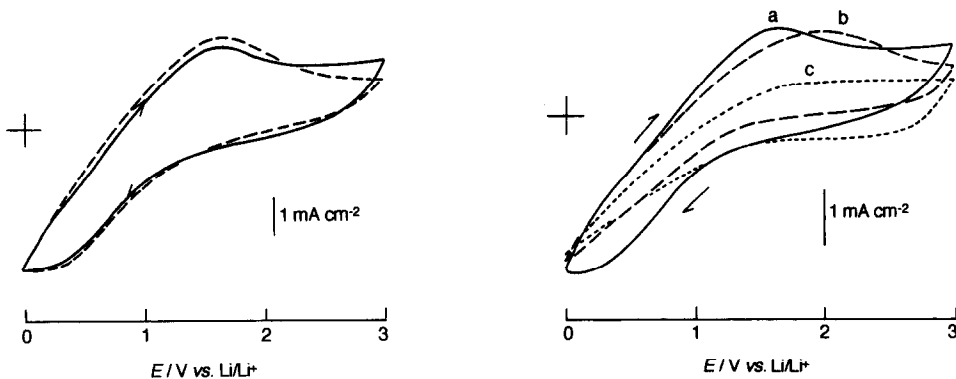Fig. 2. XRD patterns of BC_2N powder heat-treated at different temperatures.

Fig. 3. Cyclic voltammograms of BC_2N electrodes in PC (solid line) and PC + DME (dashed line) containing 1 M $LiClO_4$; scan rate: 1 mV s^{-1}, heat treatment at 1000 °C.

Fig. 4. Cyclic voltammograms of BC_2N electrodes in PC containing 1 M $LiClO_4$; scan rate: 1 mV s^{-1}, heat treatment at (a) 1000 °C, (b) at 1500 °C, and (c) at 2000 °C.

Figure 3 shows CV curves for BC_2N electrode, heat treated at 1000 °C , in PC (solid line) and PC + DME (1:1 mixture, dashed line) dissolving 1 M $LiClO_4$ (scan rate: 1 mV s^{-1}). The cathodic currents, increasing at 1.0 V (versus Li/Li$^+$) or below, are mainly based on the electrochemical intercalation (or doping) of Li into the BC_2N matrix. The anodic currents with broad peaks at ~1.5 V are accompanied by

deintercalation (or undoping) of Li from the matrix. These electrochemical processes are formulated as eqn. (2):

$$BC_2N + xLi^+ + xe^- \longrightarrow Li_x(BC_2N) \qquad (2)$$

where x denotes the doping level of Li in BC_2N ($0 \leqslant x \leqslant 4/6$). The effect of DME blending in the electrolyte solvent was rather small on the CV characteristics in the solutions containing $LiClO_4$. However, the reaction rate of intercalation/deintercalation depended on the electrolytic salt. The DME blending in the solvent was effective to improve the reaction rates in the solutions containing $LiBF_4$ and $LiPF_6$.

In Fig. 4, CV curves for BC_2N treated at different temperatures are compared with each other. The BC_2N electrode with 1500 °C treatment showed almost the same CV curve as that for the electrode with 1000 °C treatment, whereas the electrode with 2000 °C treatment gave only low currents during anodic and cathodic scans. This is probably because of disturbance of Li intercalation into the BC_2N phase by the other phase formed during the heat treatment.

Utilization of the Li intercalation/deintercalation process in the BC_2N matrix was examined for the battery reaction by a bobbin-type cell consisting of a BC_2N working and a Li counter electrodes (BC_2N/Li). Figure 5 shows typical voltage–time curves of the cell containing $LiClO_4$/PC electrolyte. The cathodic intercalation of Li into BC_2N corresponds to the charging process for the negative electrode, and the anodic deintercalation means the discharge of the electrode. The quantity of electricity passed for 330 h charging gives a theoretical intercalation level of $x = 0.58$ for $Li_x(BC_2N)$. This is approximately equivalent to the value of a stoichiometric GIC (C_6Li). The open-circuit voltage (OCV) of charged BC_2N, $x = 0.58$ in $Li_x(BC_2N)$, was 0.47 V, and that of discharged BC_2N ($x = 0$) was 1.43 V. These OCV potentials are rather positive compared with those of usual GICs, but it suggests that the electrochemical intercalation of Li in BC_2N occurs more easily than that in natural graphite.

Detailed characteristics of Li intercalation/deintercalation in the BC_2N matrix are investigated using the beaker-type three-electrode cell. Figure 6 shows the potential–time curves of the BC_2N electrodes during the charge/discharge cycles. The current density in this experiment was relatively high (1.0 mA cm^{-2}), but the level of Li intercalation (doping) was rather low ($x = 0.015$) even after the 30 min charge. The heat treatment in the BC_2N preparation much affected the charge/discharge char-
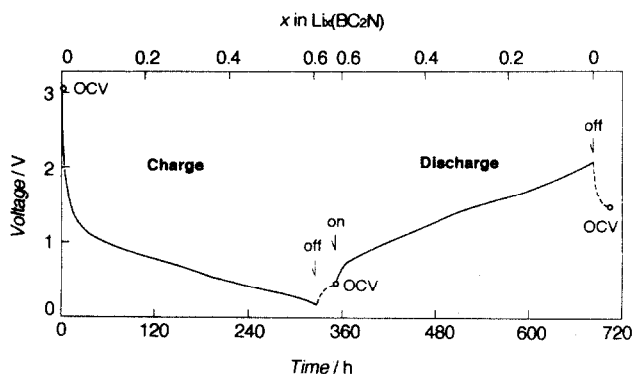

Fig. 5. Charge/discharge curves of BC_2N electrode in PC, containing 1 M $LiClO_4$; $i_{ch} = i_{dis} = 25~\mu A~cm^{-2}$; the amount of BC_2N: 51.5 mg.
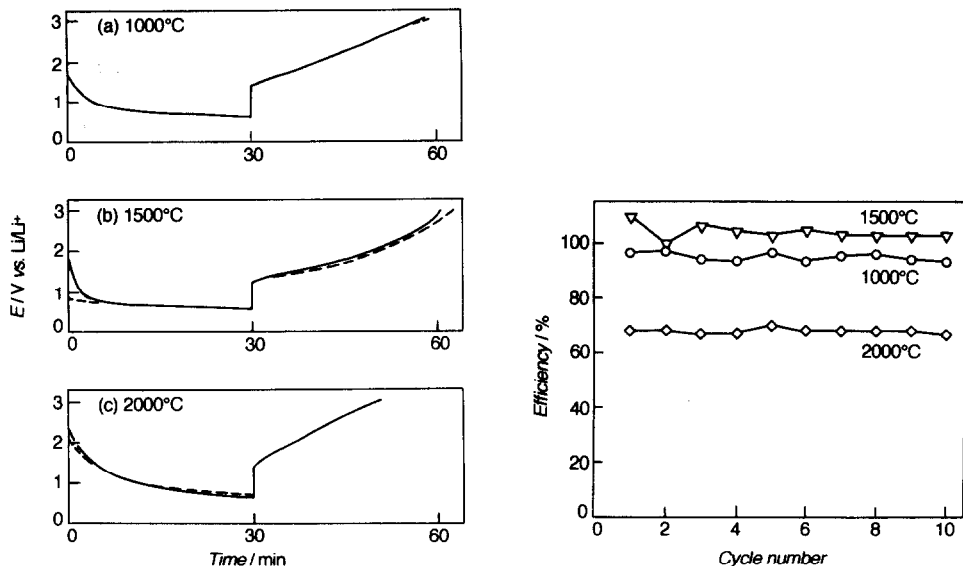
Fig. 6. Charge/discharge curves of BC_2N electrode in PC containing 1 M $LiClO_4$, at different temperatures; $i_{ch} = i_{dis} = 1.0$ mA cm^{-2}, $Q_{ch} = 1.8$ C cm^{-2}; dashed line: 1st cycle, solid line: 10th cycle; the amount of BC_2N: 85 mg.

Fig. 7. Coulombic efficiency for charge/discharge cycling of BC_2N electrode in PC containing 1 M $LiClO_4$: $i_{ch} = i_{dis} = 1.0$ mA cm^{-2}, $Q_{ch} = 1.8$ C cm^{-2}; the amount of BC_2N: 85 mg.

acteristics. The electrode using BC_2N heated at 1500 °C showed the lowest potential difference between the charge (intercalation) and discharge (deintercalation) processes. The electrode heated at 2000 °C revealed relatively short time for the discharge, suggesting that some side reaction proceeds during the charge and/or discharge processes. It is notable that there were only slight variations in the charge/discharge curves with repeated cycles. The XRD patterns of BC_2N showed slight changes in the crystal structure after the electrochemic, l Li intercalation. This would be advantageous to the practical use of BC_2N for rechargeable batteries.

The coulombic efficiency for cycling, Q(discharge)/Q(charge), is a measure of the rechargeability of the electrode. Figure 7 shows the variation of the efficiency with the cycle number. The efficiency for BC_2N heat-treated at 1000 or 1500 °C was about 95% or higher under this cycling condition, and did not show any degradation after repeated cycles. However BC_2N heat-treated at 2000 °C showed efficiencies less than 70%. These characteristics correspond to the results on the cyclic voltammetry of BC_2N heat-treated at different temperatures.

Acknowledgements

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