

Short Communication

# Boron–carbon–nitrogen compounds as negative electrode matrices for rechargeable lithium battery systems

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## Abstract

Boron–carbon–nitrogen composite (BC<sub>x</sub>N) matrices (BC<sub>3</sub>N, BC<sub>7</sub>N, and BC<sub>10</sub>N) for rechargeable lithium batteries are synthesized by a thermal decomposition method. BC<sub>10</sub>NLi<sub>0.5</sub> is prepared by the thermal decomposition of a mixture of the starting materials for BC<sub>10</sub>N and lithium hydroxide (LiOH). The charge/discharge behaviour of these layered-structure compounds is investigated in an organic electrolyte that contains lithium salts. The capacity increases with an increase in the carbon content. The LiOH treatment causes an increase in the discharge capacity of boron–carbon–nitrogen material.

*Keywords:* Negative electrodes; Boron; Carbon; Nitrogen; Rechargeable lithium batteries

## 1. Introduction

Considerable interest has been focused on the utilization of layered ‘pure’ carbon material, such as graphite, as a negative electrode matrix in secondary lithium (Li) batteries. Little is known, however, about the similar application of carbon-based layered material with other light atoms such as boron and nitrogen. The authors have synthesized a new inorganic compound, BC<sub>2</sub>N, that has a graphite-like structure and have reported its charge/discharge behaviour [1–3]. Recently, the electrochemical behaviour of some carbon–nitrogen (C–N) and carbon–boron (C–B) composite materials has been reported [4,5]. Although various boron–carbon–nitrogen (B–C–N) layered materials have been investigated [6–10], these compounds have not, to date, been applied to the negative electrode, except for the afore-mentioned BC<sub>2</sub>N compound.

This work examines the charge/discharge behaviour of BC<sub>x</sub>N ( $x = \sim 3, 7, \text{ and } 10$ ) and BC<sub>10</sub>NLi<sub>0.5</sub> as negative electrode matrices; the latter compound was prepared from a mixture of the starting materials for BC<sub>10</sub>N with lithium hydroxide (LiOH). It is considered that one of the causes for the decline in discharge capacity

may be the irreversible reaction of Li (ion) with active sites in the electrode material during charge/discharge. Thus, an attempt is made to inactivate these sites.

## 2. Experimental

BC<sub>x</sub>N was prepared by a thermal decomposition method [10] in an aqueous solution at 200 °C, or in a solid–gas phase at 400 °C. The reactions were followed by heat treatment at 1000 °C in a stream of nitrogen. On the other hand, BC<sub>10</sub>NLi<sub>0.5</sub> was prepared by thermal decomposition of BC<sub>10</sub>N with LiOH starting materials. The other conditions of this reaction were identical with those of the BC<sub>10</sub>N preparation. The actual compositions of the resulting BC<sub>x</sub>N and BC<sub>10</sub>NLi<sub>0.5</sub> were confirmed by chemical analysis and atomic absorption analysis. The reaction condition and the actual composition are summarized in Table 1. The structure of BC<sub>x</sub>N and BC<sub>10</sub>NLi<sub>0.5</sub> was characterized by X-ray diffractometry (XRD).

The electrochemical properties of the active materials, BC<sub>x</sub>N and BC<sub>10</sub>NLi<sub>0.5</sub>, were investigated in an organic electrolyte system. High-purity ethylene carbonate (EC) and 1,2-dimethoxyethane (DME) (Mitsubishi Chemical, battery grade) were used as the solvents of the electrolyte

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Table 1  
Composition and preparation conditions of various matrices

Matrix	Composition	Raw materials	Method (reaction temperature)
BC <sub>3</sub> N	BC <sub>3.0</sub> N <sub>0.95</sub>	BCl <sub>3</sub> , polyacrylonitrile	thermal decomposition (400 °C)
BC <sub>7</sub> N	BC <sub>6.8</sub> N <sub>0.7</sub>	BCl <sub>3</sub> , acrylonitrile/butadiene/styrene	thermal decomposition (400 °C)
BC <sub>10</sub> N	BC <sub>10</sub> N <sub>0.7</sub>	H <sub>2</sub> BO <sub>3</sub> , saccharose, urea	thermal decomposition (200 °C)
BC <sub>10</sub> NLi <sub>0.5</sub>	BC <sub>9.9</sub> N <sub>0.6</sub> Li <sub>0.44</sub>	H <sub>2</sub> BO <sub>3</sub> , saccharose, urea, LiOH	thermal decomposition (200 °C)

solution. Lithium perchlorate, LiClO<sub>4</sub>, (Ishizu Pharmaceutical, extra pure grade) was used as the electrolytic salt after drying.

The working electrode was prepared by mixing the active material powder with 10 wt.% poly(tetrafluoroethylene) as a binder, followed by moulding under pressure to form a tablet (diameter: 13 mm). A beaker-type three-electrode cell was used for cyclic voltammetry (CV) and open-circuit potential measurement. The counter and reference electrodes were a large surface area Li sheet and an Li chip, respectively. A beaker-type, two-electrode cell with an Li sheet as the counter electrode was used for charge/discharge cycling. The coulombic efficiency ( $E_{ff}$ ) to cycling can be defined as:

$$E_{ff} = (Q_{dis}/Q_{ch})100\% \quad (1)$$

where  $Q_{dis}$  and  $Q_{ch}$  are the quantities of electrochemical charge passed for discharging and charging, respectively. The electrochemical measurements were carried out under a dry argon atmosphere at room temperature (20 to 25 °C).

### 3. Results and discussion

The structures of BC<sub>x</sub>N and BC<sub>10</sub>NLi<sub>0.5</sub> were characterized by X-ray diffractometry (XRD), as shown in Fig. 1. These materials display a partly disordered, quasi-layered structure. The crystallinity of these materials is somewhat dependent on the preparation temperature. The matrices can be classified into two groups as follows: (i) BC<sub>3</sub>N and BC<sub>6</sub>N (thermal decomposition at 400 °C) and (ii) BC<sub>4</sub>N, BC<sub>10</sub>N, and BC<sub>10</sub>NLi<sub>0.5</sub> (thermal decomposition at 200 °C). The crystallinity decreased with a decrease in the decomposition temperature. Since no diffraction peak of Li compounds such as Li<sub>2</sub>O and Li<sub>2</sub>CO<sub>3</sub> was observed for BC<sub>10</sub>NLi<sub>0.5</sub>, Li may be bonded to the surface of BC<sub>10</sub>N crystallites.

Fig. 2 shows CV curves for BC<sub>x</sub>N and BC<sub>10</sub>NLi<sub>0.5</sub> in EC–DME (1:1 mixture by volume) containing 1 M LiClO<sub>4</sub>. The CV curves for the first cycle were different from those obtained during subsequent cycles. The curves for the tenth cycle are representative of the steady-state relations. The cathodic currents are mainly based on the electrochemical intercalation of Li into

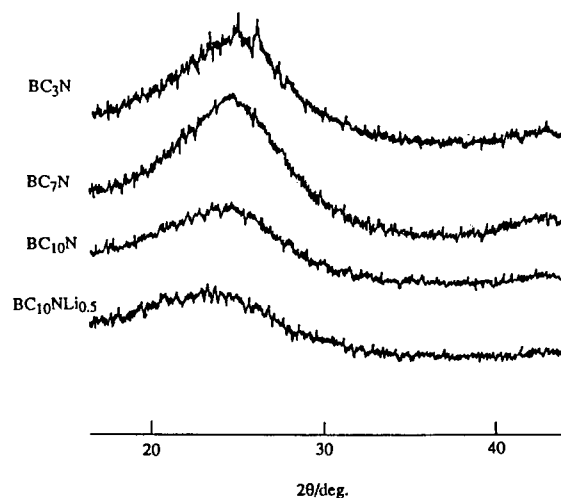


Fig. 1. XRD patterns for various electrodes.

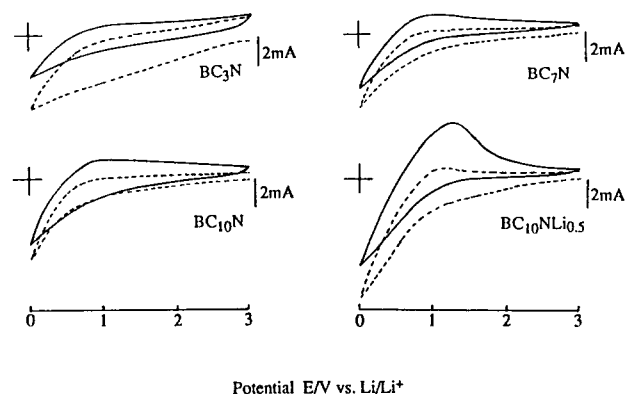


Fig. 2. Cyclic voltammograms for various electrodes in EC–DME (1:1 by volume) with 1 M LiClO<sub>4</sub>, scan rate = 1 mV s<sup>-1</sup>; (---) first cycle, and (—) tenth cycle.

the B–C–N matrix [1–3]. The anodic currents are accompanied by the de-intercalation of Li from the matrix [1–3]. An anodic current peak was observed at about 1 V (versus Li/Li<sup>+</sup>) for BC<sub>10</sub>N and BC<sub>7</sub>N electrodes. By contrast, no anodic current peak was observed for BC<sub>3</sub>N; the anodic current increased with increase in the voltage. Judging from the results of the CV measurements, the Li intercalation/de-intercalation takes place in the high voltage region when the carbon content in the matrices decreases. Furthermore, both the anodic and cathodic currents were highest in the case of the BC<sub>10</sub>NLi<sub>0.5</sub> electrode; the current response for

$BC_{10}NLi_{0.5}$  was superior to that for  $BC_{10}N$  which resembles  $BC_{10}NLi_{0.5}$  in composition but no in Li content. It is thought that one of the causes for degradation in discharge capacity may be the irreversible reaction of Li (ion) with active sites in the electrode material during charge/discharge. Treatment of raw materials for  $BC_{10}N$  with LiOH may inactivate these sites and, thereby, stabilized the discharge capacity.

The open-circuit potential of the various Li-intercalated matrices was measured after polarization under a constant current in EC–DME (1:1 by volume) that contained 1 M  $LiClO_4$ . Fig. 3 shows the variations of the potential with electrode composition,  $x$  in  $M_6Li_x$ , which was calculated from the quantity of electrical charge that was passed.  $M$  represents the atoms (B, C, and N) making up the matrix; for example, in the case of  $BC_3N$ ,  $M_6Li_x$  corresponds to  $B_{6/5}C_{18/5}N_{6/5} \cdot Li_x$ . The electrode potential exhibited a steady-state value within about 10 min after the electrical circuit was opened. The steady-state, open-circuit potentials of all the matrices decreased gradually with increasing  $x$  in the composition. Roughly speaking, the plateau potential in the potential variation decreased with an increase in carbon content in the matrices.

Fig. 4 shows the cycle dependence of the discharge capacities of the matrices during charge/discharge cycles

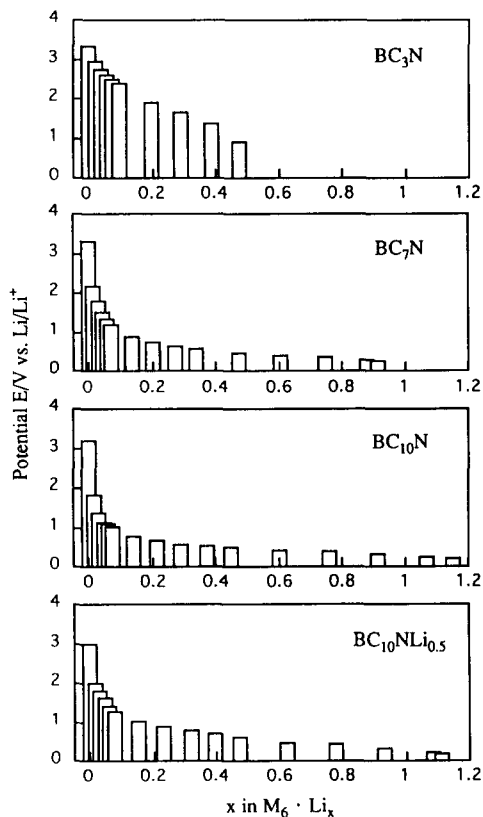


Fig. 3. Relationship between open-circuit potential and lithium content for various electrodes in EC–DME (1:1 by volume) with 1 M  $LiClO_4$ ; current density = 1.0 mA/cm<sup>2</sup>; mass of active material = 30 mg.

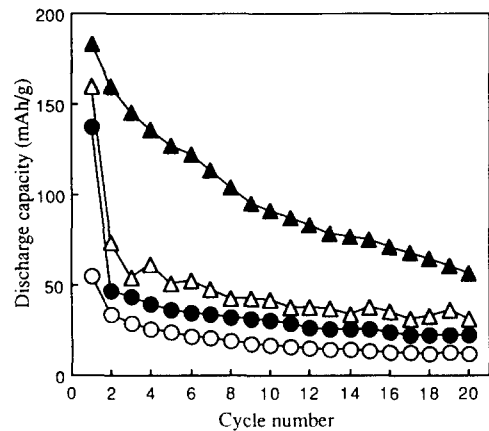


Fig. 4. Cycle dependence of discharge capacity in EC–DME (1:1 by volume) with 1 M  $LiClO_4$ ; current density = 0.3 mA/cm<sup>2</sup>; cutoff potential = 0 V (charging), and 3 V (discharging). (○)  $BC_3N$ ; (●)  $BC_7N$ ; (△)  $BC_{10}N$ , and (▲)  $BC_{10}NLi_{0.5}$ .

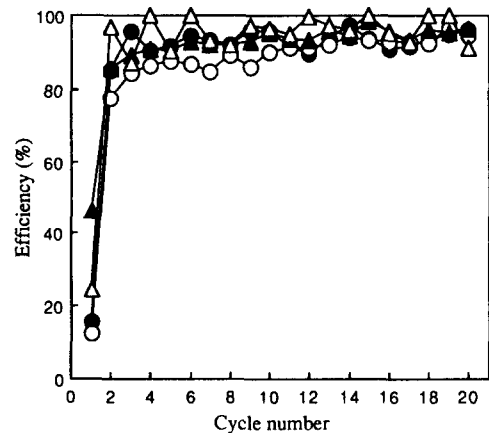


Fig. 5. Cycle dependence of coulombic efficiency in EC–DME (1:1 by volume) with 1 M  $LiClO_4$ ; current density = 0.3 mA/cm<sup>2</sup>; cutoff potential = 0 V (charging), and 3 V (discharging). (○)  $BC_3N$ ; (●)  $BC_7N$ ; (△)  $BC_{10}N$ , and (▲)  $BC_{10}NLi_{0.5}$ .

(the mass of B–C–N·Li) material was 30 mg) in EC–DME (1:1 by volume) that contained 1 M  $LiClO_4$ . The current density was 0.3 mA cm<sup>-2</sup>, and the cutoff potentials were 0 V for charging and 3 V for discharging. The order of the capacity was  $BC_{10}N > BC_7N > BC_3N$  with respect to the  $BC_xN$  matrices. The discharge capacity of  $BC_{10}NLi_{0.5}$  was highest throughout cycling. Treatment of raw materials for  $BC_{10}N$  with LiOH may be effective in increasing the capacity. The coulombic efficiencies in the above test are given in Fig. 5. After the second cycle, the efficiencies of the matrices were maintained above 80%. The discharge capacities of various matrices at first and twentieth cycles in the test are summarized in Table 2 with the corresponding charge capacities. Both the charge and discharge capacities on the first cycle increased approximately with an increase in the carbon content. On the twentieth cycle, the order of charge and discharge capacity dependent upon the carbon content did not change,

Table 2

Charge and discharge capacity of various matrices on first and twentieth cycles, electrolyte: EC–DME (1:1 by volume) with 1 M LiClO<sub>4</sub>; current density=0.3 mA/cm<sup>2</sup>; cutoff potential=0 V (charging), and 3 V (discharging)

Materials	1st cycle		20th cycle	
	Charge (mAh/g)	Discharge (mAh/g)	Charge (mAh/g)	Discharge (mAh/g)
BC <sub>3</sub> N	430	54	12	12
BC <sub>7</sub> N	600	138	24	22
BC <sub>10</sub> N	654	160	34	31
BC <sub>10</sub> NLi <sub>0.5</sub>	398	184	58	56

although each capacity was lower than that for the first cycle. BC<sub>10</sub>NLi<sub>0.5</sub> displayed the highest charge and discharge capacities on the first and twentieth cycles, except for the charge capacity on the first cycle.

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