— Communication —

Electrochemical Behavior of BC_{10}N and $\text{BC}_{10}\text{N-Li}_{0.44}$ as Negative Electrode Matrices for Secondary Lithium Batteries

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1 INTRODUCTION

Considerable interest has so far been focused on the utilization of layered "pure" carbon material such as graphite for a negative electrode matrix in secondary lithium (Li) batteries. However, little is known about the application of carbon-based layered material with other light atoms such as boron and nitrogen to the negative electrode. We synthesized new inorganic compound, BC_2N , which has a graphite like structure and reported its charge/discharge behavior¹⁻³). Although various B/C/N layered materials have been reported⁴⁻⁸), these compounds have not so far been applied to the negative electrode except for the BC_2N compound.

We report herein the charge/discharge behavior of BC_{10}N and $\text{BC}_{10}\text{N-Li}_{0.44}$ as negative electrode matrices; the latter compound ($\text{BC}_{10}\text{N-Li}_{0.44}$) was prepared by the thermal decomposition of the mixture of starting materials for BC_{10}N and lithium hydroxide (LiOH).

2 EXPERIMENTAL

BC_{10}N ($\text{BC}_{10}\text{N-I}$) was prepared by a thermal decomposition method⁸); saccharose, boric acid, and urea were reacted in aqueous solution at 200 °C, and this reaction was followed by heat treatment at 1000 °C in a stream of N_2 . On the other hand,

$\text{BC}_{10}\text{N-Li}_{0.44}$ ($\text{BC}_{10}\text{N-II}$) was prepared by thermal decomposition of the above-mentioned starting materials and LiOH. The other conditions of this reaction were identical with those of $\text{BC}_{10}\text{N-I}$ preparation. The compositions of the resulting $\text{BC}_{10}\text{N-I}$ and $\text{BC}_{10}\text{N-II}$ were confirmed by chemical analysis and atomic absorption analysis. The structure of $\text{BC}_{10}\text{N-I}$ and $\text{BC}_{10}\text{N-II}$ was characterized by X-ray diffractometry (XRD) as shown in Fig. 1. Both $\text{BC}_{10}\text{N-I}$ and $\text{BC}_{10}\text{N-II}$ showed a partly disordered quasi-layered structure: the respective interlayer spacings were 3.6 Å and 3.7 Å, and the widths of half-height (002) were 9.3° and 10.6°, respectively. Since no diffraction peak of Li compounds such as Li_2O and Li_2CO_3 was observed for $\text{BC}_{10}\text{N-II}$, Li may be bonded to the surface of BC_{10}N crystallites.

The electrochemical properties of the active materials ($\text{BC}_{10}\text{N-I}$ and $\text{BC}_{10}\text{N-II}$) were investigated in organic electrolyte systems. The working electrode was prepared by mixing the

Fig.1 XRD patterns of $\text{BC}_{10}\text{N-I}$ and $\text{BC}_{10}\text{N-II}$.

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BC₁₀N powder with 10 wt. % poly(tetrafluoroethylene) as the binder followed by molding under a pressure to form a tablet (13 mm ϕ). A beaker-type three-electrode cell was used for cyclic voltammetry (CV). 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 the counter electrode was used for charge/discharge cycling. High purity ethylene carbonate (EC), 1,2-dimethoxyethane (DME), and dimethyl carbonate (DMC) (Mitsubishi Petrochemical, Battery Grade) were used as the solvents of electrolyte solutions. Lithium perchlorate, LiClO₄, (Ishizu Pharmaceutical, Extra Pure Grade) and lithium trifluoromethanesulfonate, LiCF₃SO₃, (Morita Chemical Industries) were used for electrolytic salts after drying. The electrochemical measurements were carried out under a dry Ar atmosphere at room temperature (19-25 °C).

3 RESULTS AND DISCUSSION

Figure 2 shows CV curves for BC₁₀N-I and BC₁₀N-II in EC-DME (1:1 mixture by vol.) containing 1 mol dm⁻³ LiClO₄. The CV curves at the 1st cycle were different from those during the subsequent cycles. The curves at the 10th scan are

Fig.2 Cyclic voltammograms of BC₁₀N-I and BC₁₀N-II electrodes in EC-DME(1:1 by vol) containing 1 mol dm⁻³ LiClO₄. Scan rate : 1mV s⁻¹; Dashed line:1st cycle;Solid line:10th cycle.

representatives of the steady-state relations. The cathodic currents are mainly based on the electrochemical intercalation of Li into the B/C/N matrix¹⁻³). The anodic currents with broad peak at 1.0-1.3 V (vs. Li/Li⁺) are accompanied by the deintercalation of Li from the matrix¹⁻³). Judging from the response of the intercalation/deintercalation, BC₁₀N-II may be more suitable for the electrode matrix.

On the basis of these results, we can suppose that BC₁₀N-II has favorable properties with respect to the capacity during charging and discharging. Figure 3 represents the potential-time curves during charge/discharge cycles of BC₁₀N-I and BC₁₀N-II (The mass of B/C/N material was 10 mg.) in EC-DMC (1:1 mixture by vol.) containing 1 mol dm⁻³ LiCF₃SO₃. Recently, we reported that this electrolyte system may be suitable for the charge/discharge cycling of carbon-based electrode materials^{9,10}. The current density was 30 mA g⁻¹, and the cut-off potentials were 0 V for charging and 3 V for discharging. Figure 4 shows cycle dependence of the discharge capacities of BC₁₀N-I and BC₁₀N-II in these tests. The capacities of BC₁₀N-I and -II were somewhat larger than that of BC₂N, which was previously reported³), although respective electrolyte systems are not same. This

Fig.3 Charge/discharge curves of BC₁₀N-I and BC₁₀N-II electrodes in EC-DMC(1:1 by vol.) containing 1 mol dm⁻³ LiCF₃SO₃. Solid line:1st cycle;Dashed line:20th cycle.

Fig.4 Cycle dependence of discharge capacities in EC-DMC(1:1 by vol.) containing 1 mol dm⁻³ LiCF₃SO₃.

indicates that the BC₁₀N materials are usable as negative electrode matrices for rechargeable lithium batteries. The capacity of BC₁₀N-II was stable throughout cycling, while that of BC₁₀N-I decreased gradually. The interlayer spacing of BC₁₀N-II was slightly larger than that of BC₁₀N-I as shown in Fig. 1. Therefore, this expanded spacing of BC₁₀N-II may provide an increase in the stable discharge capacity. In addition, it is supposed that one of the origins of discharge capacity degradation may be irreversible reaction of Li (ion) with active sites in the electrode material during charge/discharge. Treatment of raw materials for BC₁₀N with LiOH may inactive these sites, stabilizing the discharge capacity; while this explanation has not been confirmed. At any rate, our method, *i.e.*, treating

raw materials for electrode matrix with LiOH, may be effective in increasing the stable capacity.

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REFERENCES

- 1) M. Morita, T. Hanada, H. Tsutsumi, Y. Matsuda and M. Kawaguchi, *J. Electrochem. Soc.*, **139**, 1227 (1991).
- 2) Y. Matsuda, M. Morita, T. Hanada and M. Kawaguchi, *J. Power Sources*, **43**, 75 (1993).
- 3) M. Ishikawa, M. Morita, T. Hanada, Y. Matsuda and M. Kawaguchi, *Denki Kagaku*, **61**, 1395 (1993).
- 4) J. Kouvetakis, R. B. Kaner, M. L. Sattler and N. Bartlett, *J. Chem. Soc., Chem. Commun.*, **1986**, 1758.
- 5) L. Maya, *J. Electrochem. Soc.*, **135**, 1278 (1988).
- 6) R. Riedel, J. Bill and G. Passing, *Adv. Mater.*, **3**, 551 (1991).
- 7) M. Kawaguchi, T. Kawashima and T. Nakajima, *Denki Kagaku*, **61**, 1403 (1993).
- 8) M. Hubáček and T. Sato, *J. Solid State Chem.*, in contribution.
- 9) M. Ishikawa, M. Asao, M. Morita, Y. Matsuda, T. Ijima and K. Suzuki, *Denki Kagaku*, **61**, 1317 (1993).
- 10) M. Ishikawa, M. Morita, M. Asao and Y. Matsuda, *J. Electrochem. Soc.*, **141**, 1105 (1994).