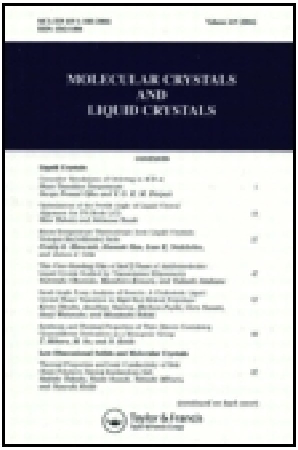

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Lithium Intercalation into BCN Alloy Derived from Pyridine-Borane Complex

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Pyridine-borane complex was synthesized by reaction of pyridine with borane-dimethyl sulfide complex. The pyridine-borane complex was used as a precursor for BCN alloy. The BCN alloy was fabricated by passing through a cross-linked pyridine-borane derivative obtained from the pyridine-borane complex by heating at 1273 K for 2 h in Ar. Turbostratic layered BCN alloy was prepared by the pyrolysis of the pyridine-borane derivative. Four coordination number of boron which was remained in both the complex and the derivative changed to three coordination number in the BCN ceramic alloy with a composition of B_2NC_4 obtained. Lithium insertion into this B_2NC_4 alloy has been attempted.

Keywords: Pyridine-borane complex; BCN alloy; Lithium battery electrode; discharge capacity; energy change for lithium insertion

INTRODUCTION

Rechargeable lithium (Li) ion batteries with carbon-based anode have been widely used. Higher Li discharge capacity of the anode materials with larger amount of Li ions has been expected. The research on new carbon-based materials attracts us to improve the anode discharge capacity for Li ion batteries. Boron-substituted carbons are well known to show a larger Li storage than that of carbon[1,2]. However, small amount of boron up to 2 wt% can be dissolved into carbon, in spite of the high-temperature heat treatment around 2300 K[3]. On the other hand, BCN ceramics with a large amount of boron and nitrogen content in the carbon have been derived from organo-borane complexes by Goto and Sasaki et al.[4, 5]. The present work has focused on the use of BCN alloy as anode material to improve Li discharge capacity, and on the Li insertion sites and energy change in the BCN alloy.

EXPERIMENTAL

A pyridine-borane complex of 0.2 mole (20 ml) and a 100 ml of xylene were poured into a flask and refluxed at 393 K for 24 h in an argon atmosphere, then a yellow solid was formed gradually. After that, xylene as a solvent was removed. The specimen obtained was milled (<75 μm) and pyridine-borane derivative was prepared. The powdered pyridine-borane derivative was heated at various temperatures in the range 573 to 1273 K for 2 h (heating rate, 250 K h^{-1}) in Ar (0.1 MPa; flow rate, 0.5 l min^{-1}) then BCN alloy was prepared. The structural change of the alloy was evaluated by FT-IR (Jasco; FT-IR 500), ^{11}B-NMR (JEOL; JNM-GX270), ^{13}C-NMR (Bruker; MSL400), X-ray diffraction (CuKα_1/ 40 kV/ 20 mA; 2θ=10 - 80 deg), gas chromatograph (Yanaco G3810; TCD; Column, Porapack N; carrier gas, He; flow rate, 50 ml min^{-1}).

Discharge experiments were performed in the following conditions: electrolyte/ solvent, 1 mole $LiClO_4$/ ethylene carbonate+ diethyl carbonate (1:1) solution; electrodes, Li metal and BCN alloy with acethylene black and polyfron moulding powder; potential, 0 to 4 V.

Semiempirical MO calculations based on MNDO (modified neglect of differential overlap)[6] method, were performed by using the semiempirical MO program MOPAC97[7]. The accuracy of the parameters in the MNDO method for C, B, N and Li atoms has been checked by performing ab initio Hartree-Fock calculations for the rather small model clusters $(BNB)_8C_{30}H_{18}$ and $C_{54}H_{18}$, for example, and their derivatives with 2 to 10 Li atoms insertion[8].

RESULTS AND DISCUSSION

BCN alloy formation process

The structure model of the BCN alloy formation process is shown in Fig. 1. Confirmed by FT-IR and ^{11}B-NMR, the stage 1 means an infusible process caused by

B-C and/ or C-N bonds formation at 393 K. The coordination number of boron in stage 1 is still 4. By thermal decomposition around 673 K, FT-IR showed C-H bonds disappearance, and gas chromatograph detected an exhaust of C_2H_4 and C_2H_6 gas from the precursor. The ^{11}B-NMR showed coexistence of 3 and 4 coordination number of boron, B-H bonds completely disappeared in stage 2. Passing through the stage 3 around 873 K, layered structure developed and ceramic formation process almost finished in stage 4 (1073 K). Layered $B_2N_1C_4$ alloy was obtained at 1073 K. The layered $B_2N_1C_4$ ceramic alloy contains trigonal coordination of boron and of carbon, and C=C double bonds. Large amount of boron can be substituted into layered carbon sheet accompanied with nitrogen addition.

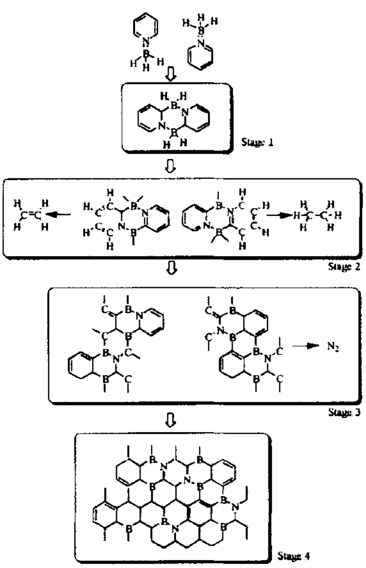

FIGURE 1 Structure model of BCN alloy.

Lithium discharge capacity

Figure 2 shows a Raman spectra of the pyridine-borane derivatives and BCN alloy. The spectra show a layered structure of the BCN alloy obtained at 1273 K. The chemical formula of the alloy obtained at 2173 K was $B_2N_1C_3$ with less carbon content than $B_2N_1C_4$ at 1073 K. The lower discharge capacity of 120 $mAhg^{-1}$ may be caused by lower carbon content.

The $B_2N_1C_4$ alloy obtained at 1073 K was heat-treated in the temperature range from 1273 to 2173 K. The chemical compositions are $B_2N_1C_{4.4}$ for 1273 K,

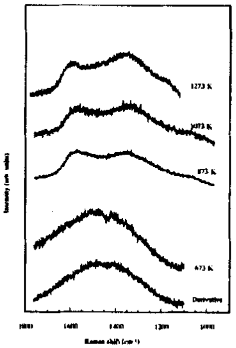

FIGURE 2 Raman spectra of pyridine-borane derivatives obtained in Ar.

$B_2N_{1.3}C_{4.8}$ for 1573 K, $B_2N_{1.4}C_{4.2}$ for 1773 K, $B_2N_1C_3$ for 2173 K, respectively. Figure 3 indicates the relationship between interlayer spacing and discharge capacity of BCN alloys derived from pyridine-borane complex in comparison with carbon. Decreasing of the interlayer spacing caused by crystallization, and increasing of the interlayer spacing caused by lower crystallinity increase the discharge capacity of carbon. The discharge capacity of the BCN alloys tend to be the same as carbon shown in Fig. 3. Li discharge capacity may follow the crystallinity and suitable carbon content in both cases. B_2NC_4 alloys tend to show one and half times as large as C at the same interlayer spacing conditions.

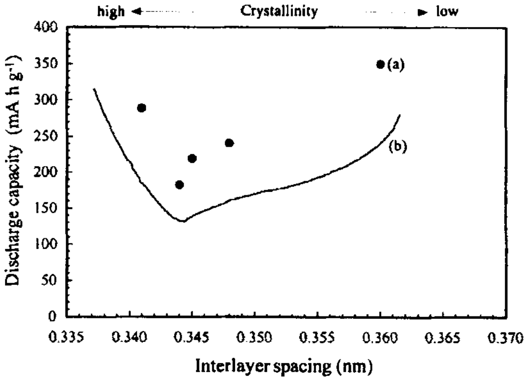

FIGURE 3 Relationship between interlayer spacing and discharge capacity of BCN alloys (a) derived from pyridine-borane in comparison with carbon (b).

MO calculations

In the previous study[8], the change in electronic properties and Li insertion energy of disordered carbons induced by boron or nitrogen substitution, by using a semiempirical molecular orbital (MO) method and model clusters such as $C_{24}H_{12}$, $C_{54}H_{18}$ and $C_{96}H_{24}$ has been reported. This investigation clarified that boron-substitution into disordered carbons creates an electron acceptor level in a lower energy region than that for the pristine disordered carbons. This lower-lying acceptor-level receives electrons from the inserted Li atoms more easily, so that the Li insertion energy for the boron-substituted disordered carbon is much larger than that for the pristine carbon. This result is consistent with the experimental result that boron-substituted carbons can store larger Li ions than a pristine carbon anode[1,2].

In the present study, we investigate the effect of substitution of BNB units

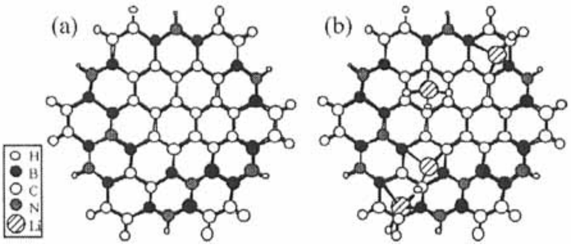

FIGURE 4 $(BNB)_8C_{30}H_{18}$ cluster (a) optimized, and Li_4-$(BNB)_8C_{30}H_{18}$ cluster (b) after Li intercalation.

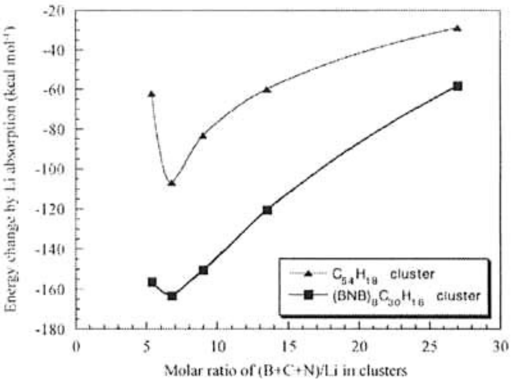

FIGURE 5 Calculated energy change by Li insertion as a function of (B+C+N)/Li ratio in the clusters.

into $C_{54}H_{18}$ sheet, considering the experimental result[9] that BNC ceramic alloys prepared from pyridine-borane complex have BNB units and a large amount of B content: the ratio of B, N and C components is 2:1:4. The most stable cluster structure of $(BNB)_8C_{30}H_{18}$ (with 8 BNB units dispersed in the $C_{54}H_{18}$ sheet) was obtained as shown in Fig. 4(a). The most stable structure of 4 Li-absorbed $(BNB)_8C_{30}H_{18}$ was also shown in Fig. 4(b). The calculation results demonstrate the Li insertion sites around carbon atoms or boron atoms, avoiding nitrogen sites.

CONCLUSIONS

BCN alloy was prepared from pyridine-borane complex by passing through the infusible pyridine-borane derivative at 1073 K for 2 h in Ar. The alloy obtained was layered $B_2N_1C_4$ with trigonal coordination number of both boron and carbon, and with C=C double bonds. Large amount of boron can be substituted into layered carbon sheet accompanied with nitrogen addition. Discharge capacity of the $B_1C_4N_{0.5}$ during lithium insertion showed 350 mAhg^{-1}.

Acknowledgments

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