

# Boronated Graphites

## -Chemical State of Boron and Electrochemical Intercalation of Lithium-

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**Abstract:** Boronated graphites were prepared by the heat treatment of the mixtures of petroleum coke and boron carbide in different ratios at 2500 °C for 1 hour in argon atmosphere. The samples were characterized by chemical analysis, XRD, XPS and electrochemical intercalation of lithium. Certain amount of boron, about 3 at%, was proved to be incorporated into graphite structure and to accelerate the development of graphite structure. The excess boron formed boron carbide in a separated phase. The increase in discharge capacity on the boronated graphites was explained by the improvement of graphite structure.

**Keywords:** boron-doping, coke, photoelectron spectroscopy, crystal structure, electrochemical intercalation.

### 1. Introduction

Boron is known to be only atom which can surely substitute carbon atoms in graphitic hexagonal layers[1]. Extensive studies on its doping have been carried out because of its accelerating effect on graphitization of host carbon materials and also its modification of electronic properties[2,3]. In relation to lithium rechargeable batteries, electrochemical performance of boron doped carbon anodes has recently been explored by different authors [4-6].

One of authors (T.S.) was interested in boron doping into graphite materials in relation to hydrogen retention as the plasma-facing wall of nuclear fusion reactors, and studied on the preparation procedures and some properties of resultant boronated graphite materials [7-9].

In the present work, detailed state analysis of boron atoms in graphite materials was done mainly using X-ray diffraction and X-ray photoelectron spectroscopy, and performance of electrochemical intercalation and deintercalation of lithium on these boronated graphite was studied.

### 2. Experimental

#### 2.1 Preparation of boronated graphites

A petroleum coke in powder of 12  $\mu\text{m}$  in size was mixed with a reagent grade boron carbide powder with the size of 3  $\mu\text{m}$  and placed in a graphite crucible. Four different mixing ratios of B<sub>2</sub>C were employed, as shown in Table 1, with the sample code used in the present paper. It was heat-treated at 2500 °C for 1

hour in argon atmosphere.

On the heat-treated sample powders, the content of boron was determined by chemical analysis, because some of boron atoms escaped from sample through the crucible during the heat treatment at such a high temperature.

#### 2.2 X-ray diffraction and X-ray photoelectron spectroscopy

The crystalline phases existed in the sample after 2500 °C treatment were identified from X-ray powder diffractogram and the interlayer spacing of graphite phase was determined by Cu K $\alpha$  radiation using high purity silicon powder as inner standard.

X-ray photoelectron spectroscopy (XPS) was carried out on each sample powders by using Mg K $\alpha$  X-rays. Binding energies  $E_b$  of B1s, O1s and N1s were determined by referring to  $E_b$  of C1s (284.3 eV).

#### 2.3 Electrochemical performance

Electrochemical performance of these sample powders was determined at room temperature in a mixed solution of ethylene carbonate (EC) and diethyl carbonate (DEC) in equal volume with 1.0 M LiClO<sub>4</sub> as an electrolyte. The cathode was prepared by painting a slurry of each graphite samples with 10 wt% polyvinylidene fluoride (PVDF) onto a copper sheet and then evaporating the solvent dimethylamine (DMA) at 80 °C. Before using, the cathode thus prepared was dried at 110 °C for one day under reduced pressure. The anode was a wire of lithium metal. Relations between potential and time during lithium

intercalation and deintercalation, *i.e.*, discharge-charge curves, were measured with a constant current of 0.2 mA during lithium intercalation (discharging) and 0.4 mA during deintercalation

(charging). Discharge-charge cycles were repeated 5 times on 2 sheets of each graphite sample. Capacity of each sample

**Table 1 Samples prepared and their characteristics**

Sample code	B <sub>4</sub> C mixed (wt%)	Boron content (at%)	Phases present	Interlayer spacing d <sub>002</sub> (nm)	Electrical conductivity (Scm <sup>-1</sup> )	Capacities	
						discharging (mA h g <sup>-1</sup> )	charging (mA h g <sup>-1</sup> )
0B	0.0	0.00	graphite	0.3364	8.04	326	323
1.5B	1.5	0.73	graphite	0.3356	8.64	314	312
3B	3.0	2.04	graphite	0.3354	0.82	321	320
5B	5.0	3.80	graphite+B <sub>4</sub> C	0.3352	0.79	310	307
10B	10.0	8.89	graphite+B <sub>4</sub> C	0.3352	0.096	272	268
NG	--	0.00	graphite	0.3354		373	368

graphite was determined from the observed curves in the potential range between 1.0 and 0.0 V during discharging and charging on each cycle. Irreversible capacity (retention) was calculated from the difference in capacities between discharging and charging.

A powder of natural graphite with averaged flake size of 7 μm was used as a reference for electrochemical performance.

Electrical conductivity of the sample sheet, which was prepared by casting the DMA slurry of the graphite samples with 10 wt% PVDF onto a sheet of polyethyleneterephthalate, was measured by four probe DC method at room temperature.

### 3. Results and Discussion

#### 3.1 Structure and state of boron in boronated graphites

In the samples containing boron in more than 3 at%, crystalline phase of B<sub>4</sub>C is clearly observed on X-ray powder pattern, as shown in Fig. 1 and tabulated in Table 1, in addition to crystalline graphite. According to the phase diagram reported [1], solid solubility of boron into graphite structure is about 3 at% at 2500°C. If we assume that this amount of boron is quenched down to room temperature in the present graphite samples, it is reasonable that B<sub>4</sub>C is detected in the samples with overall boron content above 3 at%.

It has been reported that the substitution of boron into graphite structure results in the reduction of interlayer spacing d<sub>002</sub> from the graphite value of 0.3354. In the present samples, the d<sub>002</sub>-values smaller than that of graphite are observed on all boronated graphites (Table 1). In addition, it has to be mentioned that the sharpening of three-dimensional lines, such as 101, 103 and 112, is observed, as shown in Fig. 1, which suggests the improvement in graphitic crystallinity in these

boronated samples. In the present boronated samples, therefore, the graphitization is accelerated by the substitution of boron in the structure. The sample without boron (sample 0B) gives a little larger d<sub>002</sub>-value and also broader three dimensional lines, which is consistent with the results on graphitization behavior of such kind of cokes.

XPS spectra for the samples, except NG-7, are compared with each other in Fig. 2. Oxygen detected on XPS was assumed to be due to species absorbed on the surface of the particles, because its intensity strongly scattered from sample to sample and because long evacuation time for XPS measurement (more than 2 days under a pressure of 10<sup>-8</sup> Pa) was needed. The appearance of boron in the samples mixed with B<sub>4</sub>C is reasonable, but it is unexpected that nitrogen is observed only in the samples containing boron and the peaks for boron and nitrogen appears to grow together[10]. A detailed analysis of chemical states of boron and nitrogen in these graphite materials showed that the existence of nitrogen is closely related to that of boron and binding energy values measured suggested the bond formation between boron and nitrogen, although the authors do not know yet where nitrogen atoms come from.

A pronounced decrease in electrical conductivity measured on the sheets for electrochemistry (Table 1) in the samples 3B might be due to a minute amount of precipitation of B<sub>4</sub>C, which could not be detected on X-ray powder pattern of the samples.

#### 3.2 Discharge-charge performance of boronated graphites

In Fig. 3, discharge curves for the first cycle are compared on the samples, where a part of the electricity range of 0-80 mAh/g are enlarged for easy comparison.

The discharge capacity down to the potential of 0.5 V is

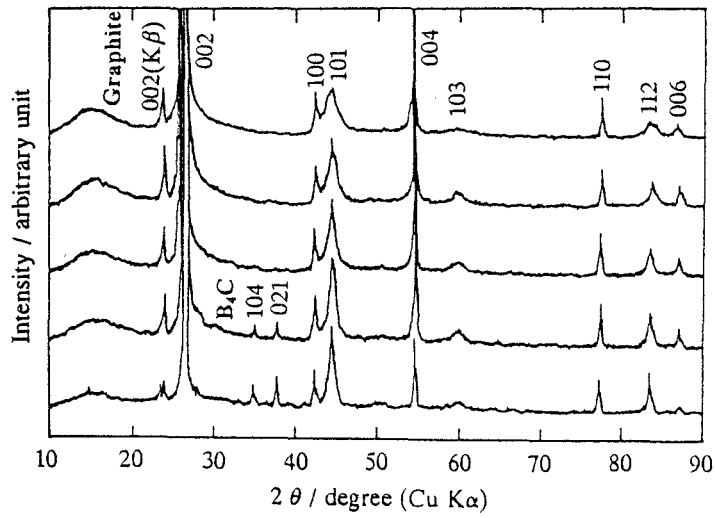


Fig. 1 XRD patterns of the samples used.

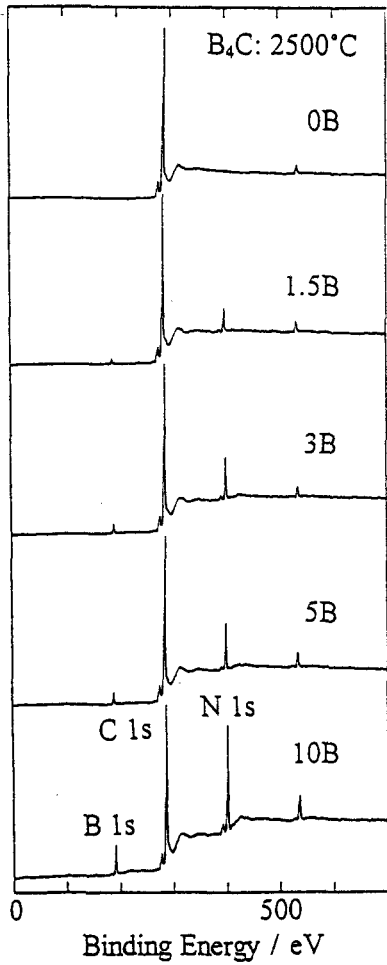


Fig. 2 XPS spectra of the samples used.

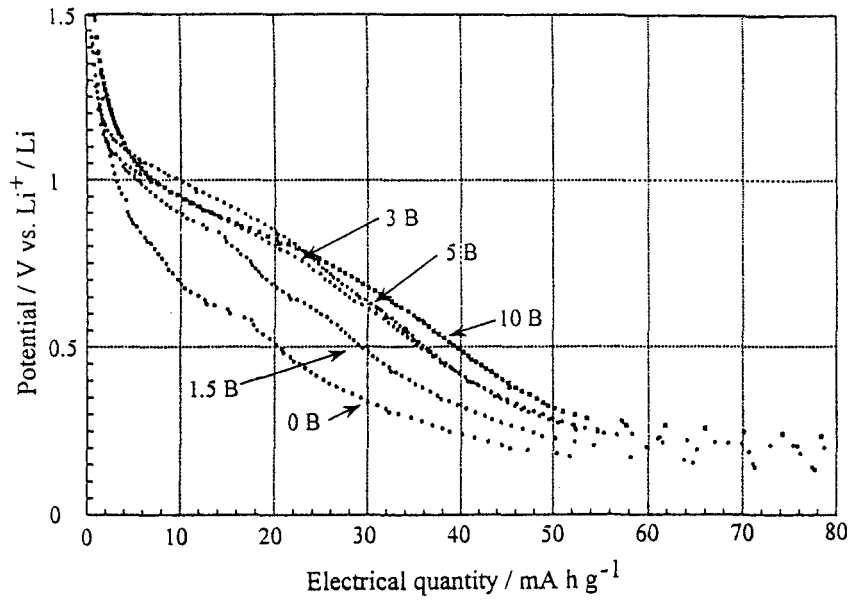


Fig. 3 Discharge curves for the first cycle on the samples.

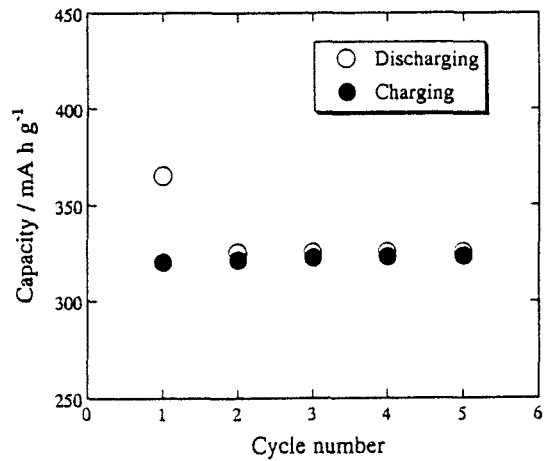


Fig. 4 Discharge and charge capacities against cycle number on the sample 3B.

larger in the boronated samples (samples 1.5B-10B) than in non-boronated ones (sample NG-7 and 0B), which agrees with the data reported by Dahn et al.[4]. The increase in capacity is more marked with the increase in boron content from 0 to 3 % (i.e., the change from the sample 0B to 3B) than with higher content (among the samples 3B, 5B and 10B). This result suggests that the substitution of boron for carbon is responsible for this increase in capacity down to 0.5 V.

In Fig. 4, capacities for discharging and charging are plotted against cycle number on the sample 3B. For the first cycle, appreciable retention of lithium in the sample is observed, but after second cycle it becomes negligibly small. On all samples used, the retention for the first cycle was 34-50 mA h g<sup>-1</sup> and that for 2nd to 5th cycles was less than 5 mA h g<sup>-1</sup>. Therefore, the capacities for discharge and charge processes are calculated by averaging those after 2nd cycle and shown in Table 1.

The capacity tends to decrease with the increase in boron content. By taking into account the segregation of certain amount of boron as B<sub>4</sub>C, the capacity for graphite phase has to be recalculated; for example, in the sample 10B, 9 at% boron is existing, where 2 at% B is supposed to locate in hexagonal carbon layers and 7 at% forms B<sub>4</sub>C particles so that the content of graphite phase must be about 92 wt%. If the capacity is recalculated on the graphite phase existed in the present boronated graphite which are mixed with B<sub>4</sub>C, it is roughly 340 mA h g<sup>-1</sup> which is a little less than the capacity for pure graphite NG-7. The sample without boron (sample 0B) gives a little lower value of capacity because of its lower degree of crystallinity.

#### 4. Conclusive Remarks

In the boronated graphites prepared in the present work, boron atoms are reasonably supposed to exist in two different states, one being substitutionally incorporated into graphite structure and the other segregated as crystalline B<sub>4</sub>C particles. The former accelerated the growth of graphite crystals, i.e., graphitization of carbon, and also affected on the discharge-charge performance in LiClO<sub>4</sub> electrolyte by increasing the capacity at the potential around 0.5 V. However, total capacity, which is interested in relation to lithium rechargeable batteries, did not change by the substitution with boron. The present results agreed with the data reported on the similar boronated graphites[4,5]. It has also been reported that the capacity of graphitized materials, such as high-temperature treated carbon materials, depends strongly on the graphitization state evaluated

by degree of graphitization P<sub>1</sub>, interlayer spacing d<sub>002</sub> and crystallite size L<sub>c</sub> [12-14]. The present results are also consistent with these published data [11-13], if the presence of B<sub>4</sub>C was taken into account, as discussed before.

Recently, it was reported that a large amount of lithium could be intercalated into boronated carbons prepared by CVD method, the authors claiming the formation of ternary B-C-N compounds [6]. So, the effect of boron substitution on capacity might be different on the crystallinity of host carbon materials, either high crystallized graphite or rather amorphous carbon. Also, it might be important to clarify the state of nitrogen in the ternary compounds reported and the present samples. It is the problem that the authors are planning to work in the next step of research.

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#### References

1. Lowell, C.E., *J. Am. Ceram. Soc.*, **50**, 142(1967).
2. Woodley, R.E., *Carbon*, **6**, 617(1968).
3. Allardice, D.J. and Walker, Jr., P.L., *Carbon*, **8**, 375(1970).
4. Dahn, J.R., Reimers, J.N., Sleigh, A.K. and Tiedje, T., *Phys. Rev. B*, **45**, 3773(1992).
5. Way, B.M. and Dahn, J.R., *J. Electrochem. Soc.*, **141**, 107 (1994).
6. Flandrois, S., Ottaviani, B., Derre, A. and Tressaud, A., *J. Phys. Chem. Solids*, **57**, 741(1996).
7. Hino, T., Ishio, K., Hirohata, Y., Yamashina, T., Sogabe, T., Okada, M. and Kuroda, K., *J. Nucl. Mater.*, **211**, 30(1994).
8. Sogabe, T., Matsuda, T., Kuroda, K., Hirohata, Y., Hino, T. and Yamashina, T., *Carbon*, **33**, 1783(1995).
9. Sogabe, T., Nakajima, K. and Inagaki, M., *J. Mater. Sci.*, **31**, 6469(1996).
10. Konno, H., Nakahashi, T. and Inagaki, M., *Carbon* (to be submitted).
11. Tatsumi, K., Zaghbi, K., Sawada, Y., Abe, H. and Ohsaki, T., *J. Electrochem. Soc.*, **142**, 1095(1995).
12. Tatsumi, K., Iwashita, N., Sakaebe, H., Shioyama, H., Higuchi, S., Mabuchi, A. and Fujimoto, H., *J. Electrochem. Soc.*, **142**, 716(1995).
13. Endo, M., Nakamura, J., Sasabe, T., Takahashi, T. and Inagaki, M., *TANSO*, **1994** (No.165), 282.

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