

# STRUCTURE AND ANODE PERFORMANCES OF VARIOUS TYPES OF GRAPHITIZED AND B-DOPED MATERIALS

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## Introduction

Recently, heteroatom-doped carbon materials  $BC_x$ ,  $BC_xN$  and  $C_xN$  have been suggested the potential applications as anode materials in Li ion batteries, because these compounds consist of layered structure [1-3]. In particular, boron-doped carbon materials have been experimentally and theoretically investigated from different points of view, not only from fundamental scientific aspects, such as electronic properties, but also potential applications, such as the high temperature oxidation protector for carbon/carbon (C/C) composite and an anode material for Li ion batteries. Because boron-doping is inducing the creation of electron acceptor level, the enhanced capacity has been expected.

The purpose of this study is not only to investigate the electrochemical properties, such as the charge/discharge capacity, voltage profile, and irreversible capacity loss, but also to estimate the boron doping effect in highly ordered carbon materials for use as anode materials in lithium ion secondary batteries.

## Experimental

The host samples were mesophase pitch-based carbon fibers (MPCFs), petroleum coke (Graphite I), and mesophase pitch-based carbon from coal tar pitch (Graphite II), respectively. Samples of these materials were heat-treated at 2800°C in a high purity argon gas (99.999 %) for 30min using a graphite resistance furnace. The boron-doped samples prepared by mixing the oxidized samples and 3 wt.%  $B_4C$ , and then heat-treating the material to 2800°C in a flow of Ar gas for 30min.

Electrochemical measurements were performed by using three-electrode test cells made of pyrex glass. Lithium metal was used both as a counter electrode and as a reference electrode. The electrolyte used was 1M solution of  $LiClO_4$  dissolved in a 50 : 50 mixture by volume of ethylene carbonate (EC) and diethyl carbonate (DEC). The specific capacity of the graphite electrode was measured by a potentiostat/galvanostat during the charge and discharge cycles in the ranges 0 to 2.8V, with a current density of 30mA/g-cabon.

## Results and discussion

Fig. 1 illustrates typical voltage profiles of the second discharge and charge for pristine graphitized and boron-doped graphite cells. The long plateaus below 0.2V correspond to the reversible intercalation of Li in graphitized and boron-doped samples. First, it should be noted that the 2nd discharge/charge capacity of boron-doped coke and Graphite I slightly decreased relative to that of the pristine samples. However, in the case of boron-doped MPCFs, the 2nd charge capacity is larger than that of undoped MPCFs. The reduced charge capacity of the boron-doped Graphite I and Graphite II samples may be related to boron occupying the lithium insertion active site, such as an edge-type site in the graphite layers and thus the presence of the boron will inhibit the lithium intercalation process. Finally, we note that the voltage profiles of boron-doped samples are higher than those of the undoped samples about 40mV/Li.

On the discharging cycle for boron-doped samples, shoulder plateaus are characteristically observed at about 1.3V, which may be caused by inducing an electron acceptor level so that lithium insertion yields a higher voltage compared to undoped samples. The irreversible capacity is calculated as the average of the capacities of the second discharge and charge process. It is interesting that the irreversible capacity loss for boron-doped samples is lower than that of the corresponding undoped samples. These results may be related to the redistribution of the Fermi level of the boron-doped samples, which is lowered by boron-doping by introducing an electron acceptor.

Figs. 2 and 3 illustrate the boron and nitrogen 1s peak at higher resolution. As expected, the  $B_{1s}$  peak appears in the boron-doped samples, but its form and position are different depending on the samples. In particular, the  $B_{1s}$  peak of the boron-doped Graphite I was split three peaks at 185.6, 187.7, and 189.8eV, which were assigned to boron from boron carbide or boron cluster, substituted in graphite plane, and incorporated nitrogen, respectively. And also, in Fig. 3, the  $N_{1s}$  peak shows the only boron-doped Graphite I. From these results, the appearance of the  $B_{1s}$  near ~190eV and  $N_{1s}$  near ~398eV peaks of boron-doped Graphite I substitutionally incorporated into graphite layers are preferentially bonding with nitrogen atoms existing in the heat-treatment atmosphere. It is

possible also that the residual nitrogen atom of cokes reacted with the boron carbide during the carbonization step and then formation of boron nitride and/or  $BC_xN$  compounds during the graphitization step.

### Conclusions

Three different forms of carbon materials have been investigated and characterized by a variety of experimental techniques and electrochemical measurements.

It is suggested that the effect of boron-doping in the three types of samples influenced the electrochemical properties due to presence of boron form. In the case of boron-doped samples, lithium is inserted at a higher voltage and shows a better cyclic efficiency, presumably because the presence of boron acts as an electron acceptor and gives increased

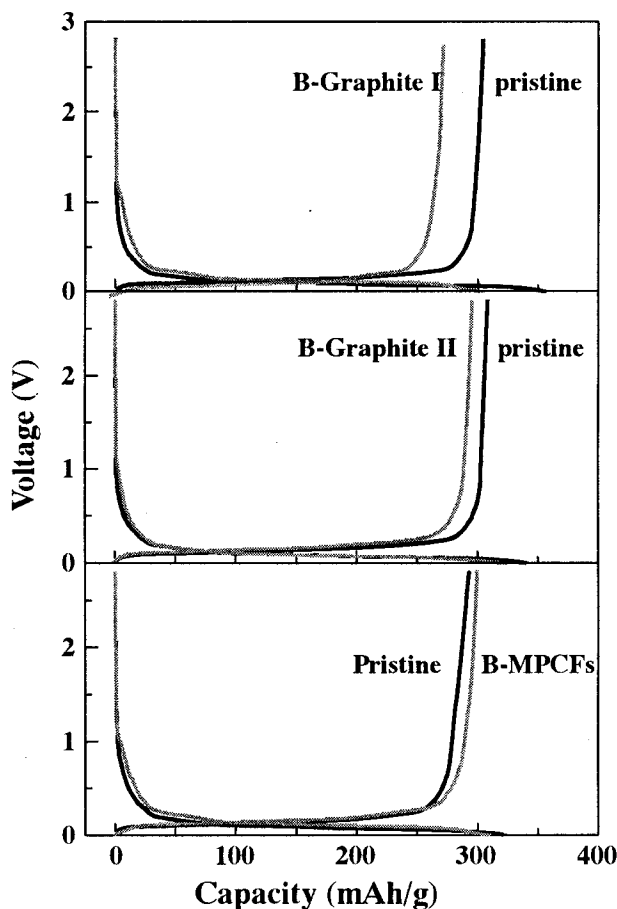


Figure 1. Change in potential during the second discharging and charging cycle of the graphitized and boron-doped samples for various graphite hosts.

mechanical strength to the graphite lattice. Also, the lithium insertion capacity depends on the structural geometry and the chemical composition of the host materials.

### References

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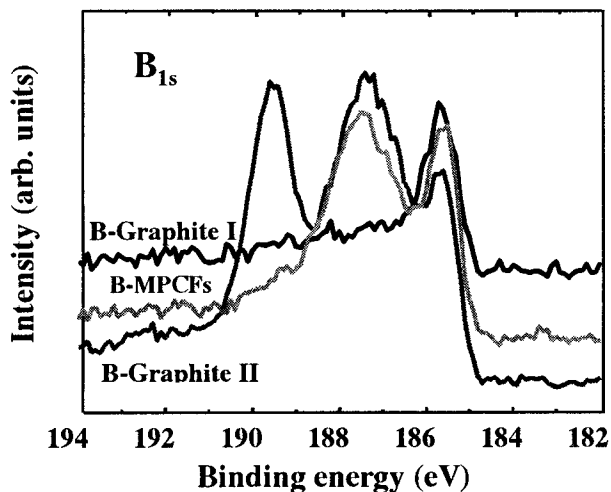


Figure 2. XPS  $B_{1s}$  spectra of graphitized and B-doped samples.

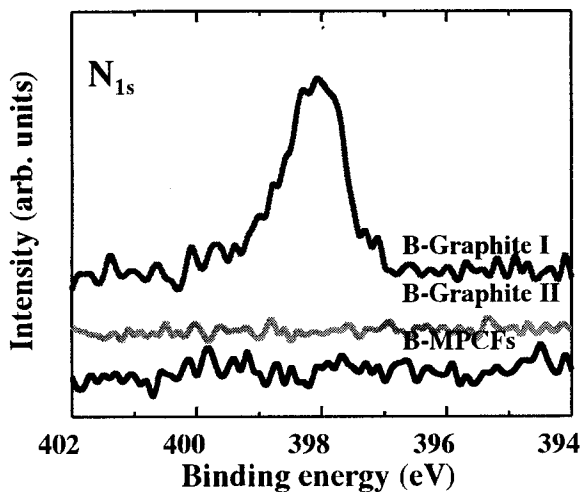


Figure 3. XPS  $N_{1s}$  spectra of graphitized and B-doped samples.