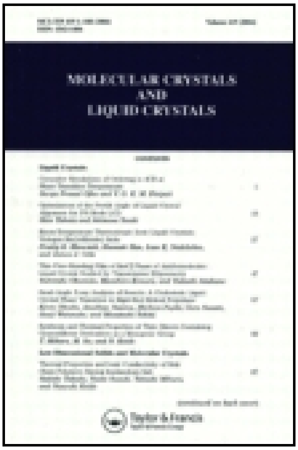

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Structure and Anode Performance of Pristine and B-Doped Graphites for Li-ion Batteries

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Structure and Anode Performance of Pristine and B-Doped Graphites for Li-ion Batteries

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The microstructure and electrochemical properties of pristine graphitized and boron-doped materials have been comparatively analyzed by x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), and electrochemical measurements. The electrochemical properties in a Li ion secondary battery of boron-doped graphitized materials depends strongly on the structural geometry and chemical composition of the pristine host materials.

Keywords: Doped carbon; Li ion secondary battery

INTRODUCTION

Recently, heteroatom-doped carbons such as BC_x, BC_xN and C_xN have been suggested for potential applications as anode materials in Li ion batteries, because these compounds consist of layered structure[1-2]. Many researchers have reported and suggested preparation methods of boron-doped carbons by co-deposition of CVD, pyrolysis of organic molecules containing boron atom, and the substitutional boron doping mechanism into carbon structures[1-2].

In the present paper, we describe the correlation between the structure and electrochemical properties of graphitized and B-doped samples for various types of carbon hosts.

EXPERIMENTAL

Mesophase pitch-based carbon fibers (MPCFs), petroleum coke (Graphite I), and carbon spheres (Graphite II) were obtained from petroleum mesophase pitch. Oxidation of the pitch fibers and the crude carbon spheres are performed in air at 300 °C and 350 °C, 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 were prepared by mixing the oxidized samples and 3 wt.% B_4C, and then heat-treating the material to 2800°C in flowing of Ar gas for 30min. Electrochemical measurements were performed by using three-electrode test cells made of pyrex glass. The working electrodes were prepared by mixing the pristine and boron-doped samples at 95 weight percent (wt.%) with poly(vinylidene fluoride) (PVDF) at 5 wt.%, using 1-methyl-2pyrrolidinone as a solvent. The electrolyte used was a *1M* solution of $LiClO_4$ dissolved in a 50 : 50 mixture by volume of ethylene carbonate (EC) and diethyl carbonate (DEC). The 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.

RESULTS AND DISCUSSION

Fig. 1 illustrates typical voltage profiles of the second discharge and charging for pristine graphitized and boron-doped graphite electrodes. These samples were prepared from a mixture of pristine material and boron carbide (B_4C) by heat treatment at 2800°C in an Ar atmosphere. The long plateaus below 0.2V correspond to the reversible intercalation of Li in graphitized and boron-doped samples. These electrochemical behaviors of the graphitized samples are almost the same as that of other highly graphitized electrodes. It should be noted that the 2nd discharge/charge capacities of boron-doped graphite I (B-Graphite I) and graphite II (B-Graphite II) slightly decreased relative to those of the pristine samples. However, in the case of boron-doped MPCFs, the 2nd charge capacity is larger than that of undoped pristine MPCFs. The reduced charge capacity of the boron-doped samples may be related to boron atoms occupying the lithium insertion active site, such as an edge-type site in the carbon layers and thus the presence of the boron will inhibit the lithium insertion process. It is worthwhile to note that the voltage profiles of boron-doped samples are higher than those of the undoped samples by about 40mV[3], and this could be useful for practical cell applications. On the discharging cycle for boron-doped samples, shoulder plateaus are characteristically observed at about 1.3V, which may be caused by filling an acceptor level with electron so that lithium insertion yields a higher voltage compared to the undoped samples[2,4]. The irreversible capacity is calculated as the average difference of the capacities for the discharge and charge processes.

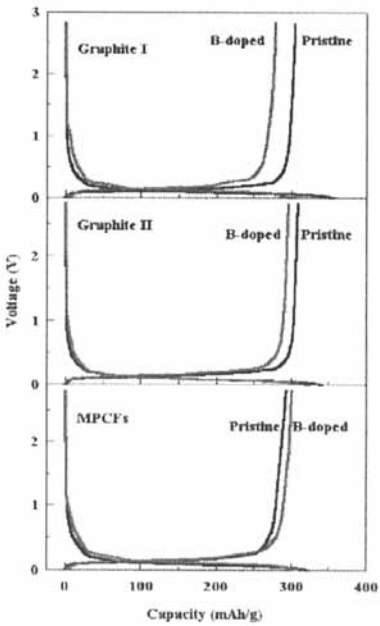

FIGURE 1. Change in potential during the second discharge/charge cycle of the pristine and B-doped samples.

TABLE 1. Results of the electrochemical tests for the pristine and B-doped samples.

Samples		Irreversible capacity (mAh/g)		Cyclic efficiency (%)	
		1st	2nd	1st	2nd
Graphite I	Pristine	103	52	75	85
	B-doped	78	25	79	92
Graphite II	Pristine	93	32	77	90
	B-doped	55	29	85	91
MPCFs	Pristine	140	35	72	89
	B-doped	84	11	82	96

It is interesting that the irreversible capacity loss for boron-doped samples is lower than that of the corresponding undoped samples (Table I). 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 in the lattice[2,4].

Fig. 2 shows the carbon 1s peak in the high resolution XPS spectra. It is interesting that the C_{1s} peak of the boron-doped samples is located at a slightly lower binding energy compared with the undoped samples. The lowering of the binding energy of the C_{1s} peak for the boron-doped samples might be due to the lowering of the Fermi level, because of the redistributed π-electrons in the graphite layer planes[4]. This result may be related to the chemical bond formation of carbon atoms with electron deficient boron atoms.

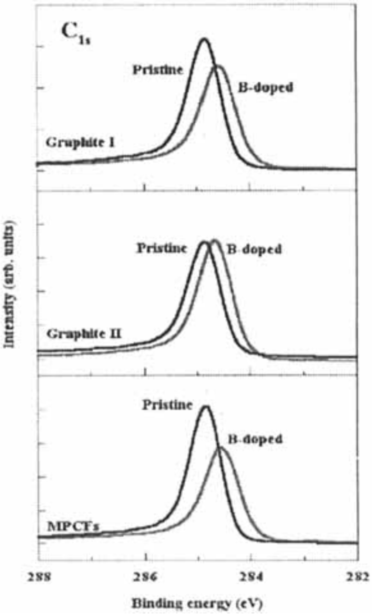

FIGURE 2. XPS C_{1s} spectra of pristine and B-doped samples.

Figs. 3 and 4 illustrate the boron and nitrogen 1s peak in the XPS spectrum. As expected, the B_{1s} peak appears in the boron-doped samples, but their forms and positions are different depending on the samples. In particular, the B_{1s} peak of the boron-doped graphite I (B-Graphite I) was split into three peaks at 185.6, 187.7, and 189.8eV, which were assigned to boron in boron carbide, in a boron cluster or boron bound to incorporated nitrogen atoms, respectively.

And also, in Fig. 4, the N_{1s} peak is observed only in B-Graphite I. From these results, the appearance of the B_{1s} level near ~190eV and the N_{1s} level near ~398eV peaks of B-Graphite I corresponds to the boron nitride formed by the reaction of B_4C with nitrogen atoms existing in the heat treatment atmosphere. It is also possible that the residual nitrogen atoms in the raw materials react with the substitutionally incorporated B atoms into graphite lattice during the carbonization step and then formed the boron nitride and/or BC_xN compounds during the graphitization step. Konno et al. demonstrated B-N bonding in B-doped graphites by XPS and suggested the possible nitrogen source as air occluded in the raw materials that are packed into a graphite crucible[5]. These phenomena should be taken into consideration seriously for industrial processes using an Acheson type furnace.

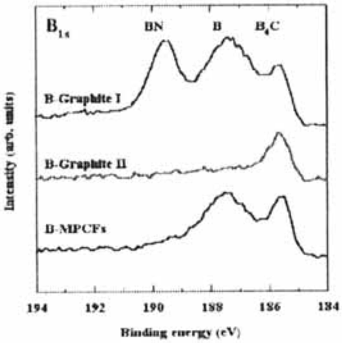

FIGURE 3. XPS B_{1s} spectra of B-doped samples.

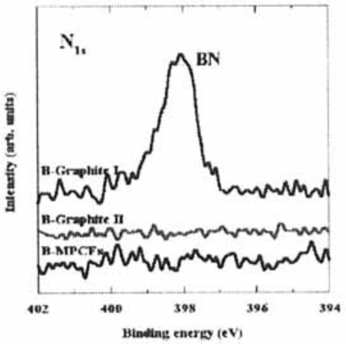

FIGURE 4. XPS N_{1s} spectra of B-doped samples.

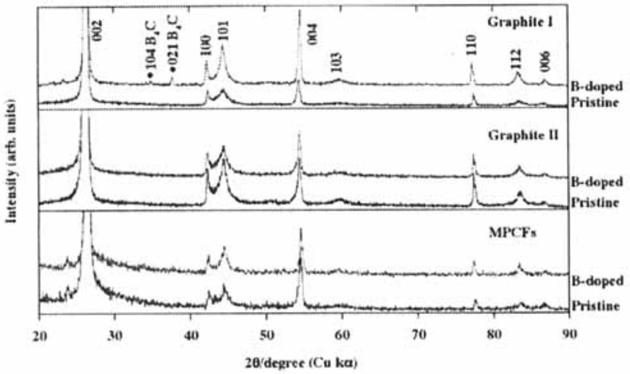

FIGURE 5. X-ray diffraction patterns of pristine graphitized and boron-doped samples.

Fig. 5 shows the X-ray diffraction patterns of pristine and B-doped samples. Peaks of boron carbide are only detected with boron-doped Graphite I. The results might be related to the boron substitutionally incorporated into graphite layers up to the concentration of about 2.5at.% at this temperature [5]. It should be noted that the (101) and (112) peaks of boron-doped samples sharply developed than that of the corresponding undoped pristine samples, which implies a improvement of crystallity of the graphite [5,6].

CONCLUSIONS

The degradation of the lithium insertion capacity observed in some kinds of boron-doped graphite might be closely related to the presence of borons with forms of boron nitride and boron carbide. Also the unexpected opposite effects of B-doping could be related to the heterogeneous growth of the crystallite dimension, L_a, due to the borons acting as a graphitization catalyst. In order to employ the more advantageous effects of boron doping, depending on the carbon materials obtained from different precursors with a wide variety of shapes and microstructures, the doping conditions including the atmospheres exposure, heating rate and some other processes should be carefully selected.

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