

# SUPER-ACTIVATED NANOPOROUS CARBON CONTAINING SUBSTITUTIONAL BORON FOR H<sub>2</sub> STORAGE

Youni Jeong and T. C. Mike Chung\*

Department of Materials Science and Engineering, The Pennsylvania State University, University park, PA 16802

## Introduction

Despite tremendous efforts in studying H<sub>2</sub> storage in various nanoporous materials, including various forms of carbonaceous (C) materials and metal-organic frameworks (MOFs), the H<sub>2</sub> storage goal (>60 mg H<sub>2</sub>/g and >45 g H<sub>2</sub>/L) is still unfulfilled for practical usage. One major problem is that effective H<sub>2</sub> physisorption requires very low temperature (77K), due to a weak van der Waals interaction, which is typically 4-7 kJ/mol. Thermodynamic considerations indicate that the H<sub>2</sub> binding energy should be 15-25 kJ/mol for ambient temperature operation.

Few early reports discussed boron substitution in C by doping graphite with inorganics, such as boron powder, boron carbide, etc. Typically, the doping of well-ordered crystalline graphite is difficult. Several researchers reported that inhomogeneous distribution because boron preferentially enters into the most disordered regions of the carbon. More recently, a similar post-carbonization process—with the aids of high energy sources (such as arc and laser)—has been applied to boron doping in well-defined carbon structures, including fullerene and nanotubes. There are also few reports using CVD process to prepare BC<sub>x</sub> material. Generally, these high energy processes produce the products that contain either very high B content (such as a stable B<sub>4</sub>C structure) or very low B content (<3 wt%) in the graphitic structure.

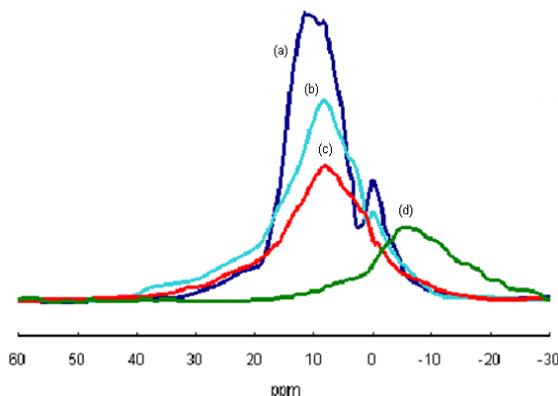
## Results and Discussion

In this paper, we systematically study a new family of porous boron-substituted carbons (BC<sub>x</sub>) with controlled structure, which are prepared by a polymeric B-precursor, i.e. poly(borachlorophenyldiacetylene) containing in situ formed inorganic additives (templates). At pyrolysis <400 °C, the B-precursor engages in facile inter-chain reactions to form dark solid with high C and B yields (>85%). Above 600 °C, the amorphous carbon-like BC<sub>x</sub> material is formed with an extended fused hexagonal ring structure. After removing the inorganic additives by water-washing, the resulting porous BC<sub>x</sub> shows a surface area 500-800 m<sup>2</sup>/g. Evidently, the pore size distribution is directly related to melting temperature and mixability of the inorganic salts. Table 1 summarizes several resulting porous BC<sub>x</sub> materials. Comparing A set, the B content

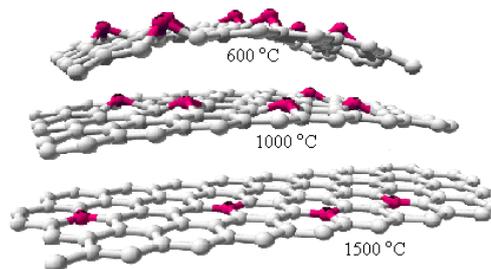
slowly decreases with the increase of the pyrolysis temperature. The composition changes from BC<sub>11</sub> at 600 °C to BC<sub>13</sub> and BC<sub>21</sub> at 800 and 1100 °C, respectively. The addition of external additives, such as NaBH<sub>4</sub> in B set, can significantly increase B content at 600-1000 °C range.

**Table 1. Summary of BC<sub>x</sub> Prepared by B-Precursor**

Run No.	B Content (wt%)		Surface Area (m <sup>2</sup> /g)	Composition (BC <sub>x</sub> )
	<sup>11</sup> B NMR	PGAA		
A-1	7.7	7.7	780	BC <sub>11</sub>
A-2	6.4	6.0	528	BC <sub>13</sub>
A-3	4.2	-	-	BC <sub>21</sub>
A-4	3.5	3.7	-	BC <sub>25</sub>
A-5	2.6	-	36	BC <sub>34</sub>
A-6	2.2	2.0	-	BC <sub>40</sub>
B-1	12.2	12.8	609	BC <sub>6</sub>
B-2	10.4	9.2	-	BC <sub>8</sub>



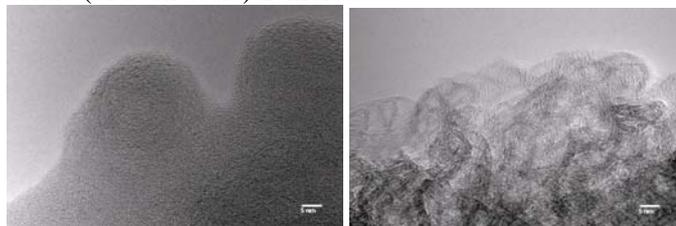
**Figure 1.** Solid state (MAS) <sup>11</sup>B NMR spectra of BC<sub>x</sub> materials prepared from pyrolysis of B-precursor at (a) 600 °C, (b) 800 °C, (c) 1100 °C, and (d) 1500 °C.



**Figure 2.** The schematic presentation of BC<sub>x</sub> materials.

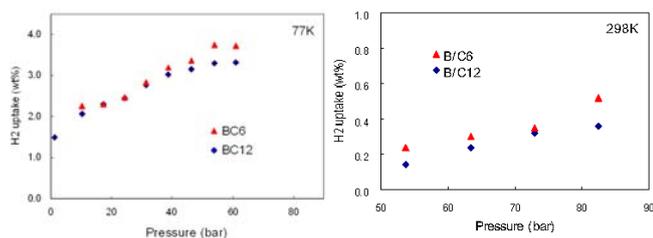
Figure 1 shows the <sup>11</sup>B MAS-NMR spectra of several BC<sub>x</sub> materials, and Figure 2 illustrates their proposed molecular structures. BC<sub>11</sub> (run A-1) shows one distinctive broad chemical shift centered at 10 ppm, corresponding to trivalent B moieties with some π-electron delocalization in the C fused rings. There is a minor peak centered at 0 ppm, which may be associated with few B moieties located at

the edge area of the porous BC<sub>11</sub> structure. As the pyrolysis temperature increases from 600 to 800 °C, the major trivalent B peak slowly moves up-field, indicating gradually increase of electron density at B and better  $\pi$ -electron conjugation in the BC<sub>13</sub> material (run A-2). On the other hand, the edge area B moieties sharply decrease in its intensity. At 1100 °C, only a trivalent B peak at 8 ppm was observed in BC<sub>21</sub> (run A-3). Evidently, the BC<sub>x</sub> fused ring structure increases its size as the pyrolysis temperature increases. Further annealing the sample at higher temperatures (1500 °C), the BC<sub>x</sub> material appears to graphitize on a larger scale (Figure 2), with a single B chemical shift abruptly moving up-field to -5 ppm in the BC<sub>28</sub> material (run A-5), which indicates that B is highly involved in  $\pi$ -electron delocalization to form very weak acidic (or even basic) B moieties.



**Figure 3.** TEM micrographs of BC<sub>x</sub> prepared at (a) 600°C and (b) 1800°C.

Figure 3 compare two TEM micrographs of BC<sub>11</sub> (run A-1) and BC<sub>40</sub> (run A-6) materials. In the BC<sub>11</sub>, prepared at 600°C, we observed fingerprint patterns with short and curved fringes, and randomly-oriented fringes between fingerprint patterns. On the other hand, the randomly-oriented stacks of several layers, with extended, straight, and parallel organized fringes were observed in the BC<sub>40</sub> material prepared at 1800°C. The stack thickness ( $L_c$ ; crystallite size) is about 2-3 nm, and the stack length (crystallite width) is in the range of 5-7 nm—consistent with the X-ray results.



**Figure 4.** Hydrogen adsorption (vs. H<sub>2</sub> pressure) for two porous BC<sub>6</sub> and BC<sub>12</sub> materials at (a) 77K and (b) 293K.

The resulting nanoporous BC<sub>x</sub> materials were used as absorbents for H<sub>2</sub> storage under various temperatures and pressure conditions. Figure 4 shows hydrogen adsorption of BC<sub>11</sub> (run A-1) and BC<sub>6</sub> (run C-1) at 77K and 293 K,

respectively. Hydrogen uptake almost follows a linear relationship with hydrogen pressure, which is quite different from C materials that reach a saturation level in relatively low pressure. About 0.37 wt% hydrogen adsorption was observed in the BC<sub>11</sub> material, having a specific surface area of 780 m<sup>2</sup>/g, at ambient temperature under 80 bars H<sub>2</sub> pressure, which is about double that of carbonaceous materials with similar surface areas. Temperature has a marked effect on the increase of the hydrogen adsorption capability. At 77 K, hydrogen adsorption reaches the 3 wt % mark—more than 7 times that at ambient temperature. This value is more than double that of the corresponding carbonaceous materials with similar surface area. Further increase of the B content in the BC<sub>6</sub> material—having a smaller specific area 609 m<sup>2</sup>/g—shows 0.54 wt% and 3.8 wt% hydrogen adsorption at 273 and 77K, respectively. Despite the reduction of surface area, the overall hydrogen adsorption capacity clearly increases. Evidently, the substituted B elements are essential in hydrogen adsorption, which enhances the surface energy for binding hydrogen. The quantitative H<sub>2</sub> binding energy on the BC<sub>11</sub> and BC<sub>6</sub> materials was estimated by adsorption isotherms (at 77 and 87 K) under low hydrogen pressure (<1 bar). The initial isosteric heat of adsorption for BC<sub>11</sub> (run A-1) and BC<sub>6</sub> (run C-1) is 12.47 and 20 kJ/mol, respectively. Both samples maintain quite high adsorption energy levels (>10 kJ/mol) to higher surface coverage. They are significantly higher than those observed in undoped carbonaceous materials (4 kJ/mole) and some metal-doped C materials.

**Acknowledgement.** The authors would like to thank the U.S. Department of Energy and the Hydrogen Sorption Center of Excellent (lead: National Renewable Energy Laboratory) for their financial support.

## References

- (1) Liu, C.; Fan, Y. Y.; Liu, M.; Cong, H. T.; Cheng, H. M.; Dresselhaus, M. S. *Science* **1999**, 286, 1127.
- (2) Yaghi, O. M.; O’Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi M.; Kim, J. *Nature* **2003**, 423, 705.
- (3) Ye, Y.; Ahn, C. C.; Witham, C.; Fultz, B.; Liu, J.; Rinzler, A. G.; Colbert, D.; Smith, K.; Smalley, R. E. *Appl. Phys. Lett.* **1999**, 74, 2307.
- (4) Lowell, C. E. *J. Am. Cer. Soc.* **1967**, 50, 142.
- (5) Kouvetsakis, J.; Kaner, R. B.; Sattler, M. L.; Bartlett, N. *J. Chem. Soc., Chem Commun.* **1986**, 1758.
- (6) Chung, T. C.; Jeong, Y.; Chen, Q.; Kleinhammes, A.; Wu, Y. *J. Am. Chem. Soc.* **2008**, 130, 1021.