

**High-capacity electrode material BC<sub>3</sub> for lithium batteries proposed by *ab initio* simulations**Alexander A. Kuzubov,<sup>1</sup> Aleksandr S. Fedorov,<sup>2,\*</sup> Natalya S. Eliseeva,<sup>1,2</sup> Felix N. Tomilin,<sup>1,2</sup> Pavel V. Avramov,<sup>2,3</sup> and Dmitri G. Fedorov<sup>4</sup><sup>1</sup>*Siberian Federal University, av. Svobodny 79, Krasnoyarsk 660041, Russia*<sup>2</sup>*Kirensky Institute of Physics, Akademgorodok 50, Krasnoyarsk 660036, Russia*<sup>3</sup>*Advanced Science Research Center, Japan Atomic Energy Agency, 2-4 Shirakata Shirane, Tokai-mura, Naka-gun, Ibaraki-ken 319-1195, Japan*<sup>4</sup>*Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Central 2, Umezono 1-1-1, Tsukuba 305-8568, Japan*

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The absorption energy and diffusion rates of lithium atoms inside graphitelike boron carbide (BC<sub>3</sub>) crystal are investigated by the *ab initio* pseudopotential density-functional method using generalized gradient approximation. It is shown that lithium may effectively intercalate this structure with the maximum lithium concentration corresponding to Li<sub>2</sub>BC<sub>3</sub> stoichiometry, which is threefold in comparison to lithium in graphite. The potential barrier values for lithium diffusion both at low and maximum concentration are about 0.19 eV, so lithium atoms inside the BC<sub>3</sub> structure can move easily. These findings suggest that boron carbide looks like a good candidate as an anode material in lithium ion batteries.

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**I. INTRODUCTION**

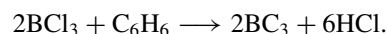
Lithium (Li) ion batteries are ubiquitously used in portable electronic devices. Recently, the batteries have been utilized in heavy applications such as power tools and electric or hybrid cars. This heavy usage is due to the fact that these batteries have a much higher energy storage capacity, a longer lifetime, and a smaller memory effect in comparison with other kinds of batteries. The electrodes in Li ion batteries operate on the basis of intercalation processes in which Li<sup>+</sup> ions are exchanged with an open host structure. Intercalation electrodes are successful because of the small structure and volume changes and a fast Li<sup>+</sup> ion diffusion rate. The commonly used Li ion intercalation anode material is *sp*<sup>2</sup>-connected carbon (petroleum coke, graphite, etc.) due to its low cost and chemical stability. However, it has a limited charge storage capacity and cannot fulfill the demands of a higher energy and power density usage and a longer lifespan needed in modern applications.

Recently,<sup>1</sup> it has been suggested that the graphitelike lithium borocarbide (LiBC) compound can release reversibly a half of lithium atoms according to the electrochemical reaction  $\text{LiBC} \rightarrow \text{Li}_{0.5}\text{BC} + 0.5\text{Li}$  with the volume change less than 3% during the charging and discharging process. This indicates that the LiBC compound can be a high-capacity cathode material for lithium ion batteries with a specific energy density of 1088 W h/kg.

In the early nineties the intercalation voltage and reversible capacity of boron-substituted graphite were investigated by electrochemical methods. The voltage and reversible capacity of Li/Li<sub>x</sub>(C<sub>1-z</sub>B<sub>z</sub>)<sub>6</sub> cells have been measured<sup>2</sup> for the range of boron concentrations  $0 < z < 0.17$ . These cells for  $z > 0$  showed greater reversible capacities than Li/petroleum coke cells, and for  $z > 0.10$  the capacities exceeded that of graphite. For example, for C<sub>0.83</sub>B<sub>0.17</sub> the reversible specific capacity was 437 mAh/g. Also these Li<sub>x</sub>(C<sub>1-z</sub>B<sub>z</sub>)<sub>6</sub> cells show an increase in the lithium intercalation voltage from 0.9 up to 1.6 V when the boron concentration  $z$  increases from 0 to 4.4%.<sup>3</sup> However, due to the chemical vapor deposition synthesis technique,

only a low boron concentration (<17%) in boron-substituted graphite has been studied. The features of lithium intercalation in the hexagonal graphitelike BC<sub>3</sub> (*g*-BC<sub>3</sub>) crystal structure are unknown and the purpose of this work is to investigate this BC<sub>3</sub> structure as a new material for electrodes in Li ion batteries.

It is known<sup>4</sup> that a boron substitution inside main carbon allotropes, diamond and graphite, can form both a diamondlike phase with tetragonal symmetry (*t*-BC<sub>3</sub>) and a graphitelike *g*-BC<sub>3</sub> phase [see Fig. 1(a)]. For the first time the layered structure of *g*-BC<sub>3</sub> was successfully synthesized more than 20 years ago by the chemical reaction of benzene and boron trichloride at 800°C:<sup>5</sup>



Experiments<sup>6</sup> as well as *ab initio* local-density approximation (LDA) calculations predicted that BC<sub>3</sub> layers have hexagonal symmetry.<sup>7,8</sup> Unfortunately, from experiments the details of the three layer stacking in the bulk material were not clear, though for some structures the electronic and structural properties were investigated.<sup>9,10</sup> Sun *et al.*<sup>11</sup> using *ab initio* LDA pseudopotential density-functional theory predicted two most stable BC<sub>3</sub> structures, a semiconductor and a metal, having ABAB and ABCABC layer stacking, respectively. The authors have shown that these phases have other layer shifts in comparison with the hexagonal graphite. Experiments also confirm the metallic property of *g*-BC<sub>3</sub>. X-ray-diffraction and *ab initio* calculations show that the distance by which layers are separated in BC<sub>3</sub> is 3.35 Å (similar to graphite).<sup>5,7</sup> This is a consequence of the weak van der Waals interaction between adjacent layers. A similar distance allows us to hope that the solvent molecules in the lithium ion batteries also will not penetrate between the layers of the BC<sub>3</sub> structure, as well as in the case of graphite. The carbon-carbon and boron-carbon bond lengths are 1.42 and 1.55 Å, respectively, suggesting that a B-C bond is weaker than a C-C bond.

Keeping in mind that lithium atoms can penetrate quite easily between adjacent graphite plates, it can be expected

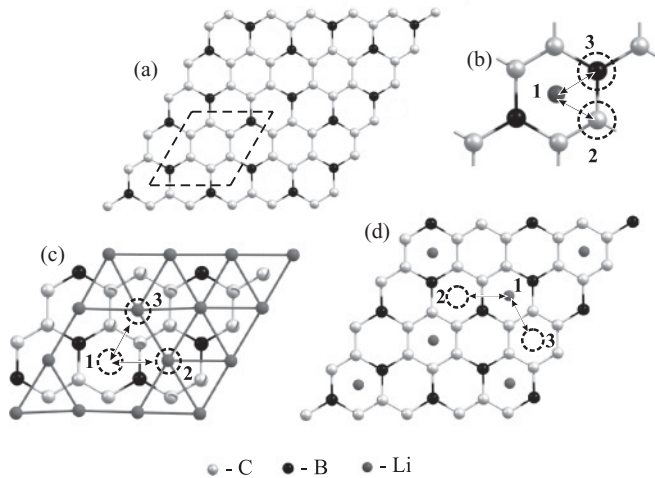


FIG. 1. (a) Plate of  $g\text{-BC}_3$  supercell used in calculations; the elementary unit cell is shown by the dotted line. (b) Jumps of a single lithium atom from position 1 to 2 or 3 inside  $g\text{-BC}_3$  of AB ordering. (c) Jumps of lithium vacancy from position 1 to 2 or 3 inside  $\text{Li}_2\text{BC}_3$  of AA ordering. (d) Jumps of the lithium atom from position 1 to 2 or 3 inside  $\text{Li}_{2/3}\text{BC}_3$  of AB ordering.

that these atoms can penetrate easily between adjacent  $g\text{-BC}_3$  plates as well. During intercalation in graphite, lithium atoms penetrate between graphite plates and partially donate their  $s$  electrons to the plates and become lithium cations. Due to the ionic repulsion, the maximum concentration of lithium between adjacent graphite plates corresponds to  $\text{LiC}_6$  with the lithium mass fraction of 8.7%.<sup>12–14</sup> At a higher lithium concentration, the Li-Li ionic repulsion exceeds the attractive energy of the lithium-carbon binding, so the structure becomes thermodynamically unstable. Under a further lithium absorption inside graphite a mixture of pure graphite and  $\text{Li}_2\text{C}_2$  compound having an orthorhombic ( $I_{mmm}$ ) lattice is formed.<sup>15</sup>

The electronic structure and vibrations of the  $g\text{-BC}_3$  structure were analyzed theoretically.<sup>16</sup> It was shown that there is a strong electron-density localization between C atoms in the all-carbon hexagonal rings, clearly indicating that the C-C bonding is stronger than the B-C bonding. However, the relatively weak B-C bonding can maintain hexagonal symmetry of the  $g\text{-BC}_3$  structure, with a weak bonding to C hexagons. Because the boron valence is lower than that of carbon,  $g\text{-BC}_3$  has an electron deficiency in comparison with graphite, and it is somewhat less stable. Lithium atoms donate  $s$  electrons into the  $\pi$  system of this electron-deficient structure, making it more stable. So one can expect that a maximum lithium concentration inside the  $g\text{-BC}_3$  structure may be higher than in the most intercalated graphite ( $\text{LiC}_6$ ). In addition, a larger electron transfer from lithium atoms to surrounding borons would lead to a wider electrostatic potential distribution in comparison with  $\text{LiC}_6$  and result in a potential barrier decrease for lithium movement. This should promote lithium migration. To verify these assumptions, we performed *ab initio* calculations of the binding energies, electronic band structures, and density of states (DOS) for a set of  $\text{Li}_x\text{BC}_3$  structures ( $\text{Li}_{2/3}\text{BC}_3$ ,  $\text{LiBC}_3$ ,  $\text{Li}_{1.5}\text{BC}_3$ , and  $\text{Li}_2\text{BC}_3$ ), intercalated by a different number of lithium atoms. The elementary unit cell of the prototype  $g\text{-BC}_3$  structure was used, which is shown in

Fig. 1(a). But for calculations of the  $\text{Li}_{2/3}\text{BC}_3$  structure, which is analogical to the maximum intercalated  $\text{LiC}_6$  structure, the unit cell consisting of  $3 \times 3 \times 1$  unit cells of a native  $g\text{-BC}_3$  structure was chosen.

## II. COMPUTATIONAL METHOD

For all calculations the plane-wave pseudopotential approach within the framework of the density-functional theory (GGA approach) was used, as implemented in VASP software.<sup>17,18</sup> The electron-ion interaction was treated with ultrasoft Vanderbilt pseudopotentials.<sup>19</sup> Using these pseudopotentials for  $\text{Li}_x\text{BC}_3$  structures allows us to reduce a cutoff energy down to 257 eV. The exchange-correlation terms were considered via the Perdew-Berke-Ernzerhof form of the generalized gradient approximation.<sup>20</sup> The  $k$ -point samplings of the first Brillouin zone (1BZ) were chosen as  $6 \times 6 \times 2$  according to the Monkhorst-Pack scheme.<sup>21</sup> All structures were relaxed until forces acting on all atoms became smaller than 0.05 eV/Å. The band structure and the DOS of the  $\text{Li}_2\text{BC}_3$  compound, having threefold lithium concentration in comparison with the  $\text{LiC}_6$  structure, are shown in Fig. 2. Analyzing the DOS of this structure, as well as the DOS of other investigated  $\text{Li}_x\text{BC}_3$  structures, it was established that all these structures are conductive, which is necessary for using them as a Li ion accumulator electrode.

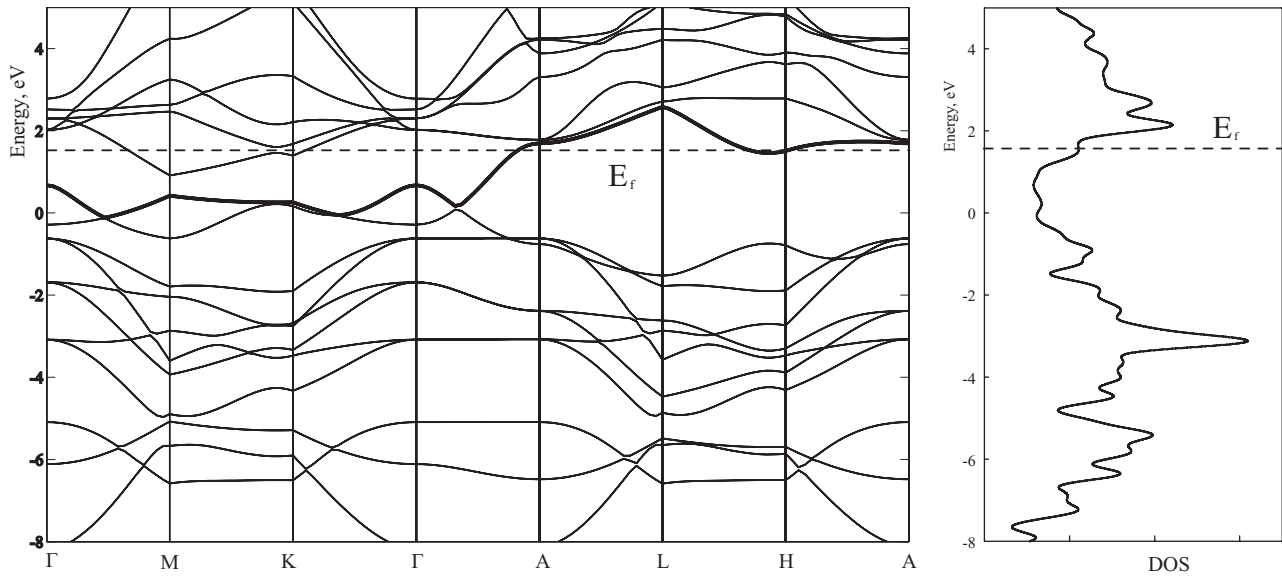
## III. RESULTS AND DISCUSSION

The binding energies of the lithium atom (the lithium chemical potential  $\mu$ ) for a set of  $\text{Li}_x\text{BC}_3$  structures were calculated as

$$xE_{\text{bind}}(\text{Li}) = E(\text{Li}_x\text{BC}_3) - E(\text{BC}_3) - xE(\text{Li}),$$

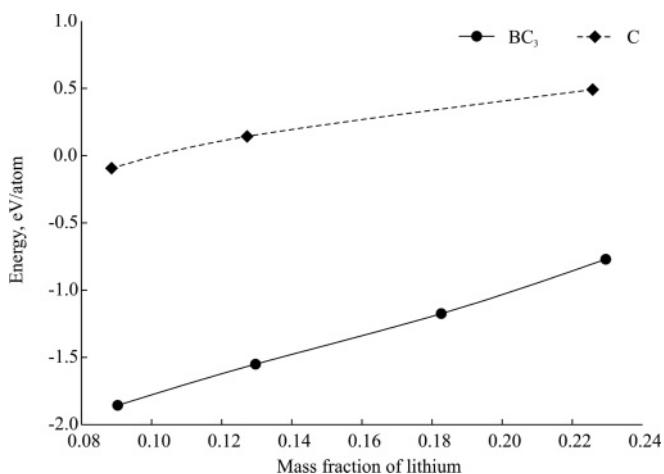
where  $E(\text{Li})$  is the energy per lithium atom in metallic lithium and similarly for  $E(\text{Li}_x\text{BC}_3)$  and  $E(\text{BC}_3)$ . The binding energies (per atom) for  $\text{Li}_{2/3}\text{BC}_3$ ,  $\text{LiBC}_3$ ,  $\text{Li}_{1.5}\text{BC}_3$ , and  $\text{Li}_2\text{BC}_3$  compounds are shown in Fig. 3. The binding energies of the three  $\text{Li}_x\text{C}$  ( $\text{LiC}_2$ ,  $\text{LiC}_4$ , and  $\text{LiC}_6$ ) structures were calculated and also shown by the dotted line in Fig. 3.

The all  $\text{Li}_x\text{BC}_3$  structures have Li binding energies in the  $-1.9$ - to  $-0.9$ -eV range relative to metallic Li. These values are essentially larger than the small chemical potential value of  $\text{LiC}_6$  ( $-0.2$  eV). In experiments the potential of  $\text{Li}_x\text{C}$  carbon electrodes containing a not too large amount of intercalated lithium can be positive relative to the lithium electrode to 0.5–0.8 V, so the calculated  $\text{LiC}_6$  binding energy correlates quite well with the experimental value of the  $\text{Li}_x\text{C}$  potential. It should be recalled that lithium chemical potential  $\mu$  is given by  $\mu = -eV$ , where  $V$  is the voltage of the cell and  $e$  is the magnitude of the electron charge. Of course, the relatively high potentials of the  $\text{Li}_x\text{BC}_3$  anode are detrimental for anode material in lithium ion batteries because they reduce the open circuit voltage (OCV) of cells on  $\approx 0.4$ –1.4 V. But the use of the  $\text{LiCoO}_2$  or  $\text{LiMn}_2\text{O}_4$  cathodes having the potential  $\sim 4$  V relative to metallic lithium will change the battery OCV from 3.6 to 2.6 V during the battery discharge. This voltage range is similar with a discharge profile of the Sony Li ion batteries having the petroleum coke anode and cell voltages variable from 3.9 to 2.5 V at the end of the discharge.

FIG. 2. Band structure and DOS of Li<sub>2</sub>BC<sub>3</sub> compound.

During calculations the structures were fully relaxed, including a shift of adjacent layers. The structures with two different initial orders of adjacent layers (AA and ABAB stacking) were calculated. Comparing the binding energies of structures with different stacking it was found that for examined lithium concentrations the structures with AA stacking have a lower energy than the ABAB structures. However, without lithium, the ABAB structure is more favorable than the AA structure with a small energy difference ( $\Delta E \approx 0.01$  eV/unit cell), in agreement with other studies.<sup>11</sup> The structures having the lowest energies were used in the discussion below.

As seen by the positive (repulsive) binding energies in Fig. 3, Li<sub>x</sub>C where  $x > 1/6$  is thermodynamically unstable in agreement with experiments.<sup>22</sup> However, Li<sub>x</sub>BC<sub>3</sub> is thermodynamically stable even for the case of Li<sub>2</sub>BC<sub>3</sub>, where lithium concentration is threefold in comparison with LiC<sub>6</sub>. In

FIG. 3. Dependence of the intercalation binding energy per lithium atom on the lithium mass fraction in *g*-BC<sub>3</sub> and graphite structures.

this structure lithium atoms occupy the centers of all hexagons formed by both carbon and boron atoms.

For possible application of Li<sub>x</sub>BC<sub>3</sub> structures as anodes in Li ion batteries it is desirable to have a high mobility of lithium ions, comparable to or higher than that for the Li<sub>x</sub>C compound. So, potential barrier values for the lithium atom jumps between potential minima inside different Li<sub>x</sub>BC<sub>3</sub> structures were calculated, for which the *g*-BC<sub>3</sub> supercell consisting of  $4 \times 4 \times 2$  unit cells and  $2 \times 2 \times 2$  *k* sampling of the 1BZ was chosen. The barrier values were calculated by the “nudge elastic band” method.<sup>23</sup> This method allows one to determine an energy optimized pathway (reaction path) between the two nearest energy minima. For the barrier calculations we considered three different path families of lithium atom jumps. The first family [see Fig. 1(b)] consists of two paths corresponding to the jump of a single lithium atom from one potential minima to another one in two different directions (1-2, 1-3) inside the ABAB BC<sub>3</sub> structure. The barrier values were equal to 0.19 and 0.15 eV, respectively. For comparison, the barrier values for the single Li atom jump inside pure graphite were calculated to be 0.44 and 0.47 eV for the 1-2 and 1-3 directions, respectively, that is in a good agreement with the previously reported value of 0.51 eV.<sup>24</sup> These values mean that lithium atoms at low concentration move more freely in the BC<sub>3</sub> structure than in the graphite. The second path family corresponds to the lithium vacancy jumps inside Li<sub>2</sub>BC<sub>3</sub> as shown in Fig. 1(c). In this structure with AA stacking all the Li atoms lie above centers of hexagons. The potential barrier values for Li atom jumps to the nearest Li vacancy were calculated to be 0.79 and 0.19 eV for 1-2 and 1-3 directions, respectively, while the barrier values inside fully intercalated LiC<sub>6</sub> are 0.49 eV.<sup>24</sup> The last path family involves the jumps of the lithium atom in two different directions (1-2, 1-3) inside partially filled Li<sub>2</sub>B<sub>3</sub>C<sub>9</sub> corresponding to the maximally intercalated graphite phase LiC<sub>6</sub> [see Fig. 1(d)]. The potential barrier values for Li jumps were found to be 0.57 and 0.66 eV, respectively. Summarizing, we found that the intercalated Li<sub>x</sub>BC<sub>3</sub> where  $x \leq 2$  is thermodynamically stable and shows a metallic conductance. Lithium atoms inside

the structures move more freely compared to the intercalated graphite  $\text{Li}_x\text{C}$  with  $x < 1/6$ .

These results indicate that the intercalated graphitelike  $\text{Li}_x\text{BC}_3$  ( $x \leq 2$ ) is a promising anode material for Li ion batteries or as an ionic conductor.

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