

## Structures and Formation Energies of $\text{Li}_x\text{C}_6$ ( $x=1-3$ ) and its Homologues for Lithium Rechargeable Batteries

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Using first principles density functional theory the formation energies of various binary compounds of lithium graphite and its homologues were calculated. Lithium and graphite react to form  $\text{Li}_1\text{C}_6$  (+141 mV) but not form  $\text{LiC}_4$  (-143 mV),  $\text{LiC}_3$  (-247 mV) and  $\text{LiC}_2$  (-529 mV) because they are less stable than lithium metal itself. Properties of structure and reaction potentials of  $\text{C}_5\text{B}$ ,  $\text{C}_5\text{N}$  and  $\text{B}_3\text{N}_3$  materials as iso-structural graphite were studied. Boron and nitrogen substituted graphite and boron-nitrogen material as a iso-electronic structured graphitic material have longer graphene layer spacing than that of graphite. The layer spacing of  $\text{Li}_x\text{C}_6$ ,  $\text{Li}_x\text{C}_5\text{B}$ ,  $\text{Li}_x\text{C}_5\text{N}$  materials increased until to  $x=1$ , and then decreased until to  $x=2$  and 3. Nevertheless  $\text{Li}_x\text{B}_3\text{N}_3$  has opposite tendency of layer spacing variation. Among various lithium compositions of  $\text{Li}_x\text{C}_5\text{B}$ ,  $\text{Li}_x\text{C}_5\text{N}$  and  $\text{Li}_x\text{B}_3\text{N}_3$ , reaction potentials of  $\text{Li}_x\text{C}_5\text{B}$  ( $x=1-3$ ) and  $\text{Li}_x\text{C}_5$  ( $x=1$ ) from total energy analyses have positive values against lithium deposition.

**Key Words** : Lithium battery, Graphites, Intercalation, Potential, Formation energy

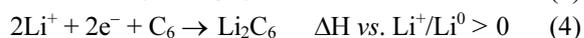
### Introduction

Carbonaceous materials including graphite have been used as active anode materials of rechargeable lithium ion batteries.<sup>1,2</sup> Lithium ions intercalate into graphite in a reversible manner. Staging phenomena of graphene sheets can take by the dominant lithium intercalation to lithium rich graphene stacks. Among lithium intercalated graphites (LIGs)  $\text{Li}_1\text{C}_6$  is known as a lithium richest compound under typical electrochemical conditions of lithium ion batteries. The *c*-axis of  $\text{LiC}_6$  elongates about 10.5% resulting in the same amount of volume expansion. Eq. (1) shows the lithium intercalation reaction to graphite. The specific capacity and the capacity density of graphite are 372 Ah/kg and 840 Ah/L applying the density of graphite as 2.26 g/mL.



specific capacity : 372 Ah/kg, capacity density : 840 Ah/L

Under typical conditions, the deposition of metallic lithium becomes thermodynamically more stable than intercalation of more of one lithium ion as shown Eq. (2)-(5).



The volume expansion (~10.5%) of  $\text{Li}_1\text{C}_6$  is relatively small compared to other anode materials such as silicon and tin. It is a reason to exhibit a good cyclic performance for graphite. As such, the key challenging issue for LIGs is to enhance the specific capacity (larger than 372 Ah/kg) and

capacity density (exceeding 840 Ah/L) with the same or better cycleability.

Theoretical studies were performed as follows; Fauster *et al.*<sup>3</sup> studied band-structures of  $\text{LiC}_6$  based on the calculated Fermi level and found that the potential of lithium-intercalated graphite was reduced for 3 eV compared to graphite. Yazami *et al.*<sup>4</sup> reported the structures of  $\text{LiC}_6$ ,  $\text{LiC}_4$ ,  $\text{LiC}_3$  and  $\text{LiC}_2$  and found that the average Li-Li distance of a  $\text{Li}_2$  pair in  $\text{LiC}_2$  is 2.46 Å. Which value is shorter than 4.26 Å in  $\text{LiC}_6$  having hexagonal structure and 3.04 Å in lithium metal also. Titantah *et al.*<sup>5</sup> performed ENLES (energy-loss near-edge structure) calculations on lithium and carbon of  $\text{LiC}_6$  and related compounds by the density functional theory (DFT) calculations using the programs of WIEN2k and Monte Carlo simulation to get distribution of the density of states (DOS) and net charge properties of lithium and carbon atoms for  $\text{LiC}_{36}$ ,  $\text{LiC}_{12}$  and  $\text{LiC}_6$ . Suzuki *et al.*<sup>6</sup> studied on the stacking structures of the lithium intercalated graphene sheets by the MO calculations using MOPAC 2000 program and discussed on the possibility of the multiple Li ion layer storage between graphene sheets. Li *et al.*<sup>7</sup> studied total energy, stability, ionization potential, electron affinity and dissociation channel of  $\text{LiC}_n$ ,  $\text{LiC}_n^+$  and  $\text{LiC}_n^-$  ( $n = 1-10$ ) using the GAUSSIAN program. Yamamoto *et al.*<sup>8</sup> studied that the chemical energy of the lithium intercalation to graphite could be obtained by the FLAPW (Wien97) calculation using by LDA-GW and GGA-PBE potential code in the year of 2004 and found that the reaction potentials of  $\text{Li}_3\text{C}_8$  ( $\text{Li}_{2.25}\text{C}_6$ ) and  $\text{Li}_{17}\text{C}_{60}$  ( $\text{Li}_{1.7}\text{C}_6$ ) (0.375 and 0.283 of  $x^{-1}$  in  $\text{LiC}_x$ ) as -500 and -230 mV ( $\text{Li}/\text{Li}^+$ ), respectively. Imai *et al.*<sup>9</sup> studied crystal structures and total energies of the lithium intercalated graphites such as  $\text{LiC}_{18}$ ,

LiC<sub>12</sub>, LiC<sub>8</sub>, LiC<sub>6</sub>, LiC<sub>4</sub> and LiC<sub>2</sub> using the Cambridge Serial Total Energy Package (CASTEP) program and the potential codes of LDA and GGA and found the following. The chemical potentials of LiC<sub>6</sub> varied with LDA and GGA potential codes as +480 mV and +230 mV, respectively. The chemical potentials of LiC<sub>4</sub> for two different structures of Aα'B and αAA stacking in lithium arrangements were evaluated as -300 mV and -30 mV with the potential code of LDA and as -430 mV and -450 mV with the potential code of GGA, respectively. The different tendency of the chemical potentials by the structures and potential codes were obtained in this study. The chemical potentials of LiC<sub>2</sub> were -860 mV and -930 mV for the LDA and GGA potential codes, respectively.

In this article the structure and the reaction potential of the lithiated graphites and its homologues were considered using the first principles calculations of VASP. The possibility of the higher lithium intercalation to graphite than 1 lithium atom per 6 carbon atoms was explored. For this exploration boron and nitrogen substituted graphite and boron-nitrogen iso-electronic structured graphitic material were also studied.

### Calculation

The total-energy calculation and full structural optimization were performed using the Vienna *ab initio* Simulation Package (VASP 4.6).<sup>10</sup> Projector augmented-wave pseudopotentials were used.<sup>11</sup> The exchange and correlation were treated within the generalized gradient approximation (GGA).<sup>12</sup> The

size of the k-mesh was chosen to be 9 × 16 × 10 for the conventional cell. To assure convergence of the energy, a cutoff value of 330 eV was used. It was found that the convergence in the total energy was better than 1 meV/atom using this cutoff energy and k-mesh grid. Total-energy minimization *via* a lattice parameter optimization and atomic position relaxation in a conjugate gradient routine was obtained by calculating the Hellmann-Feynman forces which are reduced to within the 0.01 eV/Å for each atom. Other computational and structural details are available in references.<sup>13</sup>

The reaction potentials were calculated from the total energies of reactants and products using Eq. (6).<sup>14-16</sup> The total energy calculations were performed for iso-structural C<sub>3</sub>B, C<sub>5</sub>N, B<sub>3</sub>N<sub>3</sub> using same structural data of graphite.

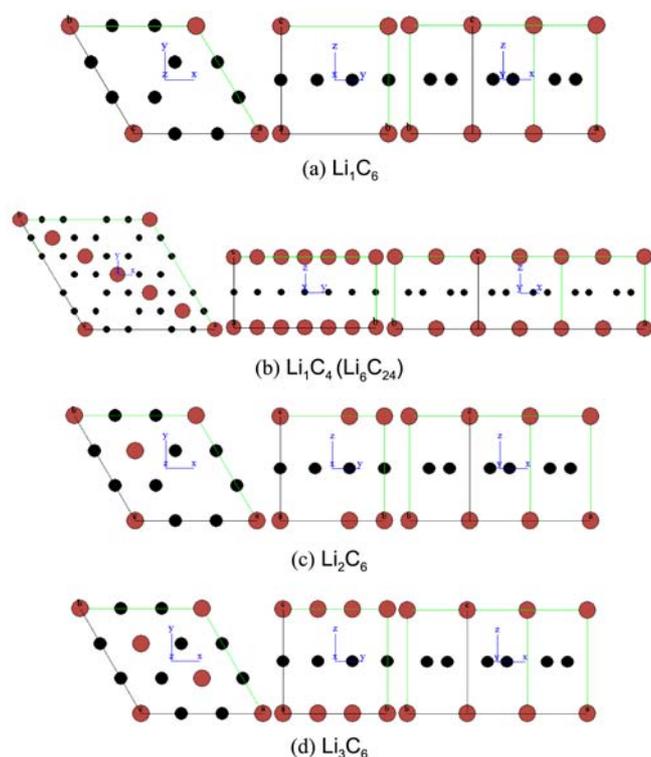
$$V(x) = \frac{\mu_{\text{Li}}^{\text{cathode}}(x) - \mu_{\text{Li}}^{\text{anode}}(x)}{-nF} \quad (6)$$

### Results and Discussion

Graphite accomplished by the piling (stacking) of graphene sheets which has continuous connections of the benzene resonance structures. Lithium can be accommodated to the center of benzene hexagon and stabilized by the delocalized *p* orbital. The higher lithium content than Li<sub>1</sub>C<sub>6</sub> can be considered such as Li<sub>1</sub>C<sub>4</sub>, Li<sub>2</sub>C<sub>6</sub> and Li<sub>3</sub>C<sub>6</sub> theoretically. The structural information was collected at Table 1 including graphite, Li<sub>1</sub>C<sub>6</sub> and hypothetical lithium graphite of Li<sub>1</sub>C<sub>4</sub>,

**Table 1.** The structural parameters for graphite and lithium intercalated graphites

Materials	Crystallographic data from inorganic database						Fully relaxed crystallographic data by VASP <i>ab initio</i> calculation					
	Structural parameters (Å, °)	Unit cell volume (Å <sup>3</sup> )	Density (g/mL)	Distance graphene layers (Å)	Distance between Li-C (Å)	Distance between Li-Li (Å)	Structural parameters	Unit cell volume (Å <sup>3</sup> )	Density (g/mL)	Distance graphene layers (Å)	Distance between Li-C (Å)	Distance between Li-Li (Å)
Graphite (P6 <sub>3</sub> /mmc)	a=2.464 c=6.711 α=90 γ=120	35.29	2.261	3.355	-	-	a=2.469 c=7.377 α=90 γ=120	38.93	2.409	3.6885	-	-
Li <sub>1</sub> C <sub>6</sub>	a=4.290 c=3.737 α=90 γ=120	59.56	2.203	3.737	2.353	3.737	a=4.319 c=3.672 α=90 γ=120	59.33	2.211	3.6723	2.334	3.672
Li <sub>1</sub> C <sub>4</sub> (Li <sub>6</sub> C <sub>24</sub> )	a=8.580 c=3.737 α=90 γ=120	59.56	2.203	3.737	2.353	2.477	a=8.7402 c=3.660 α=90 γ=120	60.532 (241.25)	2.271	3.6599	2.339	2.528
Li <sub>2</sub> C <sub>6</sub>	a=4.300 c=7.400 α=90 γ=120	59.25	-	3.700 <sup>20)</sup>	-	2.477	a=4.395 c=7.222 α=90 γ=120	60.42	2.362	3.6112	2.326	2.538
Li <sub>3</sub> C <sub>6</sub>	N.A.	-	-	-	-	2.477	a=4.488 c=3.513 α=90 γ=120	61.28	2.517	3.51293	2.307	2.591



**Figure 1.** The plane structures of the lithium intercalated graphites of (a)  $\text{Li}_1\text{C}_6$ , (b)  $\text{Li}_1\text{C}_4$ , (c)  $\text{Li}_2\text{C}_6$ , (d)  $\text{Li}_3\text{C}_6$ .

$\text{Li}_2\text{C}_6$  and  $\text{Li}_3\text{C}_6$ .

Graphite has two different stacking structures of graphene sheets as AA and ABC having the similar structural stability.  $\text{Li}_1\text{C}_6$  has a stacking structure of graphene sheets as AAA being arranged neatly as the results of the translation of graphene sheets.  $\text{Li}_x\text{C}_6$  ( $x=1.5, 2, 3$ ) may also have same AAA stacking of graphene sheets. The plane structures of  $\text{Li}_1\text{C}_6$ ,  $\text{Li}_1\text{C}_4$ ,  $\text{Li}_2\text{C}_6$  and  $\text{Li}_3\text{C}_6$  were depicted at Figure 1 considering the structural stability.

The possibility of staging between  $\text{Li}_1\text{C}_6$  and  $\text{Li}_3\text{C}_6$  was not mentioned. The structure of  $\text{Li}_2\text{C}_6$  was studied by S. Rabii and D. Geurard.<sup>17</sup>  $\text{Li}_1\text{C}_6$ ,  $\text{Li}_1\text{C}_4$ ,  $\text{Li}_2\text{C}_6$  and  $\text{Li}_3\text{C}_6$  have same stacking patterns of graphene sheets with the different ordering and content of the lithium occupation. The layer spacing of graphene sheets in  $\text{Li}_1\text{C}_6$ ,  $\text{Li}_1\text{C}_4$ ,  $\text{Li}_2\text{C}_6$  and  $\text{Li}_3\text{C}_6$  will be varied by the different interaction of each atom.

The variations of the layer spacing were presented in Table 1 as the results of the first principles calculations of VASP by the full relaxation. By the change from  $\text{Li}_1\text{C}_6$  to  $\text{Li}_1\text{C}_4$ ,  $\text{Li}_2\text{C}_6$  and  $\text{Li}_3\text{C}_6$  the layer spacing were shrunk from 3.6723 Å to 3.660 Å, 3.6112 Å and 3.5129 Å, respectively. The shrinkages of  $\text{Li}_1\text{C}_4$ ,  $\text{Li}_2\text{C}_6$  and  $\text{Li}_3\text{C}_6$  were 0.34%, 1.7% and 4.3% compared to  $\text{Li}_1\text{C}_6$ . The expansions of  $\text{Li}_1\text{C}_4$ ,  $\text{Li}_2\text{C}_6$  and  $\text{Li}_3\text{C}_6$  were 9.5%, 9.12%, 7.7% and 4.7% compared to 3,354 Å of graphite. The graphene layer spacing of  $\text{Li}_1\text{C}_6$ ,  $\text{Li}_1\text{C}_4$  and  $\text{Li}_2\text{C}_6$  have the shorter values for the calculation than that of the inorganic database and the published results. The distances of Li-Li bond in  $\text{Li}_3\text{C}_6$  was 2.591 Å to be longer than that of 2.528 Å in  $\text{Li}_1\text{C}_4$  and 2.538 Å in  $\text{Li}_2\text{C}_6$ . All distances of Li-Li bonds in  $\text{Li}_x\text{C}_6$  ( $x=1.5, 2,$

**Table 2.** The reaction energies of  $\text{Li}_x\text{C}_6$  materials from graphite and lithium

Reactions	Total energy of product (eV)	Calculated reaction energy (eV)	Calculated reaction potential (mV)	Specific capacity (mAh/g)
$\text{Li}^0$	-1.901			
$\text{C}_6$	-55.261			
$\text{Li}^0 + \text{C}_6 \rightarrow \text{Li}_1\text{C}_6$	-57.303	-0.141	+141	372
$\text{Li}^0 + \text{C}_4 \rightarrow \text{Li}_1\text{C}_4$	-38.599	0.143	-143	558
$2\text{Li}^0 + \text{C}_6 \rightarrow \text{Li}_2\text{C}_6$	-58.570	0.493	-247	744
$3\text{Li}^0 + \text{C}_6 \rightarrow \text{Li}_3\text{C}_6$	-59.376	1.588	-529	1116

3) were shorter than that of  $\text{Li}_1\text{C}_6$  (3.672 Å) and Li metal (2.978 Å). The total energies of  $\text{C}_6$ ,  $\text{Li}_1\text{C}_6$ ,  $\text{Li}_1\text{C}_4$ ,  $\text{Li}_2\text{C}_6$  and  $\text{Li}_3\text{C}_6$  were evaluated as -55.291 eV, -57.303 eV, -38.599 eV, -58.570 eV and -59.376 eV by the VASP calculations, respectively. The formation energies and potentials of  $\text{Li}_1\text{C}_6$ ,  $\text{Li}_1\text{C}_4$ ,  $\text{Li}_2\text{C}_6$  and  $\text{Li}_3\text{C}_6$  were derived from the total energies including the total energy of lithium as -1.191 eV per lithium as Table 2. The reaction potential of  $\text{Li}_1\text{C}_6$  from lithium and graphite was +141 mV which means that the formation of  $\text{Li}_1\text{C}_6$  is favorable. However the reaction potentials of  $\text{Li}_1\text{C}_4$ ,  $\text{Li}_2\text{C}_6$  and  $\text{Li}_3\text{C}_6$  were -143 mV, -247 mV and -529 mV, respectively. These negative reaction potentials have the meaning of that the deposition of lithium is easier than the formation of  $\text{Li}_1\text{C}_4$ ,  $\text{Li}_2\text{C}_6$  and  $\text{Li}_3\text{C}_6$ .

The reaction potentials of  $\text{Li}_3\text{C}_8$  ( $\text{Li}_{2.25}\text{C}_6$ ) and  $\text{Li}_{17}\text{C}_{60}$  ( $\text{Li}_{1.7}\text{C}_6$ ) (0.375 and 0.283 of  $x^{-1}$  in  $\text{LiC}_x$ ) were reported as -500 and -230 mV ( $\text{Li}/\text{Li}^+$ ) in 2004.<sup>18</sup> The reaction potential of  $\text{Li}_3\text{C}_8$  as -500 mV is similar to the reaction potential of  $\text{Li}_3\text{C}_6$  as -529 mV of this study. And the reaction potential of  $\text{Li}_{17}\text{C}_{60}$  as -230 mV is lower than the reaction potential of  $\text{LiC}_4$  as -143 mV of this report however is similar to the reaction potential of  $\text{Li}_2\text{C}_6$  as -247 mV of this study. The differences of chemical potentials were originated from the differences of the program of FLAPW (Wien97) and VASP the potential codes of LDA and GGA, and other calculation parameters. +230 mV of the reaction potential<sup>19</sup> of  $\text{LiC}_6$  calculated by using Cambridge Serial Total Energy Package (CASTEP) with the GGA potential code is different compared to +141 mV calculated by using VASP. These two different values are higher than +70 mV<sup>20</sup> as the experimental potential of  $\text{Li}_1\text{C}_6$ . The reaction potentials of  $\text{LiC}_4$  with action potentials of  $\text{LiC}_6$  of Li Total Energy Package (CASTEP) with the GGA potential code is different compared to +141 mV calculated by using VASP. These two different values are higher than +70 mV as the experimental potential of  $\text{Li}_1\text{C}_6$ . The reaction potentials of  $\text{LiC}_4$  with action potentials of  $\text{LiC}_6$  of Li with the GGA potential codation and -143 mV for VASP calculation with the same potential code of GGA, respectively, to be some different values within the same negative potentials. The reaction potentials of  $\text{LiC}_2$  with potential code of GGA were -930 mV and -529 mV for CASTEP and VASP calculations, respectively.

Tossici *et al.*<sup>21,22</sup> prepared LiC<sub>2</sub> by the mechanical ball milling<sup>23,24</sup> of lithium and graphite, assembled LiC<sub>2</sub>/Li cell, and controlled the voltage of LiC<sub>2</sub>/Li cell to get the information of deintercalation and intercalation. LiC<sub>2</sub>/Li cell showed the potential above 0 V vs. Li/Li<sup>+</sup> for the 1st deintercalation with the specific capacity of 1038 mAh/g

which was close to the theoretical values of 1115 mAh/g. The specific capacity for the next intercalation was only 368 mAh/g to form LiC<sub>6</sub> not LiC<sub>2</sub>.

Similar studies were performed for iso-structural C<sub>5</sub>B, C<sub>5</sub>N and B<sub>3</sub>N<sub>3</sub> materials. Known structural data and VASP calculated structural data were shown at Table 3, 4, 5.

**Table 3.** The structural parameters for Li<sub>x</sub>C<sub>5</sub>B as graphitic structured material

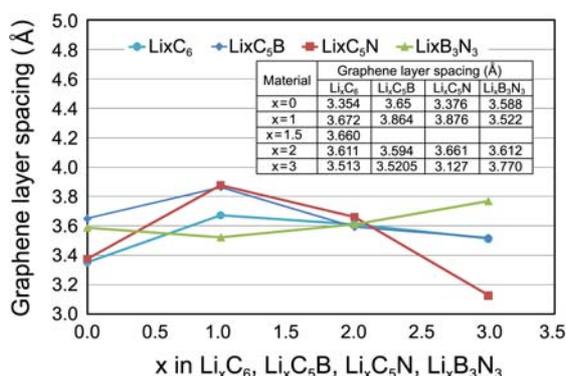
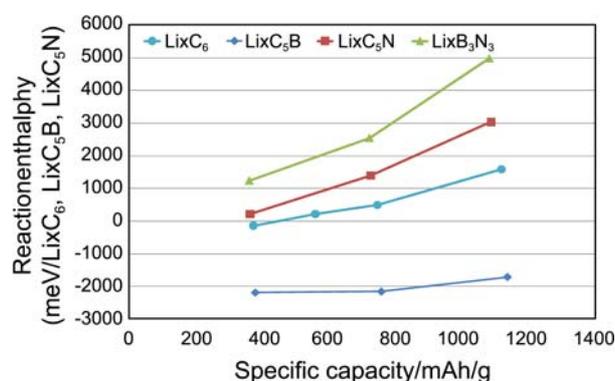
Materials	Used crystallographic data						Fully relaxed crystallographic data by VASP ab initio calculation					
	Structural parameters (Å, °)	Unit cell volume (Å <sup>3</sup> )	Density (g/mL)	Distance graphene layers (Å)	Distance between Li-C (Å)	Distance between Li-Li (Å)	Structural parameters	Unit cell volume (Å <sup>3</sup> )	Density (g/mL)	Distance graphene layers (Å)	Distance between Li-C (Å)	Distance between Li-Li (Å)
C <sub>5</sub> B(ABC)	a=4.290 c=10.062 α=90 γ=120	53.46	2.201	3.354	-	-	a=4.404 c=10.951 α=89 β=92 γ=120	61.21	1.922	3.650	-	-
Li <sub>1</sub> C <sub>5</sub> B	a=4.290 c=3.737 α=90 γ=120	59.56	2.169	3.737	2.353	3.737	a=4.418 c=3.864 α=90 γ=120	65.44	1.974	3.864	2.422	3.864
Li <sub>2</sub> C <sub>5</sub> B	a=4.290 c=3.737 α=90 γ=120	59.56	2.363	3.737	-	2.477	a=4.482 b=4.493 c=3.594 α=90 γ=120	62.72	2.244	3.594	2.286	2.570 2.635
Li <sub>3</sub> C <sub>5</sub> B	a=4.290 c=3.737 α=90 γ=120	59.56	2.556	3.737	-	2.477	a=4.569 c=3.520(5) α=90 γ=120	63.65	2.392	3.5205	2.299	2.637

**Table 4.** The structural parameters for Li<sub>x</sub>C<sub>5</sub>N as graphitic structured material

Materials	Used crystallographic data						Fully relaxed crystallographic data by VASP ab initio calculation					
	Structural parameters (Å, °)	Unit cell volume (Å <sup>3</sup> )	Density (g/mL)	Distance graphene layers (Å)	Distance between Li-C (Å)	Distance between Li-Li (Å)	Structural parameters	Unit cell volume (Å <sup>3</sup> )	Density (g/mL)	Distance graphene layers (Å)	Distance between Li-C (Å)	Distance between Li-Li (Å)
C <sub>5</sub> N(ABC)	a=4.290 c=10.062 α=90 γ=120	53.46	2.301	3.354	-	-	a=4.093 c=10.128 α=90 γ=120-	49.01	2.509	3.376	-	-
Li <sub>1</sub> C <sub>5</sub> N	a=4.290 c=3.737 α=90 γ=120	59.56	2.258	3.737	2.353	3.737	a=4.284 c=3.876 α=90 γ=120	61.62	2.183	3.876	2.251	3.876
Li <sub>2</sub> C <sub>5</sub> N	a=4.290 c=3.737 α=90 γ=120	59.56	2.452	3.737	-	2.477	a=4.379 b=4.366 c=3.661 α=90 γ=120	60.55	2.412	3.661	2.217	2.460 2.657
Li <sub>3</sub> C <sub>5</sub> N	a=4.290 c=3.737 α=90 γ=120	59.56	2.645	3.737	-	2.477	a=4.391 c=3.127 α=90 γ=120	68.93	2.286	3.127	2.497	2.479

**Table 5.** The structural parameters for  $\text{Li}_x\text{B}_3\text{N}_3$  as iso-electronic graphitic structured material

Materials	Used crystallographic data						Fully relaxed crystallographic data by VASP ab initio calculation						
	Structural parameters ( $\text{\AA}$ , $^\circ$ )	Unit cell volume ( $\text{\AA}^3$ )	Density (g/mL)	Distance graphene layers ( $\text{\AA}$ )	Distance between Li-C ( $\text{\AA}$ )	Distance between Li-Li ( $\text{\AA}$ )	Structural parameters	Unit cell volume ( $\text{\AA}^3$ )	Density (g/mL)	Distance graphene layers ( $\text{\AA}$ )	Distance between Li-B ( $\text{\AA}$ )	Distance between Li-N ( $\text{\AA}$ )	Distance between Li-Li ( $\text{\AA}$ )
isoelectronic Graphite ( $\text{B}_3\text{N}_3$ ) ( $\text{P6}_3/\text{mmc}$ )	a=2.464 c=6.711 $\alpha=90$ $\gamma=120$	35.29	2.261	3.355	-	-	a=4.3505 c=7.1767 $\alpha=90$ $\gamma=120$	117.63	2.102	3.5883	-	-	-
$\text{Li}_1\text{B}_3\text{N}_3$	a=4.290 c=3.737 $\alpha=90$ $\gamma=120$	59.56	2.203	3.737	2.353	3.737	a=4.4176 c=3.5223 $\alpha=90$ $\gamma=120$	59.53	2.270	3.5223	2.310	2.285	3.5223
$\text{Li}_2\text{B}_3\text{N}_3$	N.A.	-	-	-	-	-	a=4.4902 c=3.6121 $\alpha=90$ $\gamma=120$	63.07	2.326	3.6121	2.353	2.341	3.6121
$\text{Li}_3\text{B}_3\text{N}_3$	N.A.	-	-	-	-	-	a=4.5560 c=3.7696 $\alpha=90$ $\gamma=120$	67.76	2.335	3.7696	2.420	2.420	2.630 2.856 3.770

**Figure 2.** Graphene layer spacing of the lithium intercalated graphites and its homologues.**Figure 3.** Reaction enthalpies of the lithium intercalated graphites and its homologues.

Nitrogen substituted material has longer graphene layer spacing as 3.37  $\text{\AA}$  than  $\text{C}_6$ (graphite). Far differently, boron substituted material has 3.65  $\text{\AA}$  to show 8.8% expansion

**Table 6.** The reaction energies of  $\text{Li}_x\text{C}_5\text{B}$  materials from  $\text{C}_5\text{B}$  and lithium

Reactions	Total energy of product (eV)	Calculated reaction energy (eV)	Calculated reaction potential (mV)	Specific capacity (mAh/g)
$\text{Li}^0$	-1.901			
$\text{C}_5\text{B}(\text{ABC})$	-51.575			
$\text{Li}^0 + \text{C}_5\text{B} \rightarrow \text{Li}_1\text{C}_5\text{B}$	-55.666	-2.190	2190	378
$2\text{Li}^0 + \text{C}_5\text{B} \rightarrow \text{Li}_2\text{C}_5\text{B}$	-57.536	-2.159	1080	756
$3\text{Li}^0 + \text{C}_5\text{B} \rightarrow \text{Li}_3\text{C}_5\text{B}$	-58.991	-1.713	571	1135

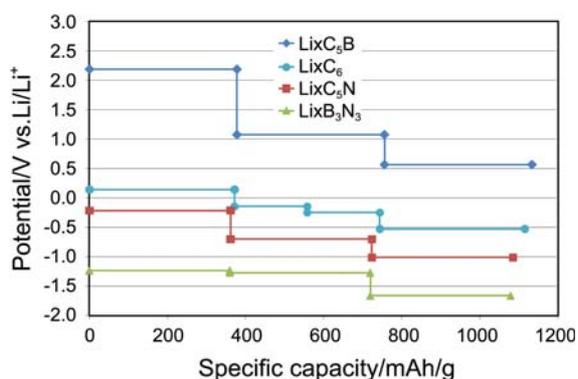
**Table 7.** The reaction energies of  $\text{Li}_x\text{C}_5\text{N}$  materials from  $\text{C}_5\text{N}$  and lithium

Reactions	Total energy of product (eV)	Calculated reaction energy (eV)	Calculated reaction potential (mV)	Specific capacity (mAh/g)
$\text{Li}^0$	-1.901			
$\text{C}_5\text{N}(\text{ABC})$	-53.369			
$\text{Li}^0 + \text{C}_5\text{N} \rightarrow \text{Li}_1\text{C}_5\text{N}$	-55.057	0.213	-213	362
$2\text{Li}^0 + \text{C}_5\text{N} \rightarrow \text{Li}_2\text{C}_5\text{N}$	-55.769	1.402	-701	724
$3\text{Li}^0 + \text{C}_5\text{N} \rightarrow \text{Li}_3\text{C}_5\text{N}$	-56.036	3.036	-1012	1086

compared to graphite.  $\text{B}_3\text{N}_3$  is iso-electronic material to graphite having 3.59  $\text{\AA}$  of layer spacing. The layer spacing of  $\text{Li}_x\text{C}_6$ ,  $\text{Li}_x\text{C}_5\text{B}$ ,  $\text{Li}_x\text{C}_5\text{N}$  materials increased until to  $x=1$ , and then decreased until to  $x=2$  and 3. Nevertheless  $\text{Li}_x\text{B}_3\text{N}_3$  has opposite tendency of layer spacing variation. Results were depicted as Figure 2. Structural data of  $\text{B}_3\text{N}_3$  was known as 2.1693  $\text{\AA}$  for a axis and 6.65626  $\text{\AA}$  for c axis with  $\text{P6}_3/\text{mmc}$  space group.

**Table 8.** The reaction energies of  $\text{Li}_x\text{B}_3\text{N}_3$  materials from  $\text{B}_3\text{N}_3$  and lithium

Reactions	Total energy of product (eV)	Calculated reaction energy (eV)	Calculated reaction potential (mV)	Specific capacity (mAh/g)
$\text{Li}^0$	-1.901			
$\text{B}_3\text{N}_3(\text{AB})$	-52.689			
$\text{B}_3\text{N}_3(\text{ABC})$	-52.690			
$\text{Li}^0 + \text{B}_3\text{N}_3 \rightarrow \text{Li}_1\text{B}_3\text{N}_3$	-53.355	1.236	-1236	360
$2\text{Li}^0 + \text{B}_3\text{N}_3 \rightarrow \text{Li}_2\text{B}_3\text{N}_3$	-53.944	2.548	-1274	720
$3\text{Li}^0 + \text{B}_3\text{N}_3 \rightarrow \text{Li}_3\text{B}_3\text{N}_3$	-53.400	4.993	-1664	1080

**Figure 4.** Reaction potential behavior of lithium intercalated graphites and its homologues as (a)  $\text{C}_6$ , (b)  $\text{C}_5\text{B}$ , (c)  $\text{C}_5\text{N}$ , (d)  $\text{B}_3\text{N}_3$ .

Total energy of each lithium composition of  $\text{Li}_x\text{C}_5\text{B}$ ,  $\text{Li}_x\text{C}_5\text{N}$  and  $\text{Li}_x\text{B}_3\text{N}_3$  were evaluated under the full relaxation condition as shown in Table 6, 7 and 8, respectively. Reaction enthalpy can be delivered from the total energy of reactants and product using described reaction equations. Reaction enthalpies were compared together at Figure 3.  $\text{Li}_x\text{C}_5\text{B}$  ( $x=1-3$ ) and  $\text{Li}_x\text{C}_5$  ( $x=1$ ) have negative reaction enthalpies against lithium metal deposition. Finally reaction potentials were also evaluated from each reaction enthalpies as shown in Table 6, 7, 8 and Figure 4.  $\text{Li}_x\text{C}_5\text{B}$  ( $x=1-3$ ) and  $\text{Li}_x\text{C}_5$  ( $x=1$ ) have positive reaction potentials against lithium deposition as indicated in enthalpy results.

### Conclusion

The first principles calculations using VASP 4.6 and the structural studies of lithium graphite and its homologues were carried out to get information of structure, total energy, reaction energy and reaction potential. The reaction potential to form  $\text{Li}_1\text{C}_6$  from lithium and graphite was calculated as +141 mV to be higher than the potential of lithium deposition. The reaction potentials to form  $\text{Li}_6\text{C}_{24}(\text{Li}_1\text{C}_4)$ ,  $\text{Li}_2\text{C}_6(\text{Li}_1\text{C}_3)$  and  $\text{Li}_3\text{C}_6(\text{Li}_1\text{C}_2)$  were calculated as -143 mV, -247 mV and -529 mV, respectively, to be lower than the potential of lithium deposition.

$\text{C}_5\text{B}$ ,  $\text{C}_5\text{N}$  and  $\text{B}_3\text{N}_3$  materials as iso-structural graphite

were studied. Boron and nitrogen substituted graphite and boron-nitrogen material as a iso-electronic structured graphitic material have longer graphene layer spacing than that of  $\text{C}_6$  (graphite). The layer spacing of  $\text{Li}_x\text{C}_6$ ,  $\text{Li}_x\text{C}_5\text{B}$ ,  $\text{Li}_x\text{C}_5\text{N}$  materials increased until to  $x=1$ , and then decreased until to  $x=2$  and 3. Nevertheless  $\text{Li}_x\text{B}_3\text{N}_3$  has opposite tendency of layer spacing variation. Reaction potentials could be evaluated from each reaction enthalpies originated from total energy of each lithium composition of  $\text{Li}_x\text{C}_5\text{B}$ ,  $\text{Li}_x\text{C}_5\text{N}$  and  $\text{Li}_x\text{B}_3\text{N}_3$ .  $\text{Li}_x\text{C}_5\text{B}$  ( $x=1-3$ ) and  $\text{Li}_x\text{C}_5$  ( $x=1$ ) have positive reaction potentials against lithium deposition. Therefore boron-substituted graphite has the possibility to have useable specific capacity range of 756 mAh/g for the potential range of 0-1 V vs.  $\text{Li/Li}^+$ .

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