First principle calculation study for structure of lithium-graphene compound

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We have calculated binding energies between bilayer graphene and lithium atom for the application of cathode of lithium-ion batteries. In this study, it is found that LiC_8 structure is the most stable structure among various lithium-graphene compound structure.

INTRODUCTION

Carbon is one of the component of all life forms and most abundant element in the following hydrogen, helium and oxygen. Graphene, which consist of carbon, is two-dimensional material and basic material of carbon nanotube, fullerene, and graphite.

Recently, graphene have been studied for applications of lithium-ion batteries, solar cell, and transistor [1]. Graphene can be obtained by mechanical exfoliation or chemical vapor deposition method. In particular, mechanical exfoliation method has more excellent performance than others [2]. In this paper, we talk about the relationship between bilayer graphene and lithium atom for the application of cathode of lithium-ion batteries.

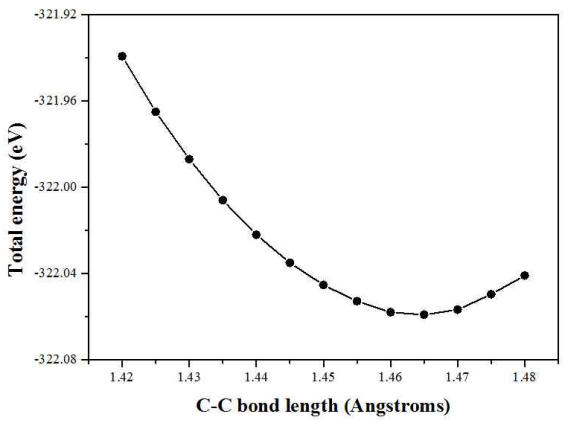

Figure 1. Total energy as a function of carbon – carbon bond length

CALCULATIONS METHODS

In this study, we have performed density functional theory (DFT) calculations within generalized gradient approximation (GGA) for exchange-correlation functional with SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) program on the EDISON (EDucation-research Integration through Simulation On the Net) web site [3]. All system is used single zeta atomic orbital basis set. All atomic coordinates are fully relaxed until the forces are less than 0.01 eV/Å. We calculated the primitive unit cell of graphene by optimizing within 1x1x1 k-sampling. For accuracy, we confirmed that carbon - carbon bond length is 1.465 Å increasing k-sampling in 5x5x1, as shown in Figure 1.

RESULTS & DISCUSSIONS

Before optimized graphene structure was found, we had defined that carbon - carbon bond length is 1. 465 Å. Primitive unit cell of graphene has three lattice vectors: two vectors are $\mathrm{a}_1 = a(\frac{3}{2}, -\frac{\sqrt{3}}{2}, 0)$ and $\mathrm{a}_2 = a(\frac{3}{2}, \frac{\sqrt{3}}{2}, 0)$, and the other vector is $\mathrm{a}_3 = c(0,0,1)$, where a and c represent carbon - carbon bond length and vacuum height, respectively.

Next, we have calculated the distance between the two graphenes when the lithium atoms are located between them. According to how lithium atoms are placed into the bilayer graphene, we

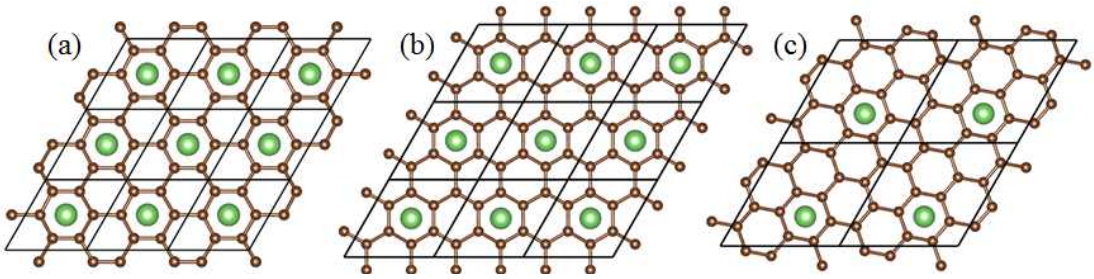

Figure 2. (a) LiC_6, (b) LiC_8 and (c) Li C_{14} super cell

consider top view of three type structure as shown in Figure 2. Figure 2 (a), (b) and (c) represent six, eight and fourteen carbon atoms of upper (or bottom) graphene per one lithium atom, respectively. Structure of Figure 2 (a), (b) and (c) are called LiC_6, LiC_8 and LiC_{14}, respectively.

When some atoms were combined, we found the most stable structure from results of calculations of binding energies. Structure of lower binding energy is more stable structure. We can calculate binding energy by using the equation (1).

$$E_b = \frac{1}{n}(E_{total} - E_{graphene} - n \times E_{Li}), \qquad (1)$$

where E_b is binding energy of lithium into bilayer graphene system, E_{total} is total energy of lithium into bilayer graphene system, $E_{graphene}$ is total energy of bilayer graphene system, E_{Li} is total energy of lithium atom, and n is the number of lithium atoms. Lower E_b of system is more stable structure than others. In this study, the number of lithium atoms is only one per super cell. So, equation (2) was used instead of equation (1).

$$E_b = E_{total} - E_{graphene} - E_{Li}. \qquad (2)$$

The results of the distance between two graphenes are ~3.7 Å, ~3.9 Å and ~6.0 Å in Figure 2 (a), (b) and (c), respectively. LiC_8 is most stable structure because binding energy of LiC_8 is the lowest than LiC_6 and LiC_{14} structure as shown in Table 1. Therefore, we can suggest that lithium-ion battery is mostly consisted of LiC_8.

CONCLUSION

In summary, we have investigated binding energies lithium atom inside between bilayer graphene to study about the cathode of lithium ion batteries. First, we have performed the calculation of carbon – carbon bond length of in the optimized primitive unit cell of graphene. And then, we have calculated the distance between two sheets of graphene when the lithium atom was located in them. As a result, we have found that the cathode of lithium-ion batteries are mostly consist of LiC_8 as a most stable structure.

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	Total energy (eV)	Li energy (eV)	Graphene energy (eV)	Binding energy (eV)
LiC6	-1948.32	-13.37	-1932.34	-2.61
LiC8	-2592.53	-13.21	-2576.28	-3.04
LiC14	-4523.90	-13.18	-4508.69	-2.03

Table 1. Binding energy of LiC_x structure

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