First-principles study on lithium absorption in carbon nanotubes

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Abstract

The Li absorption energy in carbon nanotubes and local Li–C and C–C chemical bondings have been investigated using the first-principles molecular orbital methods. It is found that the Li absorption energy is larger in the Li absorption outside the nanotube than inside the nanotube as far as the nanotube diameter is small. However, the Li outside-absorption energy decreases, whereas the Li inside-absorption energy increases with the nanotube diameter. When the nanotube diameter increases more than about 0.824 nm, the Li outside-absorption energy tends to reach a value similar to the Li inside-absorption energy. It is also shown that the distinctive chemical interactions are operating between Li and C atoms and between C atoms due to the curvature of carbon sheet in the Li absorbed carbon nanotubes. Such interactions are somewhat different from those in the Li absorbed graphite with flat carbon sheet.

1. Introduction

Various carbonaceous materials, in which lithium can intercalate reversibly, are used as the anode materials for secondary lithium-ion batteries. Graphite is one of those materials because it can be intercalated up to one lithium per six carbon atoms to form the so-called first stage graphite intercalation compound (GIC), LiC₆ [1]. However, the theoretical specific capacity of LiC₆ (372 mAhg⁻¹) is still unsatisfactory. Recently it has been reported that single-walled carbon nanotubes (SWNT) can be reversibly intercalated with lithium up to Li₁₋₇C₆ [2]. Moreover, this reversible saturation of Li composition increases to Li₁₋₇C₆ by applying a suitable ball-milling treatment to the purified SWNTs [3]. However, little has been known up to now about the fundamental difference between the lithium absorption into carbon nanotubes and into graphite. In present study, the tendency of Li absorption into carbon nanotubes with various diameters has been investigated from the first-principles total energy calculations. Moreover, the characteristics of lithium absorption into carbon nanotubes have been studied in view of local chemical bondings between lithium and carbon and between carbon atoms, and also they are compared with the results of lithium absorption into graphite.
2. Cluster models

A series of cluster models for finite length carbon nanotubes terminated with hydrogen atoms, as shown in Fig. 1, are constructed to study the electronic structures of pure (3,3), (4,4), (5,5) and (6,6) SWNT and Li-absorbed nanotubes. The cluster models for pure nanotubes are shown in Fig. 1(a)–(d) and (m). In the Li-absorbed cluster models, the limited numbers of lithium atoms are assumedly put into the inside or the outside of the nanotube. For example, in case of the Li absorbed...
(6,6) nanotube cluster models, as shown in Fig. 1(h), (l) and (n), six Li atoms are present either outside or inside the nanotube. Also, these Li atoms are assumed to locate above or below the centers of six-membered carbon rings, and to make a circuit around the middle of nanotube clusters. Such Li arrangements are presumed following the lithium occupancy sites in the first stage GIC, LiC₆ [1]. Similar to the Li absorbed (6,6) nanotube clusters, three, four or five Li atoms are put into the outside of the (3,3), (4,4) and (5,5) nanotubes respectively, as shown in Fig. 1(e)–(g). Also, one, four or five Li atoms are inserted into the inside of these nanotubes, as shown in Fig. 1(i)–(k). The diameter, $D$, of these nanotubes varies from 0.426 to 0.824 nm. The length of all these nanotube clusters is about 1.23 nm. The truncation effect of the mouth of nanotube is not examined and only the electronic structure of the central atoms is analyzed in the present study.

The geometries of the carbon skeletons as well as the positions of absorbed Li atoms are fully relaxed under $D_{nh}$ ($n = 3, 4, 5$ or 6) symmetry, and their binding energies are obtained by employing the DMol optimization calculation based on the density functional theory (DFT) [4]. Then the electronic structure and chemical bonding of these relaxed clusters are investigated using the DV-Xα molecular orbital method [5]. The numerical atomic orbitals of 1s-2p for C and Li and 1s for H are used as the basis functions for the DV-Xα calculations. The bond orders between atoms and the ionicities of constituent elements are calculated following the Mulliken population analysis.

3. Results

3.1. Li absorption energy

The diameter dependence of the binding energy of carbon nanotubes is shown in Fig. 2(a). The binding energy is set to be zero at the pure (3,3) SWNT and used as a reference in this figure. It can be seen that the binding energies of both the pure and the Li absorbed nanotubes increase with the diameter. The present results for the pure nanotubes agree well with the results calculated from the continuum elastic model [6]. According to this model, the binding energy of pure nanotube is proportional to the square of the nanotube diameter. The binding energy of the Li outside-absorbed nanotube increases with the diameter in a similar way as the pure nanotube. However, the binding energy of the Li inside-absorbed nanotube increases abruptly with the diameter. The binding energy is larger in the Li outside-absorption case than in the Li inside-absorption case except for the (6,6) SWNT in all the present calculations. As the diameter increases, the binding energy would converge to the value of graphite in case of pure nanotubes, and to the value of LiC₆ in case of Li absorbed nanotubes.

![Figure 2](n.png)

Fig. 2. Dependence of (a) binding energies of carbon nanotubes (before and after Li absorption) and (b) Li absorption energy on nanotube diameters. For convenience, the binding energy of the (3,3) SWNT is set to zero in figure (a).
The Li absorption energy, $E_{\text{absorption}}$, is defined as the change in the total energy with the Li absorption, which is a measure of the tendency to absorb Li in carbon nanotubes. It is obtained as follows:

$$
E_{\text{absorption}} = E_{\text{total}}(\text{Li}_n@\text{C}_x\text{H}_y) - nE_{\text{total}}(\text{Li})
- E_{\text{total}}(\text{C}_x\text{H}_y)
= [E_{\text{total}}(\text{Li}_n@\text{C}_x\text{H}_y) - nE_{\text{total}}(\text{Li})
- xE_{\text{total}}(\text{C}) - yE_{\text{total}}(\text{H})]
= [E_{\text{total}}(\text{C}_x\text{H}_y) - xE_{\text{total}}(\text{C}) - yE_{\text{total}}(\text{H})]
= E_{\text{binding}}(\text{Li}_n@\text{C}_x\text{H}_y) - E_{\text{binding}}(\text{C}_x\text{H}_y)
$$

Here, $E_{\text{total}}(\text{C}_x\text{H}_y)$, $E_{\text{total}}(\text{Li}_n@\text{C}_x\text{H}_y)$, $E_{\text{total}}(\text{Li})$, $E_{\text{total}}(\text{C})$ and $E_{\text{total}}(\text{H})$ are the total energies of pure nanotubes, Li absorbed nanotubes and each isolated atom, Li, C and H, shown in parentheses. $E_{\text{binding}}(\text{C}_x\text{H}_y)$ and $E_{\text{binding}}(\text{Li}_n@\text{C}_x\text{H}_y)$ are the binding energies of pure and Li absorbed nanotubes. Then the Li absorption energy is calculated from the difference in the binding energies between the pure and the Li absorbed nanotubes. As shown in Fig. 2(b), the Li outside-absorption energy decreases whereas the Li inside-absorption energy increases with the nanotube diameter. The Li outside-absorption energy is larger than the Li inside-absorption energy as far as the nanotube diameter is small. However, the difference between them decreases with increasing nanotube diameter. In fact, both the Li absorption energies tend to reach a similar value at the (6,6) SWNT with a diameter of 0.824 nm. It is interesting to note that the carbon nanotubes having diameters of about 0.8 nm are present abundantly in various experimentally synthesized nanotubes. It is supposed that the energetic tendencies of the Li outside- and inside-absorption would be very similar for the larger nanotubes. It is also noted that the Li absorption inside the (4,4) SWNT with a diameter of 0.556 nm may not occur because of the negative absorption energy.

### 3.2. Li–C chemical bonding

The changes in the ionicities of Li and C atoms and the Li–C bond length with the nanotube diameter are shown in Fig. 3(a) and (b), respectively. These results are obtained for the Li outside-absorption. The Li–C bonds have two kinds of lengths, denoted by long Li–C1 and short Li–C2 as shown in the inset of Fig. 3, because of the presence of the curvature of carbon sheet in the nanotube. The 2s electron of lithium atom moves mostly to carbon atom, so the ionic chemical interaction is mainly operating between Li and C atoms. It is found that the nearer C2 atoms have fairly large...
negative charges, but the farther C1 atoms have small negative charges. It means that the ionic interaction is much stronger between Li and C2 atoms than between Li and C1 atoms. On the other hand, in case of the Li absorbed graphite, LiC₆, all the Li–C bond lengths are the same due to the flat carbon sheet in graphite. Then all the carbon atoms would have the same negative charges and the same ionic interactions with lithium in LiC₆.

For comparison, the Li absorption into the assumed monolayered graphite is also investigated. The cluster model of the monolayered LiC₆ is constructed in the way that the Li atoms are set above the flat carbon monolayer following the Li occupancy in LiC₆. It is found that the optimized bond length between lithium and carbon atom is shorter in the monolayered LiC₆ than that in bulk LiC₆. As is shown in Fig. 3(b), the Li–C₂ bonds in the nanotubes have the similar or slightly shorter length as compared to the Li–C bond in the flat monolayered LiC₆. The Li–C₁ bond is longer than the Li–C₂ bond due to the curvature of carbon sheet, but its length decreases with the nanotube diameter and may converge to the Li–C bond length in the flat monolayered LiC₆. Also, as shown in Fig. 3(a), the ionicity of Li increases slightly with the nanotube diameter. Therefore, the Li–C ionic interaction probably becomes stronger when Li is absorbed into the larger nanotubes.

3.3. C–C chemical bonding

The changes in the bond order and the bond length between carbon atoms with the nanotube diameter are shown in Fig. 4(a) and (b), respectively. These results are presented for both the pure and the Li outside-absorbed nanotubes. It can be seen that both the C₁–C₂ and C₂–C₂ bond lengths are elongated and hence their bond strengths are weakened due to the Li outside-absorption into the nanotubes. However, the C₁–C₁ bond length is shortened and the bond strength is enhanced by the Li absorption. Also, all the bond orders between carbon atoms increase with the nanotube diameter.

According to the calculation about the Li absorption into the monolayered graphite, it is found that the bond order of the C₁–C₂ in graphite decreases from 1.00 to 0.59 due to the Li absorption. Also, the bond order of the C₁–C₁ bond (or the C₂–C₃) decreases from 0.86 to 0.54 after the Li absorption. That is to say, all the C–C bonds in graphite are elongated and weakened by the Li absorption.

![Graph showing changes in bond order and bond length between carbon atoms with nanotube diameters.](fig4.png)

Fig. 4. Changes of (a) bond orders and (b) bond lengths between carbon atoms with nanotube diameters. The inset illustrates the positions of Li, C1, C2 and C3 atoms, which are also given in Fig. 1.
4. Discussion

According to the analysis of chemical bonding, both the Li–C ionic interaction and C–C covalent interaction become stronger with increasing nanotube diameter. This helps to understand why the binding energies of the pure and the Li absorbed nanotubes increase with the diameter. However, it is out of expectation that the Li outside-absorption energy is large in the nanotubes with small diameters despite that the Li–C ionic interaction is weak in them. In order to understand it, the change of the C–C covalent interaction caused by the Li absorption must be taken into account. In fact, the positive contribution from the strengthening C1–C1 bonds described earlier is fairly large in the nanotubes with small diameters, so this should be responsible for the large Li absorption energy. Such a contribution to the Li outside-absorption energy decreases with the nanotube diameter. In graphite, there is no strengthening in the C–C bond and the Li absorption energy is expected to be lower compared to that in carbon nanotubes. On the other hand, the Li inside-absorption seems more difficult than the Li outside-absorption in the nanotubes with small diameters, and even becomes energetically unfavorable in the nanotubes smaller than the (4,4) nanotube with a diameter of 0.556 nm. It should be noted that the lithium

Fig. 5. Illustration of showing changes in the Li–C and C–C chemical bondings due to (a) Li absorption into graphite; (b) Li outside-absorption and (c) Li inside-absorption into armchair nanotube; (d) Li outside-absorption and (e) Li inside-absorption into zig-zag nanotube.
absorption is a kinetic process. So lithium diffusion path also should be considered, though it is not the aim of the present study.

It is illustrated in Fig. 5 that the Li–C and C–C chemical bondings change in different ways between the Li absorption into graphite and into carbon nanotubes. It is seen from Fig. 5(a) that the same type of Li–C ionic interactions is operating in the Li absorbed graphite. Also, the Li absorption into graphite weakens all the bonds between carbon atoms. However, this is not the case in the carbon nanotubes. For example, when lithium is absorbed outside the armchair carbon nanotube (Fig. 5(b)), strong chemical interactions are operating in those C1–C1 bonds which bridge the two neighboring six-membered carbon rings where Li is absorbed. This strengthening is primarily due to the shrinkage of the C1–C1 bond length. Such a bond shrinkage is reasonable because the repulsive Coulomb interaction between the C1 atoms is weak due to their small negative charges. But the other C1–C2 and C2–C2 bonds elongate and their strengths are weakened as in the Li absorbed graphite. The distribution and the number of the strengthening C–C bonds vary with the carbon nanotube structures (armchair type, zig-zag type, etc.) and also with the Li absorption sites (outside or inside). Several possible patterns of showing the Li–C and C–C chemical bondings in the Li absorbed carbon nanotubes are proposed on the basis of the present calculations and they are illustrated in Fig. 5(b)–(e).

5. Conclusion

The dependence of the Li absorption energy on both the diameter of carbon nanotubes and the Li absorption sites (outside or inside nanotubes) have been investigated by combining first-principles DMOl and DV-Xa techniques. It is shown that the Li outside-absorption energy decreases, but the Li inside-absorption energy increases with the nanotube diameter. The Li outside-absorption is energetically more favorable than the Li inside-absorption in the carbon nanotubes with small diameters. But the Li outside-absorption tends to have a Li absorption energy similar to the Li inside-absorption when the nanotube diameter increases more than about 0.824 nm.

A unique adjustment to the C–C bonds is characteristic of the Li absorption into carbon nanotubes. Some C–C bond strengths are enhanced by the Li absorption into the nanotubes. This is different from graphite, because every C–C bond is weakened by the Li absorption into graphite as is seen in LiC6. The strengthening of the C–C bonds leads to the high Li outside-absorption energy in the nanotubes. Also, such a strengthening effect is more prominent in the nanotubes with small diameters. The appearance of strong C–C bonds depends on the nanotube structure and the Li absorption sites. The fundamental understanding on the Li absorption into the carbon nanotubes will help to search for more advanced carbon materials as anodes for secondary Li-ion batteries.

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