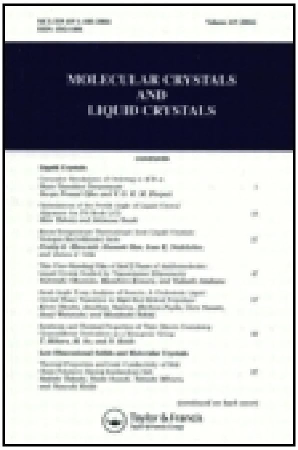

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LOCAL ELECTRONIC STRUCTURE OF LITHIUM ABSORBED IN CARBON NANOTUBES

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The Li absorption energies of single-walled armchair (6,6) and zigzag (12,0) carbon nanotubes are investigated by the first-principles molecular orbital methods. It is found that Li can be absorbed inside as well as outside these carbon nanotubes with the approximately similar absorption energy. It is still energetically favorable for Li to be absorbed both inside and outside carbon nanotubes. Furthermore, it is shown that the Li absorption weakens the covalent C-C bond, but instead forms the ionic Li-C bond which works to stabilize the Li carbon nanotube material.

Keywords: carbon nanotube; Li absorption; anode material; electronic structure

INTRODUCTION

It is well known that graphite can be intercalated up to one lithium per six carbon atoms to form the first stage graphite intercalation compound, LiC_6 [1]. Recent experiments show that carbon nanotube can absorb extra lithium atoms compared to graphite. For example, single-walled carbon nanotubes (SWNT) can be reversibly intercalated with lithium up to $Li_{1.7}C_6$ [2]. Moreover, this reversible saturation of Li composition increases to $Li_{2.7}C_6$ by applying a suitable ball-milling treatment to the purified SWNTs [2]. It is thus fundamentally interesting to clarify the reason underlying the excess reversible capacity of SWNT beyond graphite, despite the large irreversible capacity and hysteresis in SWNT on the other hand.

Lithium atoms may be intercalated into the inner cores of carbon nanotubes as a proposed mechanism for the lithium high-capacity

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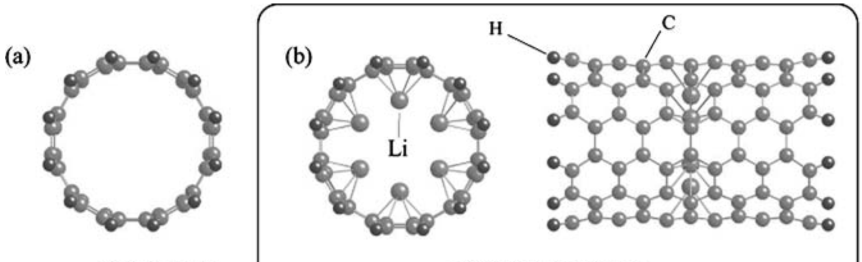
absorption [2], but this hypothesis is still hard to be proved directly from experiments. In this study, our attention has been focused mainly on the possibility of lithium absorption in both sides of single carbon sheet in the SWNTs. To treat of this problem, we have employed the first-principles calculations by assuming several possible absorption sites of lithium in carbon nanotubes. The site dependence of the Li absorption energy has been examined in detail. The modification of the chemical bonding due to the lithium absorption has also been investigated in a fundamental manner.

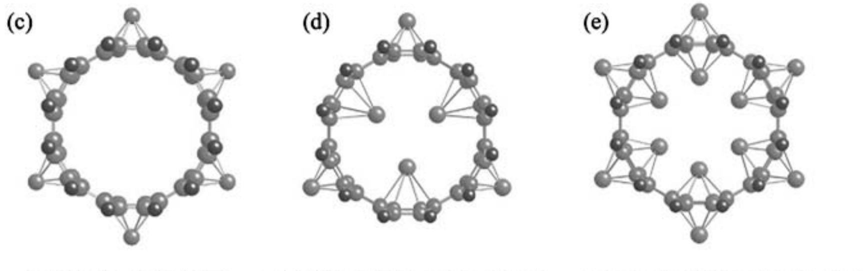
CLUSTER MODELS

As shown in Figures 1 and 2, the finite length hydrogen-terminated cluster models, $Li_nC_{132}H_{24}$ and $Li_nC_{144}H_{24}$ (n = 0, 6 or 12), are constructed to simulate the electronic structures of armchair (6,6) and zigzag (12,0) SWNTs and Li-absorbed nanotubes. In the Li-absorption models, limited numbers of lithium atoms are put inside, outside, and both sides of the



pure (6,6) SWNT

Li inside-absorption



Li outside-absorption Li inside/outside-absorption I Li inside/outside-absorption II

FIGURE 1 $Li_nC_{132}H_{24}$ cluster models used for the calculations of (a) pure nanotube (n = 0); (b) Li inside-absorption (n = 6); (c) Li outside-absorption (n = 6); (d) Li inside/outside-absorption I (n = 6) and (e) Li inside/outside-absorption II (n = 12) in (6,6) SWNT (See Color Plate VI).

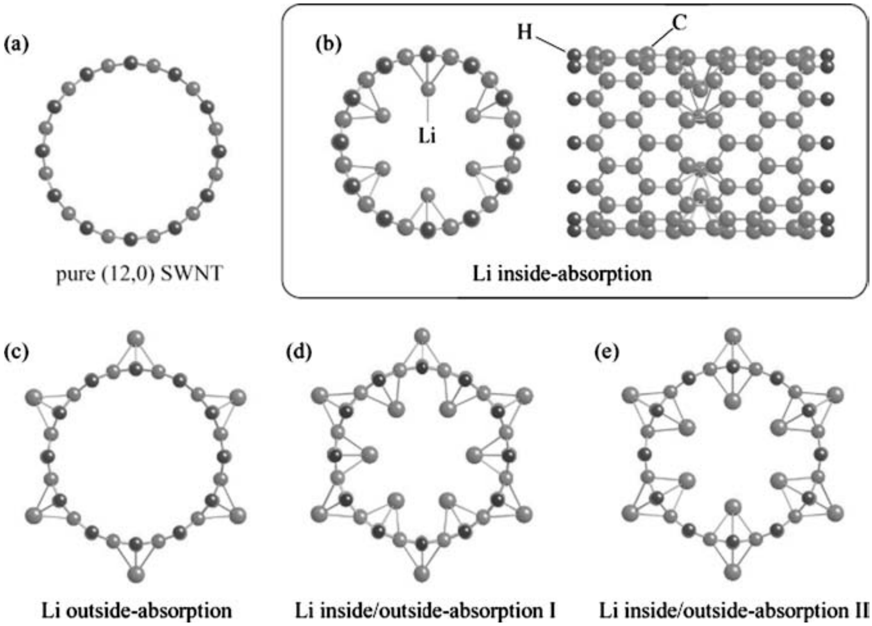


FIGURE 2 $Li_nC_{144}H_{24}$ cluster models used for the calculations of (a) pure nanotube (n = 0); (b) Li inside-absorption (n = 6); (c) Li outside-absorption (n = 6); (d) Li inside/outside-absorption I (n = 12) and (e) Li inside/outside-absorption II (n = 12) in (12,0) SWNT (See Color Plate VII).

nanotube with some assumed configurations. For example, these lithium atoms are assumed to locate above or below the centers of six-membered carbon rings, and to make a circuit around the nanotube, as shown in Figure 1 (b)–(e) and Figure 2 (b)–(e). The Li occupancies are confined in the nanotube center where the effect of tube edge becomes negligible, which is indicated by the constant optimized diameter of the nanotube center. The local stoichiometries in present models are lower that the experimental Li saturation capacity, but this does not affect the later discussion based on the comparison of the Li absorption energy between inside and outside nanotube. Also, there are other possible Li absorption sites, such as defect or edge of nanotube mouth, which may be responsible for the irreversible capacity and hysteresis in nanotubes. The comparison among these different kinds of absorption sites needs further work.

The geometries of the carbon skeletons as well as positions of absorbed Li atoms are relaxed by employing the DMol optimization calculations [3]. Then the electronic structure and chemical bonding of these optimized clusters are investigated using DV-Xα molecular orbital method [4]. The 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 analyses.

CALCULATED RESULTS

Li Absorption Energy

The Li absorption energy is a measure to show the tendency of absorbing Li in carbon nanotubes. It is calculated from the difference in the binding energy between the pure and the Li-absorbed nanotubes, and the results are shown in Table 1. It can be seen from this table that the Li absorption energy is positive in any case, which means that the nanotubes become more energetically stable with the Li absorption. For example, in case of the Li outside-absorption ($n = 6$) in the (6,6) nanotube it is 0.87 eV, only about 0.04 eV, larger than that of the Li inside-absorption. It is noted that the Li outside-absorption energy in the (12,0) nanotube is 1.16 eV, which is also 0.04 eV larger than that of the Li inside-absorption. Thus the Li outside-absorption energy is approximately similar to the Li inside-absorption energy for both the (6,6) and the (12,0) nanotubes. According to our previous investigation of showing the diameter dependence of the Li absorption energy in nanotubes [5], the Li outside-absorption energy tends to be similar to the Li inside-absorption energy when the nanotube diameter is larger than about 0.8 nm. The diameters of nanotubes studied here are 0.824 nm for the (6,6) nanotube and 0.948 nm for the (12,0) nanotube. So the present result agrees again with our previous result.

TABLE 1 Li Absorption Energies for Various Li Absorption Models in (6,6) and (12,0) SWNTs

	Li absorption model	Li absorption energy (eV/Li atom)
(6,6)	Li inside-absorption	0.83
	Li outside-absorption	0.87
	Li inside/outside-absorption I	1.04
	Li inside/outside-absorption II	0.69
(12,0)	Li inside-absorption	1.12
	Li outside-absorption	1.16
	Li inside/outside-absorption I	0.99
	Li inside/outside-absorption II	0.98

In case of the inside/outside-absorption I model for the (6,6) nanotube shown in Figure 1(d), three Li atoms are placed separately in both sides of the nanotube. The total number of Li atoms is six, the same number as the one in the inside-absorption model shown in Figure 1(b) and in the outside-absorption model shown in Figure 1(c). Its absorption energy is 1.04 eV. This indicates that the Li atom will occupy more preferably in both sides than the inside or the outside alone if the number of absorbed Li atoms does not change. On the other hand, in case of the inside/outside-absorption II model for the (6,6) nanotube shown in Figure 1(e), six Li atoms are placed separately in both sides of the nanotube. The absorption energy is 0.69 eV, which is about 0.14 eV smaller than that of the Li inside-absorption. Thus, as the number of absorbed Li atoms increases, the absorption energy per Li atom decreases, which may be explained by that the repulsive coulomb interaction between Li atoms increases with Li concentration. Similar results can be obtained from the inside/outside-absorption I and II model for the (12,0) nanotube. It is found that the absorption energy for the inside/outside-absorption II model in the (12,0) nanotube is 0.98 eV, which is also 0.14 eV smaller than that of the Li inside-absorption. Thus, a tendency to decrease the Li absorption energy from the single-side absorption to the double-side absorption in model II is similar between the (6,6) and (12,0) nanotubes. In addition, for two kinds of Li arrangements in the inside/outside-absorption I and II models of the (12,0) nanotube the difference in the Li absorption energy is only about 0.01 eV, so that the Li absorption energy is less dependent on the Li arrangements in the (12,0)nanotube with a relatively large diameter.

Ionicity and Bond Order

The chemical bonding modified by the Li absorption is investigated using the DV-Xα method. The calculated results of bond order and ionicity are shown in Figure 3 for the (6,6) nanotube and in Figure 4 for the (12,0) nanotube. Here, the bond order is a measure to show the covalent interaction between atoms, and the ionicity is a measure to show the ionic interaction between atoms through the charge transfer. It can be seen from Figure 3(a) and Figure 4(a) that the Li-C bond orders are very close to zero irrespective of the absorption models. This indicates that the covalent interaction is negligible between Li and C atoms. Instead, the ionic interaction is a main component of the Li-C chemical bonding due to the charge transfer from Li to C atoms. On the other hand, the C-C bond order of the Li-absorbed nanotubes decreases as compound to that of pure nanotubes. Our previous density functional calculations show that the C-C bond lengths increase slightly after Li absorption [6], which may be due to the repulsive coulomb interaction between C atoms with negative charges.

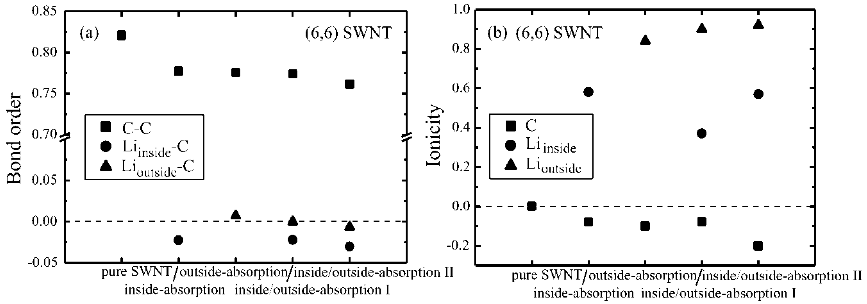


FIGURE 3 (a) Bond orders and (b) ionicities in pure and Li-absorbed (6,6) SWNT.

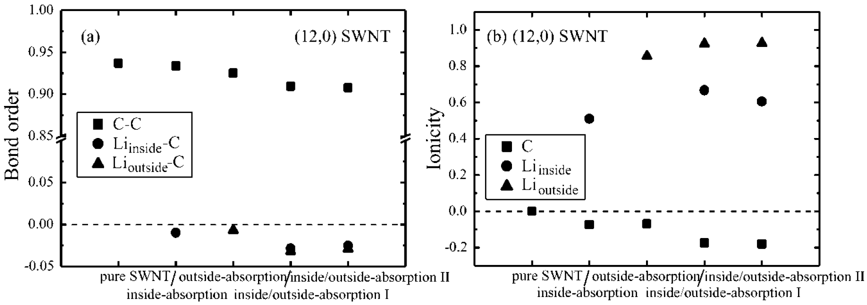


FIGURE 4 (a) Bond order and (b) ionicities in pure and Li-absorbed (12,0) SWNT.

Thus, it is evident that the C-C covalent interactions in carbon nanotubes are weakened by the Li absorption. This result is in agreement with the Raman scattering results [7], which showed a softening of the tangential vibrational modes for the C-C bond upon doping with Li.

According to the results of ionicity in the (6,6) nanotube shown in Figure 3(b), the effective charge of Li ion is +0.84 for the Li outside-absorption, but +0.58 for the Li inside-absorption. Thus, the ionicity of Li ion is larger in the Li outside-absorption than in the Li inside-absorption. This trend also can be seen in the Li inside/outside-absorption cases. Also, the ionicity of C is negative, indicating that charge transfer occurs from Li to C in the Li-absorbed (6,6) nanotube. These results indicate that the Li-C ionic interaction is stronger in the Li outside-absorption than in the Li inside-absorption. On the other hand, the C-C covalent interaction is weaker in the Li outside-absorption than in the Li inside-absorption. Both the Li-C and C-C interactions affect the Li absorption stability, and they play contrary roles in the Li absorption. As a result, the overall Li absorption tendency is very similar between the outside-absorption and inside-absorption in the (6,6) nanotube. The similar bonding characteristics also can be found for the (12,0) nanotube as shown in Figure 4(b).

CONCLUSION

The Li absorption energies of the armchair (6,6) and the zigzag (12,0) single-walled carbon nanotubes are calculated with the first-principle molecular orbital methods assuming various Li distributions. It is shown that the Li inside-absorption has the similar absorption energy as the Li outside-absorption in the nanotubes with diameter larger than about 0.8 nm. The Li absorptions both inside and outside nanotubes are proved to be still energetically favorable, though its absorption tendency decreases compared with that of the single-side Li absorption. Our results support the hypothesis of Li absorption in both sides of SWNT.

The charge transfer from Li to C occurs upon Li absorption in nanotubes, which results in the formation of Li-C ionic bonds. On the other hand, the C-C covalent bonds in nanotubes are lengthened and weakened due to Li absorption. Such chemical bonding pictures are fundamentally essential to understand the Li absorption in carbon nanotubes.

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