Density Functional Electronic Structure Calculations of Lithium Ion Adsorption on Defective Carbon Nanotubes

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The density functional theory is applied to study energetics of lithium ion adsorption on single-wall carbon nanotubes (SWNTs). We use both the local density approximation (LDA) and the generalized gradient approximation (GGA) for the exchange-correlation energy functional. The formation energies of the n = 7, 8, and 9 defective rings are calculated and their stable geometries are examined. We also estimate the lithium adsorption energies for these defective rings and the efficiency of the lithium ion battery with the defective SWNTs as the negative electrode. [DOI: 10.1380/ejssnt.2005.358]

Keywords: Density functional calculations; Carbon nanotube; Surface defects; Lithium ion

I. INTRODUCTION

Lithium-graphite intercalation compound (Li-GIC) has been extensively studied and widely used as the negative electrode in the commercial lithium ion rechargeable batteries.[1–3] It has been suggested that carbon nanotube is one of the most promising candidates to replace the Li-GIC negative electrode. Zhao et al.[4] investigated the possibility of achieving the lithium capacity of the nanotubes corresponding to the stoichiometry of LiC\(_6\) which is considerably improved compared to the Li-GIC (LiC\(_6\)). Experimentally, lithium capacity of the nanotube can be significantly increased up to the stoichiometry of LiC\(_3\) by ball-milling nanotubes into the fractured structure or chemically etching them to the short segments. Lithium could easily diffuse not only to the exterior but also to the interior through the created defects or the open-ends of such nanotubes.[5, 6] Meunier et al.[7] studied the lithium diffusion into the (5,5) and (8,0) carbon nanotubes through the defective rings by \textit{ab initio} calculations based on the density functional theory (DFT). They estimated the diffusion barrier and defect formation energies for the topological defects of (5,5) nanotube, but detailed analyses were not made for the lithium adsorption energies. Recently, we investigated the energetics of lithium ion adsorption on the defective single-wall carbon nanotubes (SWNTs) by the DFT total energy calculations.[8] In the present work we investigate stable geometries of the defective rings on the graphene, (5,5) and (8,0) SWNTs and examine the average voltage of the battery cell caused by the lithium adsorption.

II. METHOD

The total energy calculations were performed using the first–principles simulation code VASP[9, 10] with the spin polarized projector augmented-wave (PAW) method [11, 12]. Well converged cutoff energy of 300 eV was used in the plane-wave expansion and only the \(\Gamma\) point was considered in the reciprocal space integration. We used a large rectangular supercell to simulate the isolated defective graphene and SWNTs in the vacuum. The defect formation energy calculated in this way suffers from the finite-size effect due to the limitation in releasing the strain energy and eliminating the interaction between the defects and its images. We used a large supercell to eliminate or at least considerably reduce these drawbacks. Two types of SWNTs, metallic (5,5) armchair SWNT and semiconducting (8,0) zigzag SWNT, were chosen as samples in our calculations since the diameters of these SWNTs are nearly the same. The diameters of the (5,5) and (8,0) SWNTs are 6.78 Å and 6.26 Å, respectively. The size of the supercell in the radial direction was taken to be \(20 \times 20 \text{ Å}^2\) and the length in the axial direction was taken to contain six and four unit cells, which is equal to 14.76 Å and 17.04 Å for the (5,5) and (8,0) SWNTs, respectively. We also used a large supercell for the graphene sheet containing 6 × 6 unit cells (72 atoms). The size of the supercell in the vertical direction of the graphene is taken to be 6 Å, which is about twice the interlayer distance of graphite and sufficiently large to eliminate the interaction between sheets through the image cells. We used the experimental carbon–carbon bond length of graphite (1.42 Å) to construct C-C framework of the graphene and SWNTs. Atomic coordinates were relaxed using the conjugate gradient algorithm with the tolerance of 0.05 eV/Å.

III. GEOMETRY AND FORMATION ENERGY OF THE DEFECTS

We calculate the formation energies of the n = 7, 8, and 9 membered topological defective rings on a graphene, (5,5) and (8,0) SWNTs. Since the number of atoms of each defective system is the same as that of the corresponding pristine one, defect formation energy \(E_f^n\) of \(n\) membered ring can be evaluated by comparing the total energy of defective system \((E_{tot})\) with that of the pristine one \((E_{tot})\).

\[
E_f^n = E_{tot}^n - E_{tot}.
\]

There are many possible configuration of ring defect depending on the order and types of surrounding additional ring defects. Therefore the formation energy is strongly influenced by the atomic geometry of a ring. We first evaluated the defect formation energies of the defective rings.
TABLE I: Defect formation energies $E^f_n$ (in eV) of $n$ membered carbon rings calculated in the LDA and GGA.

|       | graphene | (5,5)SWNT | (8,0) SWNT |
|-------|----------|-----------|------------|
| $n=7$ | 5.00     | 3.90      | 2.81       |
| $n=8$ | 8.23     | 7.09      | 5.92       |
| $n=9$ | 13.60    | 10.07     | 8.94       |
| GGA   | 5.13     | 4.23      | 2.36       |
|       | 8.47     | 7.60      | 5.73       |
|       | 14.06    | 9.66      | 8.79       |

FIG. 1: Graphene sheet with $n = 7, 8,$ and $9$ ring defects indicated by red balls. Gray balls are the carbon atoms. Additional defective rings surrounding the center defect are painted with red ($n = 4$), yellow ($n = 5$), and green ($n = 7$) colors. Atomic bonds between neighboring carbons with the length of $\sim 1.4 \text{ Å}$ are represented by sticks.

in various geometries and determined the ground state configurations.

In Figures 1 and 2, we show the energetically favorable atomic configurations of the graphene and SWNTs with the ring defects.

We see that the $n = 7$ defective ring on graphene accompanies another $n = 7$ ring and two pentagon rings. The characteristic geometries in the presence of the defective ring on the SWNTs are different from this as shown in Figure 2.

The most energetically stable $n = 7$ defective ring on the (5,5) SWNT surface accompanies another $n = 7$ defective ring in the circumference direction, while that on the (8,0) SWNT accompanies another $n = 7$ ring in the axial direction. The results of $E^f_n$ for the most stable $n$ membered defective rings are summarized in Table I. The formation energy of $n = 7$ ring defect on the graphene is 5 eV, which is compared with $\sim 4$ eV and $\sim 2.5$ eV on the (5,5) and (8,0) SWNT, respectively. We see that the $n = 8$ defective ring on graphene accompanies two $n = 7$, one $n = 4$, and two pentagonal rings in the neighbor as shown in Fig.1. The $n = 9$ ring defect on graphene accompanies three $n = 7$, one $n = 4$, and four pentagonal rings in the neighbor. It is interesting to note that the symmetries of $n = 8$ and 9 rings on the SWNTs are no longer the same as those on the graphene. The $n = 8$ ring on the (5,5) SWNT is surrounded by four pentagonal, two $n = 7$, and two hexagonal rings and the configuration shows symmetry with respect to the axial and radial directions. We see that the $n = 7$ rings of the (5,5) SWNT cause radial contraction. Similarly, $n = 8$ ring on the (8,0) SWNT is surrounded by the same defective rings, but its configuration is different from that of the (5,5) SWNT.

The $n = 7$ and 8 defective rings cause large three-dimensional structural deformations of the SWNTs and thereby effectively release their strain energies (Table I). The defect formation energies for $n = 8$ defective rings are roughly 8 eV, 7 eV, and 6 eV for graphene, (5,5), and (8,0) SWNTs, respectively. We also note that there is no $n = 4$ defective ring in the neighbor of the $n = 8$ defective ring of the SWNTs in contrast to that of the graphene.

The $n = 9$ ring on the (5,5) SWNT is surrounded by three adjacent pairs of the pentagonal rings and three $n = 7$ rings separating each pair. The configuration of the additional defective rings in the neighbor of the $n = 9$ ring of the (8,0) SWNT is the same as that of the (5,5) SWNT, but its symmetry direction is different in the consequence of the different C-C framework of the SWNTs.

It is important to note that no structure with fused pentagons has been found in fullerenes and carbon nanotubes: this rule is called the isolated-pentagon rule (IPR[15]) and indicates that a string of pentagons is energetically unfavorable. In fact, the formation of $n=9$ defective rings in graphene, (5,5) and (8,0) SWNTs brings about the ad-
FIG. 2: Energetically most stable atomic configurations of the ring defects on the (5,5) (upper panel) and (8,0) (lower panel) SWNTs. Additional defective rings surrounding the center defect are painted by the yellow ($n=5$) and green ($n=7$) colors. Hexagons surrounding the defect are shown as blue color rings.

 joined pentagons violating the IPR, and hence it would be energetically less favorable than the formation of smaller defective rings.

IV. LITHIUM ADSORPTION ENERGY

At the initial stage of charging process of the lithium ion battery, monovalent lithium ions on the positive electrode move to the negative electrode through the separator in the battery cell. On the other hand, electrons released from the lithium atoms on the positive electrode are forced to move through an external circuit driven by the supplied electric power and are stored at the negative electrode with the adsorbed lithium ions. Therefore the balance of the total energies at the positive and negative electrodes with or without lithium ions directly correlates with the expected average voltage. This enables us to estimate the averaged power of the battery cell from the total energy calculations\[13, 14\]. Note that absolute values of the adsorption energies in their fully relaxed atomic configurations are expected to be decreased compared to that of the static calculation where the atomic configurations of the defective SWNTs are fixed in their ground states without lithium. For example, the lithium adsorption energy of $0.52$ eV\[8\] on the internal hollow site of the (5,5) SWNT without defect in the static LDA calculation is reduced to $-0.21$ eV (Table II) in its fully relaxed atomic configuration with the lithium. In the following, we examine the expected total average voltage estimated by the adsorption energies obtained in the present study. Here we consider only the upper limit of the absolute value for the adsorption energies and hence the result is valid regardless of the consideration of the structural relaxations.

The lithium adsorption energy $\Delta E$ for the defective graphene, (5,5) and (8,0) SWNTs are summarized in the Table II. By neglecting the scattering of the lithium adsorption energies of the SWNTs and interactions between lithium ions\[8\], the change in the total energy per LiC$_2$ can be roughly estimated to be $|\Delta E_{\text{LiC}_2}| = 0.5$ eV at most. This can be understood from that the net number of carbon atoms belonging to a hexagonal ring is two (more for the defective rings) and the absolute value of the lithium adsorption energy for a ring on the SWNT is typically less than 0.5 eV.

The change in the total average voltage caused by the lithium adsorption on every possible site of the defective SWNT can be rudely estimated to be $|\delta V_{ae}| \leq \ldots$
TABLE II: Lithium adsorption energy $\Delta E$ (in eV) for graphene, (5,5) and (8,0) SWNTs obtained by the LDA and GGA calculations. The interior and exterior represent the lithium adsorption on the inner and outer sides of the SWNT, respectively. The positive (negative) value indicates that the reaction is endothermic (exothermic) with respect to the metallic lithium.

|   | interior |   |   |   | exterior |   |   |   |
|---|----------|---|---|---|----------|---|---|---|
|   | n=7     | n=8 | n=9 |   | n=7     | n=8 | n=9 |   |
| (5,5) LDA | -0.21  | -0.25 | -0.38 | -0.70 | -0.18  | -0.23 | -0.30 | -1.13 |
| (5,5) GGA | 0.05   | -0.09 | -0.18 | -0.43 | 0.02   | -0.20 | -0.15 | -0.86 |
| (8,0) LDA | -0.44  | -0.42 | -0.71 | -0.69 | -0.41  | -0.39 | -0.75 | -0.56 |
| (8,0) GGA | -0.18  | -0.19 | -0.61 | -0.43 | -0.23  | -0.23 | -0.73 | -0.40 |
| graphene LDA | -0.36 | -0.45 | -0.28 | -0.62 |   |   |   |   |
| graphene GGA | -0.10 | -0.16 | 0.09  | -0.27 |   |   |   |   |

$|\Delta E_{LiC_2}/F| \approx 0.5$ V, where $F$ is the Faraday constant[13, 14]. This result for the stoichiometry of LiC$_2$ suggests that $|\delta V_{av}|$ at the experimental stoichiometry limit of LiC$_3$ is two third of that for LiC$_2$, i.e., $|\delta V_{av}'| \leq 0.3$ V. Hence the SWNTs with lithium ions adsorbed in both the exterior and interior could behave as a stable anode similar to the lithium metal anode.

V. CONCLUSION

We have calculated the formation energies of $n=7$, 8, and 9 membered topological defective rings on a graphene, (5,5) and (8,0) SWNTs. We found that the $n=7$ defective ring on graphene accompanies another $n=7$ and two pentagonal rings in the most stable geometry. The configurational geometries for the defective rings on the SWNTs are different from those on the graphene. Energetically most stable $n=7$ defective ring on the (5,5) SWNT accompanies one $n=7$ defective ring in the circumference direction. On the other hand, $n=7$ ring on the (8,0) SWNT accompanies one $n=7$ ring in the axial direction. The $n=8$ ring on the (5,5) SWNT is surrounded by four pentagonal, two $n=7$, and two hexagonal rings. The $n=8$ ring on the (8,0) SWNT is also surrounded by the same defective rings, but its configuration is different from that of the (5,5) SWNT. The geometry of the additional defective rings in the neighbor of the $n=9$ ring of the (8,0) SWNT is the same as that of the (5,5) SWNT, but its direction is different in consequence of the different C-C framework of the SWNTs. We also examined the expected total average voltage estimated by the adsorption energies for the defective graphene and the SWNTs and found that the lithium adsorption on the graphene and SWNTs is as feasible as that on the lithium metal anode.

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