Large-Scale DFT Simulation of Li-atom Insertion and Extraction in Quinons@SWCNT Rechargeable Battery Cathodes

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ABSTRACT

The system of quinone molecules encapsulated in the single-wall carbon nanotube (SWCNT) has been proposed as a next-generation cathode electrode material for rechargeable battery. We investigate the complex interaction among the SWCNT, phenanthrene-quinone (PhQ), and Li atoms in the encapsulated system by using our original DFT code. We thereby find that the shape of the SWCNT changes significantly in the relaxed state depending on the extent of Li atoms inserted. The SWCNT shows a circular cylinder shape when no Li exists. With sufficient Li atoms inserted, the SWCNT is flattened. Substantial electron transfer from the PhQs to SWCNT is found. As for the dynamics of Li atoms in insertion or extraction process, we find that the Li atoms can take either of the two paths: one is along the inner wall of the SWCNT and the other is hopping on the PhQs.

INTRODUCTION

The lithium ion battery (LIB) is presently recognized as the indispensable energy storage device for portable electronic tools as the note-PC and cellular phone. The LIB is expected to be used also in heavy machines as the electric automobile. However, the current LIB has various deficiencies: for instance, it is expensive due to the containment of rare metals as Co in cathodes. Therefore, many researches have been putting great effort to develop a new electrode material with lower cost and improved performance. Recently the system of quinone molecules encapsulated in the SWCNT, which is free from rare metals, has been proposed as a next-generation cathode electrode material [1]. In the experiment [1], the phenanthrene-quinone (PhQ) was used. The PhQ molecule is composed of 14 C, 8 H, and 2 O atoms as drawn in Fig. 1(a); that is, it has 3 benzene rings. Single PhQ can capture as much as 2 Li atoms around the two O atoms as depicted in Fig. 1(b) through our simulation. Dissolution of the PhQ toward the electrolyte, which occurs for the simple aggregate, was suppressed significantly in the encapsulated system [1].

Despite the success of the encapsulated system as the electrode material, little is known about the configuration of the PhQs in the SWCNT and about the dynamics of Li-atoms in their insertion and extraction processes. Motivated by that, in the present study, we will address those issues through large-scale, first-principles molecular-dynamics simulation. We will consider the SWCNT with its diameter corresponding to the experimental value.

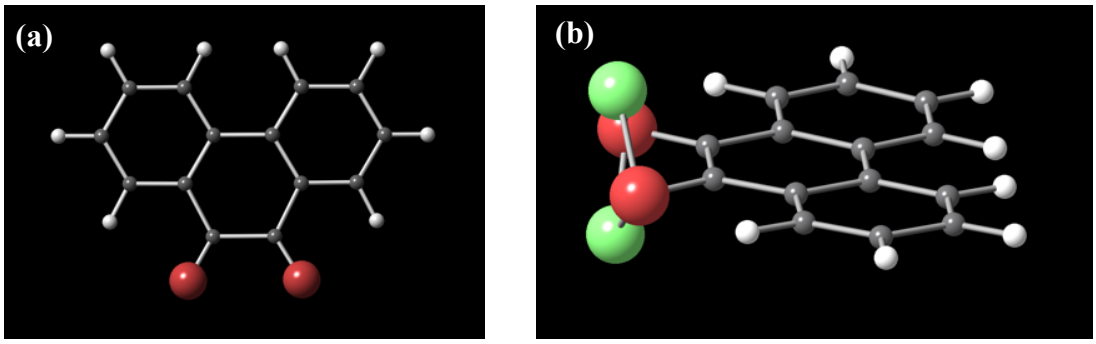

Figure 1. (a) The relaxed structure of a PhQ. (b) The relaxed structure of a PhQ with 2 Li atoms. The grey (small), white (small), red (large), and green (large) spheres represent C, H, O, and Li atoms, respectively.

METHODOLOGY AND SIMULATION SETTINGS

We adopt our divide-and-conquer-type real-space grid implementation code of the density-functional theory (DC-RGDFT) [2] with the norm-conserving pseudopotential and the PBE-GGA xc-functional. The eigenfunctions are described on the real-space grid and therefore are free from the basis set. The grid size that determines the physical accuracy in the DFT is chosen as 0.29 Å, which corresponds to the cutoff energy of 443 eV in the planewave description. The DC-RGDFT has attractive features of parallelizability and applicability to various boundary conditions in addition to the universality in target materials and capability to calculate in linear scaling. We here add the DFT-D2 [3] to the DC-RGDFT to incorporate the Van der Waals forces in an empirical manner. The system temperature is controlled with the Langevin thermostat method. We perform the following four cases of the simulation:

Case 1. Relaxation of the PhQs encapsulated in the SWCNT.
Case 2. Relaxation of the PhQs with Li atoms encapsulated in the SWCNT.
Case 3. Dynamics of Li insertion in the encapsulated system.
Case 4. Dynamics of Li extraction from the encapsulated system.

Cases 1 and 2 are considered to find the relaxed configurations of the PhQs in the encapsulated systems in two extreme settings: no Li atom exists in case 1, while 16 Li atoms exist in case 2. Figure 2 depicts the initial configurations in cases 1 and 2. The dimensions of the SWCNT are 5.11 nm in length and 1.67 nm in diameter; it is composed of 1,008 C atoms and 16 PhQs in case 1 (with 16 Li atoms in case 2). That is, 1,232 C, 128 H, and 32 O atoms in case 1 (with 16 Li atoms in case 2) as a whole. The weight percent of the PhQs is 22% in case 1, in agreement with the experimental value [1]. The periodic boundary conditions are assumed to mimic the central region of the SWCNT in experiment. Firstly, the system is heated to as high as 2,000 K in order to randomly distribute the PhQs inside the SWCNT. Secondary, the system is gradually quenched to 500 K to find the relaxed state.

Cases 3 and 4 are considered to investigate the Li dynamics, particularly the paths of Li atoms in their inserting and extraction processes. The free boundary conditions are assumed in cases 3 and 4 to mimic the end region of the SWCNT. The initial configurations of cases 3 and 4 were prepared through our separate relaxation simulation runs for about 4.5 ps (3,000 steps) at

500 K. The two ends of the SWCNT (4.18 nm in length and 1.59 in diameter; zigzag-type edge) are terminated by H atoms. The SWCNT contains 12 PhQs in case 3 (and 24 Li atoms in case 4). In case 3, we perform the simulation run by inserting the Li atoms step by step at one end followed by the relaxation process, until 24 Li atoms are inserted in total. After that, we enforce to shit the center of mass (COM) of the Li atoms at a constant velocity for about 8 ps toward the opposite end of the SWCNT. We set the velocity value as 0.26 nm/ps, which corresponds to 20% of the Li thermal velocity, expecting little modification of the Li dynamics by the COM motion. No local heating of the Li and surrounding atoms occurs because the Langevin method is used for temperature control. The present COM-shift method is quite useful for fast simulation of the Li transfer paths in a complex system, as compared to the conventional transition path calculation methods such as the nudged elastic band method.

In case 4, the total charge of the system is set to 24 in unit of the positive electronic charge to see possible effects of such a positively charged state (this relates to the charging process of the cathode). We move the COM of the Li atoms in a similar way to that in case 3. When a Li atom goes out from the end of the SWCNT, it is removed and a new Li is inserted at the other end.

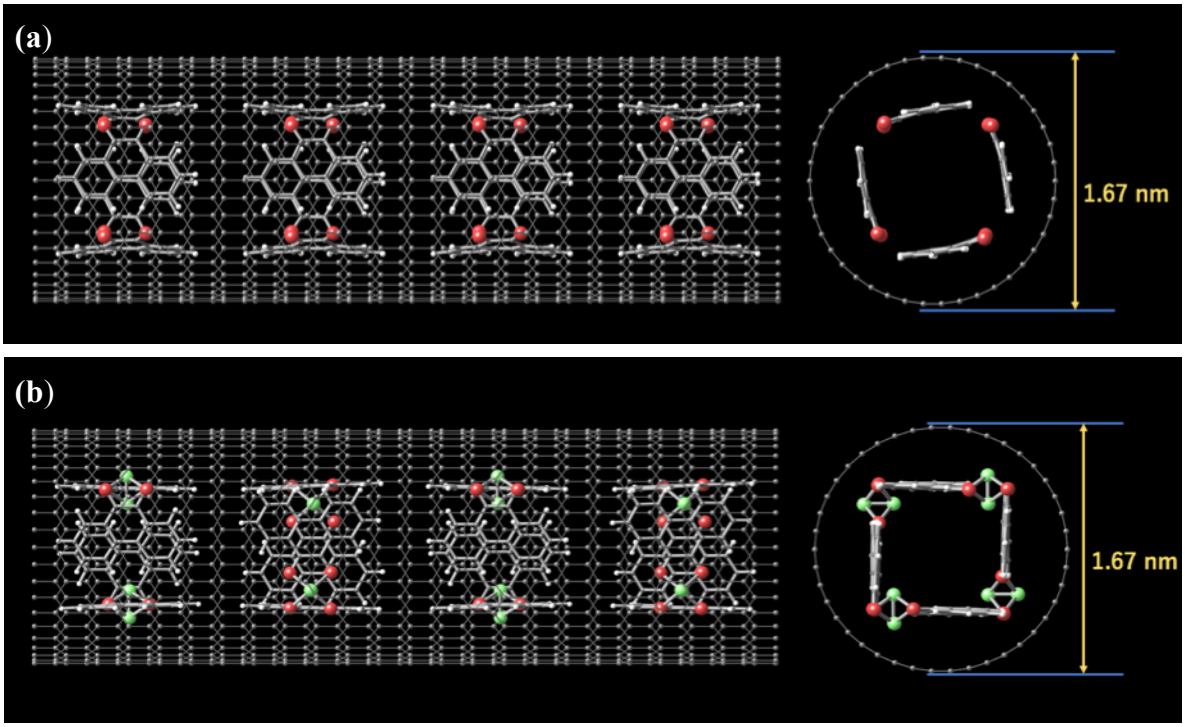

Figure 2. The initial configurations of the encapsulated systems under the periodic boundary conditions: (a) for case 1 and (b) for case 2. Four units of PhQs are placed inside the SWCNT, where the unit means 4 PhQs for case 1 and 4PhQs with 4 Li atoms for case 2.

RESULTS AND DISCUSSIONS

Prior to showing the simulation results in cases 1-4, we here explain the important findings

that we obtained in the separate calculations about the interaction among the SWCNT, PhQs, and Li atoms. One of the principal findings is that there occurs the electron-transfer from the PhQs to SWCNT by about 4 electrons per PhQ. Another is about the relaxed structure of a small mixed system of the PhQs and Li atoms as follows. In the relaxed state of the system of 2 PhQs and 4 Li atoms in vacuum, 4 Li atoms altogether work to bind all 4 O atoms of the 2 PhQs. If the system is charge neutral, 2 PhQs bend significantly around the central 4 Li atoms (like the closed butterfly wings). On the other hand, if the system is positively charged by 4 in unit of the positive electronic charge (corresponding to the degree of the charge-transfer mentioned above), 2 PhQs form a flat sheet (like the opened butterfly wings).

The simulation results in cases 1-4 are explained in the following, in conjunction with such a configuration change of 2 PhQs in vacuum depending on the charging state.

Case 1. Relaxed configuration of the PhQs encapsulated in the SWCNT

Figure 3 (a) depicts the relaxed configuration of the system in case 1. During the relaxation run, the PhQs firstly drift along the wall of SWCNT and finally form a spiral structure along the wall as seen in Fig. 3(a). We consider such a linearly connecting PhQs on the inner wall of the SWCNT reasonable from the Van der Waals and Coulomb attraction (due to the charge transfer) forces between the SWCNT and PhQs and the hydrogen bonding forces between the PhQs. The spiral periodicity is determined by the width of the PhQ-chain.

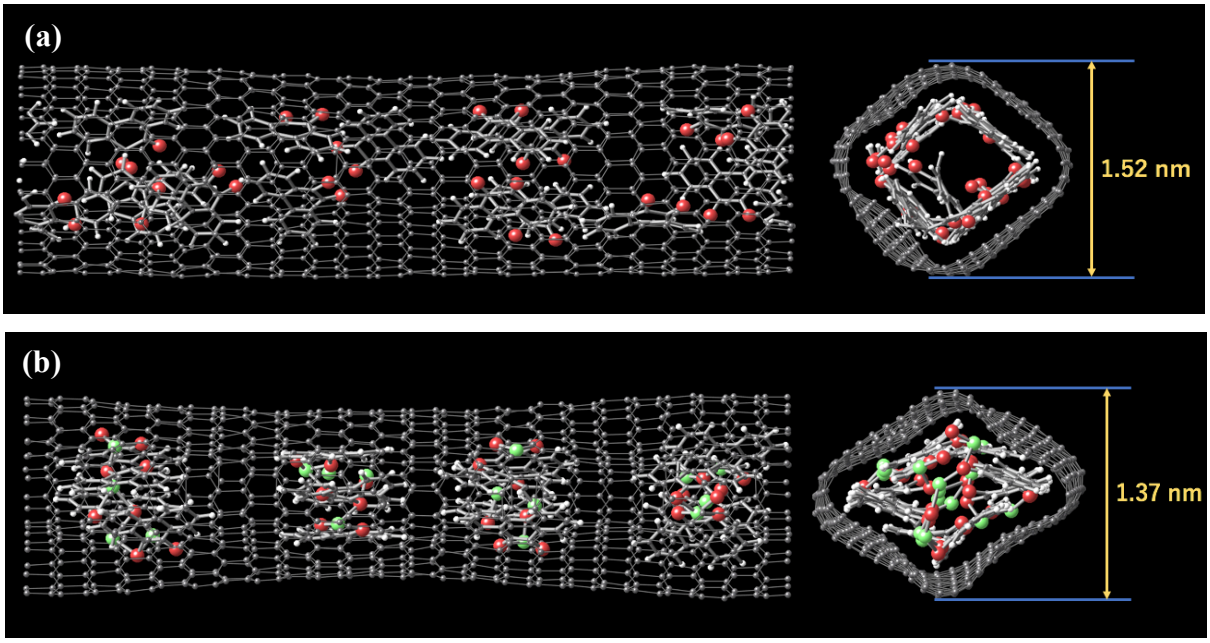

Figure 3. The relaxed structures in (a) case 1 and (b) case 2. In case 1, the SWCNT shows a round shape. In case 2, the SWCNT is flattened

Case 2. Relaxed configuration of the PhQs with Li atoms encapsulated in the SWCNT

Figure 3 (b) depicts the relaxed state of the system in case 2. The basic unit, which is

composed of 2 PhQs and 2 Li atoms, does not decompose (note: the unit mentioned in the caption of Fig. 2 is twice the basic unit). The basic unit is quite stable. A remarkable finding in case 2 in comparison to that in case 1 is that the SWCNT gets flattened to be 1.80 × 1.37 nm in size, as depicted in Fig. 3 (b). The finding corresponds well to the basic computation results mentioned at the beginning of the present section; that is, positively charged 2 PhQs with 4 Li atoms as a set change to form a flat sheet. Such a structural change of the 2 PhQs with 4 Li atoms is the reason of flattening of the SWCNT seen in Fig. 3 (b). We expect two possible effects on the Li-transfer due to the SWCNT deformation: one is to suppress the mobility of Li atoms due to formation of unsmooth surface, the other is to enhance the mobility due to the formation of layered surfaces of the SWCNT and PhQs.

Case 3. Dynamics of Li insertion to the encapsulated system

Figure 4 shows the initial and final snapshots of the simulation run in case 3. We find that the Li atoms are transferred either along the inner wall of the SWCNT or hopping on the PhQs. When the COM of the Li atoms is shifted toward the other end of the SWCNT, the PhQs gradually move also due to the attractive interaction between the PhQs and Li atoms (a PhQ goes out from the right end in Fig. 4(b)). When the Li atoms are inserted at the left-end region of the SWCNT, the end region gradually changes its shape to a flat one relating to the tendency of the PhQs to form a flat shape due to the charge-transfer between the PhQs and SWCNT. This observation suggests that the SWCNT deformation should accompany the Li insertion/extraction

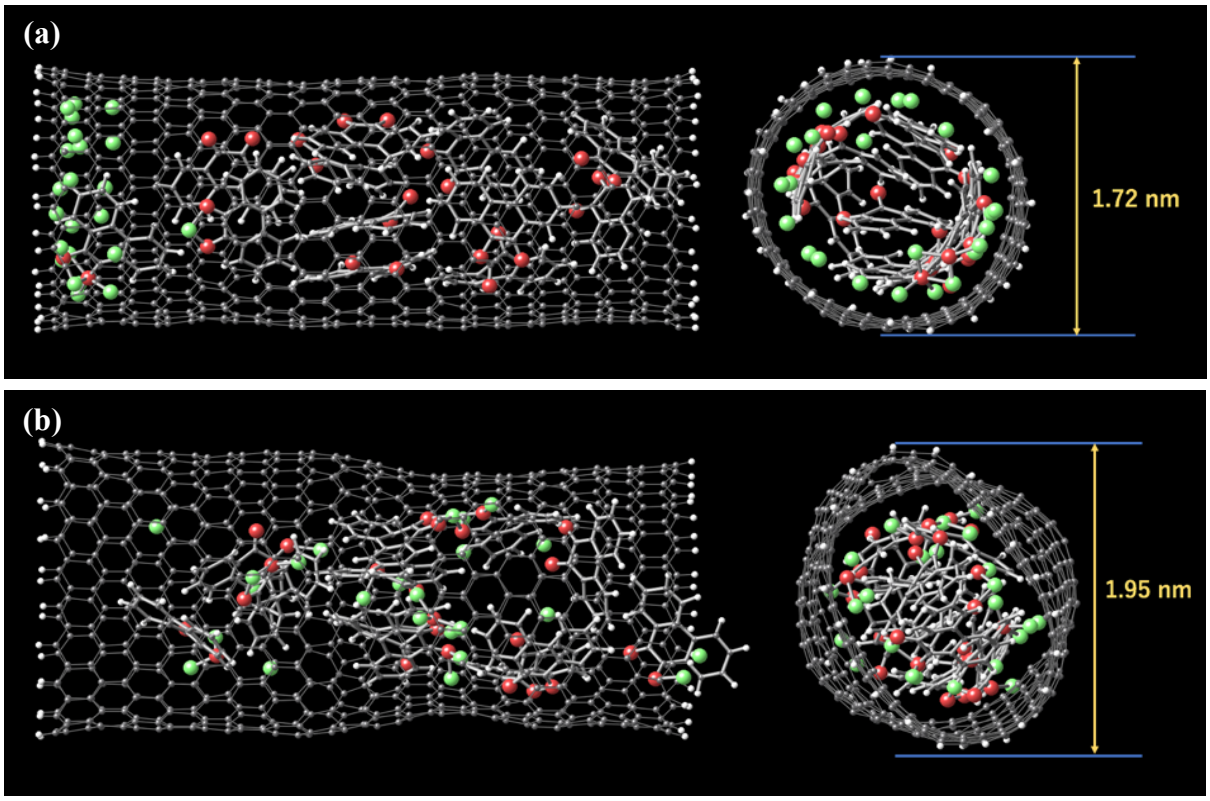

Figure 4. Snapshots of the system in case 3 where the PhQs are encapsulated in SWCNT. The Li atoms are inserted from the left end of the SWCNT. The center of mass of the Li atoms is shifted gradually toward the right end. (a) at the initial. (b) at about 8 ps.

and that such a deformation should affect the Li mobility. As for the transfer path of the Li atoms, we find that the Li atoms can take either of the two paths: one is along the inner wall of the SWCNT and the other is hopping on the PhQs.

Case 4. Dynamics of Li extraction from the encapsulated system

The simulation results in case 4 are similar to that in case 3. The SWCNT deforms to a round shape after the Li atoms are extracted from the SWCNT. The transfer path of the Li atoms can be either on along the inner wall of SWCNT or hopping on the PhQs. We here add that the length of Li-O bond is extended by 5 % due to positive charging of the system. Such a bond extension gives little effect on the SWCNT deformation while enhancing the Li-transfer.

CONCLUSIONS

We have analyzed the PhQ-encapsulated SWCNT system with or without the Li atoms by performing the first-principles molecular dynamics simulation using our original DFT code. Substantial electron transfer from the PhQs to SWCNT is found. The relaxed configurations of the SWCNT differ significantly depending on the extent of the Li atoms. The SWCNT keeps its round shape when no Li atom exists. When the Li atoms are inserted, the SWCNT is flattened. When the center of mass of the Li atoms is shifted gradually to the outside of the SWCNT, the Li atoms transfer either along the inner wall of the SWCNT or hopping on the PhQs in both . In addition, the SWCNT changes its shape to a round shape when the Li atoms go outside the SWCNT.

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