

Electronic and electrochemical properties of Li-doped carbon nanotube–zeolite complex

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The electronic and electrochemical properties of Li-doped carbon nanotube–zeolite complex are studied by first-principles calculations. There are four possible sites for Li to be doped and the reactions are all exothermic. The corresponding energy band structures follow a rigid band picture and there are charge transfers from Li to the nanotube and/or zeolite. The Li capacity of the complex can be reached to 386 mAh g⁻¹ with only a slight increase in the cell volume, and the complex may be of good cyclic stability during the charge and discharge process. Moreover, a higher voltage of about 4 V can be obtained if the complex is used in an Li-ion battery.

1. Introduction

The Li-ion rechargeable battery has been an attractive power source for its wide applications in the fields such as laptop computers, cellular telephones and other electric vehicles. Usually the Li-ion battery consists of metal oxides (such as CoO₂ and NiO₂) on the cathode side and carbon materials with Li intercalated on the anode side in the charged state.¹ Many types of carbon materials have been considered for the anode of the Li-ion battery, such as carbon black, coke, carbon fiber, graphite and so on.^{2–6} As a new member of the carbon materials family, carbon nanotubes (CNTs) have attracted a lot of attention from the science community since their discovery in 1991.⁷ The unique one-dimensional structure of carbon nanotubes also offers an interesting channel for chemical doping. In particular, Li doped carbon nanotubes were intensively investigated.^{8–15} Due to the large specific surface and curvature effect, small diameter nanotubes may exhibit more interesting doping properties compared with large ones. Recently, single-walled carbon nanotubes (SWCNTs) with very small diameters were fabricated inside the AlPO₄-5 zeolite (AFI) channels, and they were well aligned with a diameter of about 4 Å.¹⁶ The possible chiralities of these tubes are zigzag (5,0), armchair (3,3), and chiral (4,2).^{17,18} It is found that^{11,19} Li atom can be inserted into the interior of these 4 Å carbon nanotubes and there is a marked chirality dependence of the Li binding energy. In addition, the Li atom can be also doped outside and the energy is found to be more favorable.²⁰ It is thus reasonable to expect that these 4 Å carbon nanotubes could have a large Li storage capacity which may find potential applications in Li-ion batteries. In this work, we will consider Li doping in a complex system where the 4 Å carbon nanotubes are confined inside the AFI channels. We will focus on the electronic properties of the carbon nanotube–zeolite complex (tube@AFI) when Li is intercalated at several different sites. Moreover, the

electrochemical properties of the system at higher Li concentration is investigated and compared with that of graphite intercalated compounds (GICs). It should be mentioned that there is a recent study²¹ which found that the Li capacity of the carbon nanotube–zeolite complex can be reached to ~10% by weight. However, we will show in this work that such high capacity is actually accompanied with a large volume expansion which should be avoided if it is used as Li-ion battery material.

2. Computational method

Our calculations have been performed using a plane-wave pseudopotential formulation^{22–24} within the framework of density functional theory (DFT). The exchange–correlation energy is in the form of Perdew-Wang-91.²⁵ Ultrasoft pseudopotentials are used for C, Al, O, P, and Li atoms. The carbon nanotube–zeolite complex is modeled by using a supercell geometry so that the tubes are confined inside the AFI channels and arranged in a hexagonal array. The cutoff energy is set to 29 Ryd and uniform **k**-points are used along the tube axis. We choose (5,0) tube in the following discussions since its periodicity is almost perfectly commensurate with that of the AFI (one AFI elementary cell contains two zigzag (5,0) unit cells). During the geometry optimization, all the degrees of freedom (including cell shape and volume) are allowed to relax, and optimal atomic positions are determined until the magnitude of the forces acting on all atoms became less than 0.05 eV/Å.

3. Results and discussions

As known,²⁶ AFI is a type of porous aluminophosphate single crystal. Its framework consists of regularly alternating tetrahedral (AlO₄)⁻ and (PO₄)⁺ which form open one-dimensional channels packed in the hexagonal structure. The unit cell contains 72 atoms (Al₁₂P₁₂O₄₈) with lattice constant $a = 13.74$ Å and $c = 8.47$ Å. Fig. 1 is a ball-and-stick model of (5,0) tube confined inside the AFI channel, and the combined structure has a nominal formula C₄₀Al₁₂P₁₂O₄₈. For the

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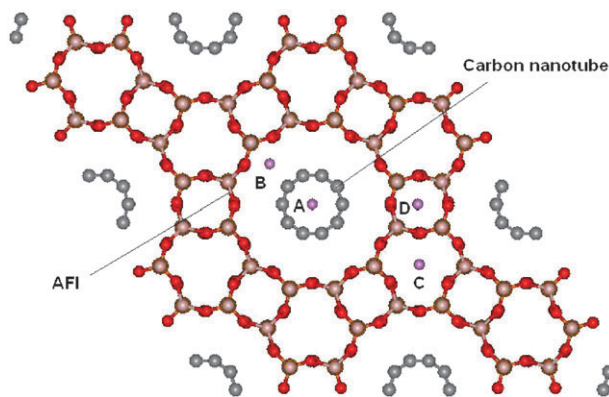


Fig. 1 Possible Li doping sites in the carbon nanotube–zeolite complex.

freestanding (5,0) tube, the Li can be doped both inside (site A) and outside the tube (site B). When the AFI is included explicitly, there are two additional sites (C and D) for Li to be intercalated. It should be mentioned that each one may have many equivalent sites in the hexagonal unit cell.

We first consider the low concentration limit such that there is only one Li atom per unit cell. Table 1 summarizes the calculated Li binding energies and volume changes for the above-mentioned doping sites. The binding energy is defined as:

$$E_b = E_{\text{Li+complex}} - E_{\text{complex}} - E_{\text{Li}} \quad (1)$$

Here $E_{\text{Li+complex}}$ is the total energy of the nanotube–zeolite complex with one Li atom doped, E_{complex} is the total energy of the complex, and E_{Li} is the total energy of Li in bcc structure. The volume change percentage is given by the expression:

$$\alpha = \frac{V - V_0}{V_0} \quad (2)$$

Here V_0 and V are the total volume of the complex system before and after Li is doped, respectively. As can be seen from Table 1, all the calculated binding energies are negative which means that the reactions are exothermic if the chemical potential of Li is set at that of bulk Li. Among all the four configurations, site B has the lowest energy and site A the highest with a difference of 0.67 eV. This value is significantly larger than that found for the outside and inside doping of freestanding (5,0) tube. The reason is that the presence of AFI will enhance Li binding at site B. It was previously found that bare AFI is not favorable for Li doping.²¹ However, when the tube is incorporated into the AFI channel, we see from Table 1 that even site C and site D are energetically favorable. Again,

Table 1 Calculated Li binding energies and volume changes for different doping sites in the carbon nanotube–zeolite complex with nominal formula of $\text{LiC}_{40}\text{Al}_{12}\text{P}_{12}\text{O}_{48}$

Doping sites	Binding energies (eV/Li)	Volume changes
A	−0.64	−0.5%
B	−1.31	0.07%
C	−1.06	−1.1%
D	−0.77	−1.8%

this suggests that the combination of carbon nanotube and AFI zeolite could be used to enhance Li binding. On the other hand, we see from Table 1 there are only slight changes of the cell volume upon Li doping at all the four sites. In particular, Li at the most energetically favorable site B leads to a very small expansion of the volume. As there are many equivalent positions for site B between the outer wall of tube and the inner wall of AFI, it is reasonable to expect that Li can be doped with a large amount without significantly destroying the nanotube–zeolite structure.

In Fig. 2, we show the calculated energy band structures for the nanotube–zeolite complex with Li doped at different sites. For comparison, the band structure of pristine complex with the same unit cell is also shown. As AFI is an insulator with large gap, the energy bands around the Fermi level mainly come from the nanotube. Without Li, we see from Fig. 2d that the complex is metallic, as characterized by the downshift of the α band in the (5,0) tube. The upper valence bands of the zeolite have little or no dispersions and are mainly located in two energy regions from -6.53 to -4.86 eV and -3.98 to -2.85 eV.²⁷ Upon doping of Li, we see from Fig. 2a–c that the band structures follow roughly a rigid band picture. That is, the Fermi levels get up-shifted when the $2s$ electron of Li atom is transferred to the nanotube–zeolite complex. However, there are obvious band-splittings due to the symmetry breaking when the Li atom is intercalated into different sites. For example, the doubly-degenerate E_{1u} and E_{2u} bands in Fig. 2d are now separated by small gaps in Fig. 2a and c for the inside (site A) and hexagonal doping (site C), respectively. Such band-splittings are more obvious in Fig. 2b since the Li atom at site B results in a serious symmetry breaking. It is interesting to see that the separated E_{2g} bands in Fig. 2d tend to degenerate again for the Li doping at site A and C. On the other hand, the Li doping also changes the positions of the AFI's bands. In particular, the upper valence bands of AFI in Fig. 2c are down-shifted by about 1.1 eV. In contrast, there is almost no shift for the AFI's bands in Fig. 2a. While for Fig. 2b, the change of the AFI bands is between these two cases. Such difference is probably due to the fact that at site A and C, the $2s$ electrons of Li are respectively transferred to the nanotube and AFI; while at site B, the electrons are given to

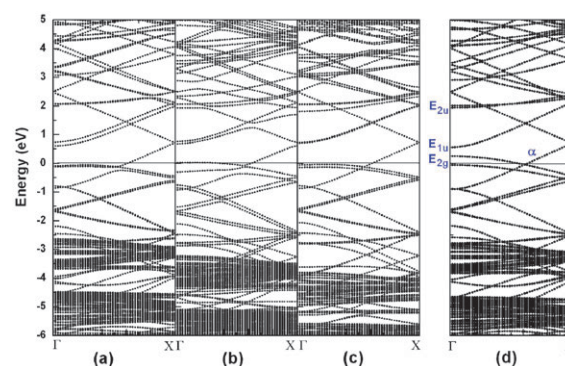


Fig. 2 Energy band structures of (a) the nanotube–zeolite complex with Li doped at site A, (b) the complex with Li doped at site B, (c) the complex with Li doped at site C, and (d) the un-doped complex. For each doping case, there is one Li per unit cell. The Fermi levels are at 0 eV.

both of them. The charge transfer can be clearly visualized by investigation of the differential charge density contour. Here the differential charge density is defined as the difference between the charge density of Li doped complex and that of the pristine complex and Li:

$$\Delta\rho = \rho_{\text{Li+complex}} - \rho_{\text{complex}} - \rho_{\text{Li}} \quad (3)$$

Fig. 3a shows the differential charge density contour on the (001) planes for the case of inside doping at site A. We see that almost all the 2s electrons of the Li atom are donated to the

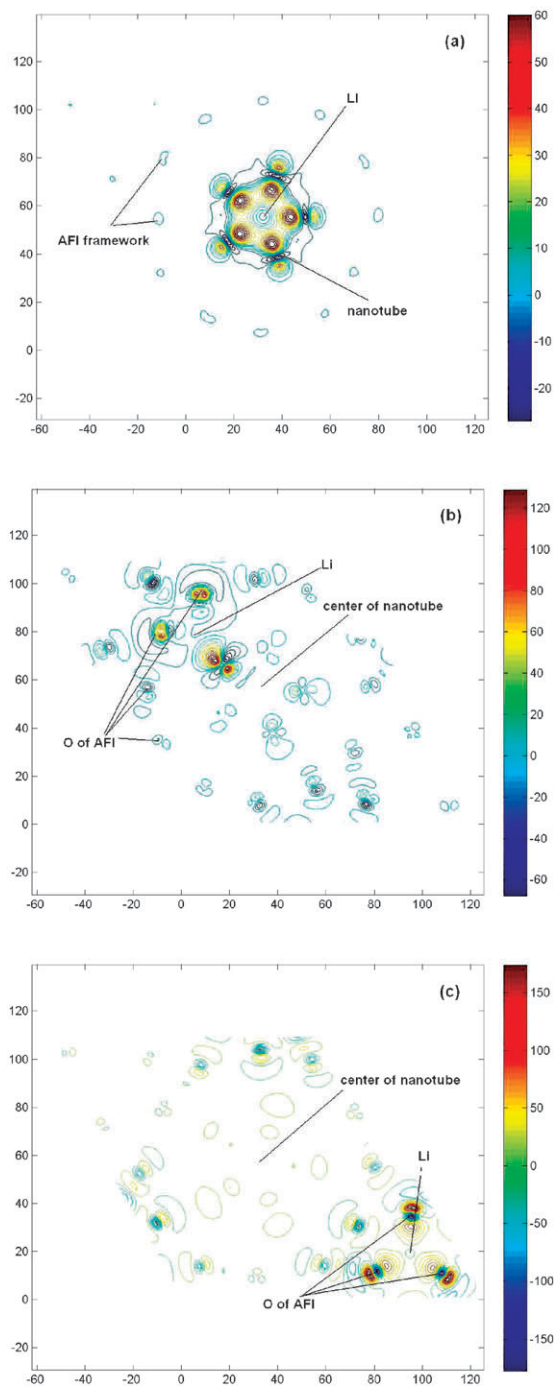


Fig. 3 Differential charge density contours on the (001) plane for Li doping at (a) site A, (b) site B, and (c) site C.

carbon wall. When the Li atom is doped in the hexagonal center of AFI (site C), we see from Fig. 3c that the charge is mainly transferred to the three nearest O atoms of the AFI framework. For the doping at site B, however, the charge is transferred to both the carbon nanotube and AFI as can be seen from Fig. 3b. This is consistent with the fact that site B has the lowest energy among all the four configurations.

We now consider the high concentration limit. It is previously reported that an exothermic doping with 36 Li per unit cell of nanotube–zeolite complex can be reached.²¹ However, we checked that such higher doping concentration causes a volume expansion larger than 10%. Moreover, the AFI framework structure is destroyed and the nanotube has a serious distortion. It is generally accepted that for the anode materials used in Li-ion battery, the volume change should be less than 5% after Li intercalation. Otherwise, the stability and safety will become a serious problem. To get a maximum intercalation capacity, we should therefore insert Li atoms as more as possible and keep the volume change within 5% at the same time. As we mentioned before, there are many equivalent positions for the four possible doping sites. In our calculations, 24 Li atoms per unit cell are evenly arranged into four alternate layers between the outer wall of nanotube and the inner wall of AFI (site B). Additionally, two Li are inserted into the center of nanotube (site A) and one to each hexagonal interstice (site C). The obtained configuration contains 28 Li atoms per unit cell with nominal formula of $\text{Li}_{28}\text{C}_{40}\text{Al}_{12}\text{P}_{12}\text{O}_{48}$, and the Li/C ratio is significantly larger than that obtained in the GICs (LiC_6). The corresponding Li binding energy is found to be -0.3 eV which means that the intercalation is still favorable at such high concentration. On the other hand, there is only a small deformation of the AFI and tube's structures (see Fig. 4a) and the volume expansion is

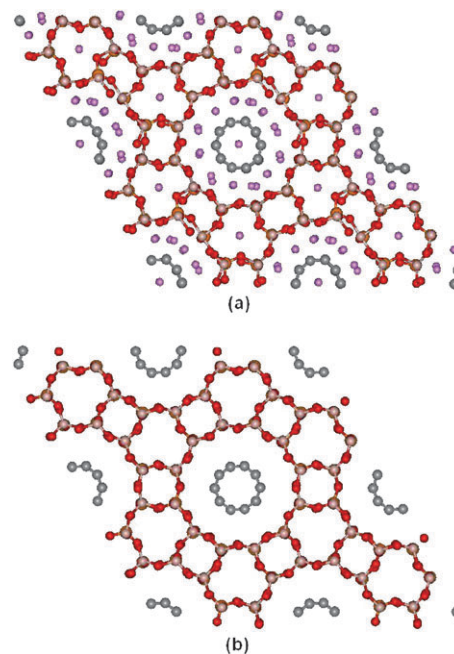


Fig. 4 The optimized structures of (a) the nanotube–zeolite complex doped with 28 Li atoms per unit cell, and (b) the relaxed structure when the 28 Li atoms are removed from the system.

found to be 4.7%. To see if such intercalation is reversible, we have done additional calculation where the 28 Li atoms are removed from the unit cell. It is interesting to find that after relaxation, the system recover to the original un-doped structure (see Fig. 4b). This suggests that the carbon nanotube–zeolite complex may have good cyclic stability when used as the anode material of Li-ion battery.

To examine the electrochemical properties, we have calculated the Li-ion intercalation capacity by using the expression:

$$C_0 = 26.8 \times n \times m_0/M \quad (4)$$

Here n is the moles of the transferred electrons. m_0 and M are respectively the mass and atomic mass of the active matter. For our complex system with 28 Li atoms per unit cell, the calculated C_0 is 386 mAh g⁻¹ which is higher than the upper limit of graphite (372 mAh g⁻¹). As known, the Li-ion battery is often described as a “rocking chair” and Li moves in and out of anode and cathode during the charge and discharge process. For the GICs, the average voltage of LiC₆/NiO₂ battery was calculated to be 3.05 V compared with the experimental value of 3.57 V.²⁸ Here we can estimate the battery voltage if the nanotube–zeolite complex is instead used as anode material. During the Li intercalation process (assuming bulk Li), we have:



The average voltage ($E^{\text{av},T}$) depends on the change of Gibbs energy (ΔG^T) in the reaction and can be given by:²⁹

$$E^{\text{av},T} = -\Delta G^T/nF \quad (6)$$

Where T denotes the absolute temperature, n is the moles of transferred electrons, and F is the Faraday constant. Usually the temperature effect is very small in the calculation of the average voltage and can be neglected. On the other hand, the change of Gibbs energy can be approximately written as:³⁰

$$\Delta G = \Delta E + P\Delta V - T\Delta S \quad (7)$$

where the 2nd term is of about 10⁻⁵ eV/Li and can be neglected compared with the 1st term. The 3rd term vanishes at zero temperature. The average voltage is thus expressed as:

$$E^{\text{av}} = -\Delta E/nF \quad (8)$$

For the minimum ($x = 1$) and maximum ($x = 28$) doping, the calculated average voltage relative to bulk Li are 0.05 and 0.01 V, respectively. On the other hand, the most popular cathode material such as CoO₂ has a voltage of 4 V relative to bulk Li.³¹ Thus our calculated small values suggest that the battery voltage can be reached to about 4 V if the nanotube–zeolite complex is used as anode material and the cathode is the conventional CoO₂ or NiO₂.

4. Summary

Using first-principles pseudopotential method, we study the electronic and electrochemical properties of Li-doped carbon nanotube–zeolite complex. The energetically favorable doping

sites are identified and the corresponding band structures and differential charge density are discussed. Without destroying the structure of the complex, the Li intercalation capacity is found to be higher than the maximum value of GICs. The good cyclic stability and higher voltage suggest that the nanotube–zeolite complex will be a promising candidate for the Li-ion battery anode.

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