Part 4

THEORY AND SIMULATIONS

28 Alkali Intercalation of Ultra-small Radius Carbon Nanotubes

H. J. Liu, J. L. Yang and C. T. Chan*
Physics Department, Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong

1.1 INTRODUCTION

We use first principles calculations to show that it is possible to intercalate ultra-small radius carbon nanotubes to form a single-atom line inside the nanotube.

Recently, single wall nanotubes (SWNT) have been successfully fabricated inside inert *AlPO4-5* zeolite channels (Tang, 1998; Wang, 2001). The nanotubes are perfectly aligned mono-sized SWNTs with ultra-small diameters of about 4 Å, confined inside the zeolite channels with inner diameters of about 7.3 Å. Due to their extremely small radius, they show unique and exciting properties, including superconducting fluctuation (Tang, 2001) with a mean field T_c of about 15 K. We consider here the possibility of modifying the properties of these nanotubes by doping. We focus on alkali atom intercalation, in anticipation that the superconductivity temperature can be enhanced if alkali doping is possible. These systems are unique as far as doping is concerned since the confinement of the nanotubes inside the zeolite channels naturally prevents the metal atoms from attaching to the outside of the SWNT. We will see below that alkali atoms inside the nanotube cannot form clusters, but have to line up as a single-atom wire. These ultra-small radius SWNTs thus have some unique structural features that make them ideal platforms for realizing a truly one-dimensional single atom wire, provided that some necessary conditions can be satisfied. These conditions are (i) the alkali atom and nanotube reaction has to be exothermic; (ii) the atoms inside the tube should not form small 3D clusters or 2D patches that are bound to the wall; (iii) the diffusion barrier inside the tube should be small; (iv) the metal atoms must find its way into the tube. We note that previous calculations (Miyamoto, 1995) have shown that intercalating K into nanotubes can be strongly

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* Corresponding author. Email: phchan@ust.hk

exothermic. The present calculations focus on ultra-small radius tubes, in particular we consider whether the insertion barrier can be overcome.

1.2 METHODLODY

The calculations (Yang, 2001) are performed within the framework of local density functional formalism. The calculations involving the insertion barrier are performed with a molecular code that considers a nanotube of finite length. For the nanotubes in zeolite channels, the dopant atoms must be able to penetrate the mouth of the nanotube, which is the only location that the outside atoms can enter the interior of these trapped SWNTs. We therefore focus on the energetics of the alkali atoms inserting through the mouth of the tube. We also did periodic unit cell calculations using a plane wave basis, which is more convenient for considering systems with higher alkali metal consideration. The finite-sized tube calculations and the periodic unit cell calculations agree well whenever they can be compared. The periodic unit cell calculations also give us band structure information and additional insight of the underlying physics.

1.3 ALKALI INTERCALATION OF (6,0) TUBE

We will first use (6,0) tube, with a diameter of about 5 Å, as the protoype ultra-small radius tube for the consideration of the alkali atom insertion into the interior of the tube.

1.3.1 K Intercalation

We now consider the doping of the (6,0) with K. The binding energy (calculated with LDA) as a function of distance measured from the geometric center of the

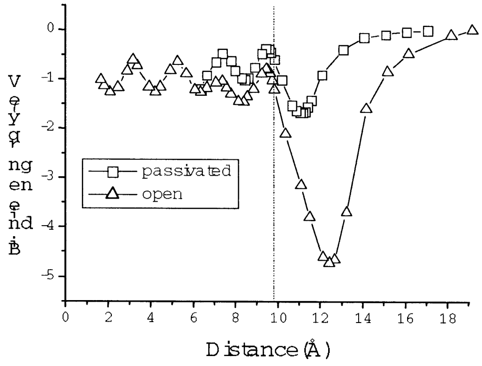

Figure 1 Binding energy per K atom as a function of distance from the geometrical center of the finite-length nanotube used for the calculation for two possible conditions of the tube mouth.

tube is shown in Fig. 1. The binding energy is calculated with a tube containing 120 carbon atoms. We consider two possible condition of the mouth of the nanotube: (i) open and unsaturated (shown as triangles in Fig. 1) and (ii) passivated by H (shown as squares in Fig. 1). For the case of a truncated tube with open, unsaturated rim, we find a deep minimum when the K atom is outside the geometric rim of the nanotube (marked by the vertical dotted line in the figure). When the K atom penetrates into the interior of the tube, it prefers to reside on the axis. We see oscillatory behavior in the binding energy as a function of position, with the lowest energy position near the center of the hexagonal rings, and the highest energy position at the zigzag ring of C atoms, and an energy difference of over 0.65 eV between the two sites so that there is a noticeable barrier for the K atoms to diffuse in the interior. If the tube mouth is passivated with H atoms, the K atom has a binding site outside the geometric edge of the tube. When the K atom penetrates into the tube, it shows the same oscillatory behavior in the binding energy as the previous case, except that the energies are higher, and which is quite reasonable since the tube with a saturated rim is less reactive in the rim region. The two binding energy curves naturally merge together when the K atom is about 4 Å deep from the tip. We have also calculated the binding energies when the K atoms penetrate the capped tube, and we found a huge barrier of over 20 eV for the K atom to penetrate the hexagonal cap. We note that if we repeat the calculation with GGA, the binding energy of the K atom is actually positive (about 0.2 eV at the lowest point), implying that the K atom has a higher energy inside the tube than outside the tube. The existence of a strong binding site outside the tube, the fairly big diffusion barrier, together with the unfavorable binding energy collectively imply that doping K into these small radius nanotubes would not be favorable from both the kinetics and thermodynamics point of view.

1.3.2 Li Intercalation

We now consider the possibility of inserting Li, a smaller alkali atom, into the tube. We used a tube of finite length containing 120 carbon atoms to model the (6,0) tubule, and we consider 3 possible conditions for the mouth of the nanotube: (i) capped, (ii) open, and (iii) saturated with H. Two Li atoms are arranged to penetrate symmetrically from both ends of the tube, one from one side, and the other on the opposite side. The energy change as Li atoms penetrate into the (6,0) nanotube through the mouth of the tube is shown in Fig. 2. The calculated results are shown as square, triangle and diamond for the case with the tube mouth capped, open, and the passivated respectively. The lines are for guiding the eye only. The zero of the binding energy refers to sum of the energy of the nanotube and free Li atoms when they are far away and non-interacting. The distance shown on the horizontal axis is measured from the geometric center of the finite sized tube used for the calculation. We first note that if the Li atom is significantly lower in energy inside the tube than outside the tube, and thus the intercalation is an exothermic process. However, the insertion barrier depends crucially on the condition of the mouth tube. If the mouth is capped (marked by squares in Fig. 2), the barrier is over 6 eV and it is unlikely that Li can penetrate the hexagonal cap.

On the other hand, there is a position of minimum energy just outside the tube mouth if the tube mouth is open and unsaturated (see the triangles). This case is not too promising for Li insertion since Li atoms will most likely be trapped in this minimum energy position and will block the entry of other Li atoms. The most promising case for Li insertion is the case in which the tube mouth is passivated by hydrogen. We see no insertion barrier and the energy just keep monotonically decreasing from outside to inside the tube. That means that the nanotube actually sucks the Li atoms in, as if a vacuum cleaner is sucking up small particles.

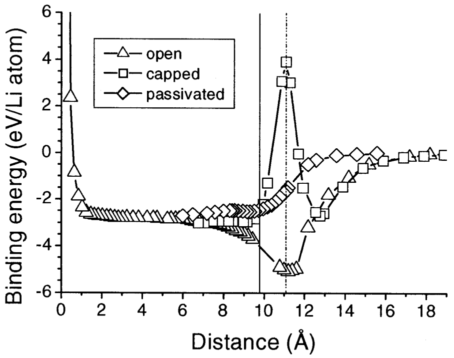

Figure 2 Binding energy per Li atom as a function of distance from the geometrical center of the finite-length nanotube used for the calculation for three possible conditions of the tube mouth. The solid line marks the rim of the open (unsaturated) nanotube, while the dotted line marks the rim of the capped nanotube.

We found that the Li atoms prefer to reside on the axis of the tube. Once inside the tube, the energy curve is very smooth. This is interesting since the tube is not a smooth cylinder, but has ring structures of the carbon atoms. This smoothness is essentially due to the small size of the Li atom. This smooth energy curve implies that there is no particularly preferred site when the Li atoms are inside the tube, sitting on the axis. That means that there is no “docking”, and the Li atoms can diffuse essentially freely along the axis, making way for additional Li atoms to enter. As have been remarked already, we are actually inserting in two Li atoms, one from each side of the tube. The fact that the energy curve suddenly shoots up when the Li atom is about 1.5 Å from the center of the finite-length tube is because the two Li atoms are now close together. Upon examining the charge density and the band structure, we found that the Li atoms give up the 2s electron to the carbon tube, leaving itself positively charged. When there are two Li atoms inside the tube, they will repel each other by Coulombic repulsion. These small radius tubes are very polarizable and they provide very good screening. That is why the energy curve is nearly flat until the two Li atoms are closer than 3 Å together. When they are further away, they literally do not see each other because of the good screening. When they are closer together than the screening length, they repel each other strongly, leading to the rapid increase of energy observed in Fig. 2.

This also has important implications as far as Li intercalation is concerned. If the Li-Li interaction is attractive, they may form small cluster or patches that clog the inside of the tube, and we will not be able to achieve the single-atom wire configuration. On the contrary, if the Li-Li interaction is strongly repulsive, there is no chance for a high concentration of inside the nanotube. What we find here is in fact the better possible scenario to form a single atom wire. The Li-Li interaction is repulsive but strongly screened. This means that the Li atoms that are already inside the tube will not block others from going in (due to the screening), but they want to keep a distance of about 3 Å away from each other so that there will not be any cluster formation.

The present result pertains to the case of low concentration. We have considered adding more Li atoms, and we found that a short (6,0) tube containing 120 carbon atoms can exothermally absorb at least 9 Li atoms (relative to a free Li atom). This implies that the tube can actually absorb a high concentration of Li exothermically. We have repeated the calculation with periodic unit cell calculations using a plane wave basis, and the results agree very well with the finite-sized tube calculations.

1.4 INTERCALATION OF 4 ANSTROM TUBES

We now consider whether intercalation is possible if the tube radius is 4 Å. There are three types of nanotubes that have diameters that are approximately 4 Å, and they are respectively (3,3), (5,0) and (4,2). There is experimental evidence (Li, 2001) that all three types of tubes are present inside zeolite channels. These three types of tubes offer us a good opportunity to study the effect of chirality on the kinetics and the energetics of the alkali doping. We repeated the insertion barrier calculation for these tubes, and found that the results are qualitatively similar to the case of (6,0). The barrier is high if the tube mouth is capped, and there are strong binding sites outside the mouth if the tube is unsaturated. If the mouth tube is passivated by hydrogen, intercalation is found to be possible with no insertion barrier and the reaction is strongly exothermic relative to atomic Li. The Li atoms still prefer to sit along axis once it is inside the tube. The Li-Li interaction is repulsive, but strongly screened as in the case of (6,0). The energy curve is also very smooth inside. We see essentially no diffusion barrier for the case of (3,3) and (4,2), and for the case of (5,0), the Li bounds slightly stronger when it is facing the hexagonal rings than facing the carbon rings, leading to a small diffusion barrier of about 0.16 eV.

When we compare the (5,0) nanotube results with those of the (6,0) nanotube that has the same chirality but a bigger radius, we found that the binding energy of Li is stronger for the case of (5,0) than (6,0). The screening is also better in the case of (5,0) than (6,0). Both of these observations are consistent with the smaller radius of the (5,0) nanotube.

One may normally expect that the radius is the key parameter in governing the reaction of the nanotube with Li, particularly that the Li atoms are residing on the axis. However, our calculations show that the heat of formation shows a marked dependence on chirality. We found that Li binds much stronger with (5,0) than (3,3). The chiral (4,2) tube is in between. For Li in (5,0) and (4,2), the heat of formation is exothermic relative to bulk Li, while for (3,3), the Li heat of formation is less than the cohesive energy of bulk Li. We further found that such a strong dependence on chirality is an intrinsic property of the tube in the sense that it does not depend on the position of the Li atoms. We have put the Li atoms outside the tube instead of inside the tube, and we found the same order in the heat of the formation. We further note that the present result does not imply that (5,0) tube is in general more reactive than (3,3). It is just for the case of alkali adsorption that the ziz-zag tube is more reactive. In fact, we have also calculated the reaction of oxygen with these tubes and we found that oxygen bonds stronger with (3,3) than (5,0).

We have also examined the electronic properties of Li intercalated inside the nanotube and we found that for all the cases we have considered, the rigid-band picture holds fairly well within 2 eV or so of the Fermi level. The Fermi level of the nanotube just get upshifted as the carbon bands are filled by the 2s electrons of the Li. This leads to a higher density of states in the Fermi level, and thus may enhance the superconducting temperature of these nanotubes.

1.5 SUMMARY

Using density functional calculations, we found that it is possible to intercalate ultra-small radius nanotubes with small alkali atoms such as Li to form a single line of atoms inside the nanotube and the Li atoms will reside on the axis. The conclusions are drawn on both kinetics and energetics considerations. If such single atom chains can be realized, it may be an interesting platform for us to learn about low dimension physics at the nano-scale.

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