

## *Ab Initio* Investigations of Lithium Diffusion in Carbon Nanotube Systems

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Li-nanotube systems can substantially improve the capacity of Li-ion batteries by utilizing both nanotube exteriors and interiors. Our *ab initio* simulations show that while Li motion through the sidewalls is forbidden, Li ions can enter tubes through topological defects containing at least nine-sided rings, or through the ends of open-ended nanotubes. Once inside, their motion is not diffusion limited. These results suggest that “damaging” nanotube ropes by either chemical or mechanical means will yield superior material for electrochemical storage.

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Carbon nanotubes not only have outstanding mechanical and electronic characteristics, but also hold considerable promise as molecular containers with applications as hydrogen fuel cells [1] and rechargeable Li batteries [2]. The key element that makes nanotubes so potentially useful as electrochemical storage devices is their structure. For instance, consider the case of Li-ion batteries. In most batteries, graphitic carbon anodes are used instead of metallic Li electrodes because of both safety and cycle efficiency concerns [3]. However, the use of graphite as a host material has some disadvantages, chief of which is the substantial reduction in the energy density as compared to metallic Li. Under optimal conditions Li intercalates into graphite to form  $\text{LiC}_6$ , which leads to a specific capacity reduction from 3860 mA h/g for metallic Li to 372 mA h/g for the graphitic anodes. In principle, the performance of these batteries would be significantly enhanced, if one could somehow boost the Li/C ratio inside the host material.

Now consider the case of carbon nanotubes, which are formed when a graphene sheet is curled up into a cylinder and the carbon atoms joined seamlessly to each other. As nanotubes form, they typically aggregate into bundles, termed *ropes* which consist of single-wall nanotubes held together by van der Waals forces. These ropes are expected to display superior energy storage capabilities provided that the Li ions can intercalate both into the channels between the nanotubes, and into the interior of the nanotubes themselves. In the ideal case, this gives an enhanced anode stoichiometry of  $\text{LiC}_2$  [4], which is considerably higher than the value of conventional Li-graphite anodes. Clearly, the key to superior battery performance using nanotubes lies in the ability of Li ions to enter and leave the nanotube interiors at a reasonable rate. To address this issue, we have investigated the dynamics of Li motion inside carbon nanotube-based systems with *ab initio* simulations. Our results show that while the entry of Li ions into pristine tubes is forbidden, the ions may enter through topological defects and open-ended nanotubes. Experimentally, such defects may be induced via suitable chemical [5] or mechanical [6–8] means. We have also calculated the diffusion barriers for Li motion in the interstitial channels between the nanotubes, and

inside the nanotubes themselves. These barriers turn out to be quite low, showing that Li motion inside nanotube systems is not diffusion limited for nanotube lengths typical of current experiments. These results have been further tested via direct large-scale *ab initio* simulations which also elucidate the effects of Li-Li ion interactions in nanotubular systems.

Experimentally, Li intercalation into nanotube systems have been performed on both multiwalled [9] and single walled [7,10,11] nanotubes. Initial results were somewhat disappointing, showing only a poor 25% increase in the reversible capacity of Li uptake relative to graphite. Moreover, the system was characterized by a very large irreversible Li capacity; i.e., most of the Li was not recovered upon cycling. These experiments suggest that very few of the Li ions actually reach the interior of the nanotubes. Subsequent experiments achieved considerably better results by first ball milling the carbon nanotube samples [7]. Not only did this dramatically reduce the irreversible capacity of the nanotubes, but it also *increased* the reversible capacity to 2.7 Li per carbon atom.

These experiments point to the important role played by the kinetics of the Li ions in nanotube systems. An aggressive ball milling treatment will clearly damage the nanotube ropes both by inducing defects into the side walls and by reducing the nanotube length via fracturing, as is shown by electron microscopy [7,8]. In order to get an understanding of how to better process nanotubes for energy storage devices, several important issues need to be addressed. For instance, what are the possible mechanisms and channels for Li ions to enter a nanotube interior? What is the rate of ion exchange? Which defects help or hinder the diffusion process?

To investigate these issues, we performed *ab initio* density functional-based calculations using a multigrid code with a real-space grid as a basis [12]. Nonlocal, norm-conserving pseudopotentials of the Troullier-Martins form [13] were included using the Kleinman-Bylander approach [14]. Calculations were carried out with a grid spacing corresponding to an effective energy cutoff of 60 Ry with a single  $k$  point. In order to calculate the diffusion pathways for the Li ions, use was made of the “adiabatic trajectory

method" [15]. In this method, the ion is pushed over the surface with a small, constant speed in a given direction, while monitoring the total energy. Note that the ion is constrained in one direction only. It is free to move in the directions perpendicular to the applied force, thereby enabling the ion to find its optimum path. All other atoms are relaxed continuously in response to the Li ion motion. This method has been found to be a viable and realistic alternative to a costly point-by-point determination of the potential energy surface [15].

Previous theoretical work [4,16] has shown that Li intercalates preferentially into the channels between nanotubes. To probe the ability of Li ions to enter and leave a nanotube interior, we calculated the energetics of a diffusion pathway for a Li atom to move through the sidewall of a metallic (5,5) armchair nanotube, as shown in Fig. 1. The pathway is characterized by two local minima which are located about 2.1 Å away from either side of the nanotube wall. In these stable positions, the Li atom is almost completely ionized. Figure 1b shows the charge density for a Li atom located in such an *external* minimum. While there is some spatial localization of the charge near the Li atom, much of the charge density is, in fact, distributed over the nanotube wall. In particular, note the appearance of a *mirror* image charge which forms on the other side of the nanotube wall. Separating the two minima on either side of the nanotube is a very large diffusion barrier of about 13.5 eV. Hence, it is virtually impossible for Li ions to enter into the interior of the nanotube via direct diffusion through the sidewalls.

Since charge transfer is one of key issues governing the Li-nanotube physics, we have repeated these calculations for a (8,0) semiconducting nanotube. As expected, the energy between the stable Li positions in/out nanotube and vacuum is *increased* by about 0.60 eV, which is close to the value of the LDA semiconducting gap for the tube. The corresponding charge distribution, given in Fig. 1d, shows that most of the charge remains localized on the nanotube wall near the Li ion. In contrast to the metallic nanotubes, the presence of a Li atom perturbs the electronic properties of a semiconducting nanotube only weakly. As may be expected, no mirror charge forms across the nanotube wall.

Because the large energy barriers prohibit Li diffusion through the walls of pristine nanotubes, other pathways into the nanotubes must be found. One such option is provided by the various topological defects that can be induced in the nanotube walls by nonequilibrium means such as ion bombardment [6], the tensile straining of nanotubes [17,18], or by more violent means such as a chemical attack or the direct mechanical grinding of the nanotubes [8]. Since all of the different topological defects consist of  $n$ -membered rings in various combinations, we calculated the diffusion barriers for Li atoms moving through such rings ranging from hexagons to enneagons (nine sides), as shown in Fig. 2. As expected, as the number of sides  $n$  increases, the barriers for Li to enter decreases, because the "holes" become larger and larger. Specific barrier heights  $\Delta E_n$ , along with the formation energies  $E_F$  for the different  $n$ -sided rings shown in Fig. 2, are summarized in Table I. It is clear that only for enneagons and

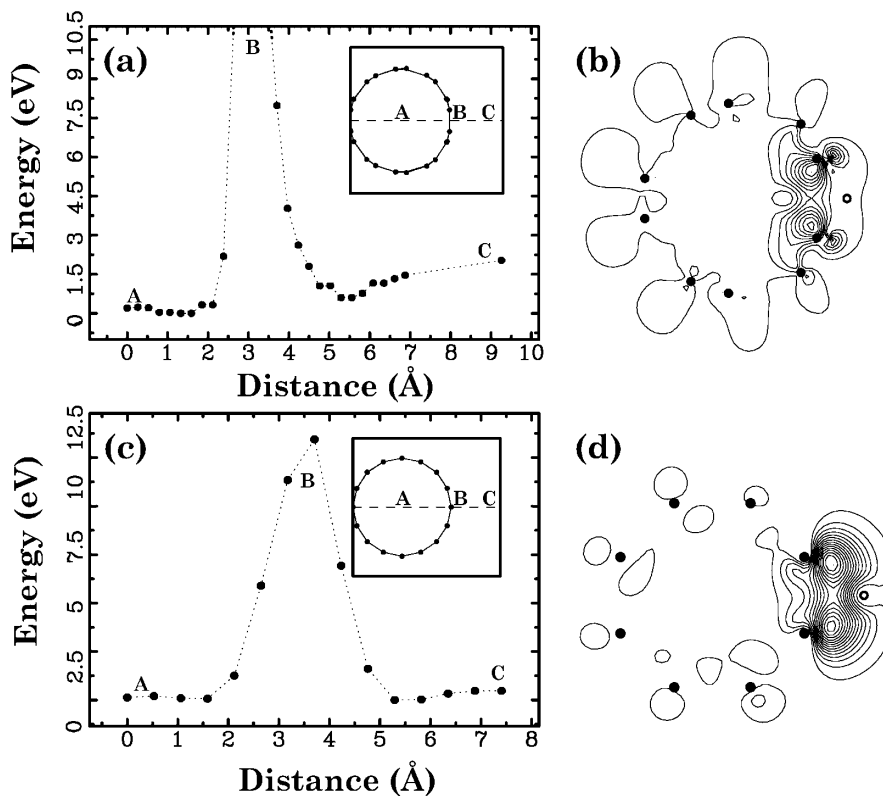


FIG. 1. Energetics of diffusion pathways for Li to move through a (a) (5,5) metallic; and (c) (8,0) semiconducting nanotube. Contour plots of the resulting charge difference distribution for a Li atom absorbed on (5,5) and (8,0) nanotubes are shown in (b) and (d), respectively. The positions of the C(Li) atoms are indicated by the filled (open) circles, respectively.

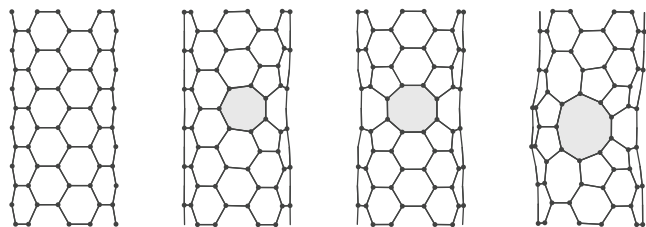


FIG. 2. Structure of the topological defects displaying different  $n$ -membered rings. The diffusion barriers through these rings and the corresponding formation energies are given in Table I.

higher-order defects can the Li ions enter and leave the nanotube relatively freely.

Aside from topological defects, an alternate way for ions to move into the nanotubes is via their *open ends*, provided that such tubes can be stabilized. To be useful, such open-ended nanotubes would have to be relatively short in order to allow for a reasonable rate of ion exchange. Experimentally, different techniques for cutting [19] and sharpening [20] nanotubes exist using both chemical and electron pulse-based techniques. Indeed, even the ball milling procedure reduces nanotube lengths from micrometers to between a few tens to hundreds of nanometers [8].

In order to understand the movement of ions through open-ended nanotubes, we have calculated the diffusion barriers for Li inside the (5,5) and (8,0) nanotubes with *ab initio* techniques. For both tubes, the ends were stabilized by saturating the nanotube tips with hydrogen. These structures were then relaxed prior to the insertion of Li atoms. The main results are as follows. For both nanotubes, there is no energy barrier for the Li ions to enter the open tubes. In fact, there is a net decrease in the energy of the system by about 1.5 eV, showing that the nanotubes actually act as an attractor for the Li ions. Similar results also hold for the Li ions entering the interstitial channel in carbon nanoropes. Once inside the nanotube (nanorope), the respective barriers for Li diffusion are  $E_b = 35$  meV (47 meV). These numbers are quite small, indicating that Li ions will be fast diffusers.

With these numbers, one can readily estimate the rate with which Li adatoms move in and out of the different nanotube systems. The time for any given diffusional hop for a Li ion is  $\sim a_o^2/(2D)$ , where the  $a_o = 2.45$  Å is the lattice constant and  $D$  is the diffusion constant given by  $D = \nu a_o^2 \exp[-E_b/k_B T]$  with  $\nu \approx 2.10^{12}$  Hz, as estimated from the potential energy curve. If we assume that

TABLE I. Diffusion barrier  $\Delta E$  and formation energy  $E_F$  for each of the topological defects shown in Fig. 2. The formation energy is measured with respect to the hexagon.

	$\Delta E$ (eV)	$E_F$ (eV)
Hexagon	13.5	0.0
Heptagon	7.5	3.5
Octagon	3.0	6.2
Enneagon	0.5	9.5

the Li ions undergo a *one-dimensional* random walk inside their respective channels, then they must undertake  $\sim N^2$  hops in order to move a distance  $L = Na$ . Thus, the time  $\tau$  for a Li ion to move in/out of a nanotube (nanorope) of length  $L$  is estimated to be  $\tau = L^2/D$ . Figure 3 shows a plot of  $\tau$  as a function of nanotube length at room temperature. From these graphs, it is clear that Li entering the nanotube channels is not diffusion limited, provided that the nanotube length is of the order of a few hundred nanometers. Hence, the key factor which controls the Li kinetics is the ability of the Li ions to reach either the open ends of the nanotube, or the interstitial channel. From geometry, one can show that the ratio between the open tube surface to the total surface is  $2\pi(R - t)^2/[\sqrt{3}(b + 2R)^2 - 4\pi R t]$ , where  $b \approx 3.3$  Å is the tube-tube separation in ropes,  $R$  is the nanotube radius, and  $t$  is one-half of the effective “thickness” of a nanotube wall, introduced in order to account for the excluded volume of the nanotube. The value of  $t$ ,  $\sim 1.0$  Å, was chosen by analyzing Fig. 1 and identifying the region that is inaccessible to Li. For nanotube radii around 7 Å, this ratio is about 50%. Both channels appear to be equally important when it comes to Li uptake. Therefore, the ideal nanotube configuration, which maximizes the Li exchange, consists of short, open-ended nanotube ropes.

The above considerations are all based on the motion of *single* Li atoms near a given nanotube structure. In practice, however, it is known that diffusion is a complex process involving what may be the concerted motion of many different Li atoms. It is therefore highly desirable to study Li diffusion with full *ab initio* molecular dynamics simulations. Unfortunately, such simulations are currently precluded because of the very large system sizes involved and the time-scale problem. As a compromise, we have therefore opted to carry out dynamical simulations using

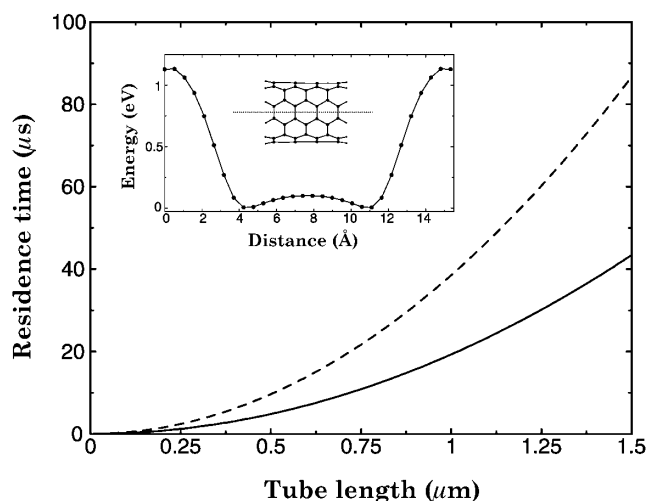


FIG. 3. Estimated residence time  $\tau$  as a function of nanotube length  $L$  at  $T = 300$  K for Li atoms in either the nanotube interior (solid line) or interstitial rope channel (dotted line). The inset shows the energetics of a typical diffusion path calculated for Li moving through an open nanotube.

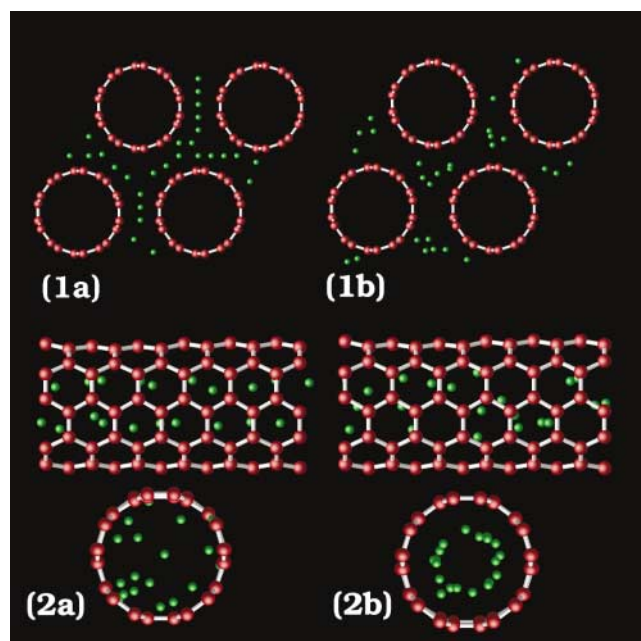


FIG. 4 (color). Snapshots of Li ions moving about charged (5,5)-based nanotube ropes (1a),(1b), and inside a charged, periodic (5,5) nanotube (2a),(2b). Here the temperature of the system was maintained at 500 K, and the time elapsed between the two frames is 5 ps each.

a frozen density approximation. As discussed, there is almost a complete charge transfer from Li to the nanotube [4], so that in the presence of many Li ions one can expect the nanotubes to be uniformly charged. Li ion motion is therefore expected to be dominated by electrostatic effects.

Figure 4 shows two results of sample runs for Li ions in the interstitial channels of a nanotube rope and in the interior of a nanotube. In each case, the electron density of the charged nanotubes was computed self-consistently and then frozen. Li ions were then added at random to the system in a  $\text{Li}_1\text{C}_6$  ratio, and then propagated via standard molecular dynamics means. In the case of nanotube ropes, the Li ions concentrate themselves in the most stable position, which is equidistant from the three neighboring nanotubes in order to minimize the electrostatic effects. The Li ions do not form aggregates, but rather chains along the main axis of the system. Electrostatic effects also dominate Figs. 4(2a) and 4(2b), which shows Li ions inside a nanotube. When placed there at random, they rearrange themselves to spread out over a cylindrical surface of radius 2.1 Å inside the (5,5) tube, while still minimizing the electrostatic repulsion. These dynamical simulations, which confirm the high Li-ion mobility inside nanotube systems, do not display any evidence of concerted Li motion.

In summary, one of the key factors in producing a superior battery based on Li/carbon nanotube technology is the ability of Li ions to exchange with the nanotube interior. We have investigated different modes for accessing these interiors with *ab initio* calculations. Our studies in-

dicating that while direct diffusion of Li ions through the sidewalls of pristine nanotubes is forbidden, the ions can enter through topological defects consisting of at least enneagons. Alternatively, Li can enter through open-ended nanotubes. Once inside, the ions are not diffusion limited, provided that the tubes are relatively short. These results are completely consistent with recent experiments, which show that a chemical or mechanical treatment of nanotube ropes that enhances these pathways will be characterized by a superior Li uptake. In addition, we have tested Li ion diffusion in nanotube systems using a frozen density approximation. The final Li arrangement in these systems is consistent with a minimization of the electrostatic energy of the system.

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