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Nanotubes for charge storage – towards an atomistic model

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ABSTRACT

We examine the insertion of alkali and halide ions into narrow nanotubes of graphite and gold by density functional theory (DFT). For tubes with diameters less than about 10 Åthe optimum position of the ion is in the center of the tube. Bader analysis and an analysis of the densities of states gave contradictory results for the charge on the halide ions, but we argue on physical grounds that they carry unit negative charge. We have calculated the energies of inserting the atoms into the tubes, where they are ionized. Because of the small system size the work function of the tubes changes during this process, which makes it difficult to interpret these energies. The surrounding tubes screen the ionic charge very effectively; thereby the ion-ion interactions are strongly reduced, which explains, why narrow tubes store charge more effectively than wider one. These effects are stronger for gold than for graphite tubes. We define an effective image radius of a cylindrical tube, and calculate the image energy experienced by the ions.

1. Introduction

The advent of nanotechnology has opened a new domain for electrochemistry, and electrode structures of nanometer size, such as pores and clusters, have become the subject of intensive investigations. They not only promise applications in catalysis, energy storage and conversion, but they also present challenges for fundamental science. A case in point is the double-layer structure in confined geometries such as nanopores. Conventional double-layer theory considers only semi-infinite electrolyte solutions, and even at high ionic concentrations the thickness of the double layer is of the order of 10 - 20 Å. This is larger than the dimensions of nanopores, which are often only a little wider than the diameters of ions or of water molecules. Obviously, simple continuum models like the Gouy-Chapman theory are useless in this case, and new models at the atomic level are called for.

In this work, we want to take a first step in this direction and consider a fundamental case, a single ion in a metal or carbon nanotube. Our work is partially motivated by recent experimental findings which indicate, that pores with radii that are so small, that solvated ions cannot enter, store charge more efficiently than wider pores – in other words, their double-layer capacity per unit area is larger [1,2]. Kondrat and Kornyshev [3] explained these unexpected findings by the image interaction between the ions and the walls of the pores. Based on these ideas, Rochester et al. [4] constructed a simple model, in which the walls of the pore were either taken to be a perfect classical metal or a Thomas-Fermi metal, and explained how the image interaction screens the Coulomb potential of a point charge and thus enables a denser packing of ions. While these explanations are certainly qualitatively correct, a description at the atomic level is missing. An important step in this direction has been taken by Merlet et al. [5] who studied the capacitance of nanoporous carbon by molecular dynamics using a corse-grained model of an ionic liquid, following earlier work by Shim and Kim [6] along the same line. We start at a more fundamental level and consider a single ion in a nanotube in order to understand its interaction with the tube and the screening of the charge. Therefore, we have performed DFT (density functional theory) calculations for a series of alkali and halide ions in nanotubes and investigated the image interaction and the concomitant screening of the Coulomb interaction quantitatively. First results for Na^+ and Cs^+ have been published in [7]; here we focus on Li^+, because of its importance in battery technology [8,9], present first results for anions, and provide details that were missing in the first paper. Again we shall contrast the behaviour of carbon tubes with that of gold tubes, since metals are known to screen charges much better than carbon [10,11]. For a related approach to lithium stored in graphite, see the very recent article of Robledo et al. [12].

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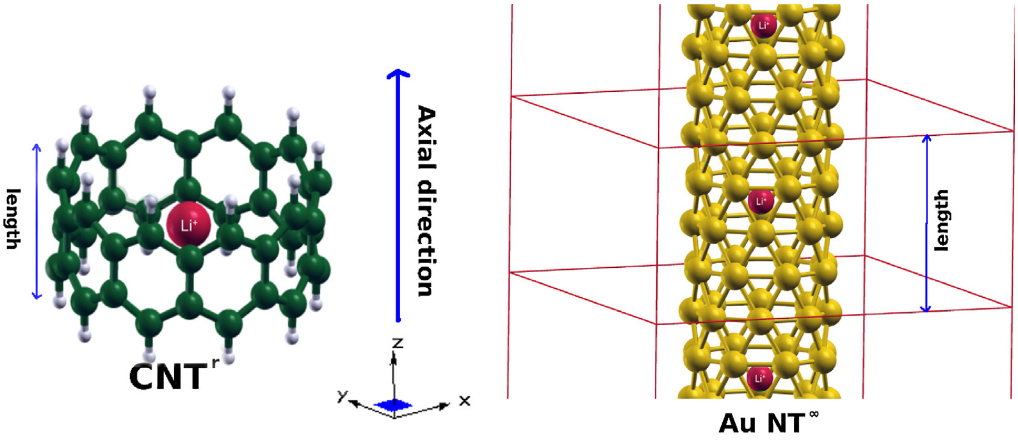

Fig. 1. Examples of lithium ions inside of gold nanotubes (right) and carbon rings (left) investigated. The red lines on the right represent the unit cell.

2. Details of the investigated systems

As in our previous publication [7] we have investigated atoms placed inside single-walled narrow carbon or gold nanotubes. In particular, we have studied alkali and halogen atoms placed into (6,6) and (8,8) gold nanotubes $(\mathrm{AuNT})^\infty$ – see [13,14], and (6,0), (8,0) and (10,0) carbon nanotubes $(\mathrm{CNT})^r$ [15]. For the AuNT^∞ we have used cyclic boundary conditions to represent infinite tubes, indicated by the superscript ∞, while the CNT are of finite size in the axial direction (see Fig. 1), which we indicate by the superscript r for ring. The CNT^rs by themselves are not stable, therefore we saturated the dangling bonds with hydrogen atoms. For comparison we shall also present a few results for infinite $(6,3)\mathrm{CNT}^\infty$, but a thorough discussion of these tubes, which have metallic properties, will be left to a future publication. The dimensions of the investigated systems are given in Table 1; the technical details of the calculations will be presented in the appendix.

2.1. Technical Details

Periodic density functional theory (DFT) calculations based on plane waves have been performed as implemented in the DACAPO code [25]. The electron-ion interactions were accounted through ultrasoft pseudopotentials [26], while the valence electrons were treated within the generalized gradient approximation (GGA) in the version of Perdew, Burke and Ernzerhof (PBE) [27]. The electron wave functions were expanded in a plane-wave basis setup to a kinetic energy cutoff of 400 eV (450 eV for the density). Brillouin zone integration was performed using the Gamma point. Spin polarization was considered in all the systems, but the results showed no net spin. Infinite CNTs were also calculated using the same computational parameters in the VASP code [28]. The obtained results were similar. For the relaxations the convergence criterion was achieved when the total forces were less than 40 meV/Å. Infinite gold nanotubes with and without ions were fully relaxed, as well as the hydrogenated and infinite carbon nanotubes.

All the systems used were neutral, but we confirmed the loss or gain of charge in the central atom by using Bader analysis method [17]. We used a dipole-correction scheme [29] in the systems that are not completely symmetric, in order to have a well-defined vacuum potential. The electrostatic part (ionic and Hartree potentials) of the local potential was calculated, but the exchange-correlation was not added. For the examination of the properties of a system this is more desirable due to the fact that the electrostatic potential converges more rapidly to the vacuum level than the total potential.

Table 1
Dimension of the empty tubes. In the carbon tubes the number of hydrogen atoms that saturate the dangling bonds equals half the number of carbon atoms. For the gold tubes the length corresponds to the length of the unit cell.

system	C atoms	diameter/nm	length/nm
$(6,0)\mathrm{CNT}^r$	24	0.484	0.500
$(8,0)\mathrm{CNT}^r$	32	0.637	0.500
$(10,0)\mathrm{CNT}^r$	40	0.789	0.500
	Au atoms	diameter/nm	length/nm
$(6,6)\mathrm{AuNT}^\infty$	24	0.545	0.960
$(8,8)\ \mathrm{AuNT}^\infty$	32	0.732	0.969

3. Results and discussion

3.1. Cation insertion

We have studied lithium, sodium, and cesium atoms, but we focus on lithium, which had not been included in our first report [7]. Initially we placed a neutral atom in the center. At the end of the calculations, in all cases we discuss here, the Bader charge on the ion was +1 within DFT error, and the stable position was at the center of the ring. Table 2 gives the insertion energies defined as:

$$E_{\mathrm{ins}} = E(\mathrm{tube} + \mathrm{ion}) - E(\mathrm{tube}) - E(\mathrm{atom}) \tag{1}$$

In our previous article we have argued that, in the absence of chemical interactions, the insertion energies should obey the equation:

$$E_{\mathrm{ins}} = I_1 - \Phi + E_{\mathrm{im}} \tag{2}$$

where I_1 is the first ionization energy (5.41 eV for Li), Φ is the work function of the tube, and E_{im} is the image energy. This equation immediately explains, why the insertion energies in the gold tubes are more favorable than in the CNT, since metals screen an external charge much better than carbon and hence provide larger image energies. However, it does not explain the small values for the CNT, nor the rather unsystematic variation with size. The application of this equation is straightforward only for real infinite tubes, where the work function does not change when an electron is transferred. In the finite systems considered here the work function becomes lower, as the electron is transferred from the alkali atom to the tube. The same argument applies to the infinite AuNT^∞, since in this case

Table 2
Insertion energies for Li^+ in various nanotubes.

system	$(6,0)\mathrm{CNT}^r$	$(8,0)\mathrm{CNT}^r$	$(10,0)\mathrm{CNT}^r$	$(6,6)\mathrm{AuNT}^\infty$	$(8,8)\mathrm{AuNT}^\infty$
E_{ins}/eV	−0.1	−0.29	−0.20	−2.39	−2.51