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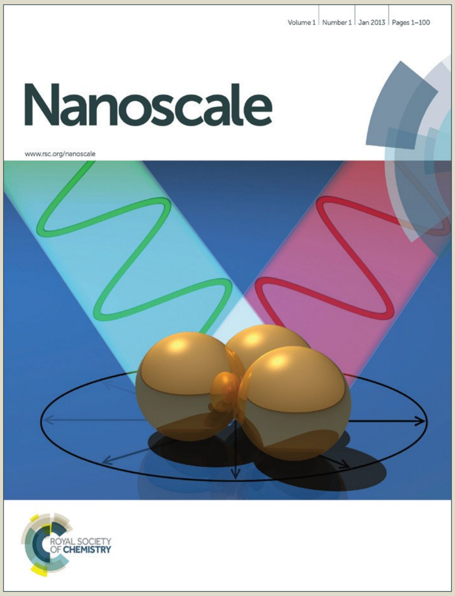

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Impact of Cation–π Interactions on the Cell Voltage of Carbon Nanotube-based Li Batteries

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Abstract

Carbon nanotube (CNT)-based Li batteries have attracted wide attention because of their high capacity, high cyclability and high energy density and are believed to be one of the most promising electrochemical energy storage systems. In CNT-based Li batteries, the main interaction between the Li^+ ions and the CNT is the cation–π interaction. However, up to now, it is still not clear how this interaction affects the storage characteristics of CNT-based Li batteries. Here, using density functional theory (DFT) calculations, we report a highly favorable impact of cation–π interactions on the cell voltage of CNT-based Li batteries. Considering both Li^+–π interaction and Li–π interaction, we show that cell voltage enhances with the increase of the CNT diameter. In addition, when the Li^+ ion adsorbs on the external wall, the cell voltage is larger than that when it adsorbs on the internal wall. This suggests that CNTs with a large diameter and a low array density are more advantageous to enhance storage performance of CNT-based Li batteries. Compared with Li^+ ions on the (4,4) CNT internal wall, the cell voltage of Li^+ on the (10,10) CNT external wall is 0.55 V higher, which indicates an improvement of about 38%. These results will be helpful for the design of more efficient CNT-based Li batteries.

Introduction

Cation–π interactions play important roles in many processes such as molecular recognition,[1-3] enzyme catalysis,[4, 5] stability of protein structures,[6-11] drug design,[12-14] and biomembranes.[15, 16] These interactions generally exist between cations and π-electron-rich carbon-based structures such as aromatic rings, graphene,[17, 18] carbon nanotubes,[19] and fullerenes. It has been widely reported that cation–π interactions greatly impact the properties and applications of these π-electron-rich carbon-based materials, including surface- or interface-charged behaviors,[20-22] wetting behavior,[23] ion distribution,[24] absorption of organic pollutants,[25-29] and the adsorption and diffusion dynamics of cations.[30-32]

How to store electrical energy with a high charge and discharge rate, high capacity, high energy density, and high cyclability[33-35] is one of the key challenges in this century. The development of nanotechnology, particularly the fabrication of nanostructures in the past decades, provides a new approach to improve the properties of energy storage materials.[36-42] Recently, a CNT-based Li battery has been reported to have a much improved lithium capacity compared with graphite, and is believed to be one of the most promising electrochemical energy storage systems.[43-49] For example, Gao and co-workers demonstrated an increase in the reversible Li capacity to 1000 mAh g^{-1} ($Li_{2.7}C_6$), after single-walled carbon nanotubes were electrochemically intercalated with lithium.[45] Theoretical studies showed that the Li/C ratio increases with the increase of the tube diameter, and can reach the stoichiometry of LiC_2.[50-53] Lee et al. reported that a functionalized carbon nanotube used as an anode can provide lifetimes in excess of thousands of cycles.[43] All of these benefits, including the high specific-surface area of CNTs and the adsorption of Li^+ ions, which reduces their over-potential, allow for faster reaction kinetics at the CNT's surface and provide it with a high capacity as an anode.[43-49, 51] We note that in CNT-based Li batteries, the main interaction between Li^+ and CNT is cation–π interactions. However, the impact of cation–π interactions on CNT-based Li batteries remains unknown.

In this paper, based on DFT calculations, we find that cation–π interactions are highly favorable to the cell voltage. In addition, when we consider both Li^+–π and Li–π interactions, the cell voltage increases with the increase of the CNT diameter.

Moreover, when the Li^+ ions adsorbs on the external wall, the cell voltage is larger than that adsorbs on the internal wall. These results indicate that CNTs with large diameters and low array densities are more advantageous for enhancing the storage performance of CNT-based Li batteries. Compared with Li^+ ions on the internal wall of (4,4) CNT, the cell voltage of Li^+ ions on the external wall of (10,10) CNT is increased by 0.55 V, which is a 38% improvement. This indicates that by careful design we should be able to greatly improve the energy density of CNT-based Li battery.

Methodology

In this work, the B3LYP[54, 55] method in the framework of DFT is employed to examine the intermolecular interactions. The electron wave functions in the Gaussian function basis are expanded. A standard all-electron basis set 6-31G(d) is used for geometry optimizations. Initially, the geometries of all CNTs and Li^+/Li@CNT systems are optimized at the B3LYP/6-31G(d) level, which is widely used in the computational study of nanostructured materials.[56-58] Then, we further calculated the single-point energy at wB97x-D/6-31G(d)[59]//B3LYP/6-31G(d) to show the effect of dispersion interactions. The zero-point energies correction is not considered in the interaction energy calculation. All calculations are carried out using the Gaussian-09 package.

The chirality plays a crucial role in Li–tube interactions. Kawasaki et al. showed that the reversible Li^+ ion storage capacity of metallic single-walled CNTs is about 5 times greater than that of semiconducting ones.[60] Based on their findings, all of the carbon nanotubes employed in this study are single-walled and of the armchair type, denoted by the chiral index (4,4), (6,6), (8,8), and (10,10). The four CNTs have an equal finite length of about 14 Å, and all dangling carbon atoms at the two open ends of the CNT are passivated by hydrogen atoms, as shown in Fig. 1. The structural distortion of single-walled CNTs is very small after the intercalation of Li^+/Li and the difference in the relaxed total energies compared with those of a rigid tube are negligible.[58, 61] Thus, the single-walled CNTs obtained by geometry optimization are kept fixed before the insertion of Li^+/Li.

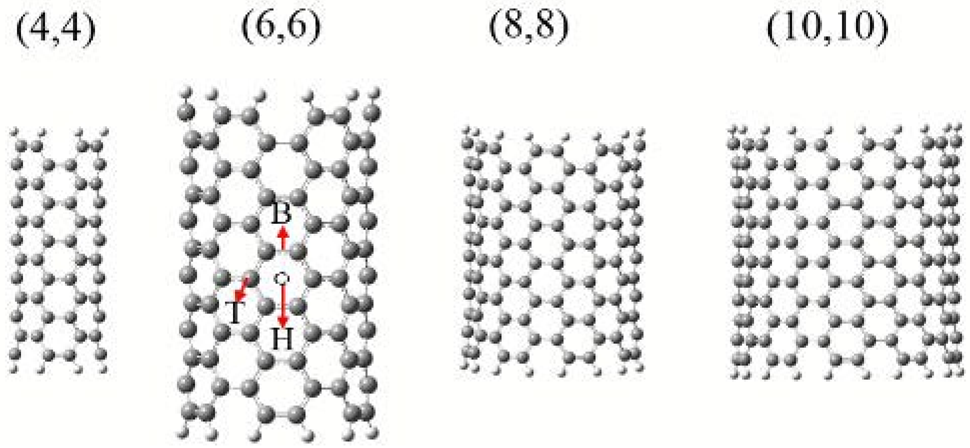

Figure 1. The side views of single-walled CNTs (4,4), (6,6), (8,8), and (10,10). The (6,6) CNT is enlarged to show the different adsorption sites, i.e., above the hollow (H), C–C bond (B), and carbon atom top (T) sites of the hexagonal ring.

Results and discussion

Adsorption of Li^+ and Li on the CNT surface

Firstly, we take the (6,6) CNT as an example to find the most stable adsorption site of Li^+ ions or Li atoms on the internal and external wall. Three different sites are considered for the adsorption of Li^+/Li: the hollow (H), C–C bond (B), and carbon atom top site (T) of the hexagonal rings (Fig. 1). The most stable structures of the internal and external adsorption of the Li^+@CNT system at the H and B sites of the (6,6) CNT are shown in Fig. 2. The adsorption at the T sites on both the internal and external wall was found to be unstable and the Li^+ moves to the H sites during the geometry optimization. The structures of the Li@CNT system are similar to that of the Li^+@CNT system and are not shown here.

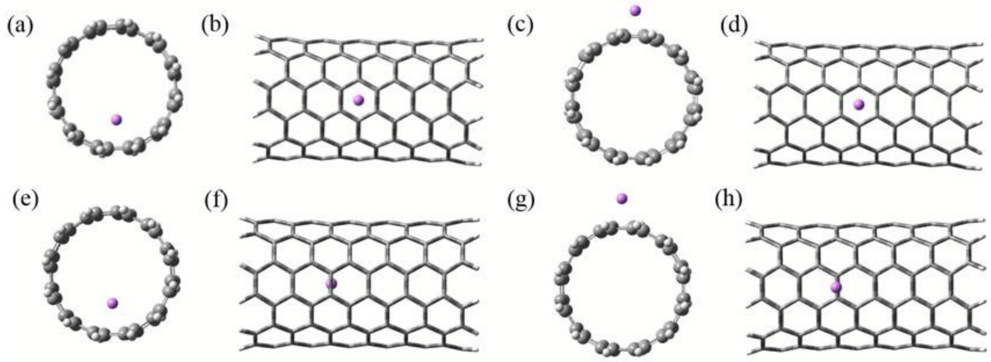

Figure 2. (a), (c), (e) and (g) are top views of the Li^+ ion internal and external adsorption at the H site and B site; (b), (d), (f), (h) are side views of Li^+ internal and external adsorption at the H site and B site.

To study the stability of Li^+/Li in the CNT, we calculated the adsorption energies of Li^+/Li@CNT clusters. The adsorption energy (E_{ads}) is defined as

$$E_{ads} = E_{Li^+/Li@CNT} - E_{CNT} - E_{Li^+/Li}, \tag{1}$$

where $E_{Li^+/Li@CNT}$, E_{CNT}, and $E_{Li^+/Li}$ are total energies of the Li^+/Li@CNT systems, the CNT, and the Li^+/Li, respectively. For Li^+/Li, the adsorption energies, average Li^+/Li–carbon distances, and transfer Hirschfeld charges for the internal and external wall adsorption at different sites of the (6,6) CNT are shown in Table 1. Adsorption energies of Li^+ and Li at the H site are 1.5 and 2.4 kcal/mol larger, respectively, than at the B site for internal adsorption, and 4.4 and 6.1 kcal/mol larger for external adsorption. The result shows that the Li^+ and Li are most stable at H site in (6,6) CNT. The most stable structures at the H sites in other CNTs are shown in the Supporting Information. The most stable adsorption site, adsorption energy and Li^+-C distance for Li^+ in (6,6) CNT are in agreement with the early study[58]. The atomic charge transfer on Li^+/Li at different sites of single walled CNT is investigated based on the method of Hirshfeld.[62] From the transfer Hirshfeld charge, we can see that there is large electron exchange between the CNTs and Li^+/Li. Analysis of the molecular orbitals and the total density of states (TDOS) of Li^+@CNT have been further employed to understand the charge exchange between the Li^+ and π electrons of carbons in CNTs (see details in the Supporting Information). From the LUMO distribution of the Li^+@CNT, we learn that there is an orbital couple between the delocalized π orbital and the unoccupied orbital of the Li^+ (see Fig. S2). In addition, the Li^+ ions has more transfer charges than the Li atoms, which is consistent with the result that the Li^+ ions have much bigger adsorption energies.

Table 1. The adsorption energies (E_{ads}), average Li^+/Li–carbon distance (R_{ion-C}), and transfer Hirshfeld charges (the initial charge of Li^+/Li minus its residual charge after adsorption in CNTs) for the internal and external wall adsorption of Li^+/Li in a (6,6) single walled CNT at B3LYP/6-31G(d) level. Three different sites are taken into consideration, that is, above the hollow (H), C–C bond (B), carbon atom top (T) of hexagonal ring. The T sites are not stable both in the internal wall and external wall, and details are not shown here. "+" and "-" in Transfer Hirshfeld charge represent that the Li^+ and Li gains and loses electrons, respectively.

Li^+/Li–CNT Clusters	**E_{ads} (kcal/mol)**	**R_{ion-C} (Å)**	**Transfer Hirshfeld Charge**
Li^+–CNT-in(H)	-55.5	2.315	+0.553
Li^+–CNT-in(B)	-53.0	2.170	+0.521

Li–CNT-in(H)	-28.1	2.311	-0.445
Li–CNT-in(B)	-25.6	2.163	-0.476
Li$^+$–CNT-out(H)	-55.5	2.330	+0.509
Li$^+$–CNT-out(B)	-50.6	2.162	+0.441
Li–CNT-out(H)	-24.4	2.298	-0.469
Li–CNT-out(B)	-18.3	2.133	-0.541

Adsorption energies of Li$^+$/Li on the most stable H sites for different single walled CNTs are shown in Fig. 3. The adsorption energy of the Li$^+$ ion is much larger than that of the Li atom, which shows that the Li$^+$–π interaction has a greater impact on this system. In addition, adsorption energies on the internal wall are larger than those on the external wall for both Li and Li$^+$, which is in agreement with earlier calculations by Khantha et al.[61] and Udomcech et al.[63] Apparently, the Li$^+$ internal adsorption energy in the internal wall is the largest in (4,4) CNT, while in (6,6), (8,8), (10,10) CNTs, it is almost equal. In the case of the external wall, adsorption energy changes little with the increase of CNT diameter. For the Li atom, the internal adsorption energy in the internal wall decreases with an increase in the tube diameter, but the change tendency of the adsorption energy on the external wall to vary with tube diameter seems not obvious.

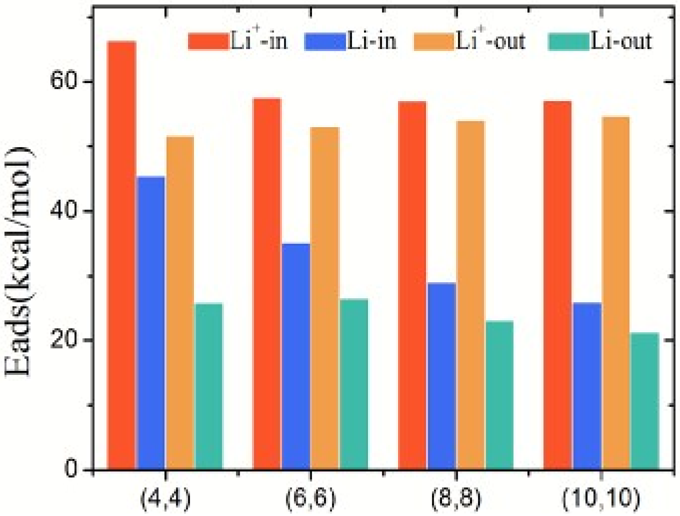

Figure 3. Adsorption energies of Li$^+$/Li on the internal and external sidewall of different single walled CNTs at wB97x-D/6-31G(d)//B3LYP/6-31G(d) level.

The cell voltage

The simplified chemical reactions involved in Li ion batteries when we consider both Li$^+$–π and Li–π interactions can be described as follows:

Anode:

$$\text{Li@CNT} \leftrightarrow \text{Li}^{+}\text{@CNT} + \text{e}^{-} \tag{2}$$

Cathode:

$$\text{Li}^{+} + \text{e}^{-} \leftrightarrow \text{Li} \tag{3}$$

Here, we are more concerned with the impact of the interaction between the Li^+ ion and the CNT on the battery, which mainly exits at the CNT-based Li battery anode. Thus the reaction at the cathode is simplified. The overall reaction is expressed by the following expression:

$$\text{Li}^{+} + \text{Li@CNT} \leftrightarrow \text{Li} + \text{Li}^{+}\text{@CNT} \tag{4}$$

The cell voltage can be determined by the Nernst equation[64, 65]

$$V_{\text{cell}} = \frac{-\Delta G_{\text{cell}}}{zF}, \tag{5}$$

where z is the charge on the Li^+ ion in the electrolyte (z=1) and F is the Faraday constant , 96500 C/mol. ΔG_{cell} is the Gibbs free energy for the chemical reaction of Li ion battery, which can be approximated as the internal energy ($\Delta G_r = \Delta E_r + P\Delta V_r - T\Delta S_r$) at 0 K since the contributions of entropy and volume effects to the cell voltage are expected to be very small (<0.01V)[37]. Thus, we can calculate the cell voltage for Li^+/Li@CNT systems by computing the change of the corresponding internal energy. The internal energy can be expressed as

$$\Delta E_{\text{tot}} = E_{\text{Li}} + E_{\text{Li}^{+}\text{@CNT}} - E_{\text{Li@CNT}} - E_{\text{Li}^{+}} \tag{6}$$

From Eq. 6, we can see that the Li^+–π interaction ($E_{\text{Li}^{+}\text{-}\pi}$) is favorable for the internal energy. Thus, based on Nernst equation, the Li^+–π interaction is beneficial to the cell voltage. We also find that the Li–π interaction ($E_{\text{Li@CNT}}$) is not favorable for the cell voltage.

Table 2. The internal energies ΔE_{tot} and V_{cell} of different Li^+/Li@CNT systems. ΔE_{tot} represents the internal energy of the chemical reaction when we consider both the Li^+–π and Li–π interactions. V_{cell} is the cell voltage calculated using the Nernst equation.

	Internal wall		**External wall**	
	ΔE_{tot} (kJ/mol)	**V_{cell} (v)**	**ΔE_{tot} (kJ/mol)**	**V_{cell} (v)**
(4,4)	−87.2	0.90	−107.9	1.12
(6,6)	−93.8	0.97	−111.0	1.15
(8,8)	−117.0	1.21	−129.5	1.34
(10,10)	−130.4	1.35	−139.9	1.45

The internal energies ΔE_{tot} and V_{cell} of different Li^+/Li@CNT systems are shown in Table 2. It can be seen that the cell voltage increases with the increase of the tube diameter. In addition, the cell voltage is larger when lithium is adsorbed on the external wall instead of the internal wall. Compared with Li^+ on the internal wall of (4,4) CNT, the cell voltage of the Li^+ on the external wall of (10,10) CNT increased by 0.55 V, which is an improvement of about 38%. Thus, CNTs with larger diameters can substantially improve the energy density and performance of Li ion batteries. We have also performed DFT calculations with two Li^+/Li adsorbed in and out the (10,10) CNT to roughly illustrate the impact of Li density on the cell voltage. With the increase of Li^+ density, the Li^+-π interaction is still beneficial to the cell voltage and the cell voltage is even larger when Li^+ adsorbs on the external wall than that on the internal wall (see details in Supporting Information).

The larger the interstitial spaces of the CNT bundles, the higher the ability for Li^+ ion intercalation. Our recent study based on *ab initio* molecular dynamics showed that Li^+ ions could quickly penetrate into the CNTs and the space between neighboring CNTs.[31] We found that Li^+ could be located between three neighboring CNTs, and these Li^+ ions were difficult to remove from the bundles of CNTs because of the strong adsorption energy. Interestingly, both our previous and present studies suggest that it’s better to use CNTs with a relatively low array density. All of these findings may be helpful to improve the energy storage capacity and energy efficiency of CNT-based Li ion batteries.

Conclusions

Based on DFT calculations, we find a highly favorable impact of cation–π interactions on the cell voltage of CNT-based Li batteries. We show that, when we consider both Li^+–π and Li–π interactions, the cell voltage increases with the increase of the CNT diameter. Moreover, when Li^+ ions adsorbed on the external wall, the cell voltage was larger than that when Li^+ adsorbed on the internal wall. These findings indicate that CNTs with a large diameter and a low array density are more advantageous to enhance the performance of CNT-based Li batteries. Compared with Li^+ on the internal wall of (4,4) CNT, the cell voltage of the Li^+ on the external wall of (10,10) CNT is increased by 0.55 V, which is an improvement of about 38%. Thus, by reasonable design we will be able to greatly improve the energy density of CNT-based Li battery[66]. Our findings provide a theoretical perspective to help design CNT-based Li batteries with large capacity and high power density.

Acknowledgement

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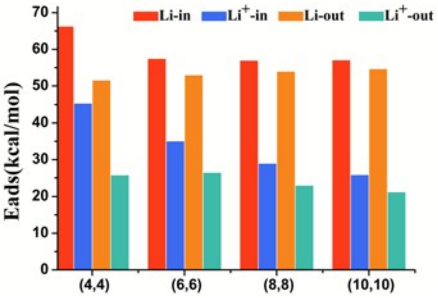

A highly favourable impact of cation–π interactions on the cell voltage of CNT-based Li batteries is reported.