

Electronic supplementary information (ESI)

Optimizing Cell Voltage Dependence on Size of Carbon Nanotube-based Electrodes in Na-ion and K-ion batteries

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Section 1. Cation— π interaction

Cation- π interaction is a non-covalent interaction. Its essence is electrostatic interaction, that is, positive charge cation and negative charge π electron cloud interaction. Therefore, it is the strongest force in the non-covalent interaction. Cation- π interaction exists widely in nature, especially in nucleic acids,^{1, 2} enzymes, histones, telomeres, biofilms and other biological systems. It plays an important role in the formation of protein structure,³⁻⁸ molecular recognition,⁹⁻¹¹ protein-nucleic acid interaction¹²⁻¹⁴ and drug-target binding. Cationic - π interactions can be divided into three categories. The first type of cation- π interaction is the interaction between simple inorganic metal cations such as Na^+ , K^+ , Mg^{2+} ions and aromatic systems. In recent years, cation- π interaction has attracted more and more attention, including ion distribution, surface or interface charge behavior, cation adsorption and diffusion kinetics, etc. It has been widely used in the absorption of organic pollutants.

Taking cation- π interaction between Na^+ and CNT(6,6) in Figure S1 as example, the 3s orbital of Na^+ interacts with the π orbital in CNT, contributing to the LUMO+3 after the adsorption of Na^+ inside CNT(6,6). This kind of cation- π interaction can be extended to similar systems like Li^+/K^+ interacted with CNT in this work.

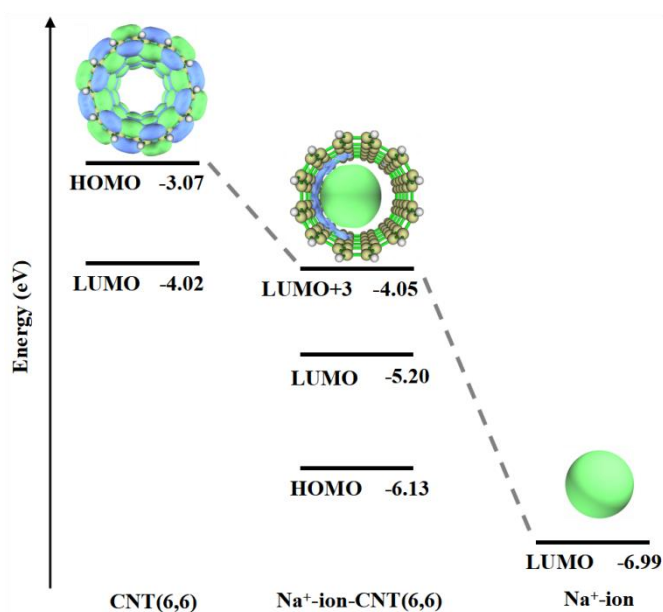


Figure S1. Orbital analysis of Na^+ adsorbed in CNT(6,6).

Section 2. The adsorption energies of $K^+/K@CNT$ system

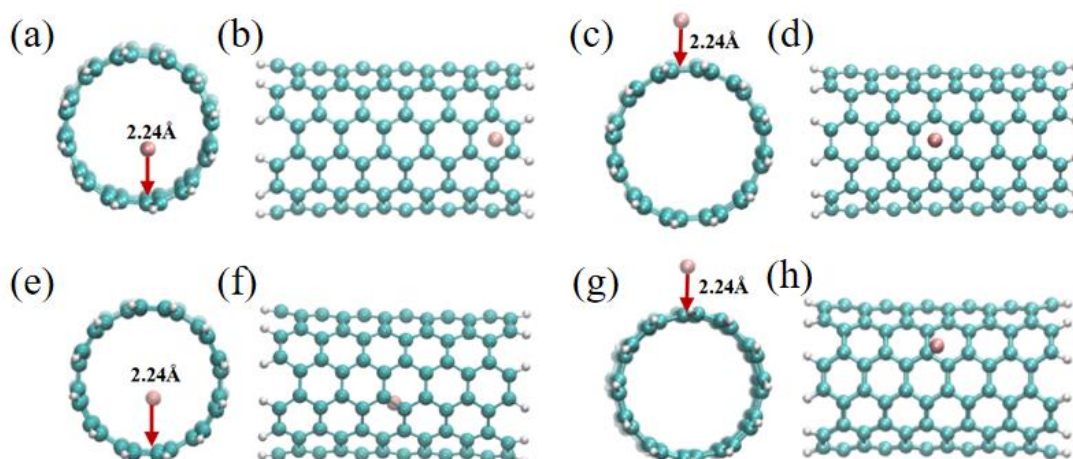


Figure S2. (a), (c), (e) and (g) The top views of the K^+ internal and external adsorption at the H site and B site; (b), (d), (f), (h) The side views of K^+ internal and external adsorption at the H site and B site. The pink globules represent Na-ion.

The (6,6) CNT is selected as a typical example to search the most stable adsorption site of K/K^+ on the internal and external wall. Three sites of the hollow (H), C–C bond (B), and carbon atom top site(T) of the hexagonal rings are firstly chose as the initial adsorption positions of K/K^+ . The adsorption at the H/B sites on both the internal and external wall was found to be stable both the K^+ which are shown in Figure S1. The optimized atomic architecture of the same element is similar to that of ionic systems, so only the structure of ionic systems is demonstrated. The adsorption at the T sites on both the internal and external wall was found to be unstable both the Na^+ and the K^+ move to the H sites during the geometry optimization.

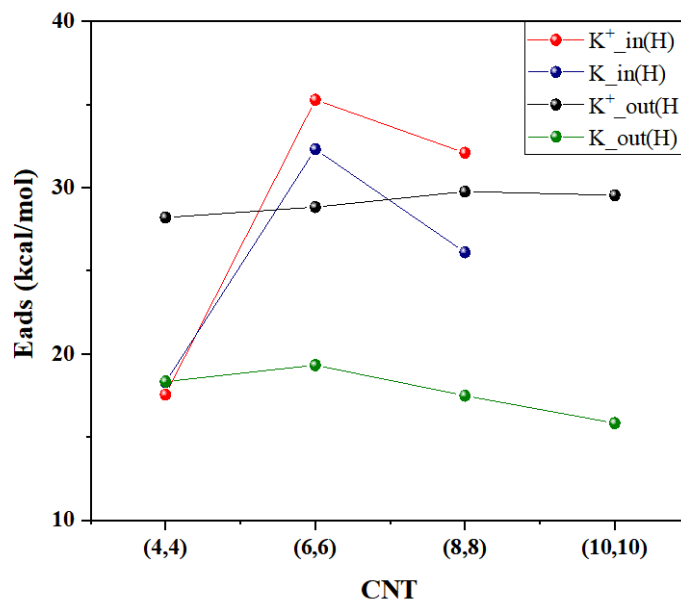


Figure S3. Adsorption energies of K^+/K on the internal and external sidewall of different single walled CNTs at the H site and at the B3LYP/ 6-31G(d) level.

Considering that the change of CNT diameter will have a certain influence on the adsorption energy and based on the above calculation results, we further calculated the adsorption energy of K^+/K at the H/B site in CNTs with different diameters. The Figure S2. shows the calculation results. It can be clearly seen from Figure S2 that when comparing the adsorption energies of systems with the same diameter and the same site, due to the influence of cation- π interaction, the adsorption energy of the $K^+@CNT$ system is greater than that of the $K@CNT$ system. Further analysis of Figure S2. shows that with the increase of the diameter of the CNTs, the adsorption energy of K-ion inside the wall of the CNTs gradually decreases, and when K-ion is adsorbed on CNTs with the same diameter and the same position, the adsorption energy inside the tube wall is greater than the adsorption energy outside the tube wall.

Section 3. The adsorption energies of Li⁺/Li@CNT system

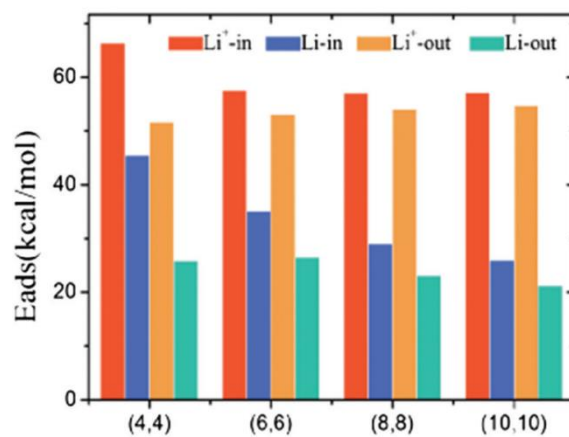


Figure S4. Adsorption energies of Li⁺/Li on the internal and external sidewall of different single walled CNTs at the H site and at the B3LYP/ 6-31G(d) level, taken from Gao *et al.*¹⁵

Table S1. The adsorption energies (E_{ads}) 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 the B3LYP/6-31G(d), taken from Gao *et al.*¹⁵

$\text{Li}^+/\text{Li}@$ CNT Clusters	E_{ads} (kcal/mol)	Transfer Hirshfeld Charge (e)
$\text{Li}^+/\text{Li}@$ CNT-in(H)	55.5	+0.553
$\text{Li}^+/\text{Li}@$ CNT-in(B)	53.0	+0.521
$\text{Li}^+/\text{Li}@$ CNT-in(H)	28.1	-0.445
$\text{Li}^+/\text{Li}@$ CNT-in(B)	25.6	-0.476
$\text{Li}^+/\text{Li}@$ CNT-out(H)	55.5	+0.509
$\text{Li}^+/\text{Li}@$ CNT-out(B)	50.6	+0.441
$\text{Li}^+/\text{Li}@$ CNT-out(H)	24.4	-0.469
$\text{Li}^+/\text{Li}@$ CNT-out(B)	18.3	-0.541

Section 4. The transfer charge of adsorbed in/out CNT(6,6)

Table S2. The transfer charge of Na⁺/Na adsorbed in/out CNT(6,6), under Mulliken, natural population analysis (NPA), hirshfeld and atomic dipole moment corrected hirshfeld population (ADCH) methods.

	Mulliken transfer charge (e)	NPA transfer charge (e)	HSirshfeld transfer charge (e)	ADCH transfer charge (e)
Na-CNT(6,6)-in	-0.71	-0.71	-0.55	-0.61
Na ⁺ -CNT(6,6)-in	0.29	0.71	0.45	0.40
Na-CNT(6,6)-out	-0.61	-0.61	-0.59	-0.73
Na ⁺ -CNT(6,6)-out	0.34	0.66	0.39	0.24

In this paper, natural population analysis (NPA), hirshfeld and atomic dipole moment corrected hirshfeld population (ADCH) methods are adopted to analyze atomic charges. The results show that the different methods demonstrate a similar phenomenon in that the adsorption site exhibits a relatively significant effect on the amount of charge transferred. Besides the NPA method which transfer charge concentrates between 0.61 e and 0.71 e, Mulliken, hirshfeld and ADCH methods all exhibit significant differences in transfer charges between ions and atoms. "Mulliken Method" is therefore simple but appropriate to analyze atomic charges in the structures of alkali metal ions/atoms that interacted with CNT.

Section 5. Different basis sets are supplemented to optimize

Table S3. The CNT(6,6) length and diameter as well as the adsorption energy of Na⁺/Na in CNT(6,6), which structures optimized by the method of B3LYP/6-31G(d), 6-311G(d) or 6-31G(d)+.

	CNT(6,6) length (Å)	CNT(6,6) diameter (Å)	Na ⁺ -CNT(6,6) adsorption energy (kcal/mol)	Na-CNT(6,6) adsorption energy (kcal/mol)
6-31G(d)	14.76	8.14	41.7	19.2
6-311G(d)	15.35	8.82	36.0	20.9
6-31+G(d)	15.38	8.85	34.7	19.8

Three commonly used basis sets of 6-31G(d), 6-311G(d) and 6-31G(d)+ are supplemented to optimize the model of Na⁺/Na adsorption within CNT(6,6). The results indicated that the calculated adsorption energy under the three basis sets was little different, showing more stable adsorption for ions rather than atoms. The adsorption energies of Na⁺ inside CNT were 41.7 kcal/mol, 30.6 kcal/mol and 34.7 kcal/mol for 6-31G(d), 6-311G(d) and 6-31G(d)+ optimization, respectively, which were all much greater than the adsorption energies of Na (19.2 kcal/mol, 20.9 kcal/mol and 19.8 kcal/mol). Additionally, 6-31G(d), 6-311G(d) and 6-31G(d)+ optimization result in CNT lengths of 14.76 Å, 15.35 Å and 15.38 Å, and diameters of 8.14 Å, 8.83 Å and 8.85 Å, respectively. In summary, the selection of the cheapest 6-31G(d) is favorable for saving computational resources and has no significant effect on the adsorption stability.

Section 6. The potential energy surface scans of Na⁺ inside the CNT (6, 6)

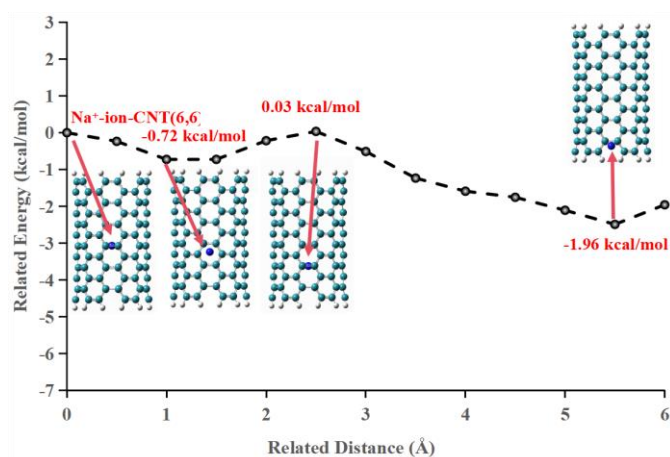


Figure S5. The potential energy surface of Na⁺ from the center of CNT(6,6) to the boundary.

In this paper, Gaussian are employed to operate the potential energy surface scans of Na⁺ inside the CNT (6, 6). Results exhibit that the energy barrier from Na⁺ at the H site to the B site is 0.76 kcal/mol, indicating an effortless diffusion kinetics. The sites in which the relative distance is increased to about 4 Å should be ignored since their Na⁺ is too close to the hydrogen atom boundary.

Section 7. The calculations for the effect of ethylene carbonate (EC) electrolytes

Table S4. The adsorption energy of Na⁺/Na-ethylene carbonate (EC) interacted inside or outside CNT(6,6).

	Adsorption Energy (kcal/mol)
Na-atom-EC-CNT(6,6)-inside	-36.46
Na-atom-EC-CNT(6,6)-outside	-32.50
Na ⁺ -ion-EC-CNT(6,6)-inside	-27.24
Na ⁺ -ion-EC-CNT(6,6)-outside	-29.03

The Table S4 shows the calculations for the effect of ethylene carbonate (EC) electrolytes¹⁷ on Na⁺/Na adsorption inside and outside CNT(6,6). The adsorption energy is calculated as

$$\Delta E_{\text{Na-ion/atom-EC-CNT(6,6)-in/out}} = E_{\text{Na-ion/atom-EC-CNT(6,6)-in/out}} - E_{\text{Na-ion/atom-EC}} - E_{\text{CNT(6,6)}}$$

Where $E_{\text{Na-ion/atom-EC-CNT(6,6)-in}}$, $E_{\text{Na-ion/atom-EC}}$ and $E_{\text{CNT(6,6)}}$ are the electronic energies of the adsorption structures of Na⁺/Na inside or outside of CNT(6,6), the electronic energies of the adsorption structures of a single Na⁺/Na with EC, and the electronic energies of the CNT(6,6), respectively. Results show that the addition of electrolyte stabilizes the Na adsorption outside CNT(6,6) rather than Na⁺. The inside adsorption structure should be excluded from discussion since both EC interact with the boundary hydrogen atoms resulting from the insufficient length of CNT. After the addition of EC, the adsorption energy of Na⁺-ion-EC outside CNT(6,6) is 29.0 kcal/mol, which is much lower than that of Na-EC outside the CNT (32.9 kcal/mol). Therefore, the addition of electrolyte had significant effect on the stability of Na⁺/Na adsorption outside the CNT(6,6), deserving more systematic exploration in the next work.

Section 8. The calculation of the adsorption of the two Na atoms in the CNT (6, 6)

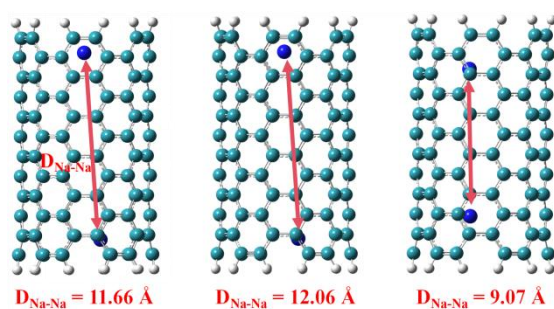


Figure S6. Geometrical structures of 2 Na atoms adsorbed in CNT(6,6).

The Figure S6 shows that the adsorption sites of these two Na atoms are close to the ends of the carbon nanotubes saturated by hydrogen and the distance between them is 9-11 Å, much larger than the distance between Na atoms in the cluster (3.3 - 3.8 Å)¹⁸. This means that the CNT system length of 14.76 Å in this work is not sufficient for exploring a large number of alkali metal atoms or ion adsorption.

Section 9. The calculation process of ΔE_{tot} and V_{cell}

The cell voltage can be determined by the Nernst equation:

$$V_{\text{cell}} = \frac{-\Delta G_{\text{cell}}}{zF} \quad (1)$$

where z is the charge on the Na^+ ion in the electrolyte ($z = 1$) and F is the Faraday constant, $96\,500 \text{ C mol}^{-1}$. ΔG_{cell} is the Gibbs free energy for the chemical reaction of Na ion battery, which can be approximated as the internal energy ($\Delta G_{\text{r}} = \Delta E_{\text{r}} + P\Delta V_{\text{r}} - T\Delta S_{\text{r}}$) at 0 K since the contributions of entropy and volume effects to the cell voltage are expected to be very small ($< 0.01 \text{ V}$).¹⁶ Thus, we can calculate the cell voltage for $\text{Na}^+/\text{Na}@ \text{CNT}$ systems and $\text{K}^+/\text{K}@ \text{CNT}$ systems by computing the change of the corresponding internal energy. The internal energy can be expressed as

$$\Delta E_{\text{tot}} = E_{\text{Na}} + E_{\text{Naion@CNT}} - E_{\text{Na@CNT}} - E_{\text{Naion}} \quad (2)$$

$$\Delta E_{\text{tot}} = E_{\text{K}} + E_{\text{Kion@CNT}} - E_{\text{K@CNT}} - E_{\text{Kion}} \quad (3)$$

From equation (2), we can see that the $\text{Na}^+ - \pi$ interaction ($E_{\text{Na}^+ - \pi}$) is favorable for the internal energy. Thus, based on Nernst equation, the $\text{Na}^+ - \pi$ interaction is beneficial to the cell voltage. We also find that the $\text{Na} - \pi$ interaction ($E_{\text{Na@CNT}}$) is not favorable for the cell voltage.

Section 10. The ΔE_{tot} and V_{cell} of $\text{Li}^+/\text{Li}@\text{CNT}$ system

Table S5. Internal energies ΔE_{tot} and V_{cell} for different $\text{Li}^+/\text{Li}@\text{CNT}$ systems taken from Gao *et al.*¹⁵

	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	1.45	-139.9	1.45

Section 11. The weak interaction of $\text{Na}^+@(\text{4,4})\text{CNT}$ system

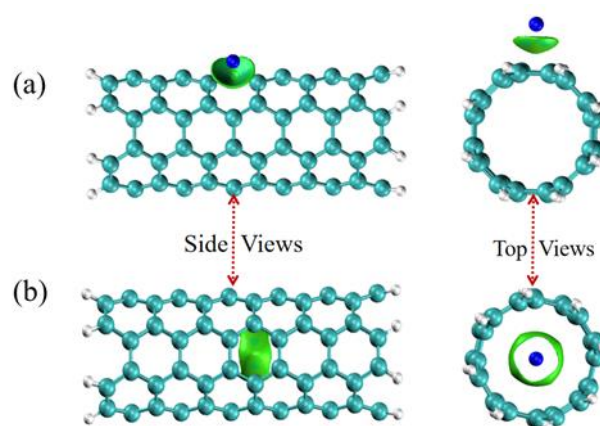


Figure S7. The weak interaction of Na^+ on the internal and external sidewall of (4,4) CNTs at the IGMH visual analysis. (a) The side and top views of the Na-ion internal adsorption at CNTs. (b) The side and top views of the Na-ion external adsorption at CNTs.

Section 12. The diffusion kinetics of alkali metal ions.

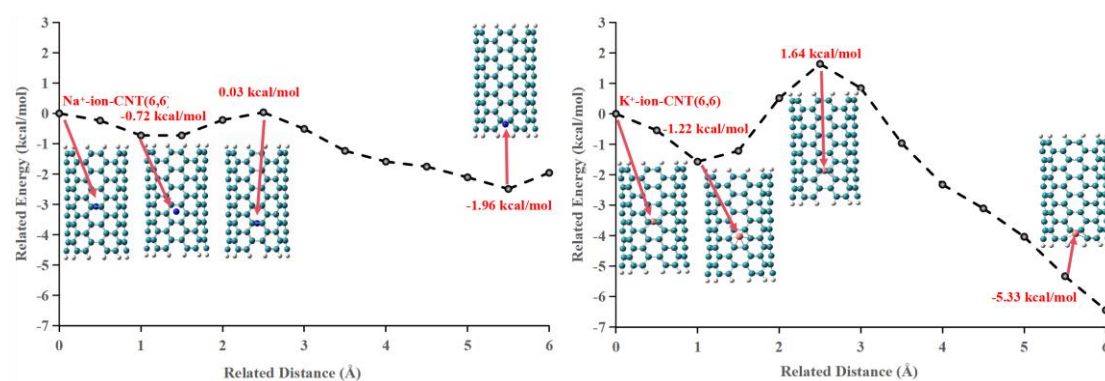


Figure S8. The potential energy surface of Na⁺(Left) and K⁺(Right) from the center of CNT(6,6) to the boundary. The energy barrier of from Na⁺ at the H site to at the B site is 0.76 kcal/mol, indicating effortless diffusion kinetics. By contrast, the energy barrier of from K⁺ at the H site to at the B site is 3.21 kcal/mol, indicating more difficult diffusion than Na⁺. The sites which the relative distance is increased to about 4 Å should be ignored since their Na⁺ is too close to the hydrogen atom boundary.

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