Supplementary Information for

Intercalation and diffusion of lithium ions in a carbon nanotube bundle by *ab initio* molecular dynamics simulations

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1. Adsorption energy of a lithium atom within a carbon nanotube in the presence of one or two Li atoms already adsorbed

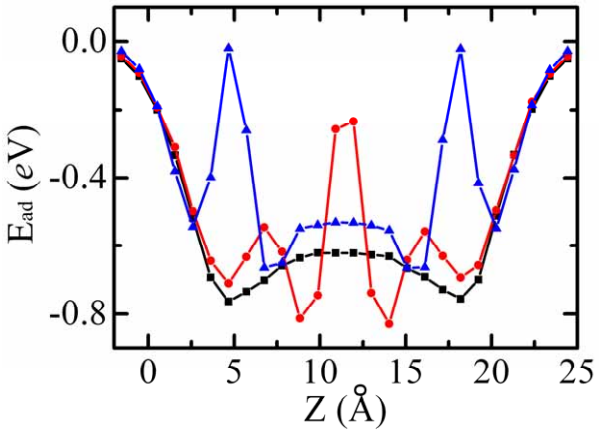

FIG. S1. Adsorption energy of a lithium atom at the center of the nanotube (r = 0.0 Å) and moving along Z direction for three cases: a) no lithium atom adsorbed within the nanotube before this Li atom moving in (-■-); b) one Li atom already adsorbed by the nanotube with Z = 11.43 Å (-●-), while r = 2.00 Å; c) two Li atoms already adsorbed by the nanotube with Z = 4.89 Å and 17.98 Å, respectively (-▲-), while r = 2.05 Å.

We performed the calculations on the adsorption energy of one Li atom in the

presence of one or two Li ions already adsorbed within carbon nanotube, the results are shown in FIG. S1. Comparing to the case without the presence of the ions already adsorbed (the black curve in FIG. S1), the barrier appears within the nanotube at the locality of the adsorbed ion, namely, Z = 11.43 Å for one ion already adsorbed (the red curve), while Z = 4.89 Å and 17.98 Å for two ions already adsorbed (the blue curve). Importantly, the height of the barrier can reach 0.6 eV, which is comparable to the depth of the potential well about -0.7 eV. Namely, the barrier from one Li ion can reduce the site-averaging adsorption energy of the other ion in the nanotube significantly. Therefore, when there is no lithium already existing, the Li ion can be stably in the nanotube. With the number of Li ions in the nanotube increasing, the number of barriers increases, which significantly reduces the adsorption energy of Li ions. This reduces the stability of the ions adsorbed in the nanotube, and promotes the ions de-intercalating the nanotube.

2. Testing whether the 10,000 fs is enough to obtain results of convergence.

A 17,100-fs simulation with the same conditions as the manuscript was done. The distributions are shown in FIG. S2.

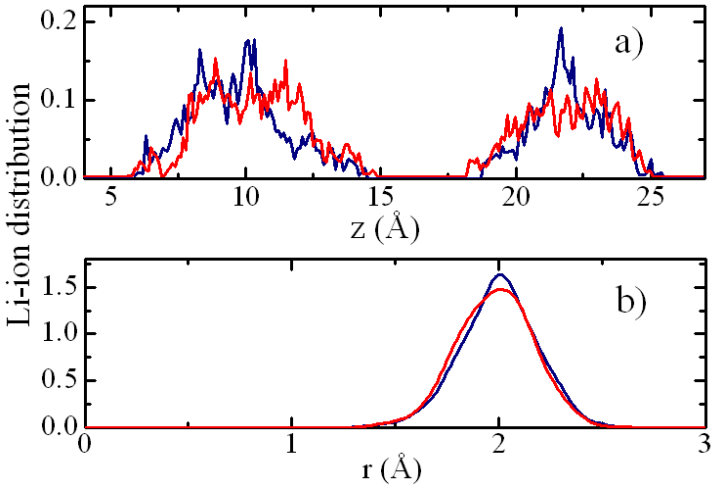

FIG. S2. A 17,100-fs simulation results of 8-Li-ion system with the same conditions as the manuscript. (a) Axial distribution of the Li ions along the z direction. (b) Radial distribution of the Li ions within the nanotube. The red curves are for the statistic results between t = 3,000 fs and 10,000 fs, while the blue curves are for the results between t = 10,000 fs and 17,100 fs.

It is observed that the axial and radial distributions of the Li ions intercalating the nanotubes from the data collected from 3,000 fs to 10,000 fs are consistent quite well with the distribution obtained from the data collected from 10,000 fs to 17,100 fs. This indicates that the simulation time of 10,000 fs is long enough to reach equilibrium in our case of low-concentration Li ions.

3. Comparison between the distributions of the system with and without the periodic boundary along z direction.

Via sampling eight initial configurations, we have performed eight 4,500-fs simulations without the periodic boundary condition along z direction (z-PBC), together with eight 4,500-fs simulations with z-PBC. From the comparison between the distributions of the two cases, it is observed that there is not significant difference between them.

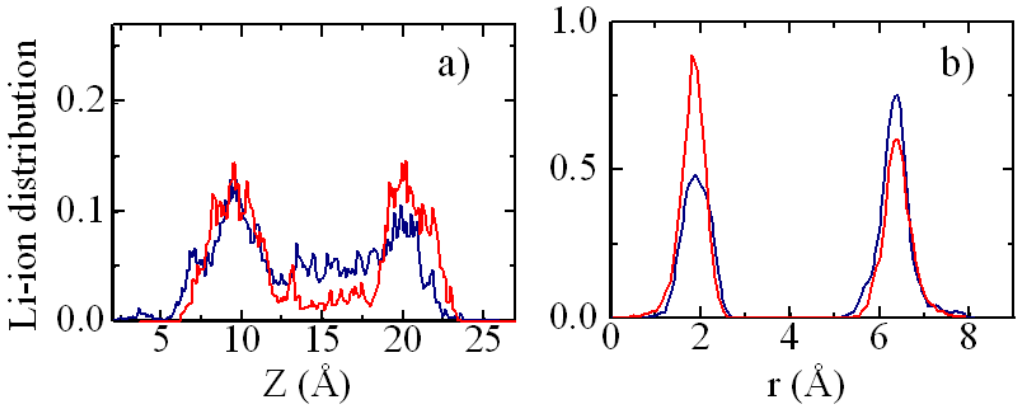

FIG. R3 Comparison between the distributions of the system with (the red curves) and without (the blue curves) the periodic boundary along z direction via sampling eight initial configurations. a,) Axial distribution of the Li ions. b) Radial distribution of the Li ions.