

Supporting Information

Computational Insights into Li_xO_y Formation, Nucleation, and Adsorption on Carbon Nanotube Electrodes in Nonaqueous Li-O_2 Batteries

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COMPUTATIONAL METHODS

All calculations in this work were performed by using CASTEP code based on periodic density functional theory (DFT).¹ The Perdew–Burke–Ernzerhof (PBE) form of the Generalized Gradient Approach (GGA) was used to perform the exchange-correlation functional.^{2,3} The plane-wave cutoff energy value and k-point Monkhorst-Pack meshes were set at 400eV and $1 \times 1 \times 3$ for all calculation involving (8,0) CNTs, respectively. Note that the same mesh size was also used by Zhou et al.⁴ For Li_xO_y ($x = 0, 1$, and 2), the appropriate Gamma centered k-point mesh density was set at least 0.04 \AA^{-1} , which were also found to be used in previous studies.⁵ Van der Waals (vdW) effects were verified to be non-negligible, and DFT-D2 of Grimme was used to correct the total energy.⁶ The BFGS algorithm was adopted to seek the most stable configuration.⁷ The convergence criterion were set as follows: $1 \times 10^{-5} \text{ eV}$ for total energy, 0.05 eV/\AA for Hellman-Feynman force, 0.002 \AA for displacement of atoms, and 0.05 Gpa for maximum stress. The initial model was constructed by placing optimized Li_xO_y molecules at random locations about $2\text{--}4 \text{ \AA}$ above the surface of the CNTs, which is similar to the approach used by Raz et al.⁸ to study the adsorption of Li_2O_2 , Na_2O_2 , and NaO_2 .

To evaluate the interaction between the adsorbate and the substrate, we calculate their adsorption energy according to the formula proposed by Liu et al.⁹:

$$E_{\text{ad}} = E_{\text{Li}_x\text{O}_y@\text{CNTs}} - E_{\text{CNTs}} - xE_{\text{Li}} - \frac{y}{2}E_{\text{O}_2} \quad (1)$$

where E_{ads} is the calculated adsorption energy, $E_{\text{Li}_x\text{O}_y@\text{CNTs}}$ and E_{CNTs} represent the energies of $\text{Li}_x\text{O}_y@\text{CNTs}$ and CNTs, respectively. E_{Li} denotes the energy of each Li atom in the body-centered cubic structure, and E_{O_2} is the energy of an isolated O_2 molecule. x and y are the stoichiometry numbers of Li and O atoms in the lithium oxide compound, respectively. In this

study, the values of x and y can be 0, 1, and 2.

When Li_2O_2 is generated, it can be divided into two cases: lithiation reaction ($\text{LiO}_2 + e^- + \text{Li}^+ \rightarrow \text{Li}_2\text{O}_2$) and disproportionation reaction ($\text{LiO}_2 + \text{LiO}_2 \rightarrow \text{Li}_2\text{O}_2 + \text{O}_2$).¹⁰ The calculation formulas for the standard free energy are as follows:

$$\Delta G_{\text{Li}_2\text{O}_2}^{\text{lith}} = E_{\text{Li}_2\text{O}_2@\text{CNTs(s)}} - E_{\text{LiO}_2@\text{CNTs(s)}} - \mu_{\text{Li(s)}} \quad (2)$$

$$\Delta G_{\text{Li}_2\text{O}_2}^{\text{disp}} = E_{\text{Li}_2\text{O}_2@\text{CNTs(s)}} + \mu_{\text{O}_2(\text{g})} - E_{(\text{LiO}_2)_2@\text{CNTs(s)}} \quad (3)$$

where E represents the total energy in DFT calculation.¹¹ $\mu_{\text{Li(s)}}$ and $\mu_{\text{O}_2(\text{g})}$ are chemical potentials of Li and O_2 , respectively. The contribution of $\Delta(TS)$ and $\Delta(PV)$ to the free energy change of a system involving condensed phases can be ignored.^{9,12-14}

Two possible generation paths were proposed to form Li_2O from Li_2O_2 , i.e., lithiation reaction ($\text{Li}_2\text{O}_2 + 2\text{Li}^+ + 2e^- \rightarrow 2\text{Li}_2\text{O}$) and disproportionation reaction ($2\text{Li}_2\text{O}_2 \rightarrow 2\text{Li}_2\text{O} + \text{O}_2$).⁹ Based on eq2 and eq3, the corresponding free energies of the two reaction paths are calculated as follows:

$$\Delta G_{\text{Li}_2\text{O}}^{\text{lith}} = \frac{1}{2} (E_{(\text{Li}_2\text{O})_2@\text{CNTs(s)}} - E_{\text{Li}_2\text{O}_2@\text{CNTs(s)}} - 2\mu_{\text{Li(s)}}) \quad (4)$$

$$\Delta G_{\text{Li}_2\text{O}}^{\text{disp}} = \frac{1}{2} (E_{(\text{Li}_2\text{O})_2@\text{CNTs(s)}} + \mu_{\text{O}_2(\text{g})} - E_{(\text{Li}_2\text{O}_2)_2@\text{CNTs(s)}}) \quad (5)$$

By introducing the Nernst equation, $\Phi = -\Delta G / ne$,¹⁵ the free energy can be expressed as

$$\Delta G = E_{\text{Li}_{x_n}\text{O}_{y_n}@\text{CNTs(s)}} - E_{\text{Li}_{x_{n-1}}\text{O}_{y_{n-1}}@\text{CNTs(s)}} - \frac{1}{2}(y_n - y_{n-1})\mu_{\text{O}_2(\text{g})} - (x_n - x_{n-1})(\mu_{\text{Li(s)}} - e\Phi) \quad (6)$$

where x_n and x_{n-1} represent the number of Li atoms in $\text{Li}_{x_n}\text{O}_{y_n}$ and $\text{Li}_{x_{n-1}}\text{O}_{y_{n-1}}$, respectively. y_n and y_{n-1} represent the number of O atoms in $\text{Li}_{x_n}\text{O}_{y_n}$ and $\text{Li}_{x_{n-1}}\text{O}_{y_{n-1}}$, respectively. e is the elementary charge, and Φ is the discharge potential.

The formation energy of $(\text{Li}_2\text{O}_2)_n$ is defined as

$$E_f = E_{(\text{Li}_2\text{O}_2)_n} - (E_{(\text{Li}_2\text{O}_2)_i} + E_{(\text{Li}_2\text{O}_2)_j} + \dots + E_{(\text{Li}_2\text{O}_2)_k}), \quad i + j + \dots + k = n \quad (7)$$

The adsorption energy (E_{ad}) required in Figure 6 is expressed as

$$E_{\text{ad}} = E_{[(\text{Li}_2\text{O}_2)_m + (\text{Li}_2\text{O}_2)_n]@\text{CNTs}} - (E_{(\text{Li}_2\text{O}_2)_m} + E_{(\text{Li}_2\text{O}_2)_n} + E_{\text{CNTs}}) \quad (8)$$

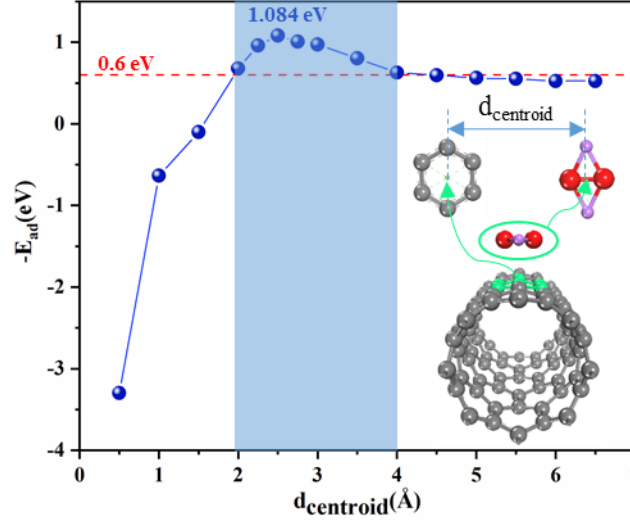


Figure S1. The effect of adsorption distance of Li_2O_2 molecule on adsorption energy. The blue region represents that the E_{ad} of $\text{Li}_2\text{O}_2@(\text{8,0})$ CNTs is larger than 0.6 eV. The dots pointed by the green arrow represent the centroids of the carbon ring and the Li_2O_2 molecule, respectively.

By calculating the adsorption energy of Li_2O_2 molecule placed at different distances (0.5–6.5 Å) above the CNT surface, we have surprisingly found that there is an optimal adsorption distance between Li_2O_2 molecule and CNTs. The atomistic structure and the corresponding adsorption energies are demonstrated in Figure S1. When the adsorption distance is less than 1.5 Å, the system of $\text{Li}_2\text{O}_2@\text{CNTs}$ is extremely unstable. However, when the adsorption distance is about 2.5 Å, the system reaches the most stable adsorption state ($E_{\text{ad}} = -1.084 \text{ eV}$). After that, as the adsorption distance continues to increase, the extent of the decrease in adsorption energy will become smaller and smaller, eventually stabilizing around -0.6 eV.

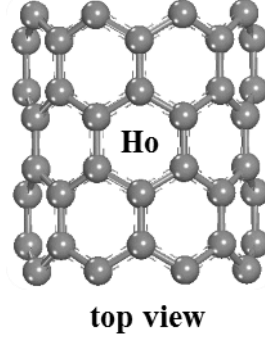


Figure S2. The hollow (Ho) on the surface of CNTs.

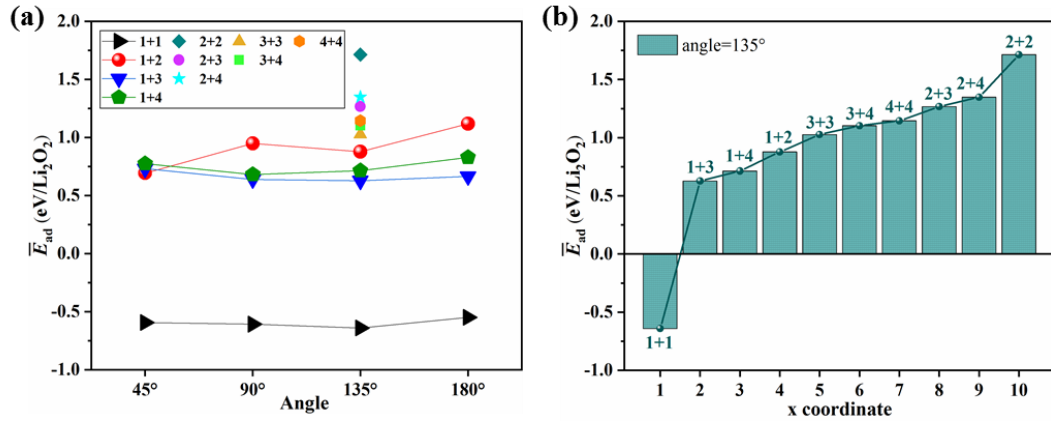


Figure S3. Influence of Li_2O_2 cluster size and relative adsorption position on average adsorption energy of each Li_2O_2 . The m and n values in $(\text{Li}_2\text{O}_2)_m$ and $(\text{Li}_2\text{O}_2)_n$ (m and $n = 1-4$) represent the number of Li_2O_2 molecules in the corresponding cluster. For example, 2+3 represents $(\text{Li}_2\text{O}_2)_2$ and $(\text{Li}_2\text{O}_2)_3$, indicating that dimers and trimers are simultaneously adsorbed on the surface of CNTs.

The presence of $(\text{Li}_2\text{O}_2)_2$ makes the average adsorption energy (1+2) is larger than 1+3 and 1+4. The orders of average adsorption energy values are $1+1 < 1+3 < 1+4 < 1+2$ and $3+3 < 3+4 < 4+4 < 2+3 < 2+4 < 2+2$ (without monomer), which indicates that the presence of the dimer $(\text{Li}_2\text{O}_2)_2$ reduces the average stability of each Li_2O_2 on the surface of CNTs. The contribution of the $(\text{Li}_2\text{O}_2)_n$ clusters with $n = 1-4$ to the average stability of each Li_2O_2 follows the order of dimer < tetramer < trimer < monomer.

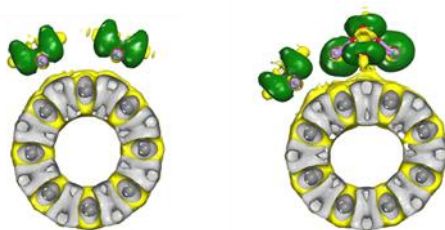


Figure S4. Charge density difference plots of monomer Li_2O_2 and dimer $(\text{Li}_2\text{O}_2)_2$ adsorbed on CNT surface. The areas of yellow and green represent the electron lost and gained, respectively.

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