Computational Insights into $\text{Li}_x\text{O}_y$ Formation, Nucleation, and Adsorption on Carbon Nanotube Electrodes in Nonaqueous Li–O$_2$ Batteries

Xiaoping Yi,† Xunliang Liu,*,† Peng Zhang,§ Ruifeng Dou,†‡ Zhi Wen,†‡ and Wenning Zhou†‡

†School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China

‡Beijing Key Laboratory of Energy Saving and Emission Reduction for Metallurgical Industry, School of Energy and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China

§ School of Energy Power and Mechanical Engineering, North China Electric Power University, Baoding 071003, China
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 400 eV 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 \(\text{Li}_x\text{O}_y\) (\(x = 0, 1,\) and 2), the appropriate Gamma centered k-point mesh density was set at least 0.04 \(\text{Å}^{-1}\), 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\(^{-5}\) eV for total energy, 0.05 eV/Å for Hellman-Feynman force, 0.002 Å for displacement of atoms, and 0.05 Gpa for maximum stress. The initial model was constructed by placing optimized \(\text{Li}_x\text{O}_y\) molecules at random locations about 2–4 Å above the surface of the CNTs, which is similar to the approach used by Raz et al.\(^8\) to study the adsorption of \(\text{Li}_2\text{O}_2, \text{Na}_2\text{O}_2,\) and \(\text{NaO}_2\).

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

\[
E_{\text{ad}} = E_{\text{Li}_x\text{O}_y\text{@CNTs}} - E_{\text{CNTs}} - xE_{\text{Li}} - \frac{y}{2}E_{\text{O}_2}
\]  

(1)

where \(E_{\text{ad}}\) is the calculated adsorption energy, \(E_{\text{Li}_x\text{O}_y\text{@CNTs}}\) and \(E_{\text{CNTs}}\) represent the energies of \(\text{Li}_x\text{O}_y\text{@CNTs}\) and CNTs, respectively. \(E_{\text{Li}}\) denotes the energy of each Li atom in the body-centered cubic structure, and \(E_{\text{O}_2}\) is the energy of an isolated \(\text{O}_2\) 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$_2$O$_2$ is generated, it can be divided into two cases: lithiation reaction ($\text{LiO}_2 + e^- + \text{Li}^+ \rightarrow \text{Li}_x\text{O}_y$) and disproportionation reaction ($\text{LiO}_2 + \text{LiO}_2 \rightarrow \text{Li}_x\text{O}_y + \text{O}_2$). The calculation formulas for the standard free energy are as follows:

$$\Delta G_{\text{Li}_x\text{O}_y}^{\text{calc}} = E_{\text{Li}_x\text{O}_y@CNTs(s)} - E_{\text{Li}_y\text{O}_x@CNTs(s)} - \mu_{\text{Li}(s)}$$

(2)

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

(3)

where $E$ represents the total energy in DFT calculation, $\mu_{\text{Li(s)}}$ and $\mu_{\text{O}_2(g)}$ 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.

Two possible generation paths were proposed to form Li$_2$O from Li$_2$O$_2$, i.e., lithiation reaction ($\text{Li}_x\text{O}_y + 2\text{Li}^+ + 2e^- \rightarrow 2\text{Li}_2\text{O}$) and disproportionation reaction ($2\text{Li}_x\text{O}_y \rightarrow 2\text{Li}_x\text{O}_y + \text{O}_2$). Based on eq 2 and eq 3, the corresponding free energies of the two reaction paths are calculated as follows:

$$\Delta G_{\text{Li}_x\text{O}_y}^{\text{calc}} = \frac{1}{2}(E_{\text{Li}_x\text{O}_y@CNTs(s)} - E_{\text{Li}_y\text{O}_x@CNTs(s)} - 2\mu_{\text{Li}(s)})$$

(4)

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

(5)

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

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

(6)

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

The formation energy of (Li$_2$O$_2$)$_n$ is defined as
\[
E_i = E_{(\text{Li}_2\text{O}_2)_{i,j,k}} - \left( E_{(\text{Li}_2\text{O}_2)_{i,j,k}} + E_{(\text{Li}_2\text{O}_2)_{i,j,k}} + \cdots + E_{(\text{Li}_2\text{O}_2)_{i,j,k}} \right), \quad i + j + \cdots + k = n
\] (7)

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

\[
E_{\text{ad}} = E_{((\text{Li}_2\text{O}_2)_{i,j,k})_{\text{CNTs}}} - \left( E_{(\text{Li}_2\text{O}_2)_{i,j,k}} + E_{(\text{Li}_2\text{O}_2)_{i,j,k}} + E_{\text{CNTs}} \right)
\] (8)

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

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

The presence of (Li$_2$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 (Li$_2$O$_2$)$_2$ reduces the average stability of each Li$_2$O$_2$ on the surface of CNTs. The contribution of the (Li$_2$O$_2$)$_n$ clusters with $n = 1–4$ to the average stability of each Li$_2$O$_2$ follows the order of dimer < tetramer < trimer < monomer.
Figure S4. Charge density difference plots of monomer Li$_2$O$_2$ and dimer (Li$_2$O$_2$)$_2$ adsorbed on CNT surface. The areas of yellow and green represent the electron lost and gained, respectively.

References


(9) Liu, Z.; De Jesus, L. R.; Banerjee, S.; Mukherjee, P. P. Mechanistic Evaluation of Li$_2$O$_2$ Formation on δ-MnO$_2$ in Nonaqueous Li–Air Batteries. ACS Appl. Mate. Inter. 2016, 8, 23028-23036.


