

## Supporting Information

# Computational Insights into $\text{Li}_x\text{O}_y$ Formation, Nucleation, and Adsorption on Carbon Nanotube Electrodes in Nonaqueous $\text{Li}-\text{O}_2$ 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).<sup>1</sup> The Perdew–Burke–Ernzerhof (PBE) form of the Generalized Gradient Approach (GGA) was used to perform the exchange-correlation functional.<sup>2,3</sup> 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.<sup>4</sup> For  $\text{Li}_x\text{O}_y$  ( $x = 0, 1$ , and  $2$ ), the appropriate Gamma centered k-point mesh density was set at least  $0.04 \text{ \AA}^{-1}$ , which were also found to be used in previous studies.<sup>5</sup> Van der Waals (vdW) effects were verified to be non-negligible, and DFT-D2 of Grimme was used to correct the total energy.<sup>6</sup> The BFGS algorithm was adopted to seek the most stable configuration.<sup>7</sup> The convergence criterion were set as follows:  $1 \times 10^{-5} \text{ eV}$  for total energy,  $0.05 \text{ eV/\AA}$  for Hellman-Feynman force,  $0.002 \text{ \AA}$  for displacement of atoms, and  $0.05 \text{ Gpa}$  for maximum stress. The initial model was constructed by placing optimized  $\text{Li}_x\text{O}_y$  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.<sup>8</sup> 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.<sup>9</sup>:

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

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

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

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

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

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

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

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

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

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

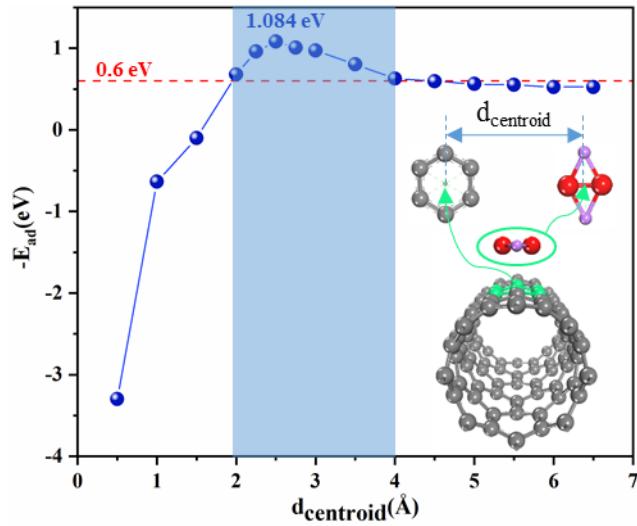
where  $x_n$  and  $x_{n-1}$  represent the number of Li atoms in  $\text{Li}_{x_n}\text{O}_{y_n}$  and  $\text{Li}_{x_{n-1}}\text{O}_{y_{n-1}}$ , respectively.  $y_n$  and  $y_{n-1}$  represent the number of O atoms in  $\text{Li}_{x_n}\text{O}_{y_n}$  and  $\text{Li}_{x_{n-1}}\text{O}_{y_{n-1}}$ ,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

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

$$E_f = E_{(Li_2O_2)_n} - (E_{(Li_2O_2)_i} + E_{(Li_2O_2)_j} + \dots + E_{(Li_2O_2)_k}), \quad i+j+\dots+k=n \quad (7)$$

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

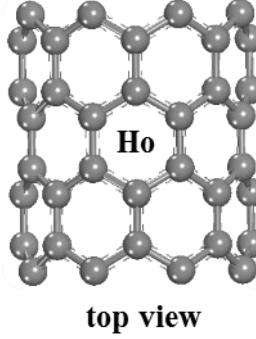
$$E_{ad} = E_{[(Li_2O_2)_m + (Li_2O_2)_n]@CNTs} - (E_{(Li_2O_2)_m} + E_{(Li_2O_2)_n} + E_{CNTs}) \quad (8)$$



**Figure S1.** The effect of adsorption distance of  $Li_2O_2$  molecule on adsorption energy. The blue

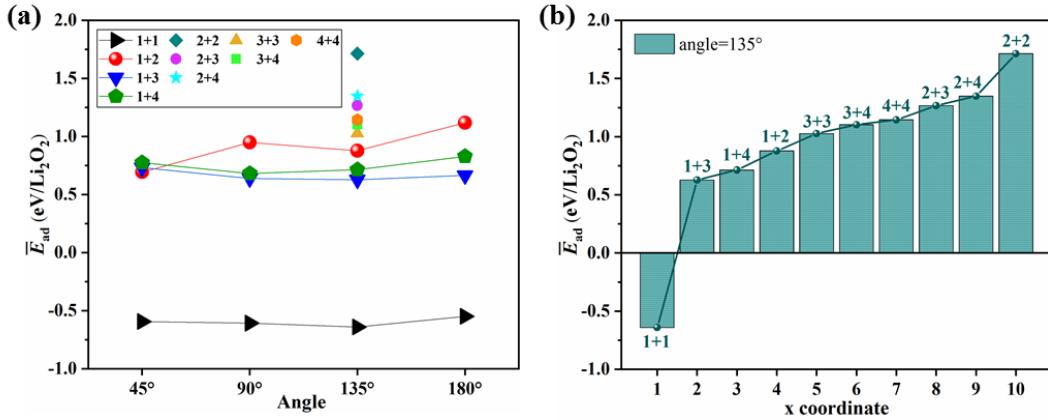
region represents that the  $E_{ad}$  of  $Li_2O_2@(8,0)$  CNTs is larger than 0.6eV. The dots pointed by the green arrow represent the centroids of the carbon ring and the  $Li_2O_2$  molecule, respectively.

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  $Li_2O_2@CNTs$  is extremely unstable. However, when the adsorption distance is about 2.5 Å, the system reaches the most stable adsorption state ( $E_{ad} = -1.084\text{eV}$ ). 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.



top view

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



**Figure S3.** Influence of Li<sub>2</sub>O<sub>2</sub> cluster size and relative adsorption position on average adsorption energy of each Li<sub>2</sub>O<sub>2</sub>. The  $m$  and  $n$  values in (Li<sub>2</sub>O<sub>2</sub>) <sub>$m$</sub>  and (Li<sub>2</sub>O<sub>2</sub>) <sub>$n$</sub>  ( $m$  and  $n$  = 1–4) represent the number of Li<sub>2</sub>O<sub>2</sub> molecules in the corresponding cluster. For example, 2+3 represents (Li<sub>2</sub>O<sub>2</sub>)<sub>2</sub> and (Li<sub>2</sub>O<sub>2</sub>)<sub>3</sub>, indicating that dimers and trimers are simultaneously adsorbed on the surface of CNTs.

The presence of (Li<sub>2</sub>O<sub>2</sub>)<sub>2</sub> 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<sub>2</sub>O<sub>2</sub>)<sub>2</sub> reduces the average stability of each Li<sub>2</sub>O<sub>2</sub> on the surface of CNTs. The contribution of the (Li<sub>2</sub>O<sub>2</sub>) <sub>$n$</sub>  clusters with  $n$  = 1–4 to the average stability of each Li<sub>2</sub>O<sub>2</sub> follows the order of dimer < tetramer < trimer < monomer.



**Figure S4.** Charge density difference plots of monomer  $\text{Li}_2\text{O}_2$  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.

## References

- (1) Segall, M. D.; Lindan, P. J. D.; Probert, M. J.; Pickard, C. J.; Hasnip, P. J.; Clark, S. J.; Payne, M. C. First-principles Simulation: Ideas, Illustrations and the CASTEP Code. *J. Phys-Condens. Mat.* **2002**, *14*, 2717-2744.
- (2) Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.
- (3) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, Molecules, Solids, and Surfaces: Applications of the Generalized Gradient Approximation for Exchange and Correlation. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *46*, 6671-6687.
- (4) Zhou, S.; Lin, S.; Guo, H. First-Principles Insights into Ammonia Decomposition Catalyzed by Ru Clusters Anchored on Carbon Nanotubes: Size Dependence and Interfacial Effects. *J. Phys. Chem. C.* **2018**, *122*, 9091-9100.
- (5) Ling, C.; Mizuno, F. Capture Lithium in  $\alpha\text{MnO}_2$ : Insights from First Principles. *Chem. Mater.* **2012**, *24*, (20), 3943-3951.
- (6) Grimme, S. Semiempirical GGA-type Density Functional Constructed with a Long-range Dispersion Correction. *J. Comput. Chem.* **2006**, *27*, 1787-99.
- (7) Fischer, T. H.; Almlöf, J. General Methods for Geometry and Wave Function Optimization. *J. Phys. Chem.* **1992**, *96*, 9768-9774.
- (8) Raz, K.; Tereshchuk, P.; Golodnitsky, D.; Natan, A. Adsorption of  $\text{Li}_2\text{O}_2$ ,  $\text{Na}_2\text{O}_2$ , and  $\text{NaO}_2$  on  $\text{TiC}(111)$  Surface for Metal–Air Rechargeable Batteries: A Theoretical Study. *J. Phys. Chem. C.* **2018**, *122*, 16473-16480.
- (9) Liu, Z.; De Jesus, L. R.; Banerjee, S.; Mukherjee, P. P. Mechanistic Evaluation of  $\text{Li}_x\text{O}_y$  Formation on  $\delta\text{-MnO}_2$  in Nonaqueous Li–Air Batteries. *ACS Appl. Mater. Inter.* **2016**, *8*, 23028-23036.
- (10) Lim, H.; Lim, H.; Park, K.; Seo, D.; Gwon, H.; Hong, J.; Goddard, W. A.; Kim, H.; Kang, K., Toward a Lithium–"Air" Battery: The Effect of  $\text{CO}_2$  on the Chemistry of a Lithium–Oxygen Cell. *J. Am. Chem. Soc.* **2013**, *135*, 9733-9742.
- (11) Hummelshøj, J. S.; Blomqvist, J.; Datta, S.; Vegge, T.; Rossmeisl, J.; Thygesen, K. S.; Luntz, A. C.; Jacobsen, K. W.; Nørskov, J. K. Communications: Elementary Oxygen Electrode Reactions in the Aprotic Li–air Battery. *J. Chem. Phys.* **2010**, *132*, 071101.
- (12) Ren, X.; Zhu, J.; Du, F.; Liu, J.; Zhang, W. B-Doped Graphene as Catalyst To Improve Charge Rate of Lithium–Air Battery. *J. Phys. Chem. C.* **2014**, *118*, 22412-22418.
- (13) Xiao, J.; Mei, D.; Li, X.; Xu, W.; Wang, D.; Graff, G. L.; Bennett, W. D.; Nie, Z.; Saraf, L. V.; Aksay, I. A.; Liu, J.; Zhang, J. Hierarchically Porous Graphene as a Lithium–Air Battery Electrode. *Nano Lett.* **2011**, *11*, 5071-5078.

(14) Ren, X.; Wang, B.; Zhu, J.; Liu, J.; Zhang, W.; Wen, Z., The Doping Effect on the Catalytic Activity of Graphene for Oxygen Evolution Reaction in a Lithium–air Battery: A First-principles Study. *Phys. Chem. Chem. Phys.* **2015**, *17*, 14605-14612.

(15) Jing, Y.; Zhou, Z. Computational Insights into Oxygen Reduction Reaction and Initial  $\text{Li}_2\text{O}_2$  Nucleation on Pristine and N-Doped Graphene in  $\text{Li}-\text{O}_2$  Batteries. *ACS Catal.* **2015**, *5*, 4309-4317.