Supporting Information

Oxidative Decomposition of Lithium Peroxide Clusters and their Relationship to Charging Potentials in Li-O_2 batteries: An Ab Initio Study

Rajeev S. Assary and Larry A. Curtiss

Materials Science Division
Argonne National Laboratories
Argonne, IL, USA, 60439

Corresponding author: assary@anl.gov (R.SA), 630-252-3536

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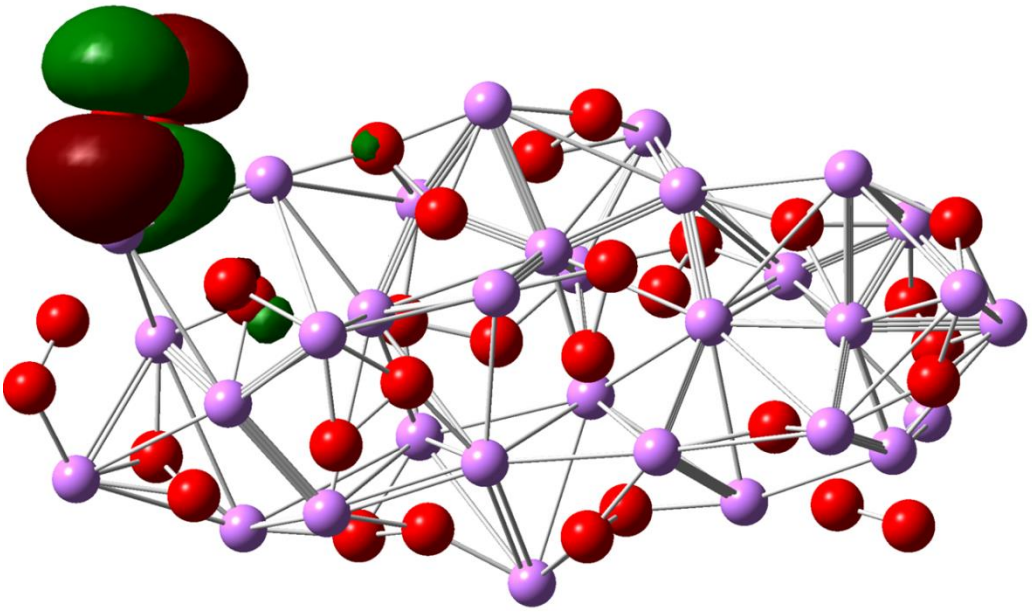
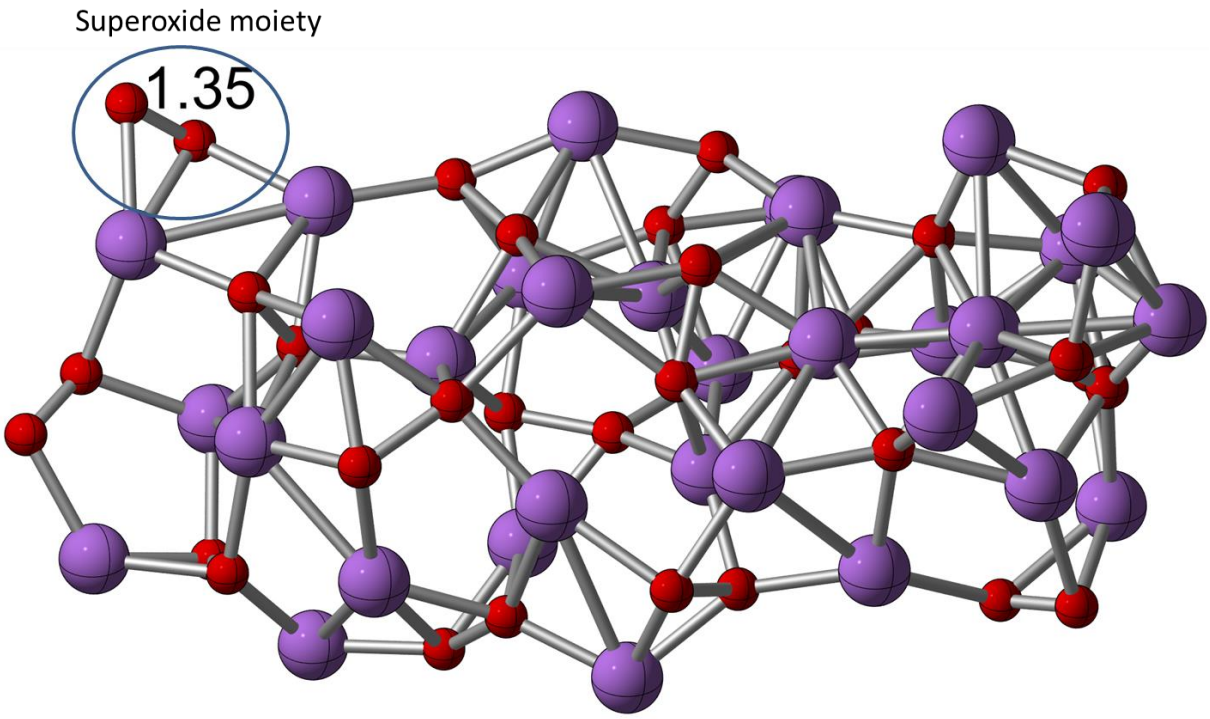
Figure S1: $(Li_2O_2)_{16}$ quintet showing HOMO and superoxide moiety on optimized structure

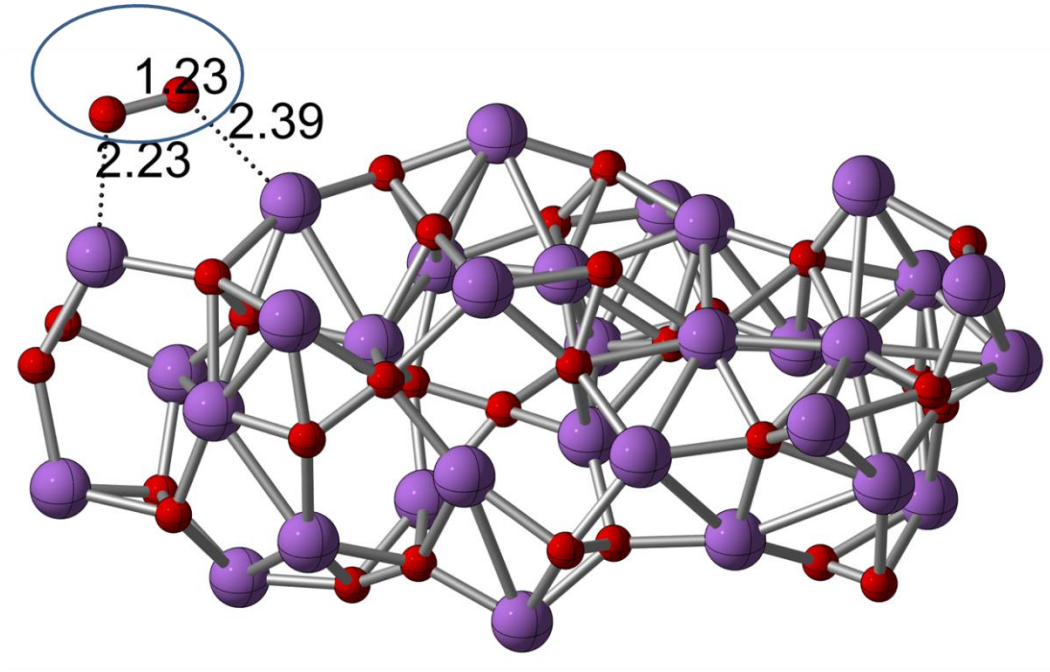


HOMO orbital of $[Li_{32}O_{32}]^{\uparrow\uparrow\uparrow\uparrow}$



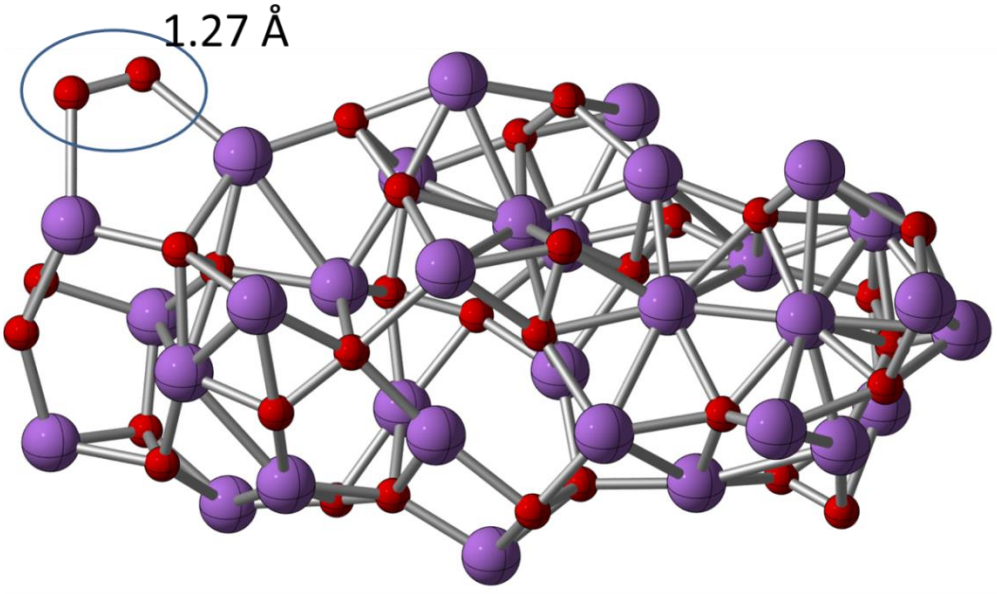
Optimized geometry of $[Li_{32}O_{32}]^{\uparrow\uparrow\uparrow\uparrow}$ cluster

Fig S2 $(Li_2O_2)_{16}$ cation sextet following oxidation of peroxide unit of $(Li_2O_2)_{16}$ quintet (Fig. S2)



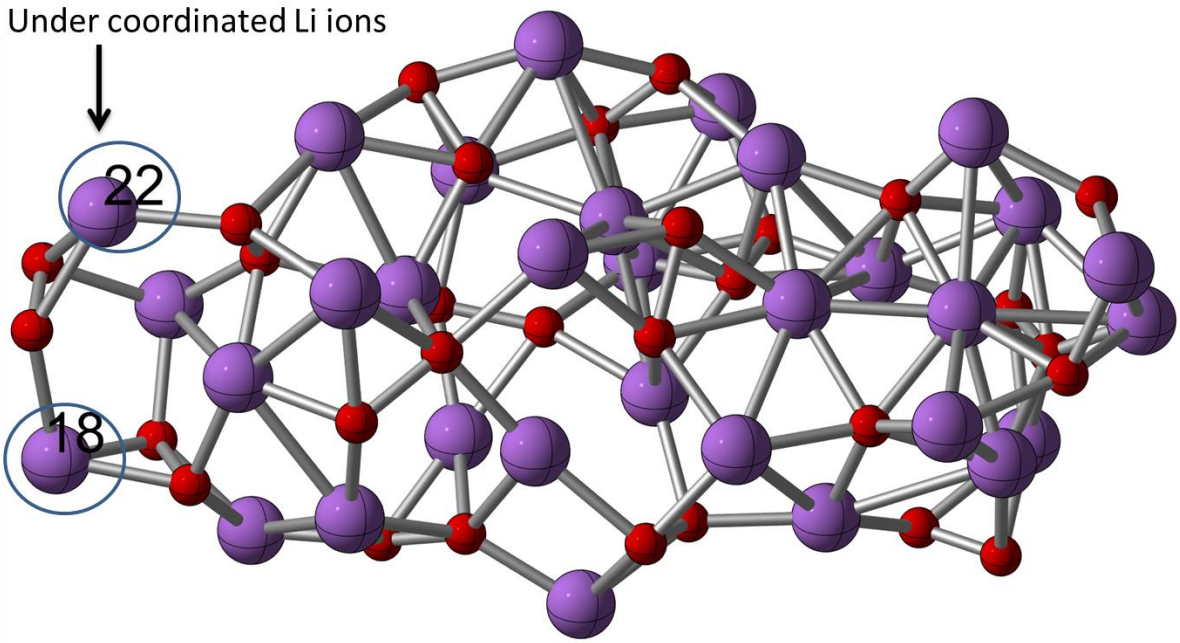
Optimized geometry of $[Li_{32}O_{32}]^{+}\uparrow\uparrow\uparrow\uparrow\uparrow$cluster

Fig S3 $(Li_2O_2)_{16}$ cation quartet following oxidation of superoxide unit of $(Li_2O_2)_{16}$ quintet (Fig. S2)



Optimized geometry of $[Li_{32}O_{32}]^{+}\uparrow\uparrow\uparrow$ cluster

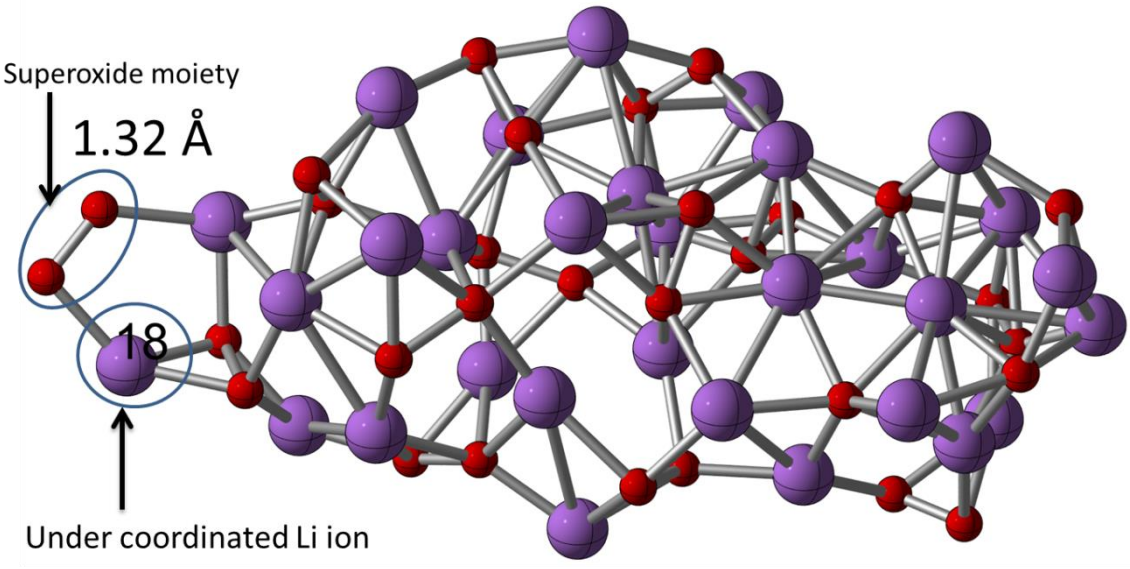
Fig S4 $Li_{32}O_{30}$ cation following O_2 removal of from $(Li_2O_2)_{16}$ cation sextet (Fig. S3)



Optimized geometry of $[Li_{32}O_{30}]^{+}\uparrow\uparrow\uparrow$ cluster

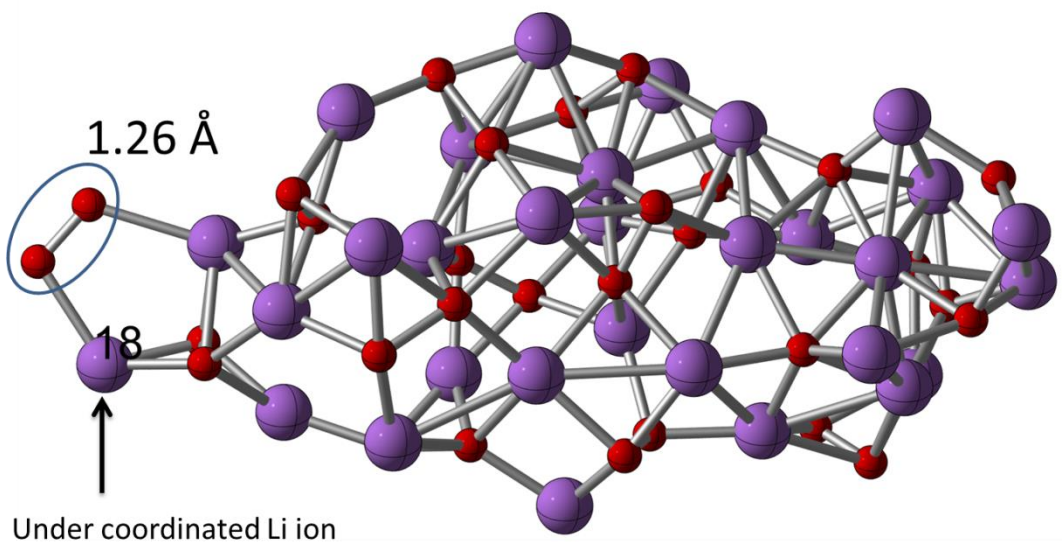
Note : The high-lighted Li ions are under coordinated surface ions are more likely to be removed from the cluster by the solvent molecules (like TEGDME) during charging.

Fig S5. $Li_{31}O_{30}$ structure following Li^+ cation removal from $Li_{32}O_{30}$ cation quartet (Fig. S5)



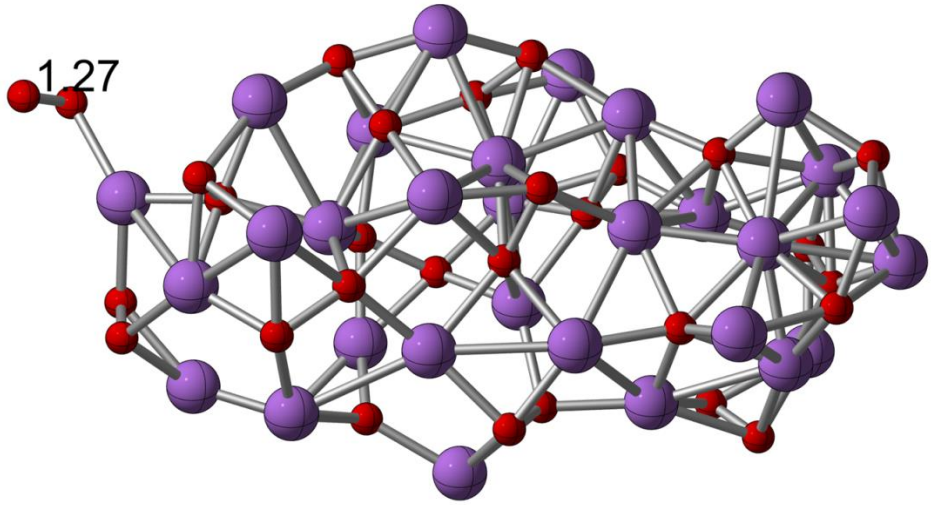
Optimized geometry of $[Li_{31}O_{30}]\uparrow\uparrow\uparrow$ cluster

Fig S6 $Li_{31}O_{30}$ cation following oxidation of $Li_{31}O_{30}$ (Fig. S6)



Optimized geometry of $[Li_{31}O_{30}]^{+}\uparrow\uparrow\uparrow\uparrow$ cluster

Fig. S7 $Li_{30}O_{30}$ structure following Li^{+} cation removal from $Li_{32}O_{30}$ cation quartet (Fig. S5) (Note that the structure shown in Fig S8 is a local minimum and the superoxide moieties can **make strong covalent bonds with Li ions upon changing the dihedral angles).**



Optimized geometry of $[Li_{30}O_{30}]\uparrow\uparrow\uparrow\uparrow$ cluster

Figure S8. Optimized structures of some non-stoichiometric lithium-oxide species computed at the B3LYP/6-31+G(d) level of theory. .