Supporting Information

Interactions of Dimethoxy Ethane with Li_2O_2 Clusters and Likely Decomposition for Li-O2 Batteries.

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Table S1. Computed electronic energy difference (ΔE_e) between lowest energy triplet and singlet energy state of $(Li_2O_2)_4$ cluster in eV.

Method	ΔE_e (eV) = E(Triplet) – E(Singlet)
G4MP2	-0.17
B3LYP/6-31G(2df,p)	-0.45
B3LYP/6-31+G(d)	-0.45
PBE/6-311+G(2df,p)//B3LYP/6-31+G(d)	-0.47
B3LYP/6-311+G(2df,p)//B3LYP/6-31+G(d)	-0.46
MP2/6-311+G(2df,p)//B3LYP/6-31+G(d)	-0.20
wB97XD/6-311+G(2df,p)//B3LYP/6-31+G(d)	-0.24
M062X/6-311+G(2df,p)//B3LYP/6-31+G(d)	-0.01
PBE0/6-311+G(2df,p)//B3LYP/6-31+G(d)	-0.39

Table S2A: The statistics of energy fluctuation (in eV) from AIMD run (Fig. 3) of ~ 400 fs for few selected DME-$(Li_2O_2)_4$ complex (at T = 300 K)

System	$(Li_2O_2)_4$ –DME complex			
	E_{tot}(min)	E_{tot}(avg)	E_{tot}(max)	E_{tot} fluctuation
Triplet	-6756.4097	-6756.3008	-6755.4573	0.9524
Singlet	-6756.3825	-6756.2192	-6755.1852	1.1973

Table S2B: The statistics of energy fluctuation (in eV) from AIMD run (Fig. 3) of ~ 200 fs for few selected DME-$(Li_2O_2)_4$ complex at equilibrated temperature T ~ 300K

System	$(Li_2O_2)_4$ –DME complex			
	E_{tot}(min)	E_{tot}(avg)	E_{tot}(max)	E_{tot} fluctuation
Triplet	-6756.4097	-6756.3008	-6756.2464	0.1633
Singlet	-6756.3825	-6756.2192	-6756.0831	0.2994

Table S **3** Computed enthalpy of activation in solution (gas values are given in parenthesis) for the breaking of CO bond breaking of dimethoxy ethane by lithium peroxide singlet and triplet clusters. Calculations were performed at the B3LYP/6-31+G(d) level of theory.

species	**ΔH^{TS} (eV)**
$(Li_2O_2)_4$-Singlet	1.4 (1.5)
$(Li_2O_2)_4$-Triplet	2.05 (1.85)

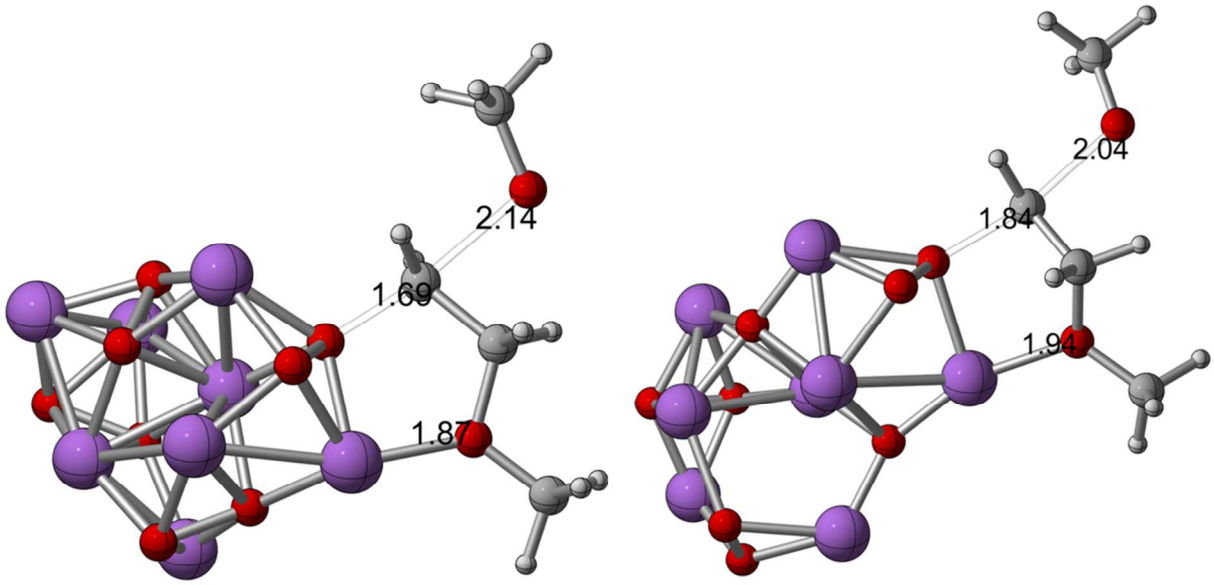

Figure S1.. optimized transition state structures for the C-O bond breaking of the DME by lithium peroxide singlet and tetramer clusters. Selected bond lengths are also given in Å.

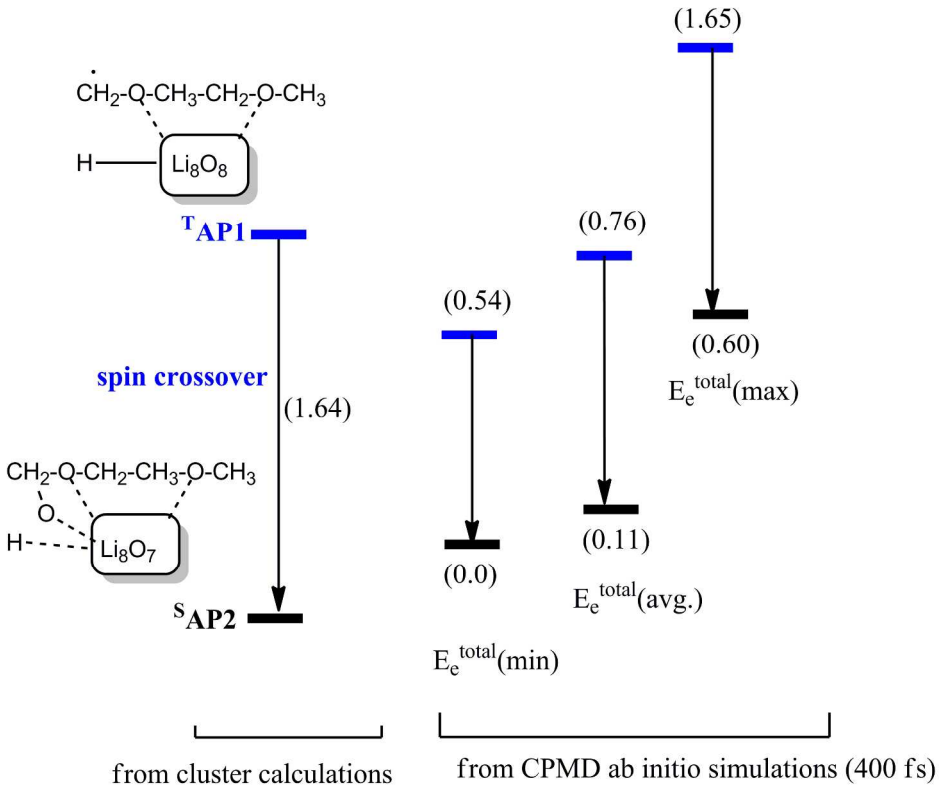

Figure S 2 . Comparison of electronic energies of species ^{T}AP1 and ^{S}AP2 from cluster (gaussian 09) and abinitio dynamics simulation (CPMD). All energies are given in eV. The maximum energy fluctuation found in ab initio dynamics simulation are 0.6 and 1.11 eV respectively for ^{S}AP2 and ^{T}AP1.

Complete Citation for Gaussian 09

Gaussian 09, Rev C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.