Electronic supporting information (ESI)

Singlet oxygen vs triplet oxygen: functions of 2D-MoO_3 catalyst in conquering the catastrophic parasitic-reactions in lithium- and sodium-oxygen batteries

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Fig. S1 is the thermodynamic process used to exam the accuracy of our calculations. The following equation can be utilized to calculate ΔG:

$$\Delta G = -E_b(\mathrm{Li}) + \Delta G_1 + \Delta G_2 + E_b(\mathrm{Li_2O_2}) \quad \backslash^* \text{ MERGEFORMAT (1)}$$

where E_b(Li) and E_b(Li_2O_2) denote the binding energies of Li and Li_2O_2, respectively. The data we adopted could be acquired form Table S1.

Table S2 listed the static dielectric constant,[1] and refractive index[1] of ten aprotic solvents (Acetone, DE, DMSO, DMA, DMF, DME, MeCN, DEC, THF, DOL) for reorganization energy calculations. The calculated reorganization energies of LiO_2 and NaO_2 are also listed.

Fig. S2 are the partial density of states of (a) $2LiO_2$, (b) $Li^3O_2{}^3O_2Li$, (c) $Li^1O_2{}^3O_2Li$, (d) $2NaO_2$, (e) $Na^3O_2{}^3O_2Na$, (f) $Na^1O_2{}^3O_2Na$ adsorbed the 2D-MoO_3 nanosheet.

Fig. S3 records the relationship between the static dielectric constant and the Gibbs free energy change (eV) of disproportionation reaction of (a) singlet and (b) triplet oxygen.

Table S1. Binding energies (in eV) of X, XO_2 and X_2O_2 (X=Li or Na) in LOBs or SOB**s**

X=Li or Na	O_2	X	XO_2	X_2O_2
LOBs (X=Li)	-0.698	3.689	1.566	4.321
SOBs (X=Na)	-0.698	3.578	2.166	7.366

Table S2. The static dielectric constant, refractive index, and calculated reorganization energy (in eV) for LiO_2 and NaO_2

Solvents	Static Dielectric Constant	Refractive Index	Reorganization Energy for LiO_2	Reorganization Energy for NaO_2
Acetone	20.7	1.359	1.199	0.702
DE	4.335	1.353	0.767	0.449
DMSO	46.7	1.479	1.059	0.621
DMA	37.781	1.437	1.113	0.652
DMF	37.219	1.431	1.122	0.657
DME	7.3	1.379	0.945	0.554
MeCN	35.688	1.344	1.278	0.748
DEC	2.82	1.384	0.407	0.238
THF	7.4257	1.407	0.901	0.528
DOL	2.2189	1.401	0.143	0.084

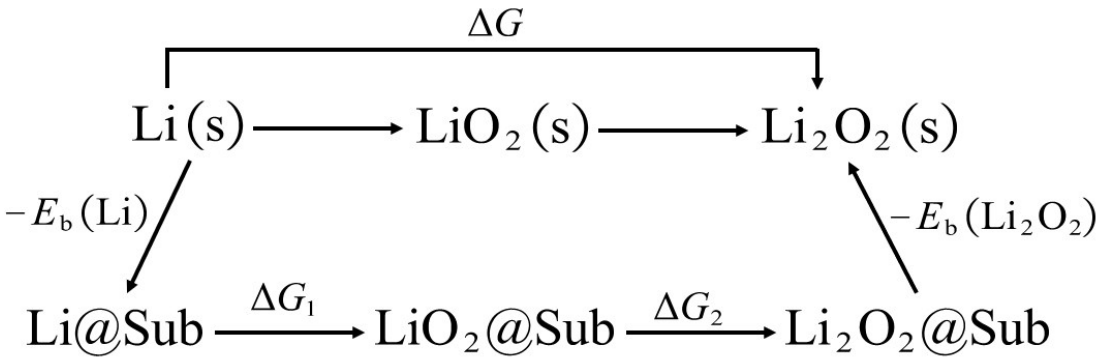

Fig. S1 The thermodynamic process we choose to calculate and exam the Gibbs energy change of Li_2O_2 (ΔG) in LOBs and SOBs.

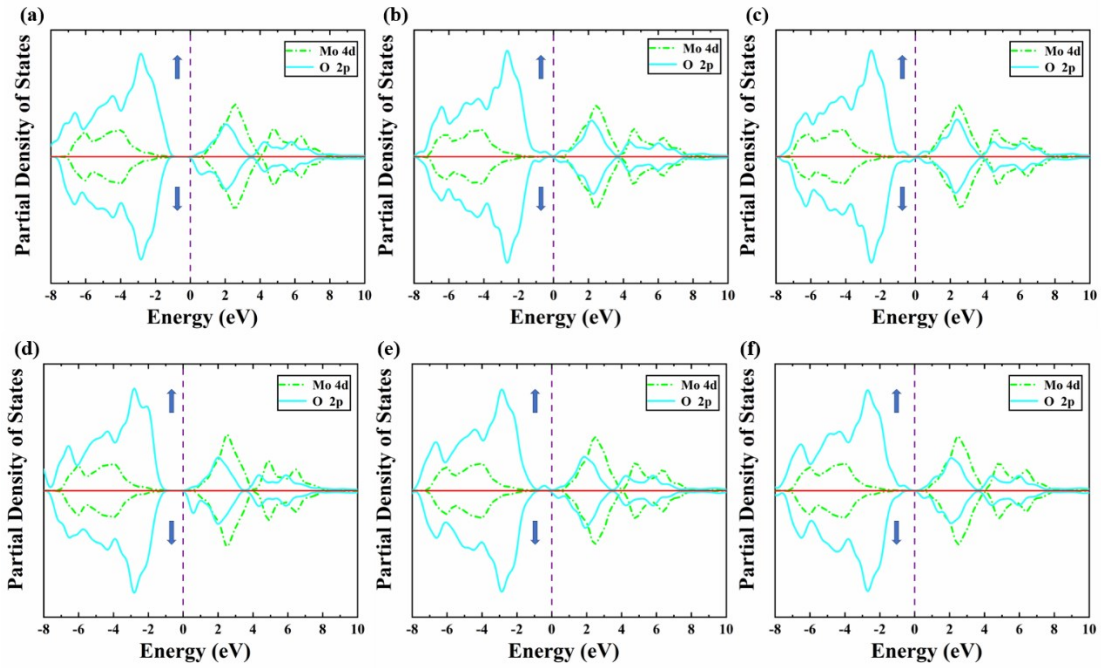

Fig. S2 Partial density of states (PDOSs) of (a) $2LiO_2$, (b) $Li^3O_2{}^3O_2Li$, (c) $Li^1O_2{}^3O_2Li$, (d) $2NaO_2$, (e) $Na^3O_2{}^3O_2Na$, (f) $Na^1O_2{}^3O_2Na$ adsorbed 2D-MoO_3. The blue and green lines represent Mo 4d and O 2p orbitals, respectively. The two arrows (↑ and ↓) in the figures demonstrate spin-up and spin-down electrons, respectively.

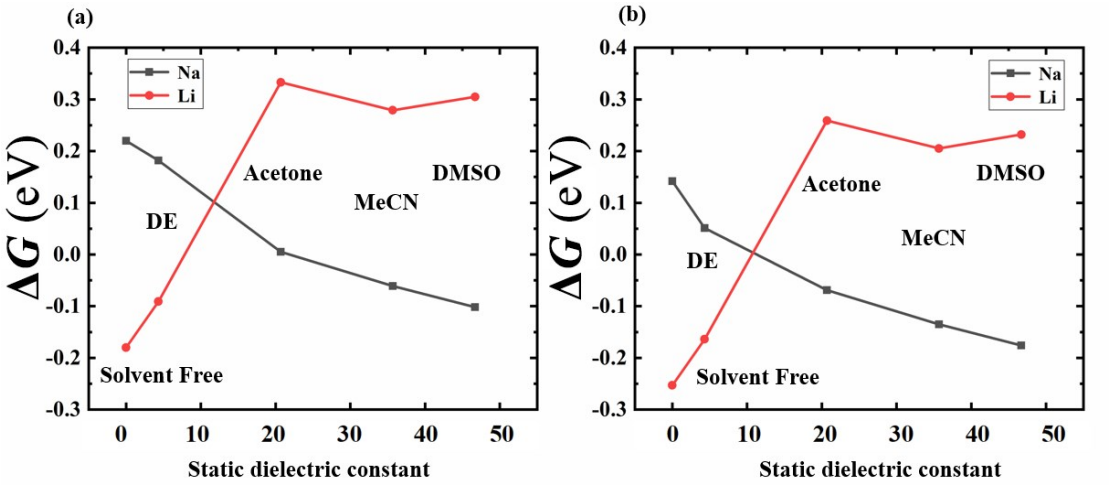

Fig. S3 The relationship between the static dielectric constant and the Gibbs energy change of disproportionation reaction of (a) singlet and (b) triplet oxygen.

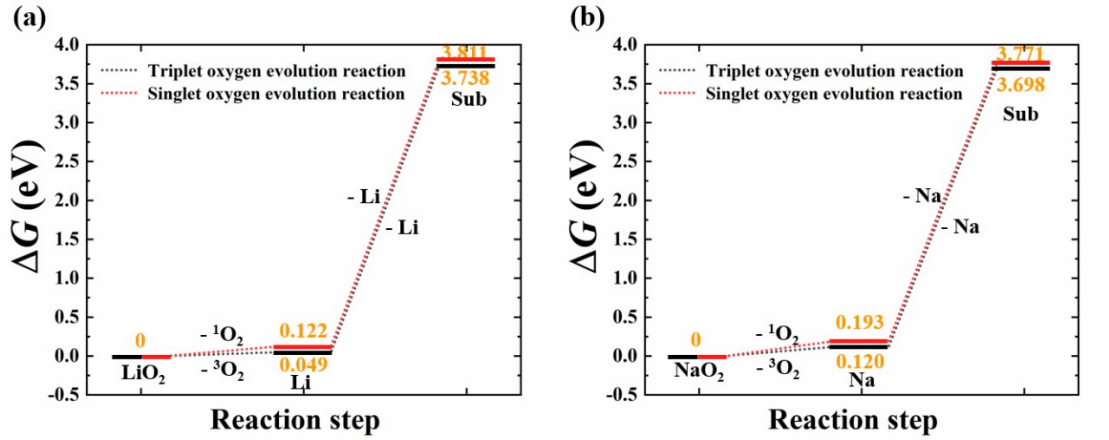

Fig. S4 Gibbs free energy changes of the evolution of XO_2 for (a) X=Li and (b) X=Na at open circuit potential (U=0 V).

Reference

1. J. R. Rumble, D. R. Lide and T. J. Bruno, *CRC handbook of chemistry and physics : a ready-reference book of chemical and physical data*, Boca Raton : CRC Press, 99th edition / editor-in-chief John R. Rumble associate editors, David R. Lide, Thomas J. Bruno.. edn., 2018.