Electrolyte-controlled discharge product distribution of Na-O_2 battery: A combined computational and experimental study

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Electronic supplementary information

Table S1. Experimental and theoretical equilibrium voltages (V) of Na_2O, Na_2O_2 and pyrite NaO_2 at 300 K with respect to solid Na metal and O_2 gas.

Formation energy	This work	Other reports[1]	Experiment[2]
$\Delta G(Na_2O)$	-1.87	-2.00	-1.96
$\Delta G(Na_2O_2)$	-2.27	-2.31	-2.33
ΔG(pyrite NaO_2)	-2.38	-2.28	-2.26

Reference

1 S. Kang, Y. Mo, S. P. Ong, G. Ceder, Nano Lett., 2014, 14, 1016–1020.
2 M. W. Chase, *NIST-JANAF thermochemical tables*. *4th ed.*, American Chemical Society; American Institute of Physics for the National Institute of Standards and Technology, Washington, DC, 1998.

Table S2. Reaction Free energies of different sodium oxide discharging products.

Reaction	ΔG(reaction)/eV
$2NaO_2+Na=Na_3O_4$	-2.12
$3NaO_2+2Na=Na_5O_6$	-3.83
$NaO_2+Na=Na_2O_2$	-1.95
$Na_3O_4+Na=2Na_2O_2$	-1.78
$3Na_3O_4+Na=2Na_5O_6$	-1.30
$Na_5O_6+Na=3Na_2O_2$	-2.01
Na_2O_2+O2=$2NaO_2$	-0.57
Na_3O_4+O2=$3NaO_2$	-0.39
Na_5O_6+O2=$5NaO_2$	-1.20

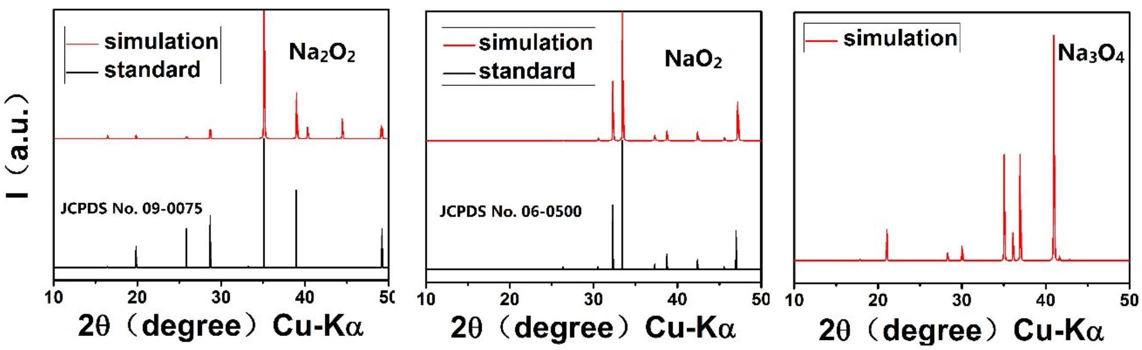

Figure S1 Computational and experimental XRD characterizations for Na_2O_2, NaO_2, and Na_3O_4. Note that no experimental XRD data was reported.

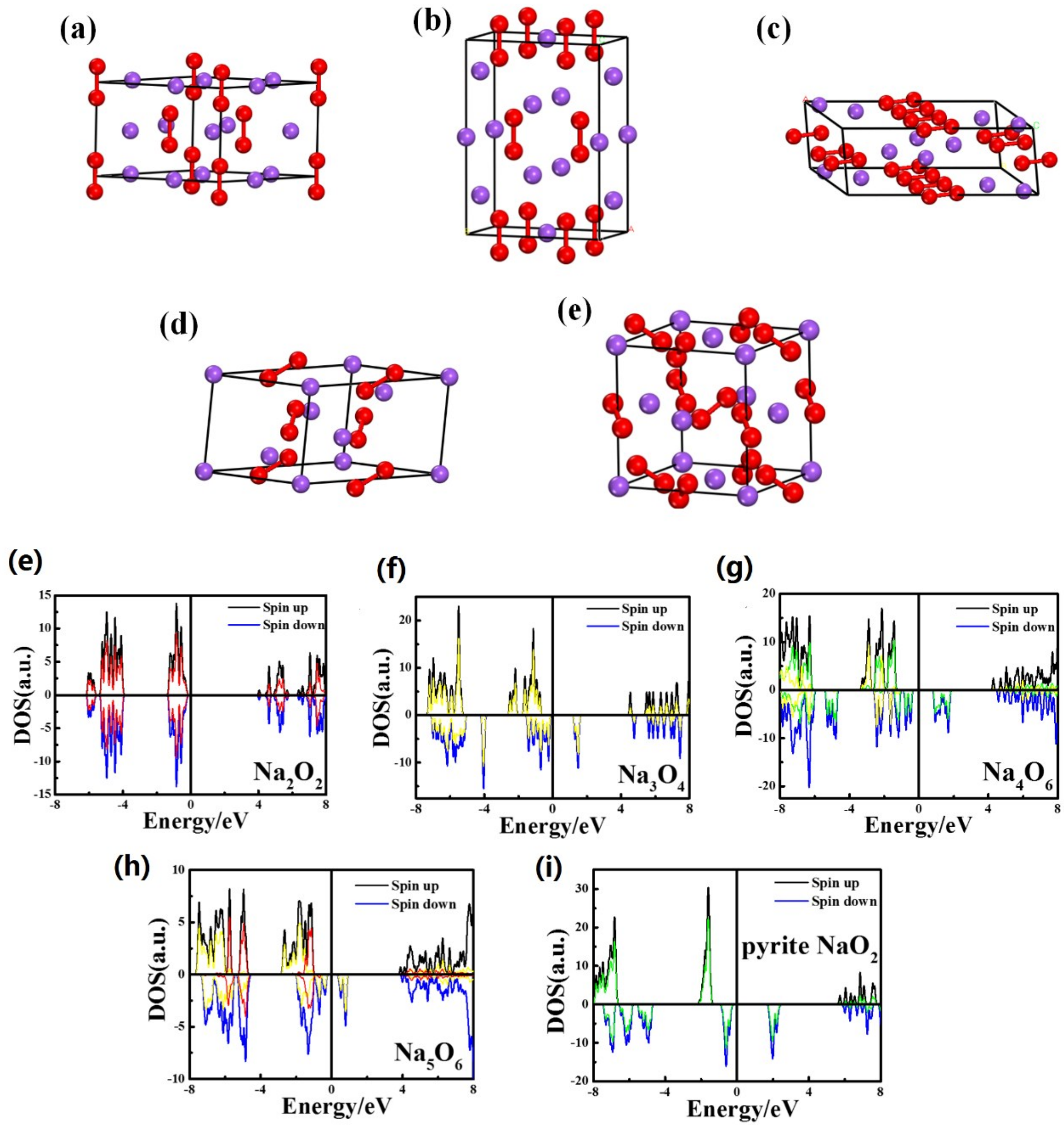

Figure S2. Conventional unit cell of (a) Na_2O_2, (b) Na_3O_4, (c) Na_4O_6, (d) Na_5O_6 and (e) pyrite NaO_2. The purple and red balls represent Na and O atoms, respectively. The bond lengths of O–O in these species are listed in Table 1. HSE-calculated total density of states of (e)Na_2O_2, (f)Na_3O_4, (g)Na_4O_6, (h)Na_5O_6 and (i)pyrite NaO_2. The red, green and yellow states are the projected DOS of peroxide, superoxide and Na_3O_4-type oxygen atoms

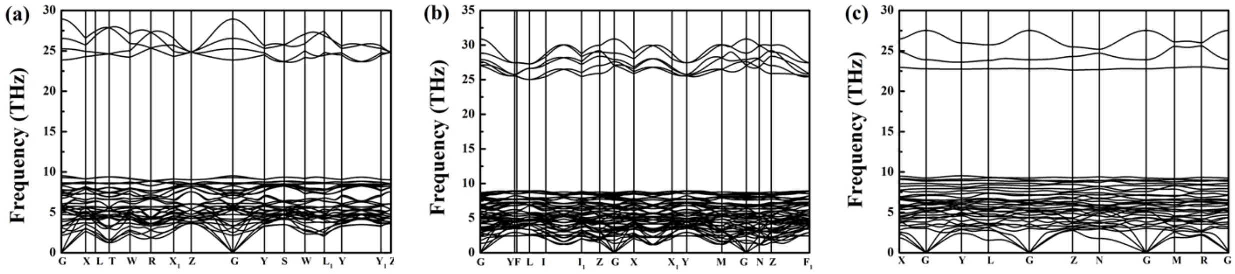

Figure S3. Phonon dispersions for (a) Na_3O_4, (b) Na_4O_6 and (c) Na_5O_6.

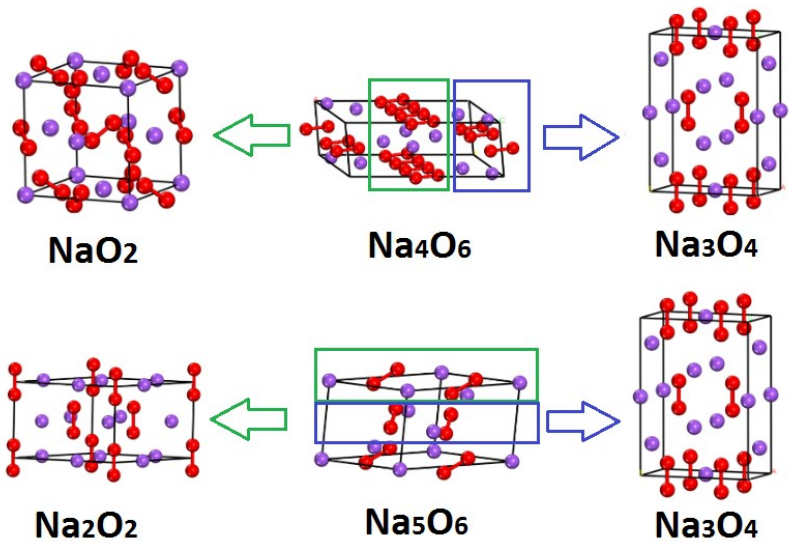

Figure S4. The structural similarity analysis of O_2^{n-}anions in Na_4O_6 and Na_5O_6 by compared with NaO_2, Na_2O_2, and Na_3O_4.

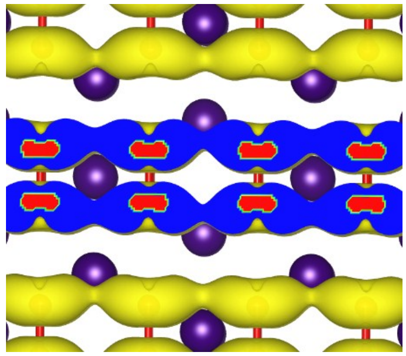

Figure S5. Partial charge density plot around Fermi level of Na_3O_4 (isosurface value of 0.005 eV).

Table S3. Calculated Surface Energies of the Low-Index Surfaces of Na_2O_2, Na_3O_4, Na_5O_6 and Pyrite NaO_2 under the Most Oxidizing and Reducing Conditions (in meV/Å^2)

species	orientation	most oxidizing condition	most reducing condition
Na_2O_2	(0001)	24.0	36.6
	(010)	24.4	40.1
	(110)	24.2	29.9
	(100)	24.3	40.1
Na_3O_4	(010)	19.6	37.8
	(100)	42.5	42.5
	(001)	3.4	11.8
	(00)	42.4	42.4
	(10)	21.3	22.3
Na_5O_6	(001)	15.8	14.0
	(101)	32.5	27.4
	(011)	15.6	12.5
	(010)	19.3	18.2
	(100)	32.8	33.3
pyrite NaO_2	(100)	2.4	2.4
	(110)	10.1	10.1
	(111)	1.7	6.5

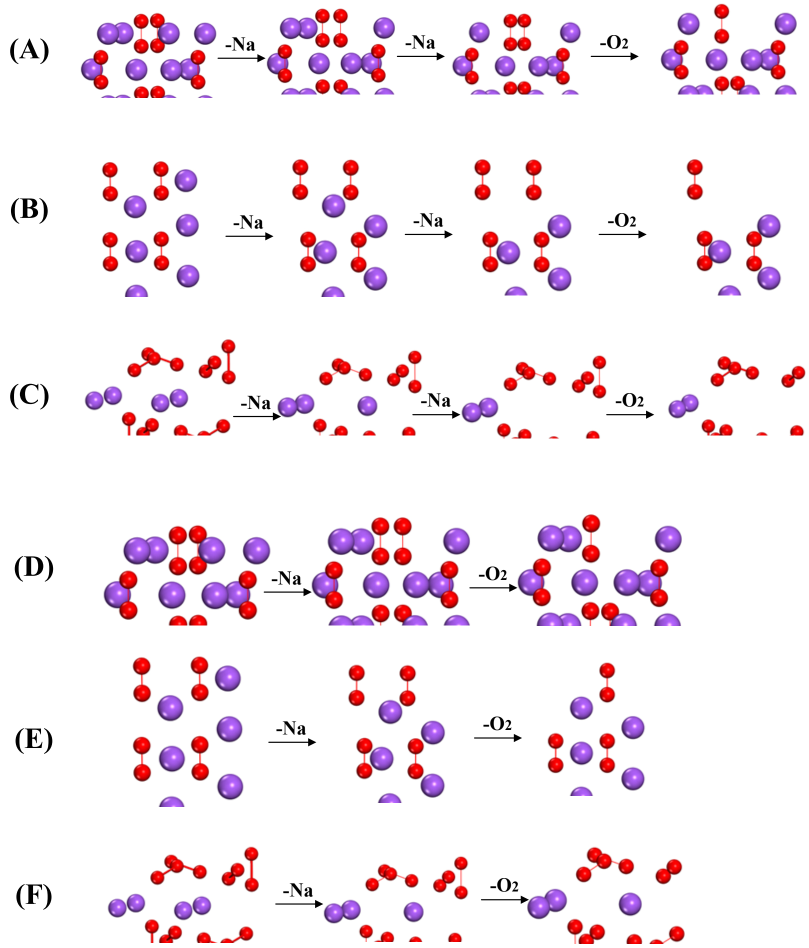

Figure S6. Structural evolution corresponding to $Na^+ \rightarrow Na^+ \rightarrow O_2$ reaction paths on the (0001) surface of Na_2O_2 (A), the (001) surface of Na_3O_4 (B) and the (111) surface of NaO_2 (C) and Structural evolution corresponding to $Na^+ \rightarrow O_2$ OER paths on the (0001) surface of Na_2O_2 (D), the (001) surface of Na_3O_4 (E) and the (111) surface of NaO_2 (F). Different kinds of elements are represented by different colors in that: Sodium (purple), Oxygen (red).

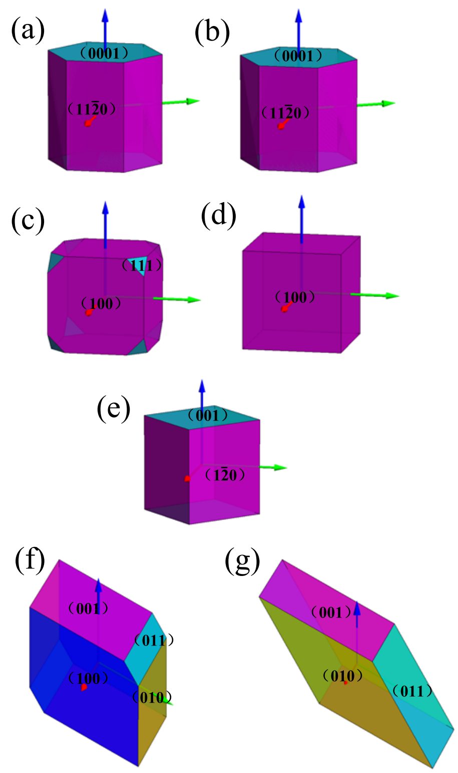

Figure S7. Wulff Shapes of (a), (b) Na_2O_2, (c), (d) pyrite NaO_2 and (e) Na_3O_4, (f), (g) Na_5O_6 during the OER on the corresponding surfaces. The left side (a), (c) and (f) are for the most oxidizing conditions, and the right side (b), (d) and (g) are for the most reducing conditions for each product. The lower-middle (e) is for both the most oxidizing and reducing conditions for Na_3O_4.