Supporting Information

Electronic Structure of Sodium Superoxide Bulk, (100) Surface, and Clusters using Hybrid Density Functional: Relevance for Na-O_2 Batteries

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Summary: Further details of computational details, density of states using PBE+U (Figure S1), optimized structures of additional $(NaO_2)_n$ clusters (Figure S2), and selected interatomic distances (Table S1) are reported here . In addition, the optimized coordinates of relevant bulk, surface, and clusters are also provided (Tables S2-S10).

Computational details

Bulk NaO_2. The NaO_2 structure ($Pa\bar{3}$ space group) was optimized using a Monkhorst−Pack[1] grid with 5×5×5 **k**-point sampling, which guarantees a tight convergence within 0.001 Å. We found that a ferromagnetic ordering of the moments on all O_2^- species is energetically preferred, with a total magnetic moment of 1.0 μ_B/O_2^-.

NaO_2(100) surface. As a $Fm\bar{3}m$ bulk NaO_2 has the O_2 dimer orientations disordered, we approximate here its (100) surface by those of ordered $Pa\bar{3}$. Surface calculations were performed using a slab model cut along the (100) direction, containing 5 atomic NaO_2 layers with the two bottom layers fixed to their bulk PBE-optimal positions. We considered at least 14 Å of vacuum between slabs. Models containing extra atomic layers or larger vacuum regions do not have significant qualitative impact on the computed electronic properties. Due to the high computational cost of HSE06 functional, only PBE geometry was considered. For PBE (HSE06) calculations we used a Monkhorst−Pack[1] grid with 7×7×1 (5×5×1) **k**-point sampling.

$(NaO_2)_n$ clusters. We used a 17×17×17 $Å^3$ cubic box to compute $(NaO_2)_3$ as well as nonplanar $(NaO_2)_4$ and $(NaO_2)_6$ clusters. Planar-ring $(NaO_2)_4$ and $(NaO_2)_6$ as well as nonplanar $(NaO_2)_8$ clusters were computed using a 19×19×19 $Å^3$ box, while for planar-ring $(NaO_2)_8$ clusters we used a 23×23×23 $Å^3$ box. These simulation boxes are large enough to ensure that repeated image interactions were negligible. All calculations were carried out at the **Γ** point. Formation energies per NaO_2 unit were calculated with respect to the optimized NaO_2 monomer in gas phase using a 17×17×17 $Å^3$ cubic box. Zero-point corrected formation energies were computed from harmonic vibrational frequencies, which were calculated numerically by building the Hessian dynamical matrix through finite displacements of ±0.01 Å from the optimized structures.

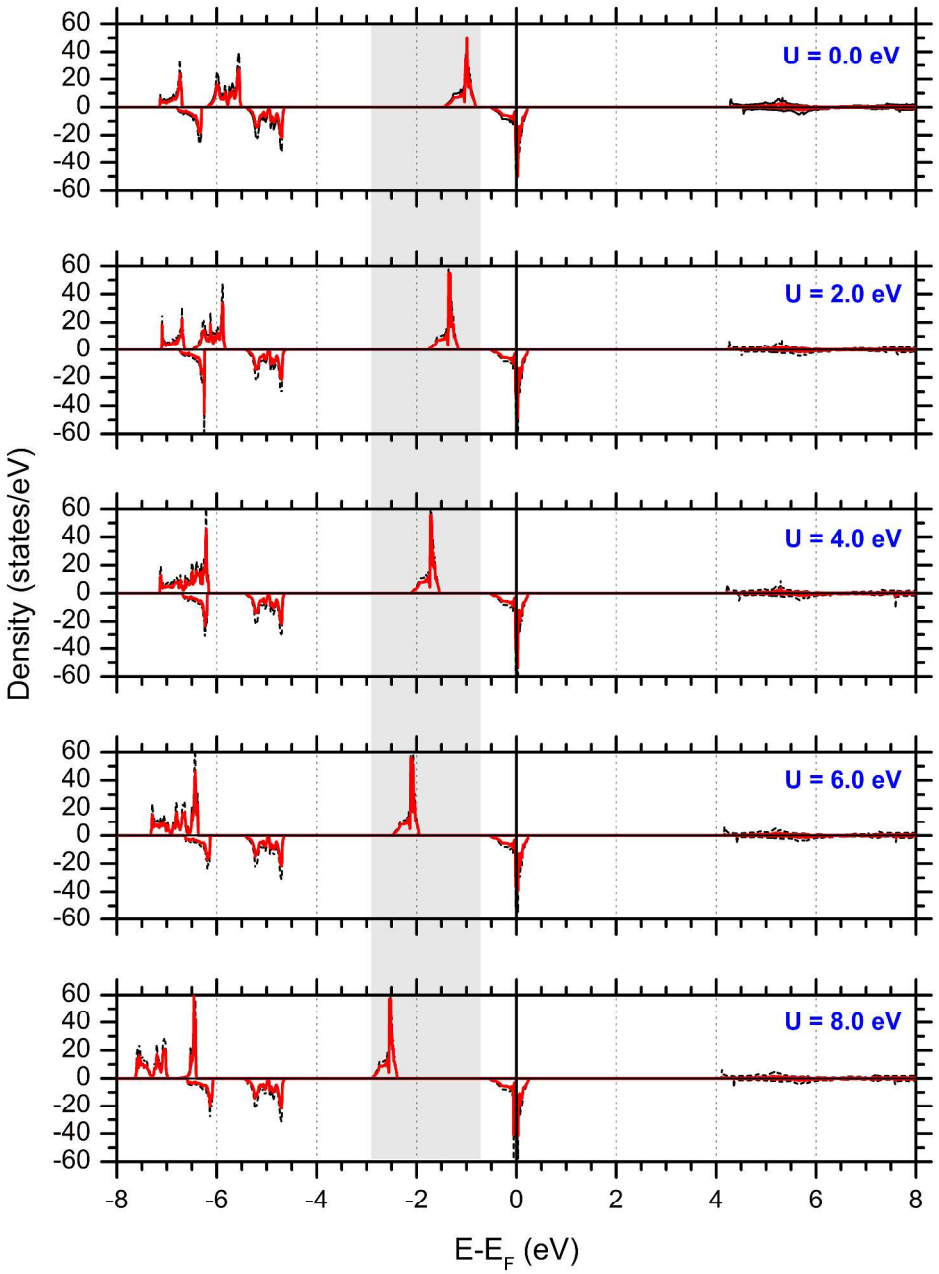

Figure S1. Density of states for bulk NaO_2 as a function of the U term using PBE+U. The black dashed (red solid) lines are the total DOS (PDOS projected onto the p orbitals of oxygen atoms). Positive (negative) values correspond to spin up (down) states.

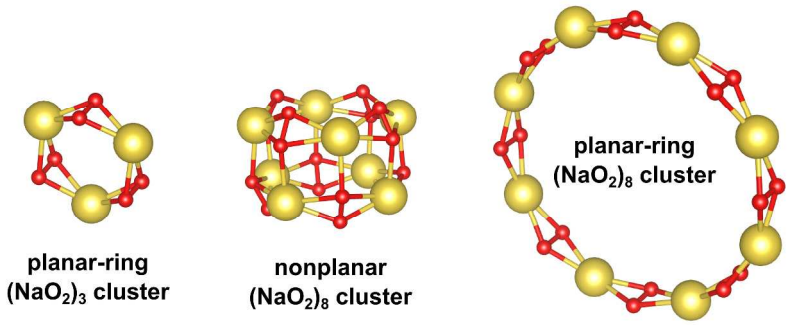

Figure S2. Optimized structures of planar-ring $(NaO_2)_3$, nonplanar $(NaO_2)_8$, and planar-ring $(NaO_2)_8$ clusters. Yellow and red spheres are Na and O atoms, respectively.

Table S1. Averaged interatomic distances (in Å) between different pairs of first nearest neighbor atoms in $(NaO_2)_n$ clusters using PBE and HSE06. Bulk NaO_2 (pyrite phase) is also included for comparison.

		PBE			HSE06		
	geometry	Na–Na	O–O	Na–O	Na–Na	O–O	Na–O
$(NaO_2)_3$	planar-ring	3.849	1.374	2.291	3.815	1.342	2.272
$(NaO_2)_4$	planar-ring	4.077	1.374	2.283	4.040	1.342	2.265
	nonplanar	3.537	1.362	2.324	3.544	1.331	2.318
$(NaO_2)_6$	planar-ring	4.228	1.374	2.280	4.195	1.342	2.260
	nonplanar	3.919	1.364	2.336	3.933	1.334	2.347
$(NaO_2)_8$	planar-ring	4.282	1.374	2.280	4.252	1.342	2.264
	nonplanar	4.182	1.366	2.345	4.182	1.335	2.342
NaO_2	bulk	3.895	1.354	2.427	3.880	1.326	2.422

Table S2. Lattice vectors (in Å) and optimized atomic fractional coordinates of bulk NaO_2 (pyrite phase) using HSE06.

a = 5.4866 a_x + 0.0000 a_y + 0.0000 a_z
b = 0.0000 b_x + 5.4866 b_y + 0.0000 b_z
c = 0.0000 c_x + 0.0000 c_y + 5.4866 c_z

atom	x	y	z	atom	x	y	z
Na	0.00000	0.00000	0.00000	O	0.93023	0.43023	0.06977
Na	0.50000	0.00000	0.50000	O	0.06977	0.56977	0.93023
Na	0.00000	0.50000	0.50000	O	0.43023	0.06977	0.93023
Na	0.50000	0.50000	0.00000	O	0.56977	0.93023	0.06977
O	0.56977	0.56977	0.56977	O	0.06977	0.93023	0.43023
O	0.43023	0.43023	0.43023	O	0.93023	0.06977	0.56977

Table S3. Supercell lattice vectors (in Å) and optimized atomic fractional coordinates of NaO_2(100) surface using PBE.

a = 5.5087 a_x + 0.0000 a_y + 0.0000 a_z
b = 0.0000 b_x + 5.5087 b_y + 0.0000 b_z
c = 0.0000 c_x + 0.0000 c_y + 25.8106 c_z

atom	x	y	z	atom	x	y	z
Na	0.00000	0.00000	0.01537	O	0.07200	0.92800	0.10671
Na	0.99564	0.99398	0.22995	O	0.07758	0.95083	0.32233
Na	0.00125	0.02077	0.44324	O	0.92800	0.42800	0.03073
Na	0.00000	0.50000	0.12208	O	0.94186	0.41745	0.24597
Na	0.99905	0.51359	0.33796	O	0.91888	0.43527	0.45860
Na	0.50000	0.50000	0.01537	O	0.42800	0.42800	0.10671
Na	0.50436	0.49398	0.22995	O	0.42242	0.45083	0.32233
Na	0.49875	0.52077	0.44324	O	0.57200	0.92800	0.03073
Na	0.50000	0.00000	0.12208	O	0.55814	0.91745	0.24597
Na	0.50095	0.01359	0.33796	O	0.58112	0.93527	0.45860
O	0.57200	0.57200	0.13745	O	0.92800	0.07200	0.13745
O	0.57940	0.57522	0.35325	O	0.92060	0.07522	0.35325
O	0.42800	0.07200	0.00000	O	0.07200	0.57200	0.00000
O	0.43344	0.07260	0.21533	O	0.06656	0.57260	0.21533
O	0.42985	0.09711	0.43630	O	0.07015	0.59711	0.43630

Table S4. Lattice vectors (in Å) and optimized atomic fractional coordinates of a nonplanar $(NaO_2)_6$ cluster using HSE06.

a = 16.5261 a_x + 0.0000 a_y + 0.0000 a_z
b = 0.0000 b_x + 16.5261 b_y + 0.0000 b_z
c = 0.0000 c_x + 0.0000 c_y + 16.5261 c_z

atom	x	y	z	atom	x	y	z
Na	0.42943	0.46433	0.36890	O	0.37684	0.46387	0.62296
Na	0.42865	0.34419	0.57303	O	0.37775	0.56944	0.44474
Na	0.42863	0.58377	0.57371	O	0.45319	0.59447	0.43058
Na	0.59225	0.46378	0.64220	O	0.64424	0.56935	0.56696
Na	0.59298	0.34423	0.43723	O	0.56833	0.59322	0.58059
Na	0.59293	0.58417	0.43781	O	0.56830	0.33480	0.57995
O	0.37784	0.35875	0.44409	O	0.64433	0.35843	0.56660
O	0.45329	0.33383	0.42978	O	0.64522	0.46437	0.38792
O	0.45218	0.46386	0.65196	O	0.56933	0.46442	0.36040

Table S5. Lattice vectors (in Å) and optimized atomic fractional coordinates of a nonplanar $(NaO_2)_4$ cluster using HSE06.

a = 16.5261 a_x + 0.0000 a_y + 0.0000 a_z
b = 0.0000 b_x + 16.5261 b_y + 0.0000 b_z
c = 0.0000 c_x + 0.0000 c_y + 16.5261 c_z

atom	x	y	z	atom	x	y	z
Na	0.35072	0.33227	0.64276	O	0.33800	0.47579	0.65354
Na	0.49594	0.35315	0.50046	O	0.35382	0.55328	0.63739
Na	0.32654	0.49583	0.51296	O	0.47874	0.36288	0.69675
Na	0.47787	0.49799	0.66860	O	0.49085	0.31378	0.63411
O	0.51625	0.48647	0.53578	O	0.36238	0.31568	0.50211
O	0.46026	0.48578	0.47793	O	0.29693	0.36079	0.51471

Table S6. Lattice vectors (in Å) and optimized atomic fractional coordinates of a planar-ring $(NaO_2)_6$ cluster using HSE06.

a = 19.0261 a_x + 0.0000 a_y + 0.0000 a_z
b = 0.0000 b_x + 19.0261 b_y + 0.0000 b_z
c = 0.0000 c_x + 0.0000 c_y + 19.0261 c_z

atom	x	y	z	atom	x	y	z
Na	0.49738	0.72242	0.46524	O	0.53234	0.75398	0.57433
Na	0.49666	0.72434	0.68374	O	0.46190	0.63349	0.39493
Na	0.49683	0.32662	0.68743	O	0.53241	0.63363	0.39444
Na	0.49709	0.52330	0.36843	O	0.46155	0.41349	0.39657
Na	0.49679	0.52642	0.78318	O	0.53206	0.41354	0.39722
Na	0.49629	0.32590	0.46904	O	0.46115	0.29584	0.57844
O	0.53187	0.63631	0.75533	O	0.53167	0.29548	0.57828
O	0.46135	0.63616	0.75513	O	0.53219	0.41592	0.75749
O	0.46182	0.75417	0.57410	O	0.46166	0.41580	0.75769

Table S7. Lattice vectors (in Å) and optimized atomic fractional coordinates of a planar-ring $(NaO_2)_4$ cluster using HSE06.

a = 19.0261 a_x + 0.0000 a_y + 0.0000 a_z
b = 0.0000 b_x + 19.0261 b_y + 0.0000 b_z
c = 0.0000 c_x + 0.0000 c_y + 19.0261 c_z

atom	x	y	z	atom	x	y	z
Na	0.57036	0.39115	0.61434	O	0.53571	0.49735	0.36195
Na	0.57110	0.60458	0.61310	O	0.60621	0.49745	0.36209
Na	0.57074	0.60394	0.40171	O	0.53532	0.34984	0.50835
Na	0.57098	0.39119	0.40256	O	0.60583	0.34969	0.50854
O	0.53576	0.64629	0.50734	O	0.60591	0.49796	0.65294
O	0.60628	0.64616	0.50720	O	0.53540	0.49819	0.65279

Table S8. Lattice vectors (in Å) and optimized atomic fractional coordinates of a planar-ring $(NaO_2)_3$ cluster using HSE06.

a = 16.5261 a_x + 0.0000 a_y + 0.0000 a_z
b = 0.0000 b_x + 16.5261 b_y + 0.0000 b_z
c = 0.0000 c_x + 0.0000 c_y + 16.5261 c_z

atom	x	y	z	atom	x	y	z
Na	0.59565	0.46399	0.64127	O	0.55453	0.35192	0.57310
Na	0.59351	0.34903	0.44127	O	0.63567	0.35228	0.57203
Na	0.59404	0.58019	0.44198	O	0.63420	0.46476	0.37909
O	0.63633	0.57606	0.57259	O	0.55302	0.46494	0.37920
O	0.55516	0.57684	0.57368				

Table S9. Lattice vectors (in Å) and optimized atomic fractional coordinates of a nonplanar $(NaO_2)_8$ cluster using HSE06.

a = 19.0261 a_x + 0.0000 a_y + 0.0000 a_z
b = 0.0000 b_x + 19.0261 b_y + 0.0000 b_z
c = 0.0000 c_x + 0.0000 c_y + 19.0261 c_z

atom	x	y	z	atom	x	y	z
Na	0.42741	0.38868	0.39684	O	0.44750	0.49894	0.34053
Na	0.42744	0.60903	0.39751	O	0.38506	0.49894	0.37260
Na	0.42635	0.60712	0.61674	O	0.44732	0.66527	0.50783
Na	0.42589	0.38681	0.61610	O	0.38406	0.63489	0.50712
Na	0.56871	0.49648	0.66280	O	0.55030	0.61683	0.38977
Na	0.57009	0.65337	0.50809	O	0.61332	0.59510	0.41165
Na	0.57054	0.49898	0.35247	O	0.55055	0.38086	0.38938
Na	0.56974	0.34210	0.50722	O	0.61277	0.40344	0.41273
O	0.38336	0.49698	0.64044	O	0.54869	0.37867	0.62535
O	0.44547	0.49682	0.67312	O	0.61197	0.40030	0.60411
O	0.44695	0.33061	0.50608	O	0.61190	0.59191	0.60302
O	0.38375	0.36110	0.50595	O	0.54945	0.61458	0.62565

Table S10. Lattice vectors (in Å) and optimized atomic fractional coordinates of a planar-ring $(NaO_2)_8$ cluster using HSE06.

a = 23.0261 a_x + 0.0000 a_y + 0.0000 a_z
b = 0.0000 b_x + 23.0261 b_y + 0.0000 b_z
c = 0.0000 c_x + 0.0000 c_y + 23.0261 c_z

atom	x	y	z	atom	x	y	z
Na	0.49656	0.33217	0.61458	O	0.46775	0.72629	0.35176
Na	0.49745	0.33268	0.27362	O	0.52601	0.72638	0.35196
Na	0.49690	0.67416	0.61377	O	0.52682	0.59549	0.22342
Na	0.49730	0.67477	0.27345	O	0.46854	0.59533	0.22328
Na	0.49727	0.50322	0.68401	O	0.46865	0.41185	0.22298
Na	0.49649	0.26146	0.44396	O	0.52693	0.41178	0.22326
Na	0.49658	0.74598	0.44362	O	0.46780	0.28147	0.35211
Na	0.49800	0.50363	0.20371	O	0.52606	0.28139	0.35240
O	0.46801	0.59494	0.66431	O	0.46725	0.28150	0.53565
O	0.52627	0.59493	0.66400	O	0.52552	0.28115	0.53577
O	0.52576	0.72573	0.53525	O	0.52602	0.41119	0.66506
O	0.46749	0.72541	0.53523	O	0.46777	0.41140	0.66515

References

(1) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188−5192.