Supporting Information

Labile Oxygen Participant Adsorbate Evolving Mechanism to Boost Oxygen Reduction in $SmMn_2O_5$ with Dual Coordination Crystal Fields

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Contents:

S1. The derivation details of the Gibbs free energy (△G) from binding energy (△E) based on the AEM

Under alkaline conditions, the ORR elementary steps of the 4e- reaction process based on the AEM are shown in equations S1-S4 (OER follows the mechanism of its reverse reaction process):

$O_2 + e^- + OH^* \rightarrow OO^* + OH^-$ (S1)

$OO^* + e^- + H_2O \rightarrow OOH^* + OH^-$ (S2)

$OOH^* + e^- \rightarrow O^* + OH^-$ (S3)

$O^* + e^- + H_2O \rightarrow OH^* + OH^-$ (S4)

where * represents the adsorption site of the catalyst. At different cell potential, the ΔG for each step can be calculated by:

$$\Delta G_1 = G_{OO*} + G_{OH-} - G_{e-} - G_{OH*} - G_{O2}$$

$$= G_{OO*} + [G_{H2O} - {}^1/_2\, G_{H2} + eU\ ] - G_{OH*} - [2G_{H2O} - 2G_{H2} + 4.92]$$

$$= G_{OO*} - G_{OH*} - G_{H2O} + {}^3/_2\, G_{H2} - 4.92 + eU$$

$$= G_{OO*} - G^* - (2G_{H2O} - 2G_{H2}) - G_{OH*} + G^* + (2G_{H2O} - 2G_{H2}) - G_{H2O} + {}^3/_2\, G_{H2} - 4.92 + eU$$

$$= \Delta G_{OO^*} - (\ G_{OH*} - G^* - G_{H2O} + {}^1/_2\, G_{H2}) - 4.92 + eU$$

$$= \Delta G_{OO^*} - \Delta G_{OH^*} - 4.92 + eU$$

$$\Delta G_2 = G_{OOH*} + G_{OH-} - G_{e-} - G_{OO*} - G_{H2O}$$

$$= G_{OOH*} + [G_{H2O} - {}^1/_2\, G_{H2} + eU\ ] - G_{OO*} - G_{H2O}$$

$$= G_{OOH*} - G_{OO*} - {}^1/_2\, G_{H2} + eU$$

$$= G_{OOH*} - G^* - (2G_{H2O} - {}^3/_2\, G_{H2}) - G_{OO*} + G^* + (2G_{H2O} - {}^3/_2\, G_{H2}) - {}^1/_2\, G_{H2} + eU$$

$$= \Delta G_{OOH^*} - [G_{OO*} - G^* - (2G_{H2O} - 2G_{H2})\ ] + eU$$

$$= \Delta G_{OOH^*} - \Delta G_{OO^*} + eU$$

$$\Delta G_3 = G_{O*} + G_{OH-} - G_{e-} - G_{OOH*}$$

$$= G_{O*} + [G_{H2O} - {}^1/_2\, G_{H2} + eU\ ] - G_{OOH*}$$

$$= G_{O*} - G_{OOH*} + G_{H2O} - {}^{1}/_{2}\, G_{H2} + \mathrm{eU}$$

$$= G_{O*} - G^{*} - (G_{H2O} - G_{H2}) - G_{OOH*} + G^{*} + (G_{H2O} - G_{H2}) + G_{H2O} - {}^{1}/_{2}\, G_{H2} + \mathrm{eU}$$

$$= \Delta G_{O^{*}} - [G_{OOH*} - G^{*} - (2G_{H2O} - {}^{3}/_{2}\, G_{H2})] \;) + \mathrm{eU}$$

$$= \Delta G_{O^{*}} - \Delta G_{OOH^{*}} + \mathrm{eU}$$

$$\Delta G_4 = G_{OH*} + G_{OH-} - G_{e-} - G_{O*} - G_{H2O}$$

$$= G_{OH*} + [G_{H2O} - {}^{1}/_{2}\, G_{H2} + \mathrm{eU}\ ] - G_{O*} - G_{H2O}$$

$$= G_{OH*} - G_{O*} - {}^{1}/_{2}\, G_{H2} + \mathrm{eU}$$

$$= G_{OH*} - G^{*} - (G_{H2O} - {}^{1}/_{2}\, G_{H2}) - G_{O*} + G^{*} + (G_{H2O} - {}^{1}/_{2}\, G_{H2}) - {}^{1}/_{2}\, G_{H2} + \mathrm{eU}$$

$$= \Delta G_{OH^{*}} - [G_{O*} - G^{*} - (G_{H2O} - G_{H2})\ ] + \mathrm{eU}$$

$$= \Delta G_{OH^{*}} - \Delta G_{O^{*}} + \mathrm{eU}$$

S2. The elementary steps of the 4e- reaction process via the lattice oxygen-mediated mechanism (LOM)

The 4e$^-$ ORR process was calculated based on the reverse lattice-oxygen participation mechanism (LOM) which was proposed by Mefford et al. [1-5]

$$H_2O + e^- + OH^* \rightarrow (H^*_{O-site} + OH^*) + OH^- \quad (S5)$$

$$(H^*_{O-site} + OH^*) + e^- \rightarrow (V_O + OH^*) + OH^- \quad (S6)$$

$$(V_O + OH^*) + O_2 + e^- \rightarrow (V_O + OO^*) + OH^- \quad (S7)$$

$$(V_O + OO^*) + e^- + H_2O \rightarrow OH^* + OH^- \quad (S8)$$

S3. The Gibbs free energy diagram of the $(125)_4$ cluster under AEM and LAM

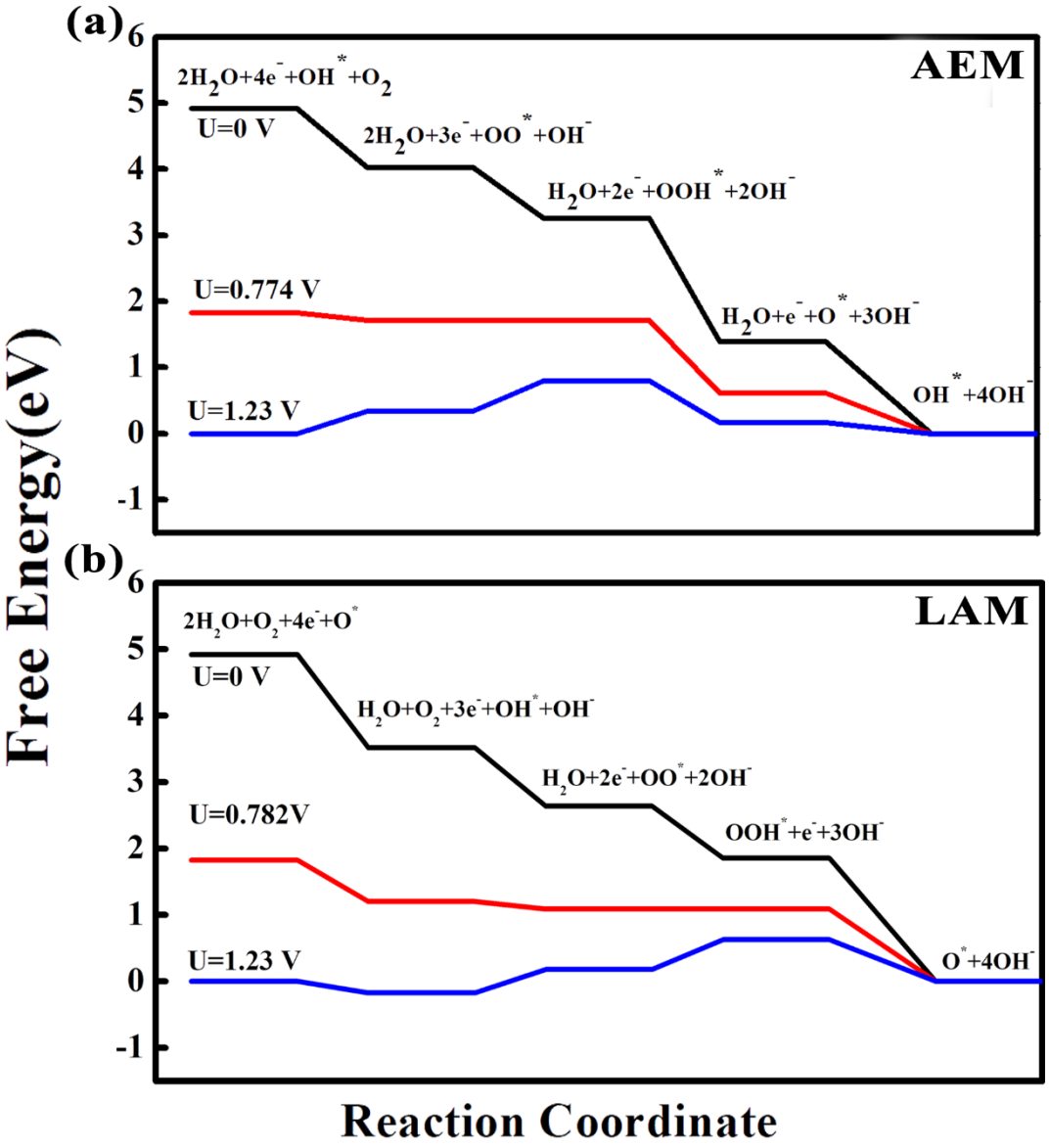
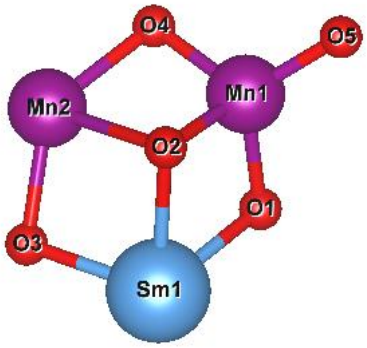


Figure S1. Free energy diagrams for oxygen reduction reaction (ORR) over $SmMn_2O_5$ $(125)_4$ cluster based on (a) the adsorbate evolution mechanism (AEM)), (b) the labile oxygen participant adsorbate evolving mechanism (LAM) at zero cell potential (U=0), at the equilibrium potential (U=1.23 V), and at the highest potential (U=0.774V for AEM and U=0.782V for LAM) where all reaction steps are exothermic.

S4. The Bader charge of each atom in the ground state structure of the $SmMn_2O_5$ (125) n (n= 1, 2, 3, 4, 8) clusters before the intermediates are adsorbed.

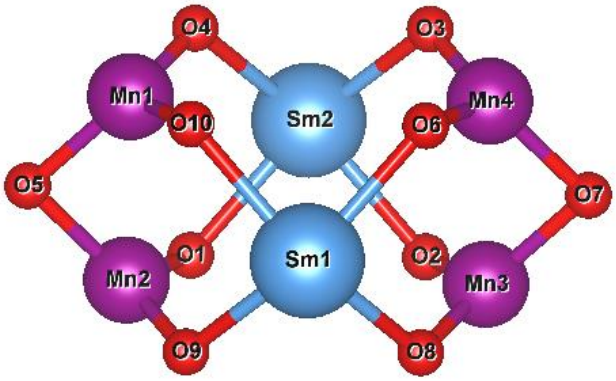
The Bader charge difference is defined between the number of valence electrons of the atoms in the clusters and the number of valence electrons of the element. And based on this definition, the Bader charge of all atoms in the ground state configuration of the $SmMn_2O_5$ (125) n (n= 1, 2, 3, 4, 8) clusters was calculated.

$(125)_1$ cluster:



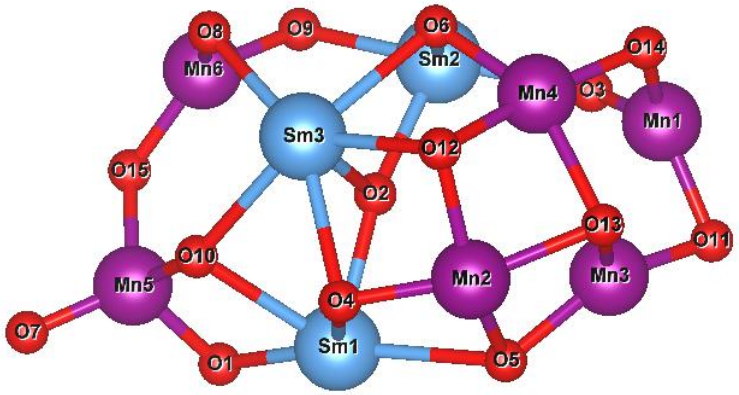
	O_1	O_2	O_3	O_4	O_5	Sm	Mn_1	Mn_2
Charge(e)	6.98	7.05	7.16	6.93	6.66	9.13	5.34	5.75
Valence Electron(e)			6			11	7	
Bader charge(e)	0.98	1.05	1.16	0.93	0.66	-1.87	-1.66	-1.25

$(125)_2$ cluster:



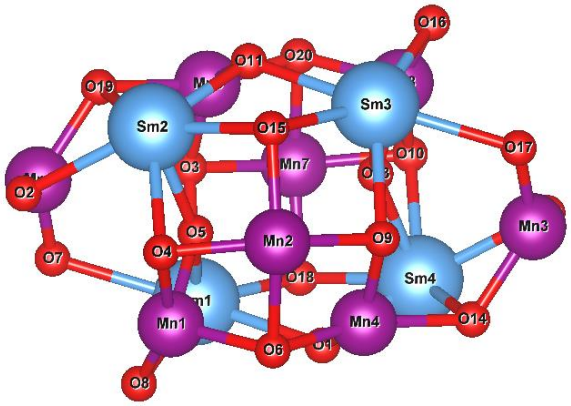
O1	0.9653	O2	0.9765	O3	0.9791	O4	0.9808
O5	0.8692	O6	0.9883	O7	0.8695	O8	0.9804
O9	0.9789	O10	0.9761	Sm1	-2.0467	Sm2	-2.0469
Mn1	-1.3684	Mn2	-1.3556	Mn3	-1.366	Mn4	-1.3805

$(125)_3$ cluster:



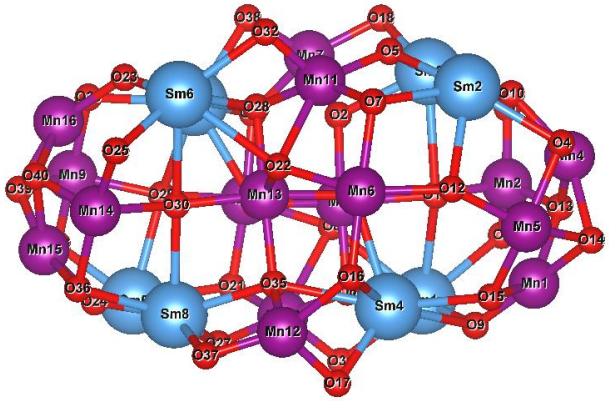
O1	0.9422	O2	1.2475	O3	0.9914	O4	1.1185	O5	1.117
O6	1.1552	O7	0.619	O8	0.9685	O9	0.9937	O10	1.0198
O11	0.9029	O12	1.0718	O13	0.9968	O14	0.9197	O15	0.8739
Sm1	-2.0394	Sm2	-2.0373	Sm3	-2.0735				
Mn1	-1.3825	Mn2	-1.4818	Mn3	-1.1796				
Mn4	-1.4997	Mn5	-1.6799	Mn6	-1.5639				

$(125)_4$ cluster:



O1	1.1715	O2	0.925	O3	1.097	O4	1.0852	O5	1.0999
O6	1.0029	O7	0.9074	O8	0.9111	O9	1.0952	O10	1.0819
O11	1.1705	O12	0.9256	O13	1.0987	O14	1.0516	O15	1.1687
O16	0.9086	O17	0.9085	O18	1.17	O19	1.051	O20	1.0047
Sm1	-2.1185	Sm2	-2.059	Sm3	-2.1147	Sm4	-2.0594		
Mn1	-1.6226	Mn2	-1.4981	Mn3	-1.5424	Mn4	-1.5822	Mn5	-1.583
Mn6	-1.5389	Mn7	-1.4977	Mn8	-1.6185				

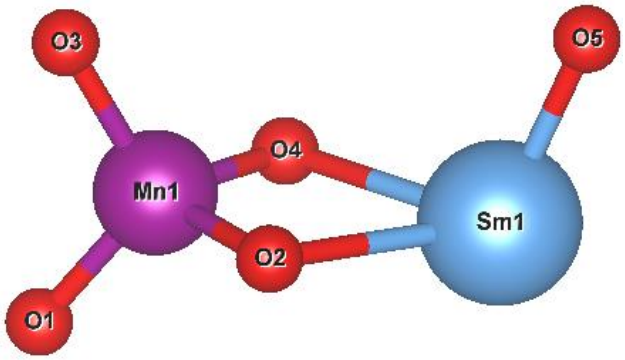
$(125)_8$ cluster:



O1	0.8109	O2	0.8721	O3	0.9098	O4	0.9205	O5	0.9457
O6	0.9554	O7	0.9662	O8	0.9828	O9	1.0007	O10	1.0071
O11	1.0188	O12	1.0274	O13	1.0314	O14	1.033	O15	1.0341
O16	1.0447	O17	1.0569	O18	1.0571	O19	1.0577	O20	1.0621
O21	1.0692	O22	1.0702	O23	1.0717	O24	1.0718	O25	1.0756
O26	1.08	O27	1.0859	O28	1.0931	O29	1.1007	O30	1.1027
O31	1.1028	O32	1.1094	O33	1.1313	O34	1.1335	O35	1.1518
O36	1.1518	O37	1.1774	O38	1.1853	O39	1.1882	O40	1.2001
Sm1	-2.0756	Sm2	-2.059	Sm3	-2.1132	Sm4	-2.101		
Sm5	-2.0429	Sm6	-2.0707	Sm7	-2.1024	Sm8	-2.112		
Mn1	-1.5398	Mn2	-1.6784	Mn3	-1.717	Mn4	-1.5178		
Mn5	-1.5194	Mn6	-1.5923	Mn7	-1.6272	Mn8	-1.5713		
Mn9	-1.5428	Mn10	-1.6521	Mn11	-1.6586	Mn12	-1.6093		
Mn13	-1.7015	Mn14	-1.4875	Mn15	-1.5319	Mn16	-1.5234		

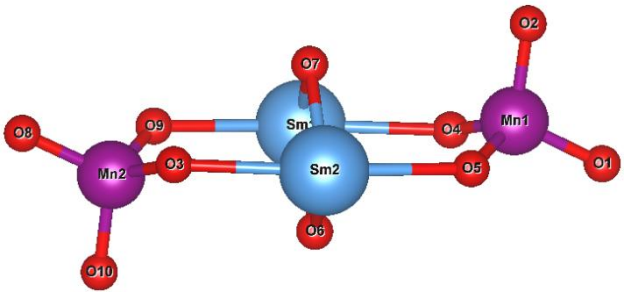
S5. The Bader charge of each atom in the ground state structure of the (115) n (n= 1, 2, 3) clusters before the intermediates are adsorbed

$(115)_1$ cluster:



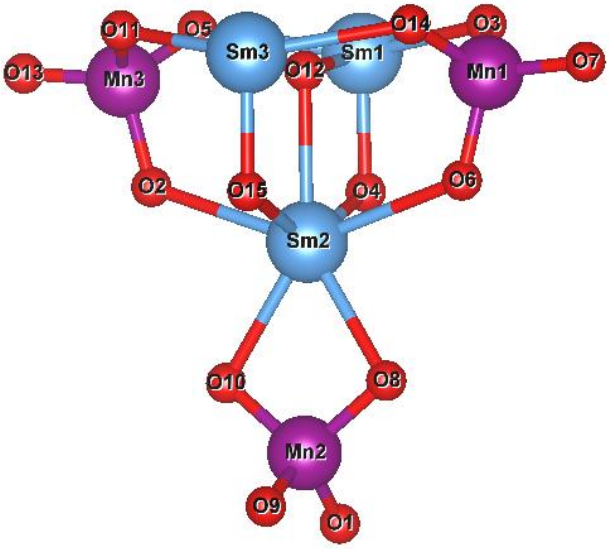
O1	0.5194	O2	0.7597	O3	0.4997	O4	0.7585	O5	1.0013
Sm1	-1.8219								
Mn1	-1.7167								

$(115)_2$ cluster:



O1	0.5033	O2	0.5176	O3	0.7812	O4	0.7830	O5	0.7828
O6	1.0985	O7	1.0972	O8	0.4977	O9	0.7831	O10	0.5185
Sm1	-1.9430	Sm2	-1.9393						
Mn1	-1.7435	Mn2	-1.7371						

$(115)_3$ cluster:



O1	0.5245	O2	0.6323	O3	0.7562	O4	1.1311	O5	0.7536
O6	0.6256	O7	0.4762	O8	0.7310	O9	0.5215	O10	0.7290
O11	0.7572	O12	1.1998	O13	0.4760	O14	0.7558	O15	1.1253
Sm1	-1.9359	Sm2	-2.1053	Sm3	-1.9358				
Mn1	-1.7450	Mn2	-1.7222	Mn3	-1.7508				

S6. The side view of the (001) slab of $SmMn_2O_5$ with N atoms passivation

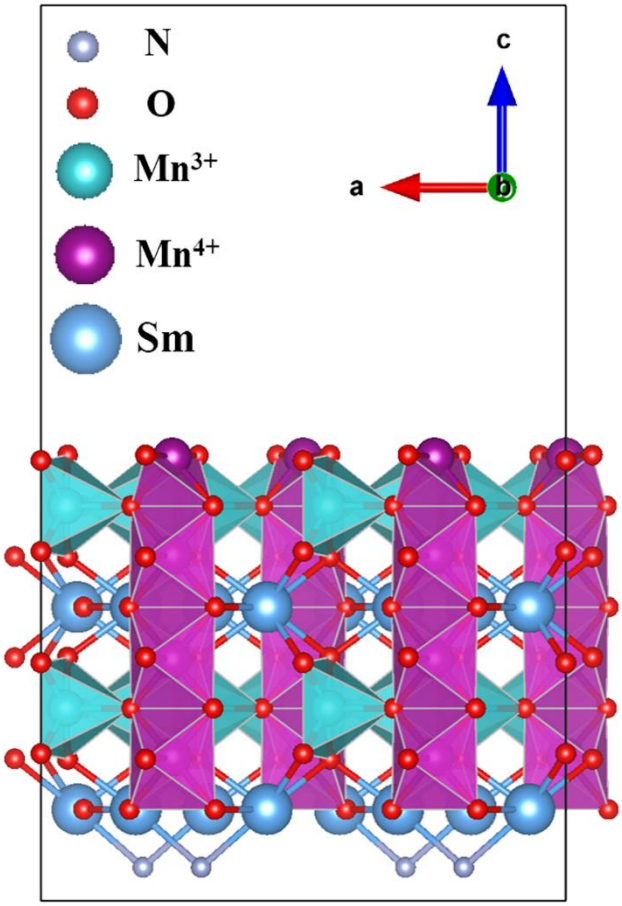


Figure S2. Side view of the 8-layers (001) slab of $SmMn_2O_5$ with passivation by N atoms. The N, O, Mn^{3+}, Mn^{4+} and Sm atoms are labeled as grey, red, green, purple, and blue, respectively.

S7. The Gibbs free energy diagrams of the (001) slab of $SmMn_2O_5$ without and with O vacancy under AEM

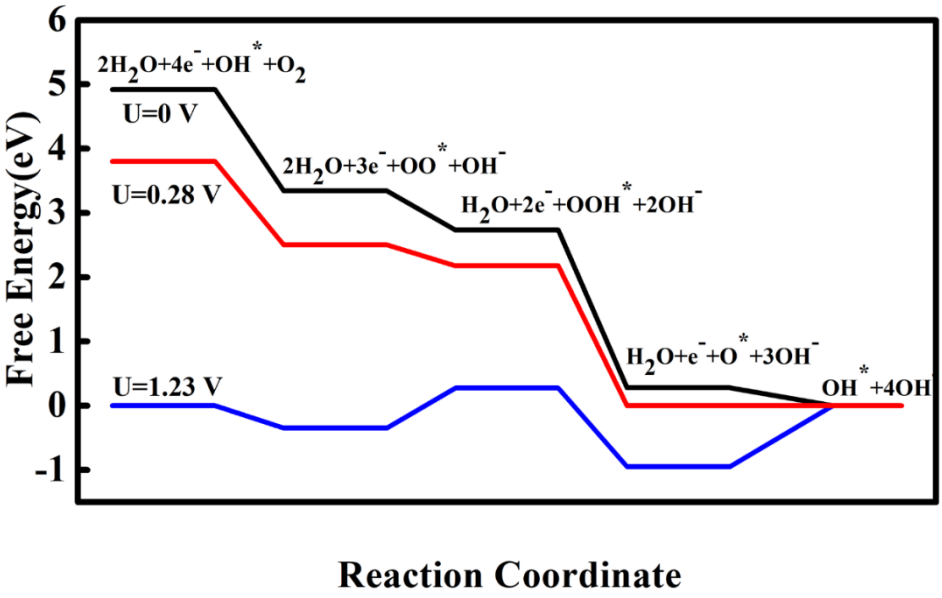


Figure S3. Free energy diagrams for oxygen reduction reaction (ORR) over $SmMn_2O_5$ (001) slab based on the AEM at zero cell potential (U=0), at the equilibrium potential (U=1.23 V), and at the highest potential (U=0.28V).

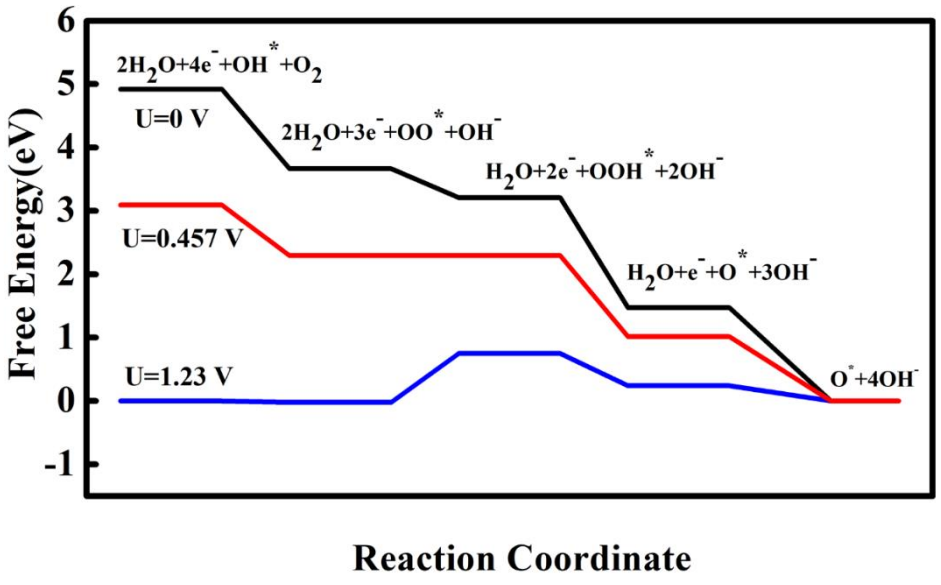


Figure S4. Free energy diagrams for oxygen reduction reaction (ORR) over $SmMn_2O_5$ (001) slab with oxygen deficiency based on the AEM at zero cell potential (U=0), at the equilibrium potential (U=1.23 V), and at the highest potential (U=0.457V).

S8. The Gibbs free energy diagrams of the (001) slab of $SmMn_2O_5$ under LOM and LAM

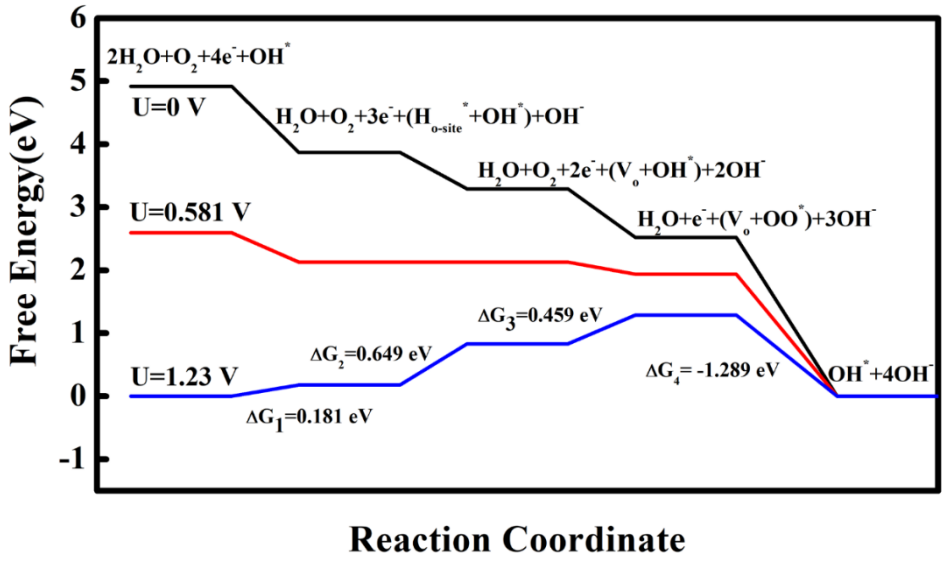


Figure S5. Free energy diagrams for oxygen reduction reaction (ORR) over $SmMn_2O_5$ (001) slab based on the LOM at zero cell potential (U=0), at the equilibrium potential (U=1.23 V), and at the highest potential (U=0.581V).

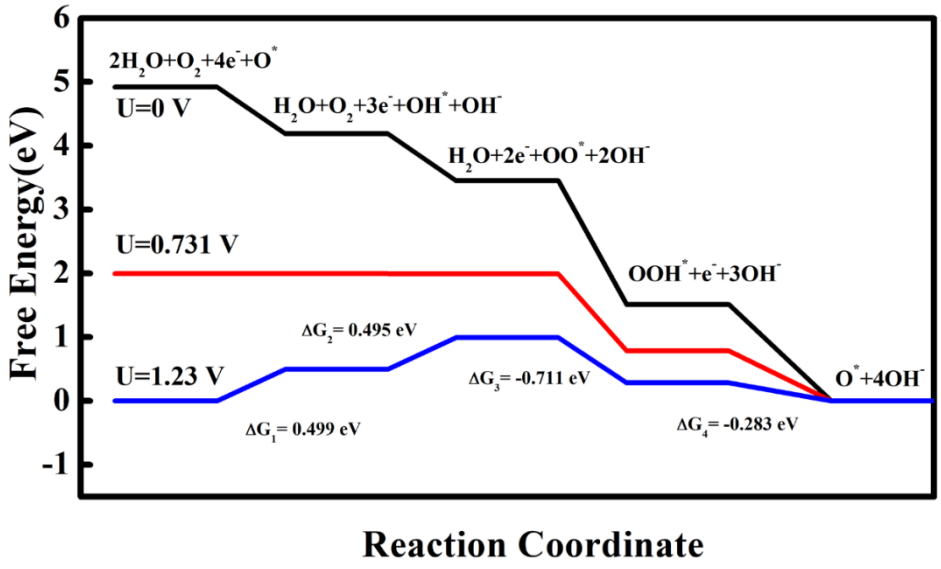


Figure S6. Free energy diagrams for oxygen reduction reaction (ORR) over $SmMn_2O_5$ (001) slab based on the LAM at zero cell potential (U=0), at the equilibrium potential (U=1.23 V), and at the highest potential (U=0.731V).

Supplementary References

S1. J. T. Mefford, X. Rong, A. M. Abakumov, W. G. Hardin, S. Dai, A. M. Kolpak, K. P. Johnston and K. J. Stevenson, *Nat. Mater.*, 2016, **7**, 11053.

S2. X. Rong, J. Parolin and A. M. Kolpak, *ACS Catal.*, 2016, **6**, 1153-1158.

S3. A. Grimaud, O. Diaz-Morales, B. Han, W. T. Hong, Y. L. Lee, L. Giordano, K. A. Stoerzinger, M. T. M. Koper and Y. Shao-Horn, *Nat. Chem.*, 2017, **9**, 457-465.

S4. J. S. Yoo, Y. Liu, X. Rong and A. M. Kolpak, *J. Phys. Chem. Lett.*, 2018, **9**, 1473-1479.

S5. J. S. Yoo, X. Rong, Y. Liu and A. M. Kolpak, *ACS Catal.*, 2018, **8**, 4628-4636.