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Supporting Information for

Theoretical Study of Y-doped Na_2ZrO_3 as a High-capacity Na-rich Cathode Material Based on Anionic Redox

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CONTENTS

Table S1 Variation of lattice parameters (in %) obtained by optimizing Na_2ZrO_3 under PBE, PBE-D3 and PBE-D2 methods compared with experimental values.

	Δa/a	Δb/b	Δc/c	Δβ/β
PBE	0.73	0.79	0.94	0.03
PBE-D3	0.16	0.10	0.55	0.02
PBE-D2	0.25	0.24	1.90	0.07

Determination of *U* in PBE+*U*.

The GGA is unable to describe the local oxygen polarons due to self-interaction errors. As early as 2005, Nalon et al.[1] successfully applied the DFT+*U* method to the study of defective oxide Li-doped MgO and also illstrated that this method can also be applied to localized O 2*p* hole states.[2] And the addition of *U* to the O 2*p* orbitals has been widely used in theoretical investigations of many materials.[3-11]

In this work, we also have a discussion on the selection of the appropriate *U* value. With Na removed from Na_2ZrO_3, oxygen oxidation reactions occur in the system, accompanied with changes of its magnetic moments. The magnetic moment is one of the references to determine whether the oxygen hole polarons is localized or non-localized. Through calculations, we find that the magnetic moments of eight oxygens in the conventional cell of $Na_{16-x}Zr_8O_{24}$ change significantly during the desodiation (The magnetic moment of oxygens are mainly concentrated on O1, O2, O3, O4, O13, O14, O15 and O16, and the absolute value of the magnetic moment of the other oxygens are less than 0.01 μ_B, which is negligible). Therefore, we tested the effects of different *U* values applied to the 2p orbitals of O in $Na_{15}Zr_8O_{24}$ on the magnetic moments of O. The PBE+U results were compared with the ones by HSE06 functional in Table S1.

Here, we introduce a parameter *r* (*r* represents the change-ratio), defined as:

$$\boldsymbol{r = \frac{\mu_{B-tot} - \mu_{B-sum}}{\mu_{B-tot}}}$$

where $\mu_{B\text{-total}}$ represents the sum of magnetic moments of all oxygens and $\mu_{B\text{-sum}}$ represents the sum of magnetic moments of the corresponding 8 oxygens. As shown in Table S1, when $U = 0$, the hole is delocalized and the difference between $\mu_{B\text{-total}}$ and $\mu_{B\text{-sum}}$ is large (the change-ratio is 41.92%). With the value of *U* increasing, *r* decreases continuously. When $U = 6$ eV, the change-ratio (*r*) is close to those obtained by HSE06 functional. Hence, $U = 6$ eV was chosen for O of $Na_{16-x}Zr_8O_{24}$ ($0 < x < 16$) in the PBE+*U* calculation.

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Table S2 The magnetic moments (μ_B) of eight oxygens in $Na_{15}Zr_8O_{24}$ by PBE+*U*-D3 and HSE06-D3.

Method	*U* (eV)	Magnetic moments (μ_B) of eight oxygens in $Na_{15}Zr_8O_{24}$										
		O1	O2	O3	O4	O13	O14	O15	O16	$\mu_{B\text{-}sum}$	$\mu_{\text{B-total}}$	*r* (%)
PBE+*U*-D3	0	0.031	0.031	0.011	0.011	0.200	0.200	0.006	0.006	0.496	0.854	41.92
	1	0.013	0.013	0.005	0.005	0.313	0.313	0.002	0.002	0.666	0.876	23.97
	2	0.006	0.006	0.003	0.003	0.368	0.368	0.001	0.001	0.756	0.886	14.67
	3	0.003	0.003	0.003	0.003	0.395	0.395	0.001	0.001	0.804	0.902	10.86
	4	0.002	0.002	0.002	0.002	0.414	0.414	0.001	0.001	0.838	0.916	8.52
	5	0.002	0.002	0.002	0.002	0.431	0.431	0.000	0.000	0.870	0.936	7.05
	6	0.001	0.001	0.002	0.002	0.446	0.446	0.000	0.000	0.898	0.950	5.47
	7	0.001	0.001	0.002	0.002	0.460	0.460	0.000	0.000	0.926	0.968	4.34
	8	0.001	0.001	0.001	0.001	0.474	0.474	0.000	0.000	0.952	0.988	3.64
HSE06-D3	-	0.002	0.002	0.002	0.002	0.420	0.42 0	0.000	0.000	0.848	0.902	5.99

Table S3 Distances (Å) between different types of oxygen and surrounding Na and Zr atoms of NZO by PBE+*U*-D3. [a]

	Zr1	Zr2	Na1	Na2	Na3	Na4
O_A	2.114	2.103	2.366	2.334	2.517	2.539
O_B	2.107	2.107	2.372	2.335	2.551	2.515
O_C	2.131	2.121	2.374	2.285	2.442	2.432

[a] Zr1 represents the Zr atom farther from the O atom, and Zr2 represents the Zr atom closer to the O atom. Na1 represents the Na atom in the mixed layer, Na2 is opposite to Na1, and Na3 and Na4 are opposite to Zr1 and Zr2, respectively (details are in **Figure S1**).

Table S4 Comparison of lattice parameters of $Na_{32}Zr_{16}O_{48}$ and $Na_{32}Zr_{14}Y_2O_{47}$ from the PBE+*U*-D3 functional and experimental data.[a]

	a (Å)	b (Å)	c (Å)	b (°)
$Na_{32}Zr_{16}O_{48}$	5.61	9.74	11.07	100.00
$Na_{32}Zr_{14}Y_2O_{47}$	5.64	9.79	11.03	100.09
Experimental (for Y-Na_2ZrO_3)	5.633	9.815	11.120	99.764

[a] Even though the calculations are based on the 2×1×1 supercells, the lattice parameters here refer to the conventional cell for batter comparison with the experimental values.

Table S5 Lattice constants and volumes of the lowest-energy $Na_{16-x}Zr_8O_{24}$ (x = 1 ~ 12) by PBE+U-D3.

x	a (Å)	b (Å)	c (Å)	α(°)	β (°)	γ (°)	V (Å3)	Volume change[a] (%)
0	5.59	9.70	11.02	90.00	100.00	90.00	588.23	-
1	5.61	9.76	11.01	90.00	100.39	90.00	592.39	0.71
2	5.62	9.85	10.97	90.00	100.35	90.00	597.35	1.55
3	5.66	9.93	10.98	90.00	100.95	90.00	606.13	3.04
4	5.70	10.07	10.87	90.00	100.65	90.00	613.24	4.25
5	5.71	10.22	10.72	89.47	99.40	88.89	616.77	4.85
6	5.69	10.39	10.37	89.27	96.09	87.46	609.16	3.56
7	5.70	10.52	10.28	88.22	95.56	89.64	613.01	4.21
8	5.69	10.71	10.12	87.90	94.42	91.17	613.98	4.38
9	5.72	10.79	10.11	85.32	94.99	91.80	619.34	5.29
10	5.73	10.87	9.97	88.73	94.11	90.78	619.54	5.32
11	5.90	11.30	8.34	62.73	93.03	96.16	491.32	-16.48
12	5.94	11.97	9.34	52.95	96.83	103.23	515.50	-12.37

[a] Relative to the initial $Na_{16}Zr_8O_{24}$ conventional unit cell, i.e., x = 0.

Table S6 The magnetic moments of oxygens[a] of $Na_{16-x}Zr_8O_{24}$ calculated by PBE+*U*-D3 and HSE06-D3 functionals, whose absolute values are greater than 0.01 μ_B.

	x	O1	O2	O3	O4	O13	O14	O15	O16	$\mu_{B\text{-sum}}$ [b]	$\mu_{B\text{-total}}$ [b]
PBE+*U*-D3	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	1	0.00	0.00	0.00	0.00	0.45	0.45	0.00	0.00	0.90	0.95
	2	0.00	0.00	0.00	0.00	0.45	0.45	0.45	0.45	1.80	1.90
	3	0.46	0.46	0.00	0.00	0.45	0.45	0.46	0.46	2.74	2.86
	4	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46	3.68	3.82
	5	0.42	0.51	0.53	0.40	0.31	0.61	0.00	0.00	2.78	2.85
	6	0.00	0.00	0.34	0.58	0.34	0.58	0.00	0.00	1.84	1.91
	7	0.00	0.00	0.33	0.60	0.00	0.00	0.00	0.00	0.93	0.95
	8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	9	-0.43	-0.45	0.00	0.00	0.00	0.00	0.00	0.00	-0.88	-0.91
	10	0.00	0.00	0.00	0.00	-0.43	-0.46	-0.46	-0.41	-1.76	-1.81
	11	0.00	0.00	-0.51	-0.36	0.45	0.44	0.41	0.47	0.90	0.91
	12	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.43	3.44	3.53
HSE06-D3	1	0.00	0.00	0.00	0.00	0.42	0.42	0.00	0.00	0.84	0.88

[a] The magnetic moment of oxygens are mainly concentrated on O1, O2, O3, O4, O13, O14, O15 and O16, and the absolute value of the magnetic moment of the other oxygens are less than 0.01 μ_B, which is negligible.

[b] $\mu_{B\text{-sum}}$ represents the sum of magnetic moments of the corresponding 8 oxygens (O1, O2, O3, O4, O13, O14, O15 and O16), and $\mu_{B\text{-total}}$ is the sum of magnetic moments of all oxygens.

Table S7 The magnetic moments of oxygens[a] of $Na_{16-x}Zr_8O_{24}$ calculated by PBE-D3 functional, whose absolute values are greater than 0.06 μ_B.

	x	O1	O2	O3	O4	O13	O14	O15	O16	$\mu_{B\text{-sum}}$[b]	$\mu_{B\text{-total}}$[b]
PBE	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	1	0.03	0.03	0.01	0.01	0.20	0.20	0.01	0.01	0.50	0.85
	2	0.03	0.03	0.03	0.03	0.27	0.27	0.28	0.28	1.22	0.72
	3	0.35	0.35	0.01	0.01	0.33	0.33	0.36	0.36	2.10	2.55
	4	-0.38	-0.38	0.38	0.38	0.38	0.38	-0.38	-0.38	0.00	0.00
	5	0.39	0.40	0.40	0.38	0.36	0.43	0.00	0.00	2.36	2.56
	6	0.00	0.00	-0.37	-0.42	0.37	0.42	0.00	0.00	0.00	0.00
	7	0.00	0.00	-0.37	-0.43	0.00	0.00	0.00	0.00	-0.77	-0.85
	8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	9	-0.20	-0.21	-0.06	-0.07	-0.01	-0.01	-0.11	-0.12	-0.79	-0.84
	10	0.19	0.19	0.18	0.20	0.19	0.19	0.20	0.19	1.53	1.68
	11	-0.19	-0.17	-0.30	-0.26	-0.36	-0.36	-0.33	-0.35	-2.32	-2.53
	12	-0.38	-0.38	0.39	0.38	0.39	0.39	0.39	0.39	1.57	1.63

[a] The magnetic moment of oxygens are mainly concentrated on O1, O2, O3, O4, O13, O14, O15 and O16, and the absolute value of the magnetic moment of the other oxygens are less than 0.06 μ_B, which is negligible.

[b] $\mu_{B\text{-sum}}$ represents the sum of magnetic moments of the corresponding 8 oxygens (O1, O2, O3, O4, O13, O14, O15 and O16), and $\mu_{B\text{-total}}$ is the sum of magnetic moments of all oxygens.

Table S8 Migration energy barriers[b] of Na ion by PBE+*U*-D3 in different pathways from the mixed layer to the pure Na layer of NZO and Y-NZO along *c* direction.

	Migration barriers (eV)	
Paths	NZO	Y-NZO
Na2 → Na4	0.56 (0.80)	0.50 (0.60)
Na2 → Na5	0.52 (0.80)	0.75 (0.61)
Na2 → Na6	0.53 (0.80)	0.62 (0.62)
Na2 → Na3	0.52 (0.75)	0.77 (0.77)
Na2 → Na15	0.48 (0.76)	0.58 (0.72)
Na2 → Na16	0.48 (0.76)	0.55 (0.63)

[b] The reverse migration barriers are shown in brackets.

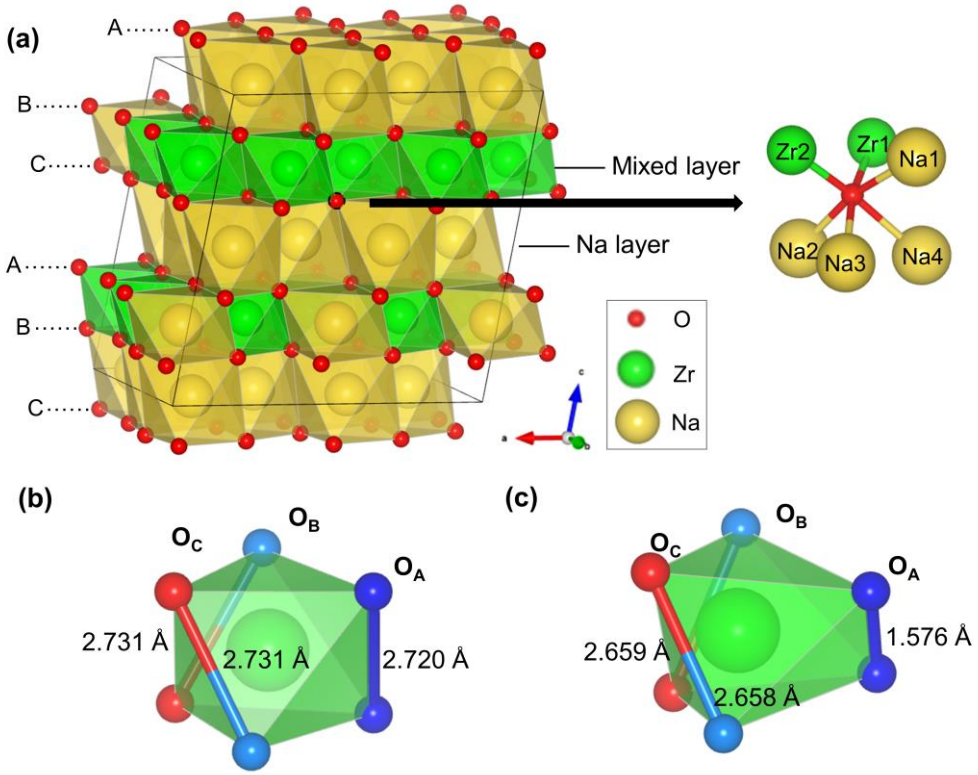

Fig. S1 (a) The coordination environment of oxygen and (b) the ZrO_6 octahedron from the initial Na_2ZrO_3 compound using PBE+*U*-D3 functional. (c) The ZrO_6 octahedron after half Na desodiation (PBE+*U*-D3). The blue, light blue and red balls in (b) and (c) represent O_A, O_B and O_C, respectively.

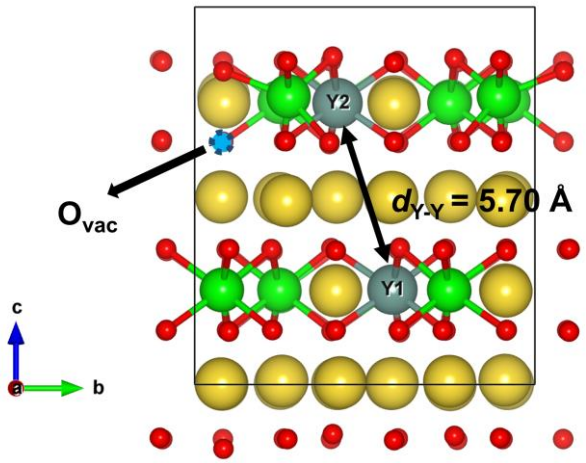

Fig. S2 The structure of Y-doped NZO with the lowest energy by PBE+*U*-D3.

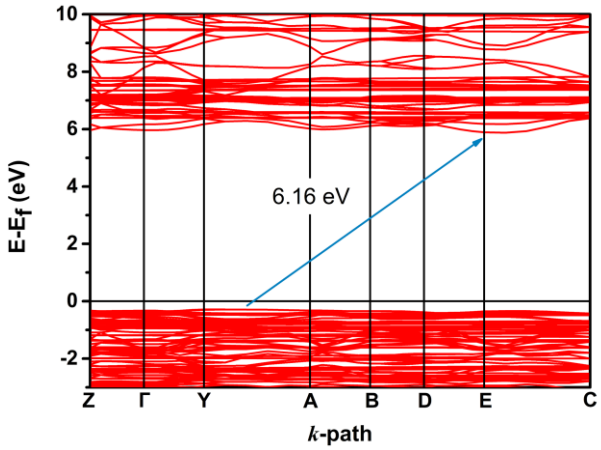

Fig. S3 Band structure of NZO calculated using HSE06-D3, showing an indirect band gap of 6.16 eV.

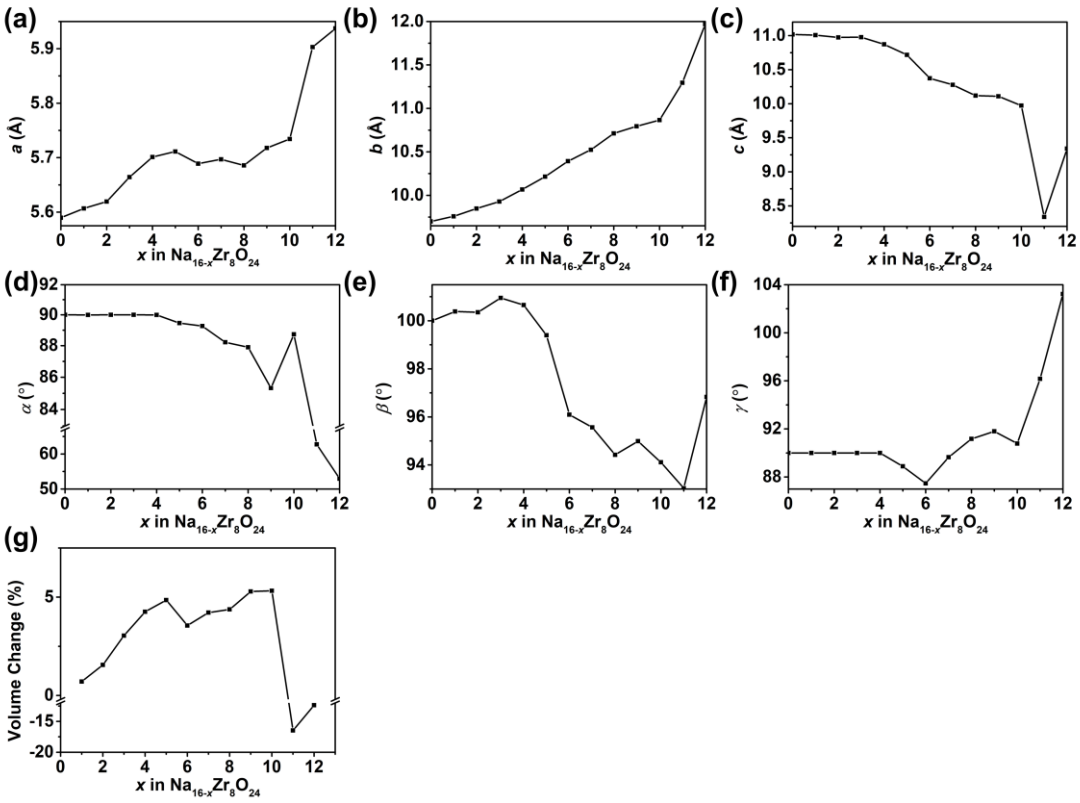

Fig. S4 The variation of lattice constants *a*, *b*, *c*, *α, β, γ* and volumes with *x* in $Na_{16-x}Zr_8O_{24}$ by PBE+*U*-D3.

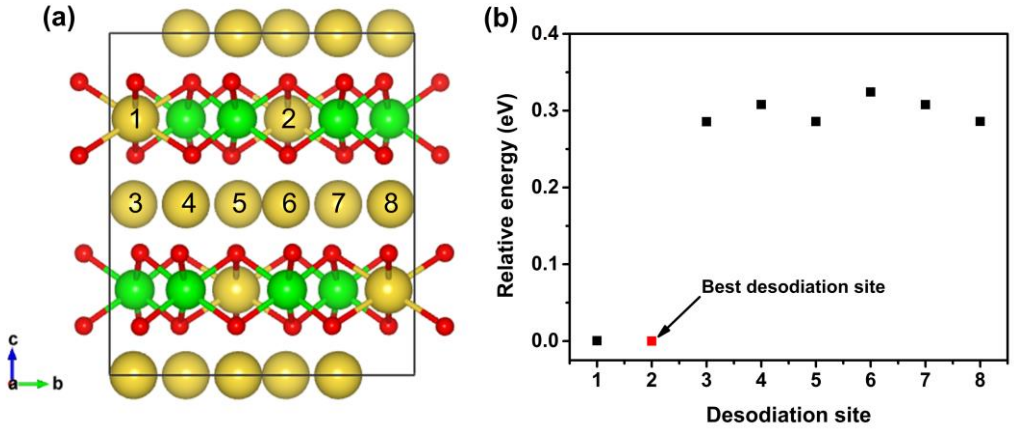

Fig. S5 (a) The structure of NZO with different Na atoms at the mixed $Na_{1/3}Zr_{2/3}$ layer and pure Na layer labelled. (b) The relative energies of $Na_{15}Zr_8O_{24}$ with a Na vacancy at different positions. The best desodiation site is in the mixed layer.

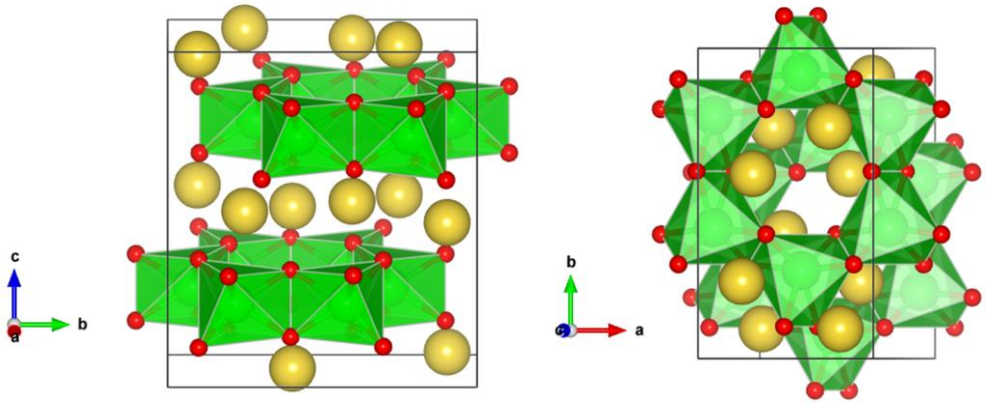

Fig. S6 The frame structure of ZrO_6 honeycomb layer and pure sodium layer alternately arranged from different views after all of Na atoms in the mixed layer are removed. The red and yellow ball represent the O and Na, respectively. The green octahedron represents ZrO_6.

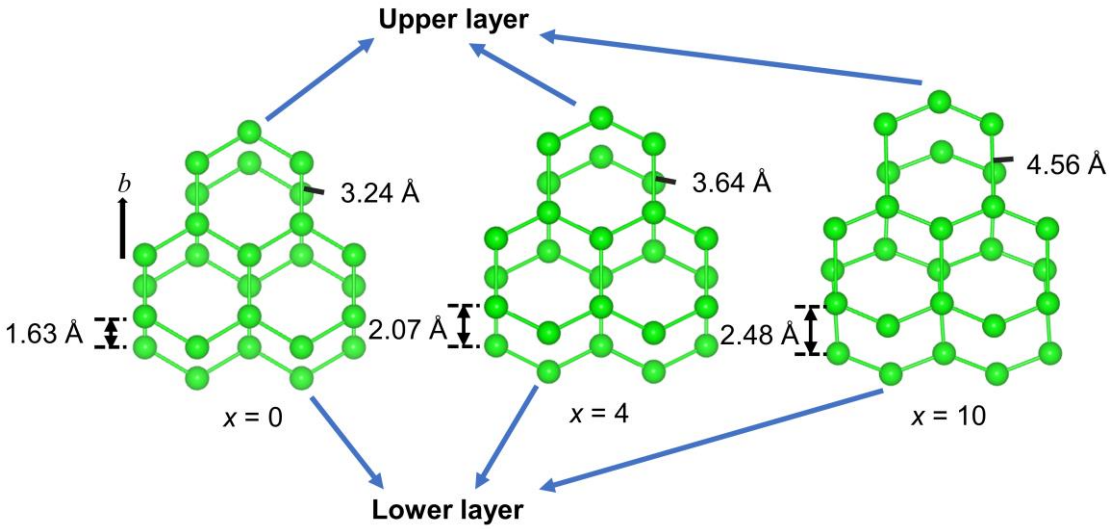

Fig. S7 Honeycomb structures of Zr in $Na_{16-x}Zr_8O_{24}$ (x = 0, 4, 10). The lower distances 1.63, 2.07, 2.48 Å are the shifts between the upper and lower honeycomb structure of Zr along *b* direction. The upper distances 3.24, 3.64, and 4.56 Å are the Zr-Zr distances.

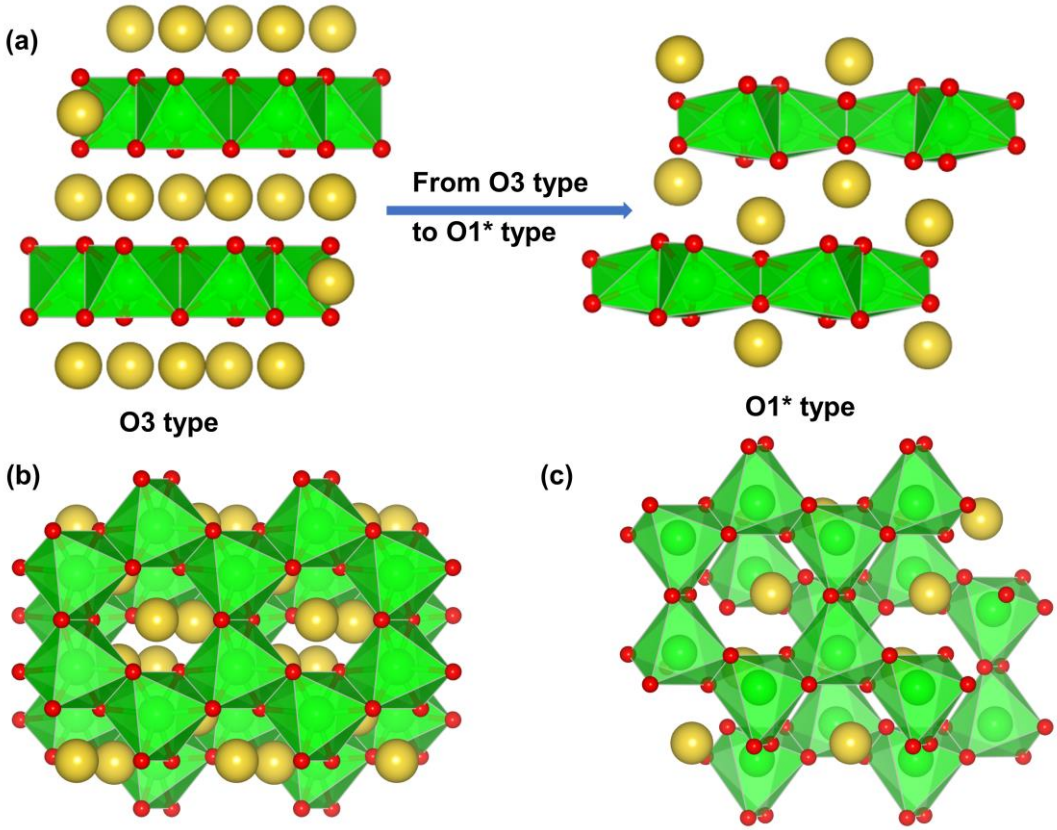

Fig. S8 (a) The newly formed O1*-type structure after removing 8Na from $Na_{16}Zr_8O_{24}$. The top view of O3 (b) and O1* (c) type.

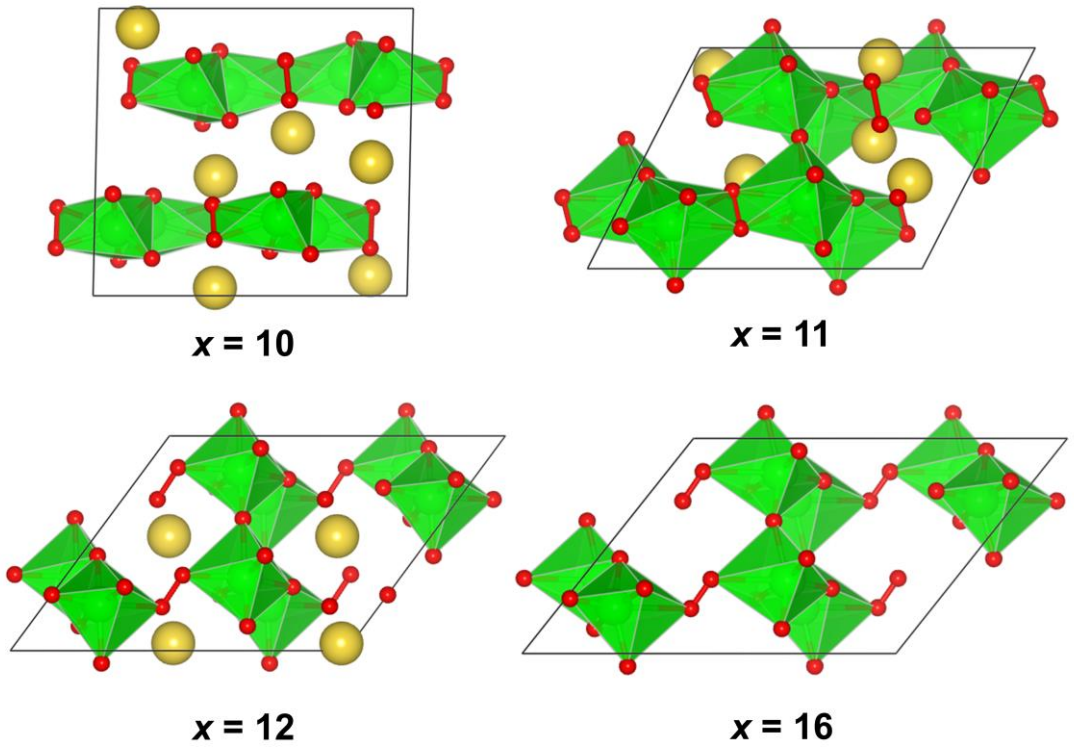

Fig. S9 The structures of $Na_{16-x}Zr_8O_{24}$ (x = 10, 11, 12 and 16) and layer structures will be completely distorted and shift to ZrO_3 phase when x > 10.

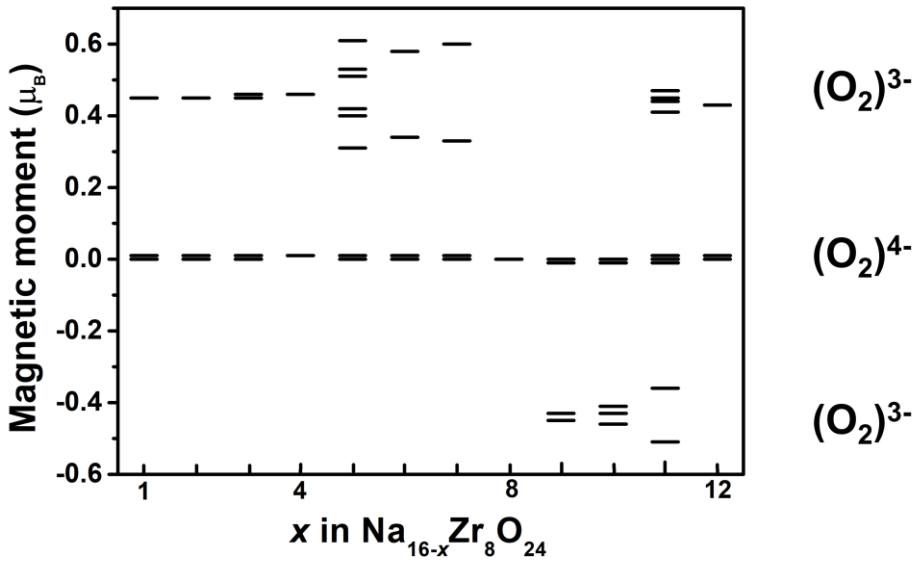

Fig. S10 The magnetization of O ions during desodiation of NZO by PBE+*U*-D3.

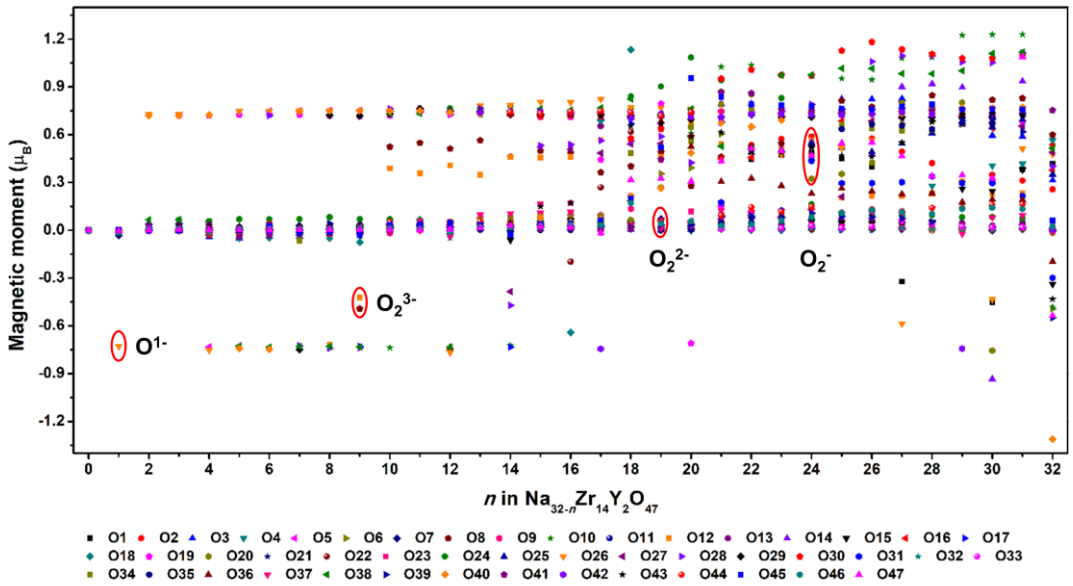

Fig. S11 The magnetization of O ions during desodiation of optimal $Na_{32-n}Zr_{14}Y_2O_{47}$ ($0 \leq n \leq 32$) by PBE+*U*-D3. The various symbols represent the 47 unique O ions in Y-NZO.

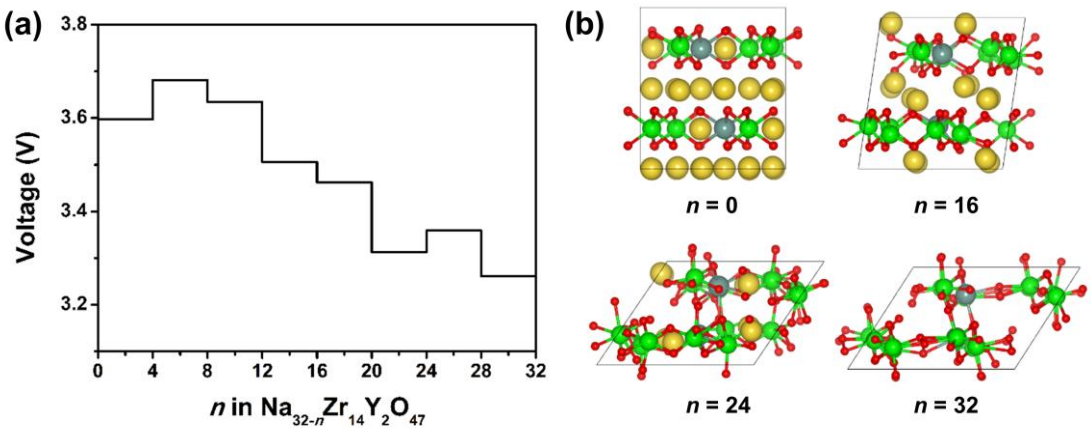

Fig. S12 (a) The calculated desodiation potentials of $Na_{32-n}Zr_{14}Y_2O_{47}$ ($0 \leq n \leq 32$) by PBE+*U*-D3. (b) The optimal structures of $Na_{32-n}Zr_{14}Y_2O_{47}$ for n = 0, 16, 24, and 32, respectively.