Electronic Supplementary Information for

Atomistic understanding of structural evolution, ion transport and oxygen stability in layered $NaFeO_2$

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Table 1S. The lattice parameters of Na_xFeO_2 (x = 1, 0.67, 0.5 and 0.33) and the average thickness of FeO_6 (d1) and NaO_6 slabs (d2), unit spacing (d), and bond distance of Fe-O (d_{Fe-O}) in them.

	x	***a***	***b***	***c***	***α***	***β***	***γ***	**d1**	**d2**	**d**	**d_{Fe-O}**
Expt.[a]	1	3.03	3.03	16.10	90	90	120				
	0.36	5.27	2.90	5.92	90		90				
Calc.[b]	1	3.04	3.04	16.10	90	90	120	2.18	3.18	5.37	2.07
	0.67	2.99	2.99	16.57	90	90	120	2.12	3.40	5.52	2.03
	0.5	5.23	2.94	5.94	90	108	90	2.08	3.58	5.65	2.00
	0.33	5.19	2.94	5.99	90	107	90	2.03	3.71	5.74	1.98

Note: [a] data from reference 1; [b] data calculated in this work.

Table 2S. The energy barriers for Na hop in $NaFeO_2$ with different in-plane and out-of-plane (c-direction) strains.

strain	+6.25%	+5%	+3%	+1%	0	-1%	-3%	-5%	-6.25%
Ea(*ab*) / eV	---	0.175	0.182	0.202	0.209	0.214	0.232	0.252	---
Ea(*c*) / eV	0	0.013	0.062	0.156	0.209	0.269	0.400	0.580	0.709

The energy of Na_xFeO_2 (x = 1, 0.67, 0.5 and 0.33) with O1, O2 and O3 stacking, where O3 stacking further includes the C2/m and R$\bar{3}$m structure, are calculated. The results are shown by solid black line with solid squares in Figure 1S, indicating that the O3 stacking Na_xFeO_2 has the lowest energy in the range of $0.33 \leq x \leq 1$. Therefore, the O3 stacking Na_xFeO_2 tend not to transit into the O1 nor O2 even when as much as 0.67 Na ions removed. Moreover, for x = 1 and 0.67, the R$\bar{3}$m structured Na_xFeO_2 is energetically more stable than the C2/m structured, while the latter is energetically more stable than the former when x = 0.5 and 0.33, consistent with the experimental results and confirming the rationalization of our models. When biaxial strain within 0.03 or uniaxial strain within 0.05 is applied, the O3 stacking Na_xFeO_2 still has lower energy than the O1 and O2 stacking Na_xFeO_2, although the C2/m structured Na_xFeO_2 may display slight lower energy than the R$\bar{3}$m structured when x = 1 and 0.67 or the R$\bar{3}$m structured Na_xFeO_2 may show slight lower energy than the C2/m structured when x = 0.5 and 0.33 at some certain strains. One thing to notice is that the energy difference of R$\bar{3}$m and C2/m structured Na_xFeO_2 at these special strains is in the order of 0.01 eV or smaller, which is about the error of the DFT calculations and negligible compared with the energy change in diffusion barriers and $\triangle G$ caused by the strains (in the order of 0.1 eV or larger). Moreover, the R$\bar{3}$m structure (at x = 1 and 0.67) or the C2/m structure (at x = 0.5 and 0.33) can be maintained in most cases when strain applied since the strains applied in this work is rather small. Therefore, we directly applied strains on the R$\bar{3}$m-structured Na_xFeO_2 at x = 1, 0.67 and the C2/m-structured Na_xFeO_2 at x = 0.5 and 0.33.

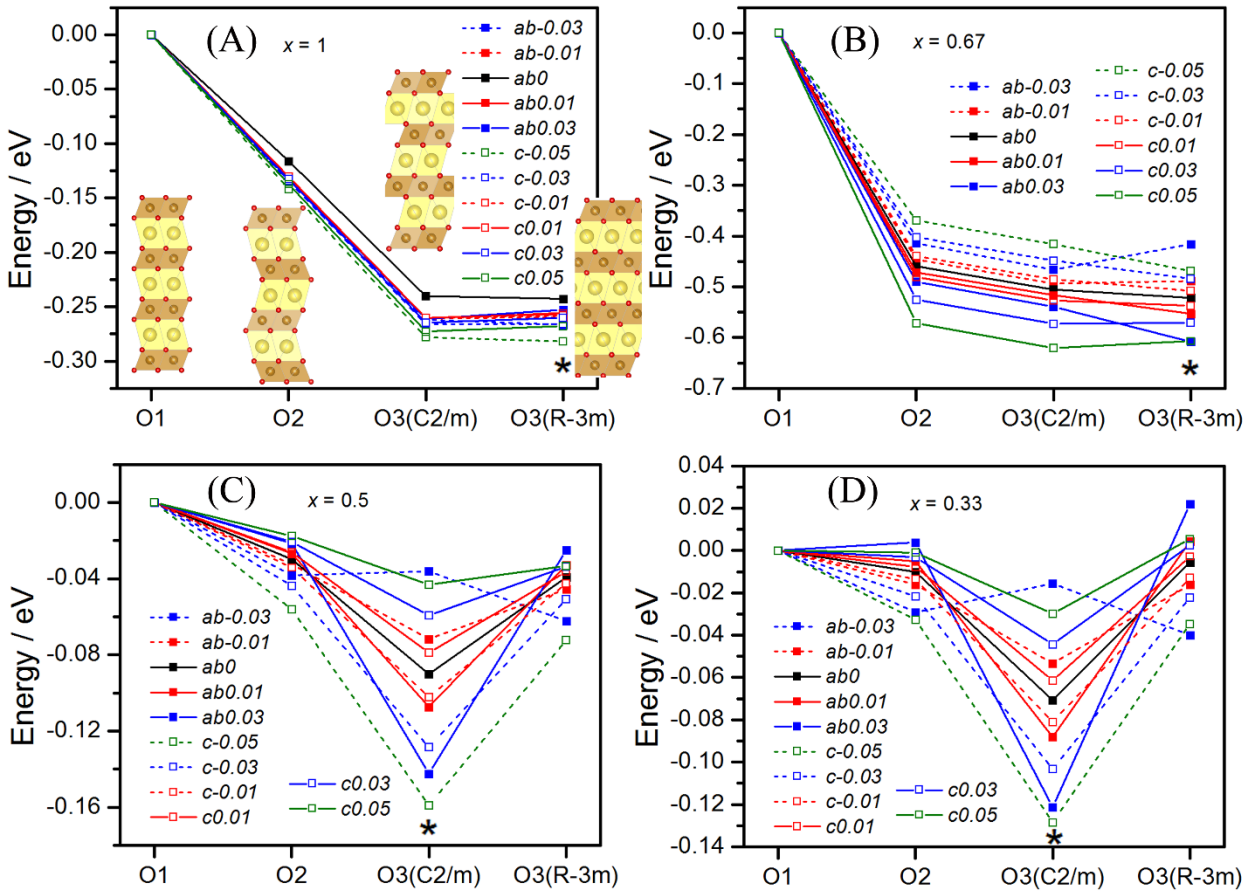

Figure 1S. Total energy of Na_xFeO_2 in the O1, O2 and O3 (including C2/m and R$\bar{3}$m) stacking structures under strains (positive for tension and negative for compression in the *ab* plane or in the *c*-direction) at x = 1 (A), 0.67 (B), 0.5 (C) and 0.33 (D). The energy of Na_xFeO_2 with the O1 stacking is set to zero.

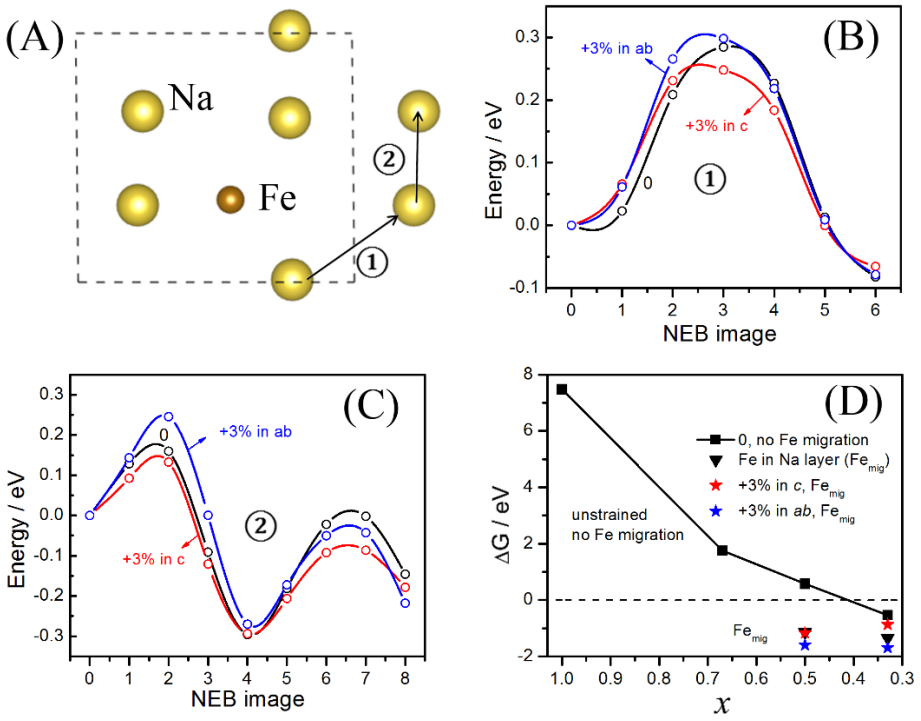

Figure 2S. Diffusion energy barriers for Na ion along two continuous pathways (A) after Fe^{3+} ion moving into the Na layer with or without strains (B and C for pathway 1 and 2, respectively). Gibbs free energy ($\triangle G$) of O_2 release (D) from $Na_{0.33}FeO_2$ and $Na_{0.5}FeO_2$, each containing one Fe^{3+} at the Na layer without strain (inverted black triangles), with 3% uniaxial tension in *c*-direction (red stars), 3% biaxial tension in the *ab* plane (blue stars). $\triangle G$ of O_2 release from Na_xFeO_2 (x = 1, 0.67, 0.5 and 0.33) without strain is shown in black line with squares for comparison.

References

1. Y. J. Li, Y. R. Gao, X. F. Wang, X. Shen, Q. Y. Kong, R. C. Yu, G. Lu, Z. X. Wang and L. Q. Chen, *Nano Energy*, 2018, **47**, 519.