Electronic Supporting Information (ESI)

Theoretical understanding of oxygen stability in Mn−Fe binary layered oxides for sodium-ion batteries

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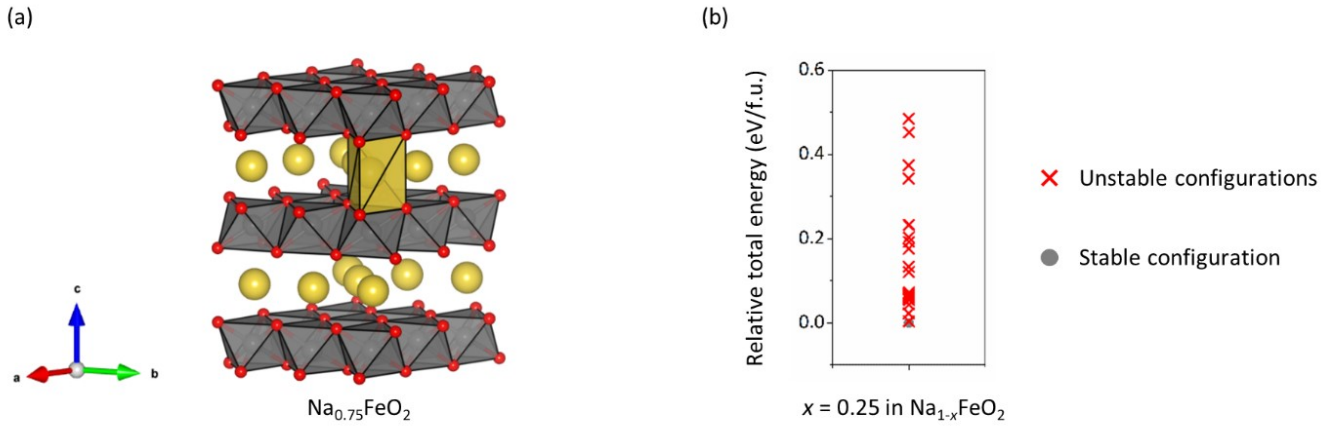

Figure S1. (a) An atomic structure of $Na_{0.75}FeO_2$, which is modeled by referring to the structural information of NMFO.[1] (b) Relative total energies considering all possible Na/vacancy mixed cases at x = 0.25 in $Na_{1-x}FeO_2$ (containing 8 f.u.). Stable configuration (gray filled circle) indicates the ground state structure having the lowest DFT energy.

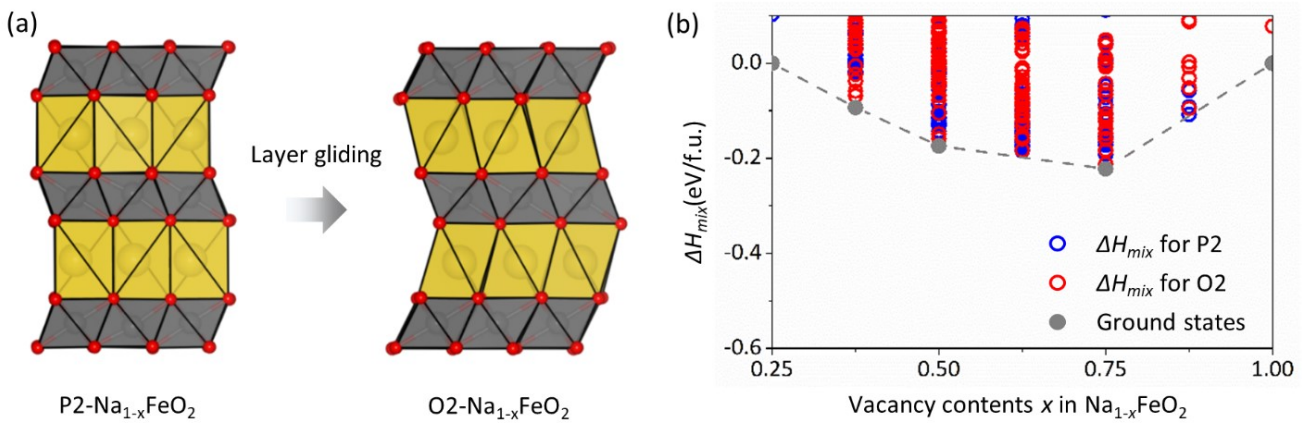

Figure S2. (a) The atomic structures of P2-$Na_{1-x}FeO_2$ and O2-$Na_{1-x}FeO_2$ at x = 0.25. The atomic models of pristine O2 stacking NFO were obtained by gliding transition metal slabs by (1/3, 2/3, 0) direction of P2-NFO ground state structure.[2] (b) Convex hull diagram considering possible phase transition during charging process. Filled gray circles on the dashed line indicates the ground states, which means the lowest ΔH_{mix} values among values at thermodynamically stable phases determined by convex hull analysis. The rest of the ΔH_{mix} values were named according to their stacking sequence of the atomic models.

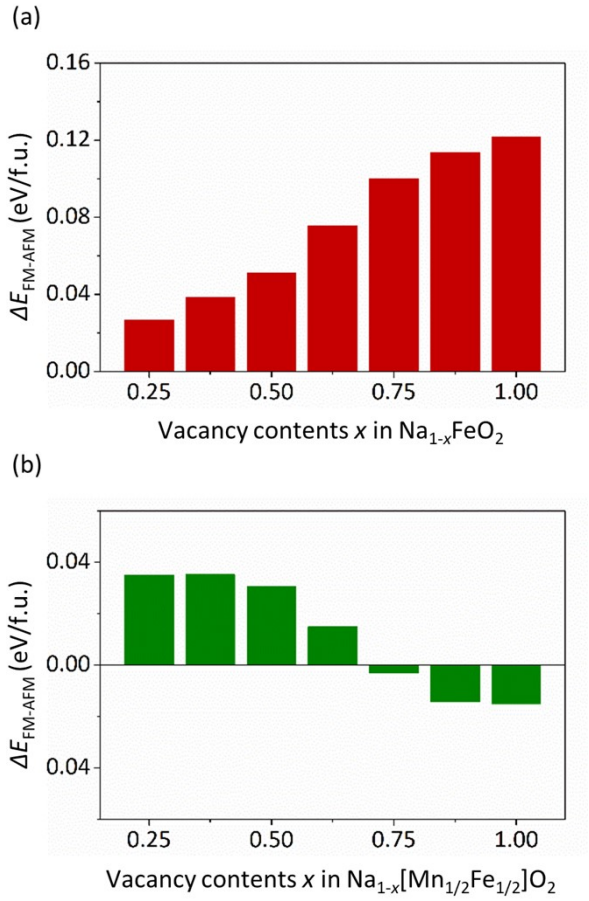

Figure S3. Energy difference between the ferromagnetic (FM) and antiferromagnetic (AFM) (ΔE_{FM-AFM}) of (a) $Na_{1-x}FeO_2$ and (b) $Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ in the vacancy range of $0.25 \leq x \leq 1.0$. The $\Delta E_{FM-AFM} > 0$ indicates that AFM is the energetically favorable spin ordering, whereas negative energy difference ($\Delta E_{FM-AFM} < 0$) presents that FM is the stable magnetic ordering.

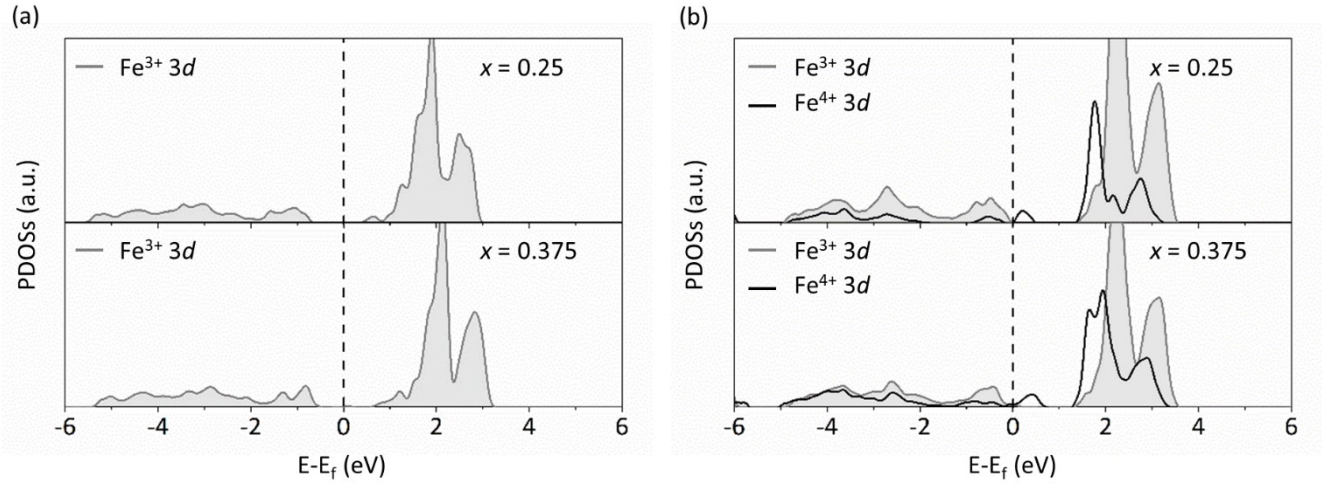

Figure S4. Partial density of states (PDOSs) of Fe^{3+} (gray) and Fe^{4+} (black) *3d*-electron at $x = 0.25$ and 0.375 for (a) $Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ and (b) $Na_{1-x}FeO_2$. The change of PDOSs for Fe^{3+} in the valence band (-1.0 eV ≤ $E-E_f$ ≤ 0.0 eV) and those for Fe^{4+} in the conduction band (0.0 eV ≤ $E-E_f$ ≤ 1.0 eV) presents the cationic redox reaction of Fe^{3+}/Fe^{4+} during $0.25 \leq x < 0.5$ in $Na_{1-x}FeO_2$

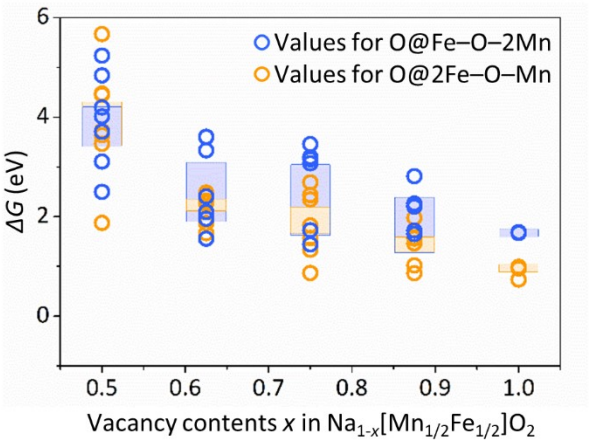

Figure S5. *ΔG* values for O@Fe-O-2Mn (blue) and O@2Fe-O-Mn (orange). Orange and blue shaded regions represent confidence interval 75% for values of O@Fe-O-2Mn and O@2Fe-O-Mn, respectively, indicating that the majority of *ΔG* values for each oxygen site are highly localized within the confidence interval.

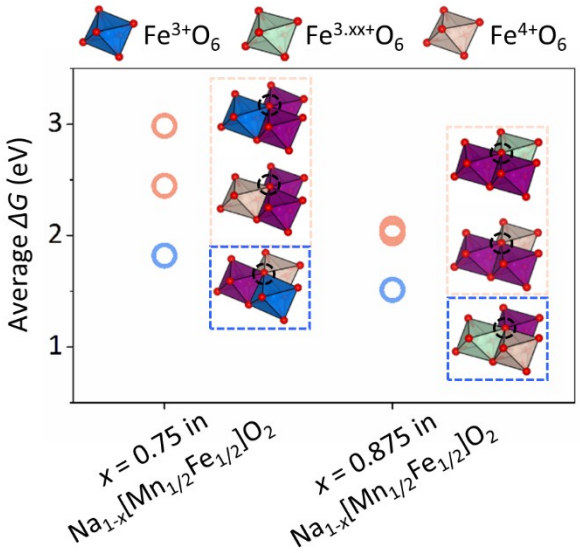

Figure S6. Averaged *ΔG* of oxygen surrounded by various Fe oxidation numbers in the ground states of $Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ at x = 0.75 and 0.875. To clearly compare the energy value with respect to the valence of surrounding Fe ions, the error bar is not included. Blue circles and orange circles present energy values for 2Fe−O−Mn and Fe−O−2Mn oxygen site. The blue and orange dashed boxes highlight that oxygen site classified by Fe coordination numbers can be further divided according to the valence states of surrounding Fe ions.

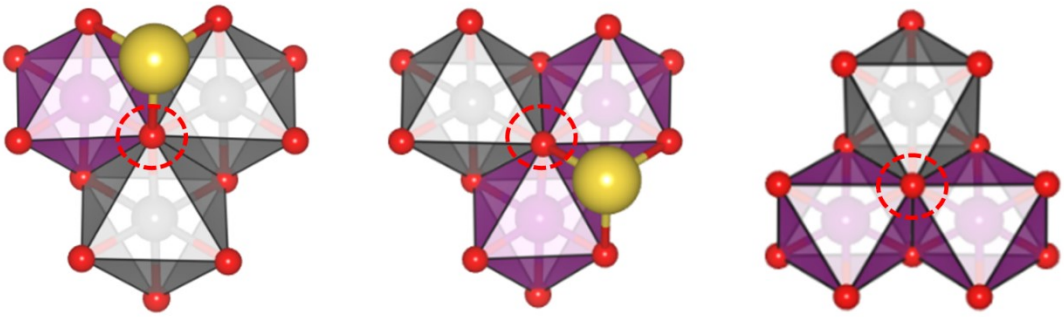

Figure S7. The surrounding Na environment around oxygen having the ΔG values used to calculate averaged ΔG of O@2Fe−O−Mn and O@Fe−O−2Mn at x = 0.625. As shown in figure, all O@2Fe−O−Mn atoms are coordinated with adjacent Na atom, whereas, Na atoms are not presented around the majority of O@Fe−O−2Mn atoms (~67%).

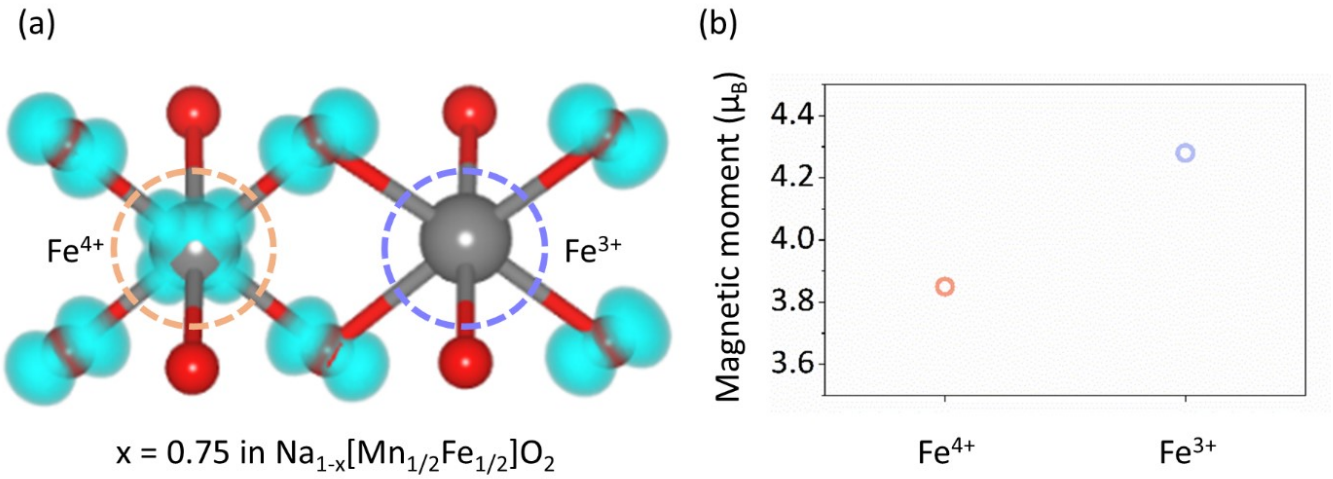

Figure S8. (a) Calculated spatial hole densities for Fe atoms at $x = 0.75$ in $Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$. Light orange and blue dashed circle represents Fe^{4+} and Fe^{3+} atoms, respectively. (b) Calculated magnetic moment of Fe^{4+} and Fe^{3+} ions. The calculated magnetic moment value of Fe^{3+} (~4.3 μ_B) is well agreed to that of high-spin state of the Fe^{3+} (4.4 μ_B) ions, which was measured from neutron diffraction analysis.[3]

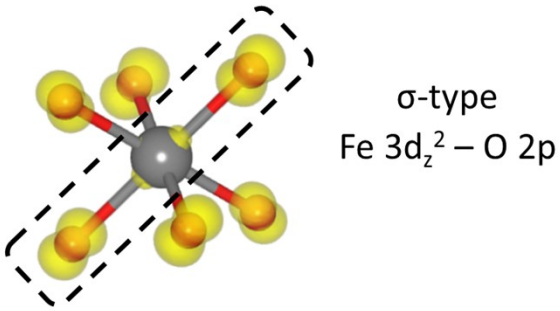

Figure S9. The spatial electron densities of $Fe^{4+}O_6$ at x = 1.0 in $Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$, which was calculated in the energy range of $-1.0 \leq E - E_f \leq 0.0$. Yellow iso-surface represents electron densities. As shown in Figure S5, d_z^2 orbital surrounds Fe^{4+} atom and is arranged toward O 2*p* orbital, which indicates σ-type Fe $3d_z^2$-O 2*p* molecular orbital.

References

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2 F. Tournadre, L. Croguennec, I. Saadoune, D. Carlier, Y. Shao-Horn, P. Willmann and C. Delmas, *J. Solid State Chem.*, 2004, **177**, 2790-2802.

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