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Electronic Supporting Information (ESI)

Unlocking veiled oxygen redox in Na-based earth-abundant binary layered oxide

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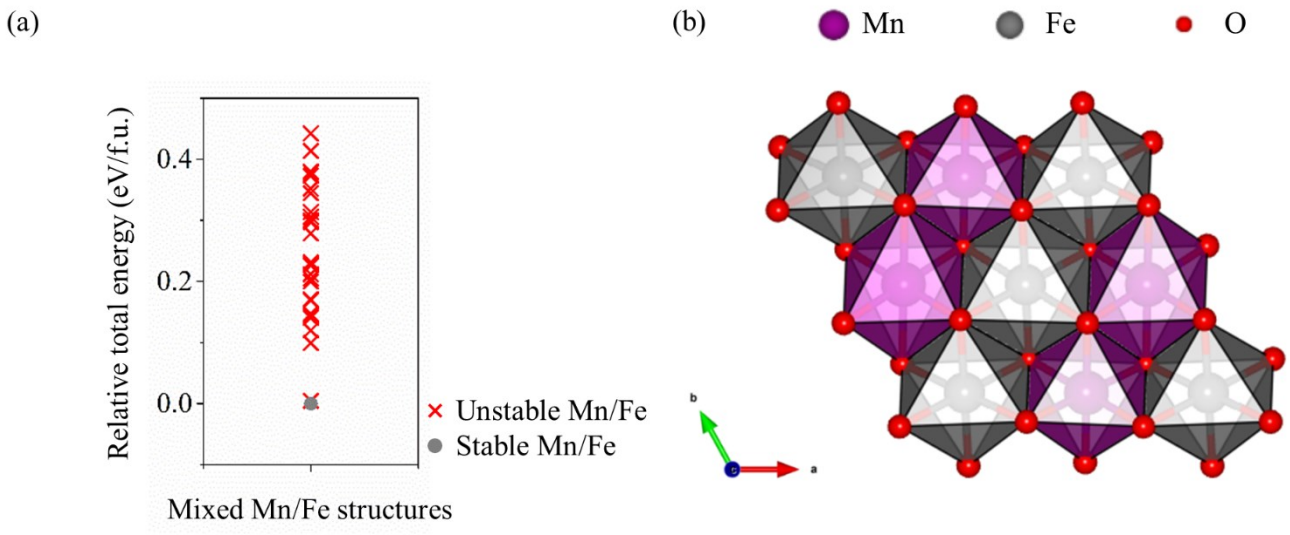

Figure S1. (a) Relative total energies of 30 Mn/Fe mixed structures having the lowest electrostatic energy among all possible Na/vacancy (x = 0.25) and Mn/Fe (y = 0.5) mixed cases in $Na_{1-x}[Mn_{1-y}Fe_y]O_2$ (containing 8 f.u.). The lowest total energy (gray filled circle) indicates the atomic configuration at the ground state among the mixed structures and (b) the corresponding $[Mn_{0.5}Fe_{0.5}]O_2$ slab in $Na_{0.75}[Mn_{0.5}Fe_{0.5}]O_2$.

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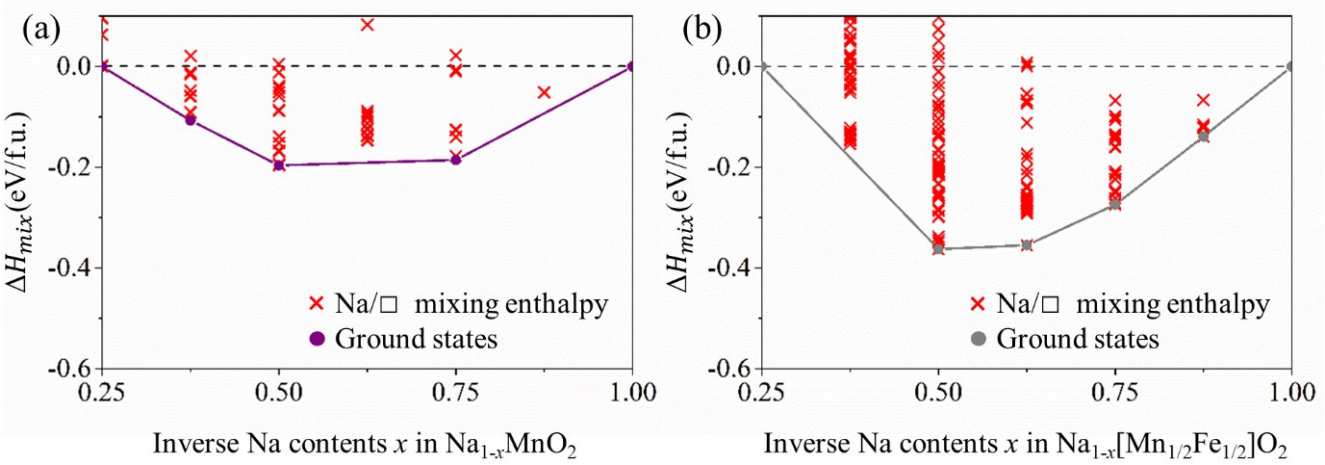

Figure S2. Convex hull diagram for (a) $Na_{1-x}MnO_2$ and (b) $Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ oxides. Filled circles on the tie line indicates the lowest ΔH_{mix} at thermodynamically stable phases determined by convex hull analysis, and the rest energies were expressed as Na/□ mixing enthalpy (red-colored cross).

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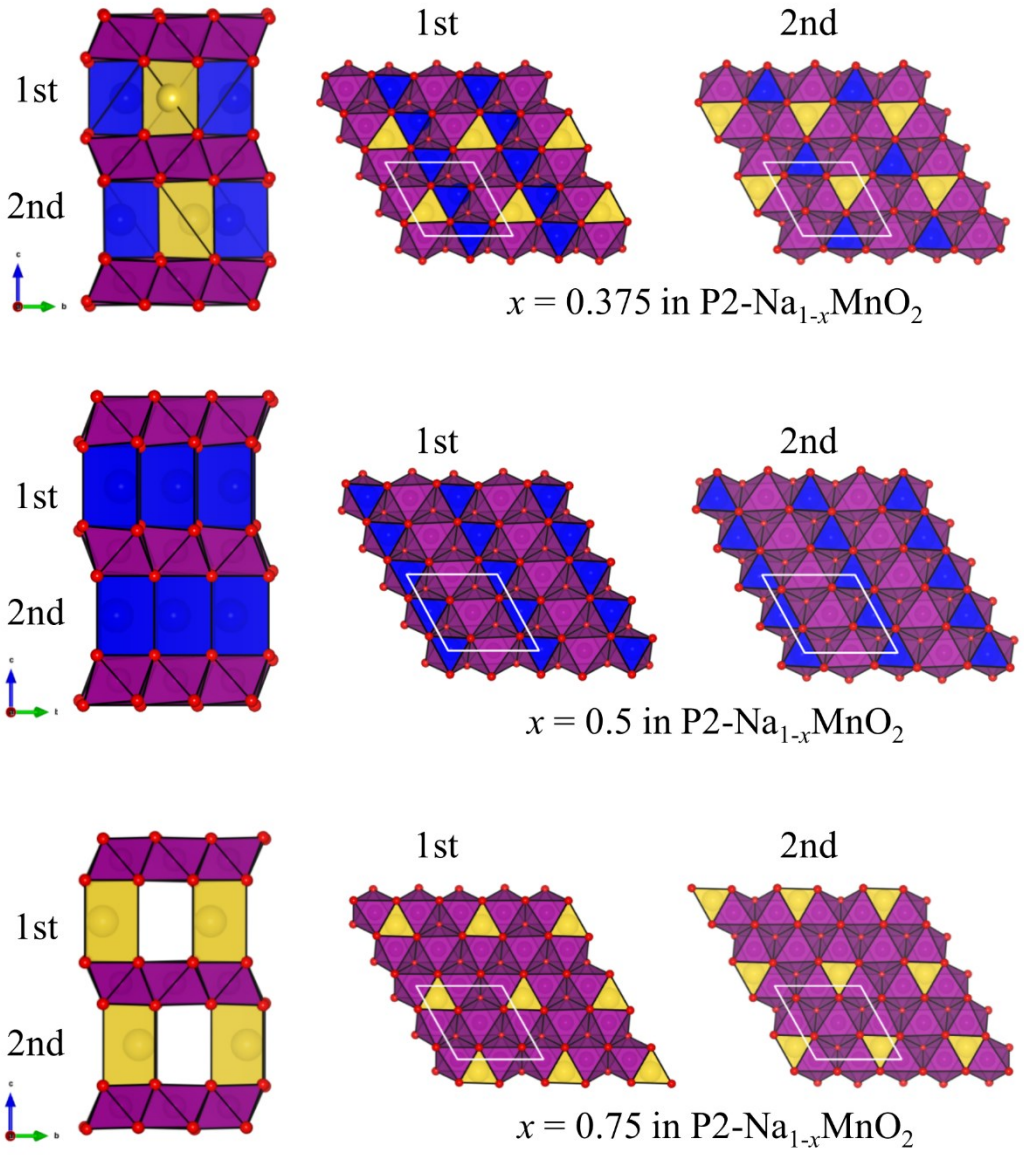

Figure S3. The relaxed ground state structures (left) and the arrangement of Na (right) at x = 0.375, 0.5 and 0.75 in $Na_{1-x}MnO_2$. Each Na_e and Na_f prismatic site is displayed in yellow and blue.

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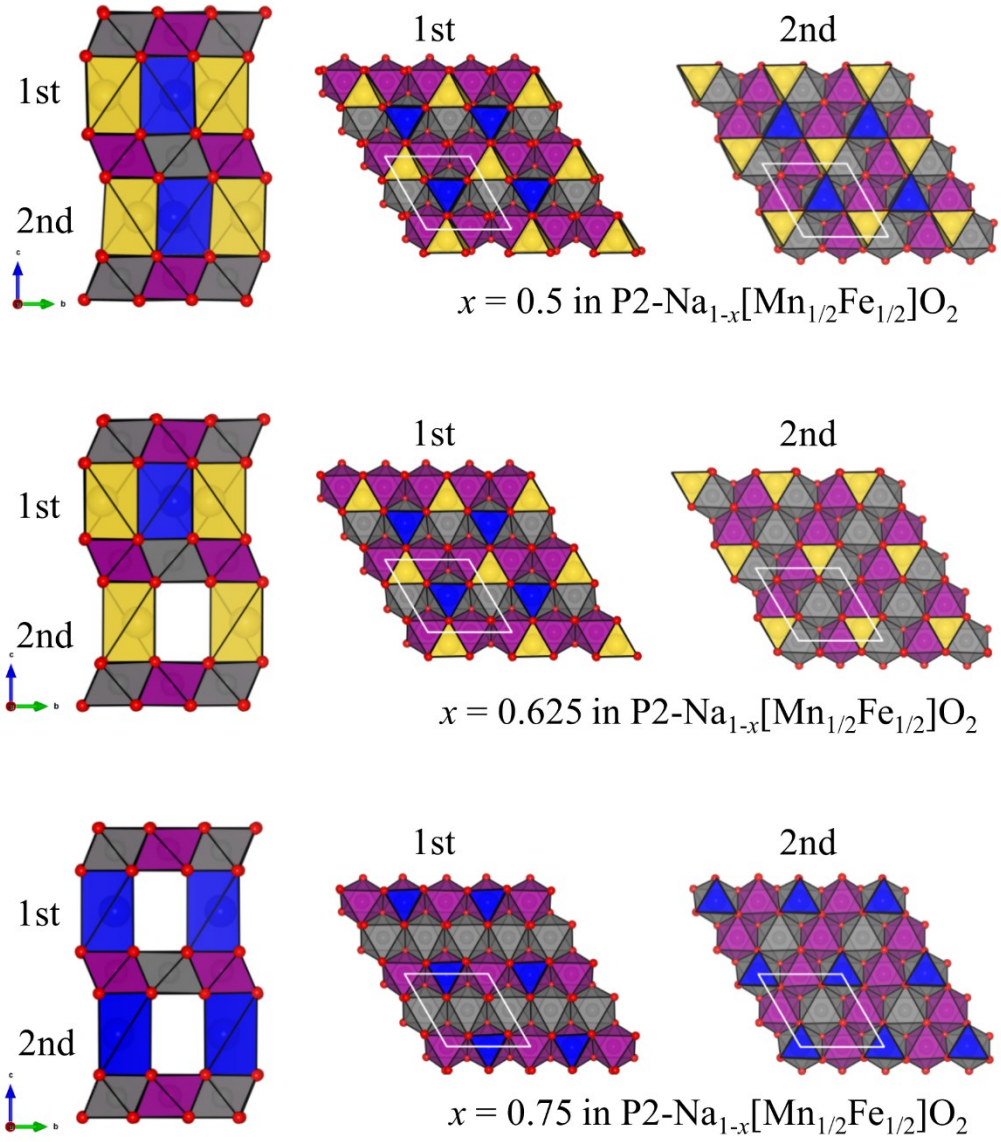

Figure S4. The relaxed ground state structures (left) and the arrangement of Na (right) correspond to x = 0.5, 0.625 and 0.75 in $Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$. Each Na_e and Na_f prismatic site is displayed in yellow and blue.

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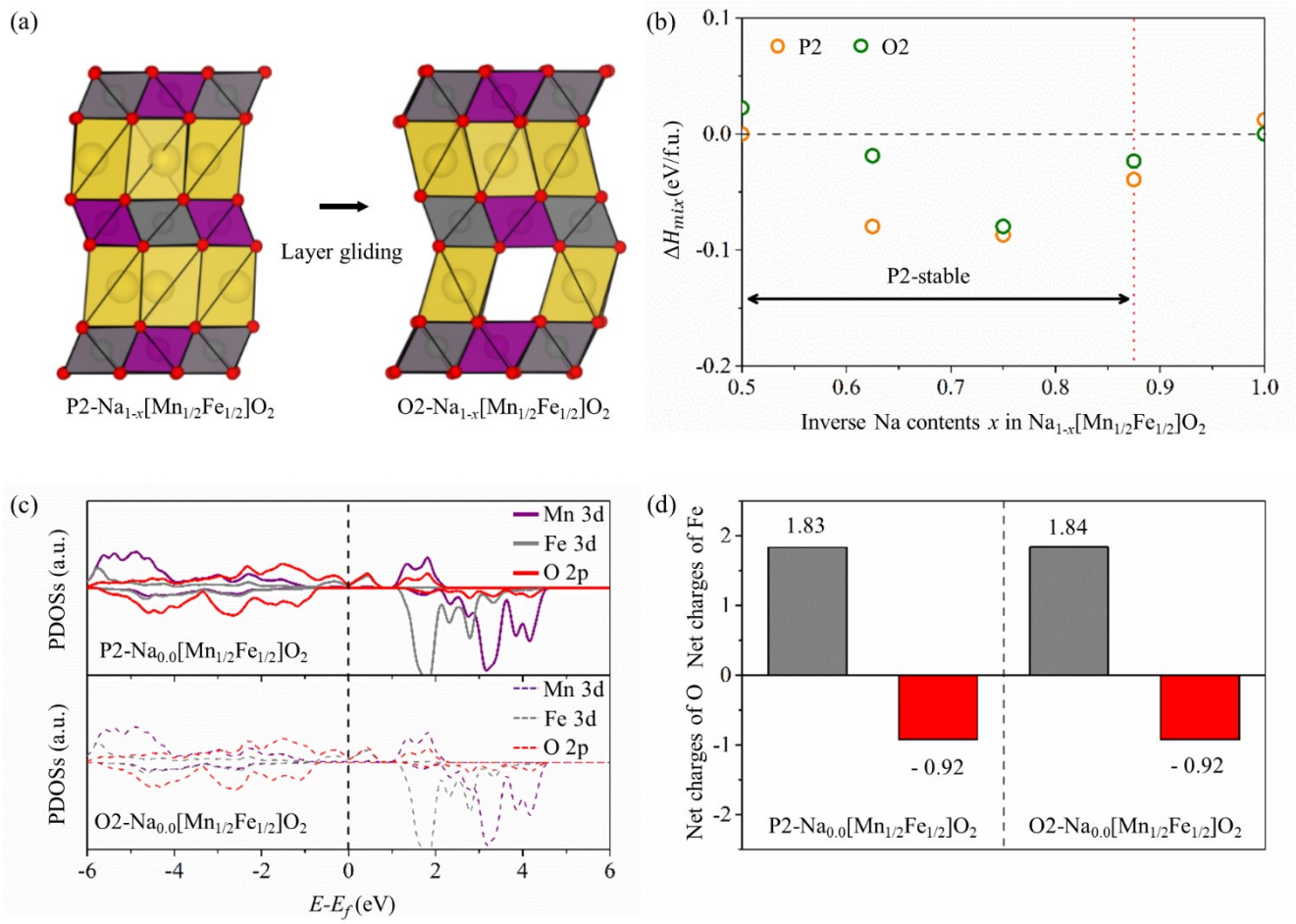

Figure S5. (a) The atomic structures of P2-$Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ and O2-$Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ (x = 0.5). The letters P and O stand for prismatic and octahedral sites, in which sodium ions can accommodate. The atomic models of O2-$Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ (x = 0.5, 0.625, 0.75, 0.875 and 1.0) were obtained, considering that P2-O2 stacking transition results from slabs (slabs in dashed box) glided by (1/3, 2/3, 0) direction in P2-structures.[1] (b) Phase stability of P2-$Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ against O2-$Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ as a function of the inverse Na contents(x) in $Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$. It has been observed that P2-O2 stacking transition were generally occurred at high voltage in various types of sodium layered oxide cathodes,[2] therefore we calculated formation energies of mixing enthalpy (ΔH_{mix}) for P2- and O2-$Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$, restricting to the high voltage range ($0.5 \le x \le 1.0$). On the basis of obtained phase stability diagram, P2-$Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ are more stable than O2-$Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ within the range ($0.5 \le x \le 0.875$). In order to explore the possibility whether the stacking transition affect the redox mechanism, PDOSs of Mn and Fe 3d-electron and O 2p-electron at x = 1.0 in P2-$Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ (solid line) and O2-$Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ (dashed line) were comparatively scrutinized (Figure S5c). PDOSs are plotted with varying energy referenced to the fermi level (E_f) for each compound. The electronic structures for P2-$Na_{0.0}[Mn_{1/2}Fe_{1/2}]O_2$ and O2-$Na_{0.0}[Mn_{1/2}Fe_{1/2}]O_2$ are almost identical, indicating that the P2-O2 stacking transition would not affect the redox mechanism of NMFO at high voltage. The calculated average net charges of Fe (gray bar graphs) and O (red bar graphs) in P2-$Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ and O2-$Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$ at x = 1.0 are almost same, which is well consist with the previous electron structure results (Figure S5d).

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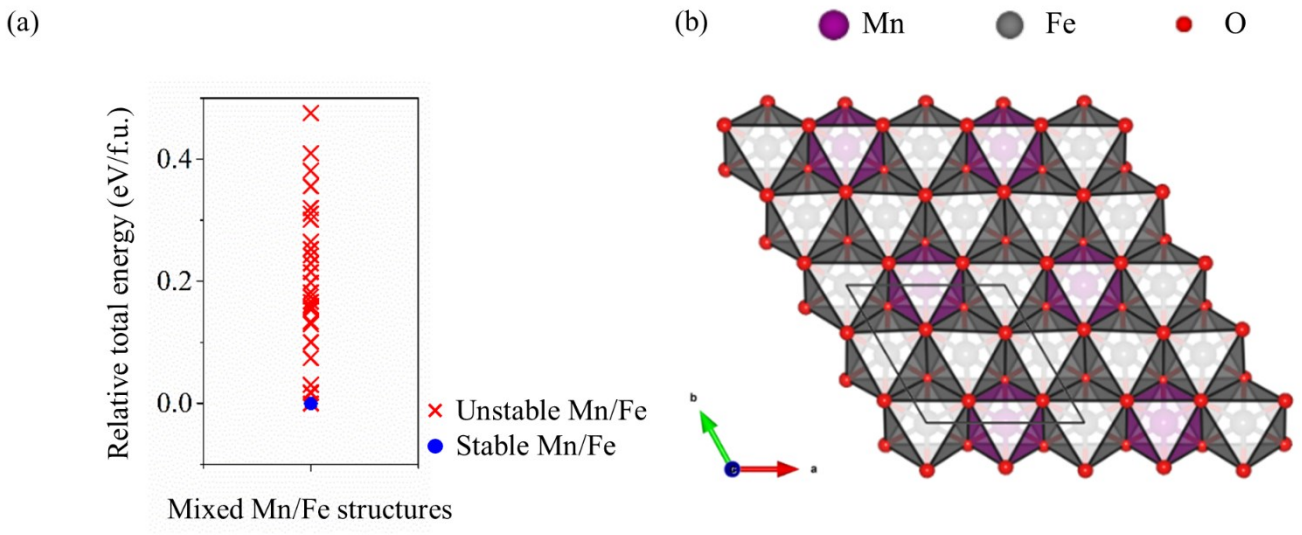

Figure S6. (a) Relative total energies of 30 Mn/Fe mixed structures having the lowest electrostatic energy among all possible Na/vacancy (x = 0.25) and Mn/Fe (y = 0.625) mixed cases in $Na_{1-x}[Mn_{1-y}Fe_y]O_2$ (containing 8 f.u.). The lowest total energy (blue filled circle) indicates the atomic configuration at the ground state among the mixed structures and (b) the corresponding $[Mn_{0.625}Fe_{0.375}]O_2$ slab in $Na_{0.75}[Mn_{0.625}Fe_{0.375}]O_2$. The honeycomb-like arrangement of Mn and Fe resemble the Mn/Fe orderings determined from the previous theoretical literature.[3]

	a lattice parameter (Å)	*b lattice parameter* (Å)	*c lattice parameter* (Å)
Calculated values ($x = 0.375$ in $Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$)	3.004	2.98	11.383
Experimentally measured values ($x = 0.33$ in $Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$)	2.934	-	11.224

Table S1. Calculated lattice parameters of $Na_{0.625}[Mn_{1/2}Fe_{1/2}]O_2$ ($x = 0.375$ in $Na_{1-x}[Mn_{1/2}Fe_{1/2}]O_2$) and experimentally measured lattice parameters of P2-$Na_{2/3}[Mn_{1/2}Fe_{1/2}]O_2$ [4] in a unit cell size.

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