Electronic Supplementary Information

Suppressing O-type stacking and cation migration with Mg and Si doping in P2-type Fe-Mn layered oxides for sodium-ion cathodes

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Supplementary note 1. Cationic Potential to select P2 structure

We validate a new concept called cationic potential developed by Zhao et al¹ has been used in the design of Na-ion layered cathodes. This concept is defined by the cation's electron density, its polarizability, and the normalization with the anion's electron density.¹

Cationic potential (ϕ_{cation}) is defined by $\phi_{cation} = \frac{\phi_{TM} \cdot \phi_{Na}}{\phi_0}$; where $\phi_{TM}, \phi_{Na}, \phi_0$ represent weighted average of the ionic potentials of TM (transition metal), Na and O ions, respectively.

 $\phi_{TM} = \sum \frac{w_i \cdot n_i}{R_i}$, w_i , n_i , R_i are the content, charge state and radius of the TMs, respectively. Similarly, $\phi_{Na} = \frac{x}{R_{Na}}, \phi_0 = \frac{-2}{R_0}$, Where, x is the content of Na, R_{Na} and R_0 are the radius of Na

and O ions, respectively.

According to our findings based on cationic potentials (Table S1), the P2 phase is stable in pristine (x=0.67) Na_xFe_{0.5}Mn_{0.5}O₂, Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O₂, and Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O₂. Additionally, powder X-ray diffraction experiments confirmed the presence of the P2 phase in pristine $Na_xFe_{0.5}Mn_{0.5}O_2$ and $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$.²

Table S1. Cationic potential for Na=0.67 in NFMO, Mg-NFMO and Si-NFMO. If cationic potential is higher than 12.29 at Na=0.67 then it will stabilize P2 structure.

Materials	Cationic potential
$Na_xFe_{0.5}Mn_{0.5}O_2$	12.848
$Na_{x}Mg_{0.11}Fe_{0.22}Mn_{0.67}O$	13.177
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Supplementary note 2. Phase diagram.

We calculated the region of stability (Fig. S1) in the chemical potential space of Fe and Mn for $Na_xFe_{0.5}Mn_{0.5}O_2$, $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$, and $Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O_2$, considering several competing materials. The results indicate good probabilities for the formation of these materials. The Chemical Potential Limits Analysis Program (CPLAP) code³ was used to generate multidimensional chemical potential space, considering the O-rich limit, while keeping Na as a dependent variable. The stability region for $Na_xFe_{0.5}Mn_{0.5}O_2$ is larger than the other two doped materials when examining the range of μ_{Fe} and μ_{Mn} within stable regions. Nevertheless, the formation of Mg-doped and Si-doped materials is also probable.



Fig. S1 Region of stability (green shaded region) at O-rich condition for (a) $Na_xFe_{0.5}Mn_{0.5}O_2$, (b) $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$, and (c) $Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O_2$ in two-dimensional space spanned by μ_{Fe} and μ_{Mn} .



Fig. S2 Convex hull for (a) $Na_xFe_{0.5}Mn_{0.5}O_2$, (b) $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$, and (c) $Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O_2$. In $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$, a clear deflection of the hulls from P2 to O2 at Na=0.0 state and for $Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O_2$, P2 and O2 hulls remain same.



Fig. S3 P2/O2 structural phase stability with different level of theories.



Fig. S4 Density of states of $Na_xFe_{0.5}Mn_{0.5}O_2$ (first column), $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$ (second column) and $Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O_2$ (third column) using PBE+U+D3. Each row corresponds to different limit of desodiation (x) as mentioned in the left.



Fig. S5 Metal arrangements in their layers with P2 structure for $Na_xFe_{0.5}Mn_{0.5}O_2$, $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$ and $Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O_2$ and (d) a representative honeycomb (hc) superstructure. Atom and polyhedron colour key: Mn (purple), Fe (cyan), O (red), Mg (green), Si (blue). It is to be noted that hc-arrangement of $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$ and $Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O_2$ and $Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O_2$ were same where Mg was replaced by Si. Fe and Mn each have 6 neighbours of each other's in $Na_xFe_{0.5}Mn_{0.5}O_2$.

Supplementary note 3. Fe-ion migration pathway

In the parent oxide $Na_xFe_{0.5}Mn_{0.5}O_2$ (x=0.0), Fe ion migrates to the Na-layers via octahedraltetrahedral-octahedral pathway (Figs. 3 and S6). To elucidate the energy barrier height for this pathway, we have performed nudged elastic band (NEB) calculations using end-point structures extracted from the AIMD trajectory of $Na_xFe_{0.5}Mn_{0.5}O_2$. Five images for the diffusion species were generated along the path at equal distances using the interpolation method, and the intermediatory images were optimised using the climbing image NEB algorithm within the *VASP* code, in conjunction with *vtst* optimiser.⁴⁻⁷ The NEB results reveal energy barriers of 0.22 eV for migration from tetrahedral to octahedral sites, and 0.52 eV for the reverse path.



Fig. S6. Migration pathways for Fe ions (brown) from tetrahedral to octahedral sites within $Na_0Fe_{0.5}Mn_{0.5}O_2$, as indicated by dotted circles. Color: Fe(brown), Mn(magenta), O(red).

Supplementary note 4. Thermodynamic stabilities of intermediate structures extracted from the AIMD trajectory

To verify the thermodynamic stability of Fe-migration and O-dimer formation, we optimized the geometries with the r²SCAN functional and ensured energy convergence, using structures extracted from the AIMD trajectory. The results indicate that the Fe-migrated structures in Na_xFe_{0.5}Mn_{0.5}O₂ during the AIMD simulations are thermodynamically feasible (Fig. S7a). Furthermore, we found configurations involving Mg and Fe migrations in Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O₂ followed by O-dimer formation, which are also thermodynamically stable (Fig. S7b).



Fig. S7 Energies with time using r²SCAN functional for (a) $Na_xFe_{0.5}Mn_{0.5}O_2$, (b) $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$, (c) $Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O_2$. These are optimized energies of intermediate structures taken from AIMD trajectories as shown in Fig. 3.

We note that AIMD simulations for Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O₂ were performed at T=500 K and 900 K. However, no significant difference was observed at these two temperatures for Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O₂. The optimized energies for intermediate structures obtained from the T=900K AIMD trajectory of Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O₂ using r²SCAN at 0 K vary within 15 meV, as shown in Fig. S7c, a range consistent with thermal vibrations (~30 meV). This indicates that structures without migration are thermodynamically stable.

Supplementary note 5. Honeycomb structure

Our calculated energy difference between the honeycomb and the lowest energy structure is 25 meV per formula unit for $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$. For $Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O_2$, the difference is 42 meV per formula unit. Previous studies have suggested that $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$ might adopt a honeycomb arrangement in the transition metal layers.² Therefore, we conducted AIMD simulations for honeycomb structures to confirm the effect of superstructure on cation migration.

In addition to the kinetics studies, we investigated how the honeycomb superstructures affect cation migration and O-dimerisation in all three materials. The local ordering of metal atoms in the transition metal layers for both the lowest energy structures and honeycomb superstructures are shown in Fig. S5.

From the AIMD calculations on the honeycomb structures, we identified Fe migration in $Na_xFe_{0.5}Mn_{0.5}O_2$ (Fig. S8) and Mg migration in $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$, similar to earlier results. Additionally, there was also intra-planar O-dimer formation for a 30 ps trajectory in $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$ (Fig. S9). However, in $Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O_2$, we did not see any cation migration (Fig. S10) in the hc structure, similar to the lowest energy structure. Overall, these comparative studies suggest superstructure has a minor effect on cation migration, while the metal-oxygen bonding character likely plays a more significant role in these Fe-Mnbased layered oxides.



Fig. S8. Structures at different time steps for $Na_xFe_{0.5}Mn_{0.5}O_2$ with honeycomb superstructure. Atom and polyhedron colour key: Mn (purple), Fe (blue), O (red).



Fig. S9. Structures at different time steps for $Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O_2$ with honeycomb superstructure. Atom and polyhedron colour key: Mn (purple), Fe (blue), O (red), Mg (green). The O-dimer formations are shown by yellow dotted circles.



Fig. S10. Structures at different time steps for $Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O_2$ with honeycomb superstructure. Atom and polyhedron colour key: Mn (purple), Fe (blue), O (red), Si (yellow).



Fig. S11. (a) ICOHP for Mg-O and Si-O bonds and (b) Mean ICOBI for metal-oxygen bonds at different de-sodiated limits.

Supplementary note 6. Effect of k-mesh and cell size

We confirmed that the Fe migration in Na_xFe_{0.5}Mn_{0.5}O₂ is not an artefact caused by our unitcell size, k-mesh. We doubled-checked with a 4 × 3 × 1 cell size, 2 × 2 × 2 k-mesh. In all cases, Fe migration occurs consistently, indicating that this phenomenon is robust. The results of these simulations are shown in Fig. S12. Based on these findings, we performed our AIMD simulations for Na_xMg_{0.11}Fe_{0.22}Mn_{0.67}O₂ and Na_xSi_{0.11}Fe_{0.22}Mn_{0.67}O₂ at the top of the charge with our initial settings of a 1 × 1 × 1 k-mesh and the PBE+U+D3 functional.



Fig. S12. Structures at different time steps for $Na_xFe_{0.5}Mn_{0.5}O_2$ with (a) $4 \times 3 \times 1$ supercell and (b) $2 \times 2 \times 2$ k-points . Mn, Fe and O are in magenta, cyan and red colours, respectively.

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