

ADVANCED ENERGY MATERIALS

Supporting Information

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Direct Observation of Alternating Octahedral and Prismatic Sodium Layers in O₃-Type Transition Metal Oxides

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SUPPLEMENTARY INFORMATION

Direct observation of alternating octahedral and prismatic sodium layers in O3-type transition metal oxides

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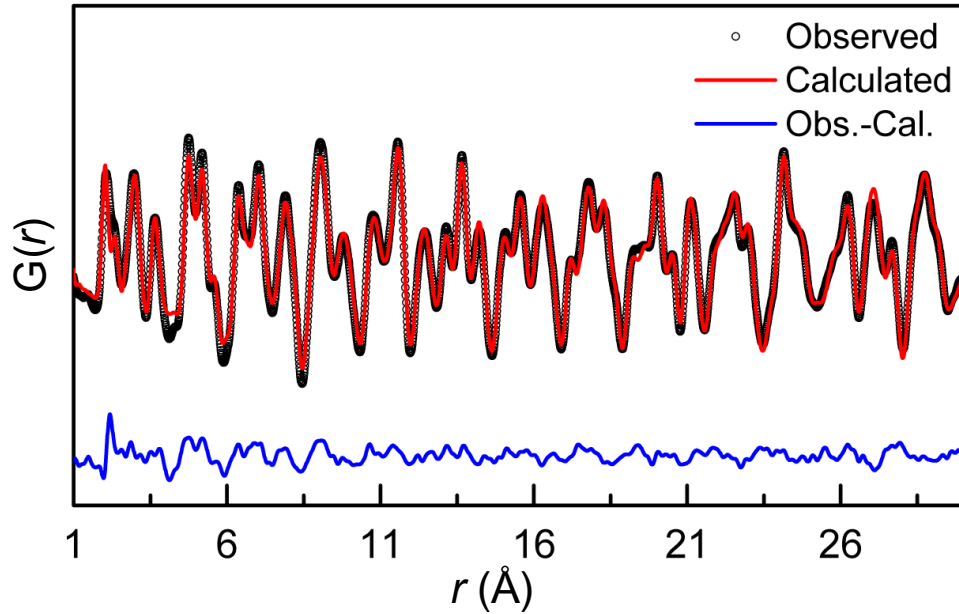
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Keywords: Energy storage, Na-ion batteries, Layered structure, O3 structure, OP2 structure

Table S1. Rietveld fitting results for neutron diffraction of NaTFCN

Space group	a	c	Volume	R_{wp}	R_{exp}	GoF
$R\bar{3}m$	2.9893(4) Å	16.0155(0) Å	123.943 Å	4.008	2.98	0.002
SOF (Na, 3a site) = 1						
SOF (TM, 3b site) = 0.25 Ti, 0.25 Fe, 0.25 Co, 0.25 Ni						
SOF (O) = 2						
Temperature coefficient, B (Na) = 0.714						
Temperature coefficient, B (TM) = 0.404						
Temperature coefficient, B (O) = 0.519						

**Figure S1.** Neutron PDF of NaTFCN in the high-Q range**Table S2.** Structural parameters of NaTFCN obtained from neutron PDF refinement

Fitting range	TM-O	TM-TM/Na-Na (in-plane)	TM-Na	Na-O	Na slab spacing	TM slab spacing	Na-TM height
3.3-30 Å	2.03	2.99	3.18	2.36	3.21	2.12	2.67

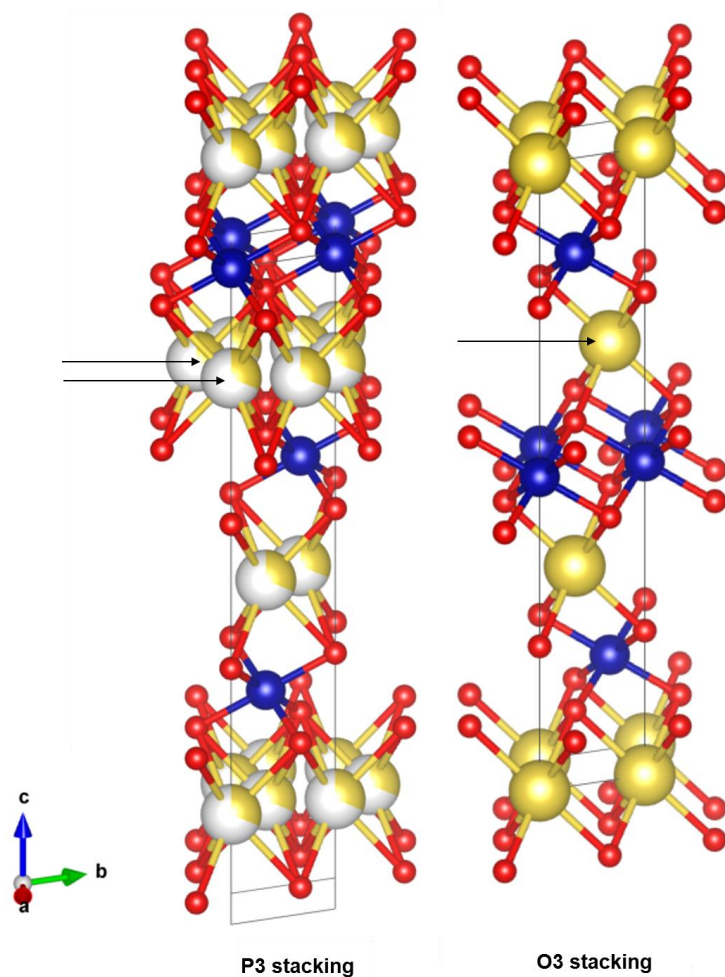


Figure S2. Here we show the P3 (left) and O3 (right) model structures oriented to the electron beam direction, $[100]$. Blue, red, and yellow spheres represent transition metal, oxygen, and sodium, respectively. Black arrows indicate the Na sites in each structure. In P3, the two types of prismatic sites over which sodium disorders are slightly overlapping from the perspective of the electron beam direction. In contrast, O3 contains a single sodium octahedral site.

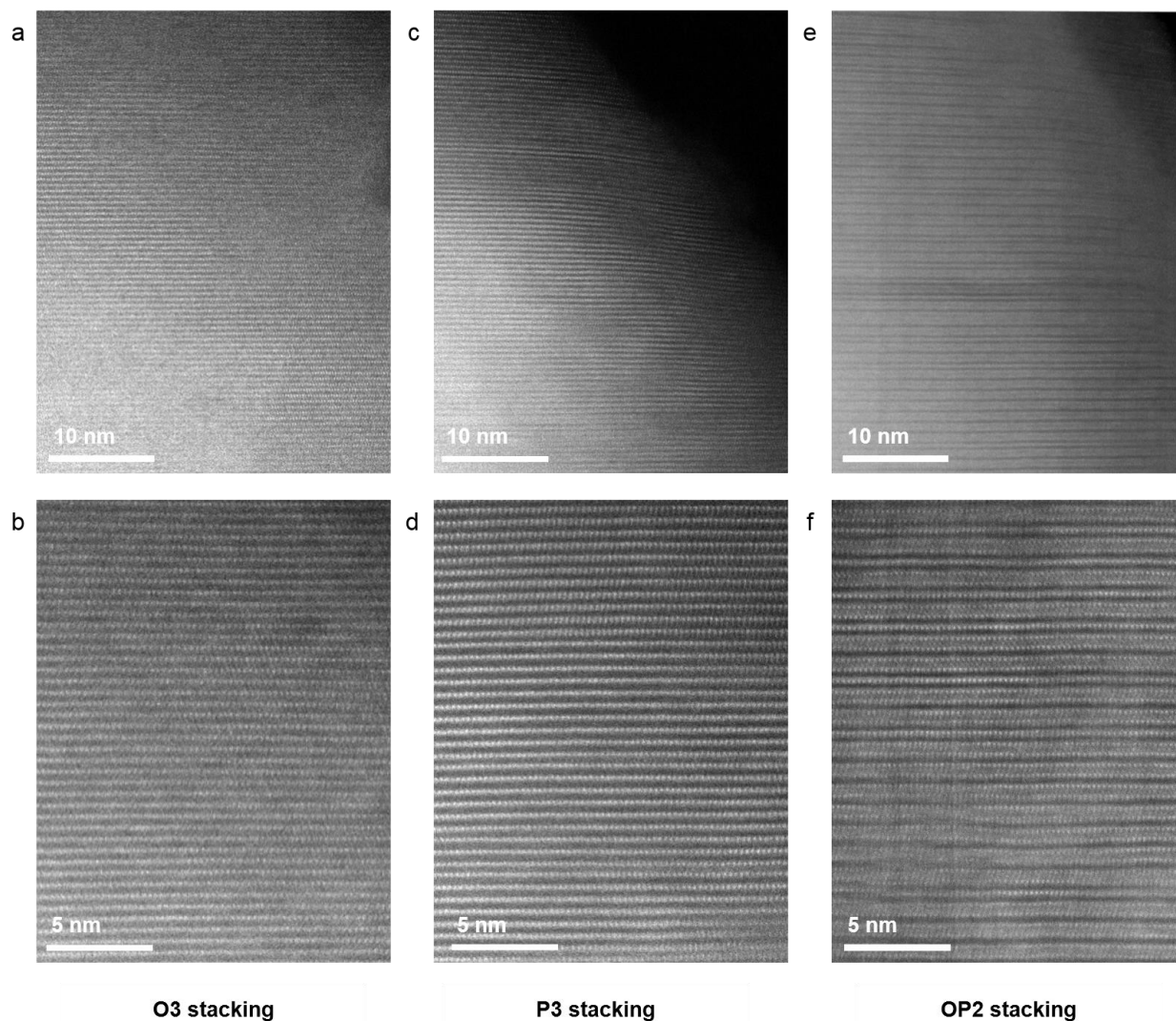


Figure S3. Low magnification HR-STEM images of O3 (a and b), P3 (c and d), and OP2 (e and f) stacking.

Comparison of the low-magnification HR-STEM images of the O3, P3, and OP2 structures. The alternating bright and dark contrast of Na layers are clearly visible in the OP2 structure (Figure 3 e and f). The OP2 particle is characterized by a “stripe pattern” in which the alternating intensity of Na layers from the O layer (Figure S3a and b) and the P layer (Figure S3c and d) is bright and dark, respectively.

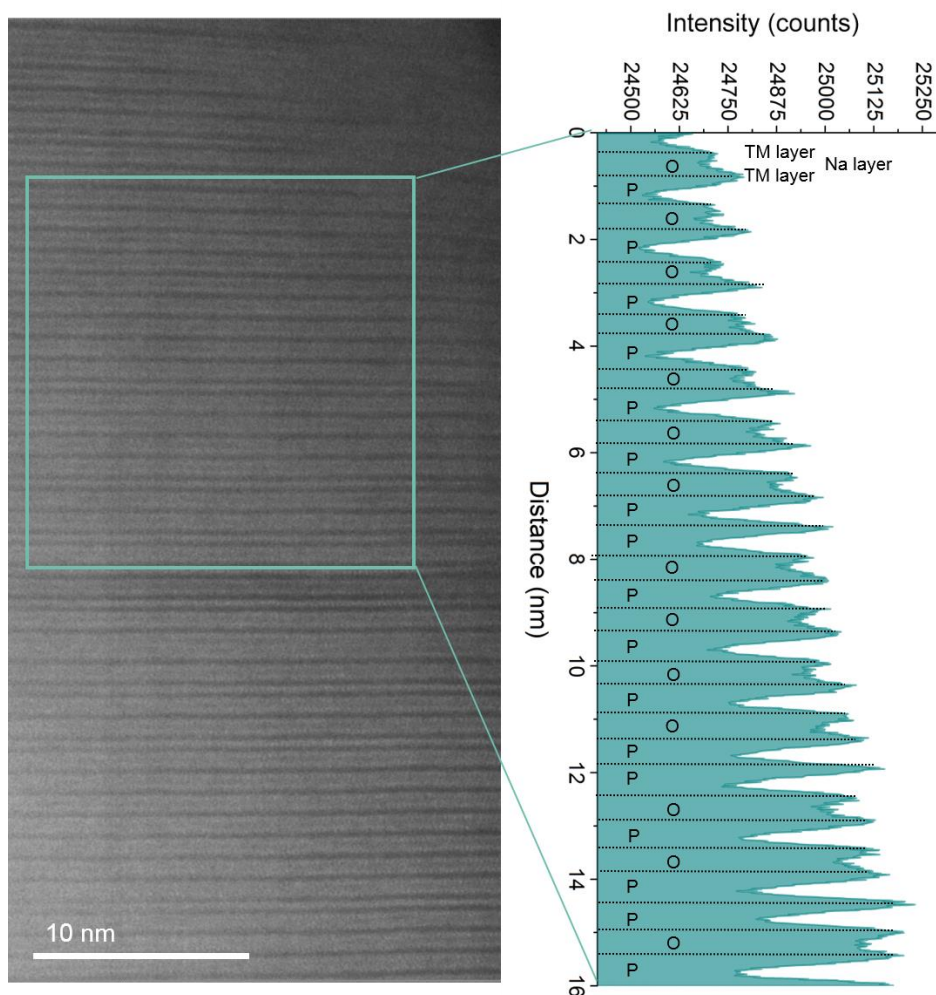


Figure S4. HR-STEM image of the OP2 structure. The right panel shows integrated signals of intensity from the transition metal and Na layers. The O and P stacking mostly alternate, but occasionally two consecutive P layers are observed.

Figure S4 shows the HR-STEM image of the OP2 structure (left) and the intensity profile of integrated signals from cation layers (inset, right). Specifically, the transition metal layers (containing Ti, Fe, Co, and Ni) have higher intensities than Na layers because they contain heavier elements. Therefore, the intensities from Na layers are the troughs of the intensity profile. As demonstrated in the main text (Figures 3e-f), of the Na layers, we assign bright intensity as O stacking and dark intensity as P stacking, leading us to deduce from the inset that around 75% of the stacking sequence alternates O/P while 25% of the stacking is consecutively P stacking. Evidently, the structure exhibits mainly O/P stacking, so is labelled as OP2. These statistics are consistently observed in low-magnification STEM images.

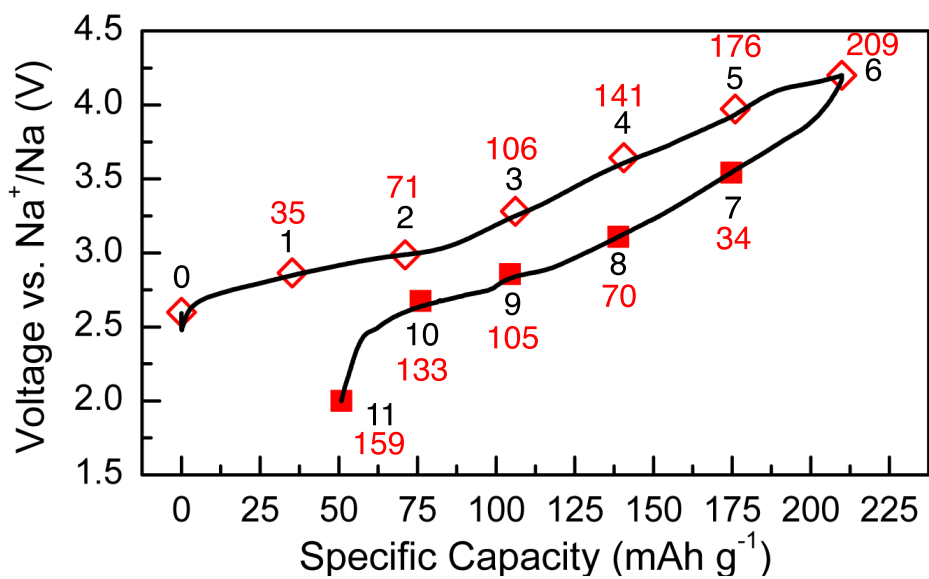


Figure S5. Here we show a representative voltage-capacity profile of NaTFCN used to collect *ex situ* XAS samples.

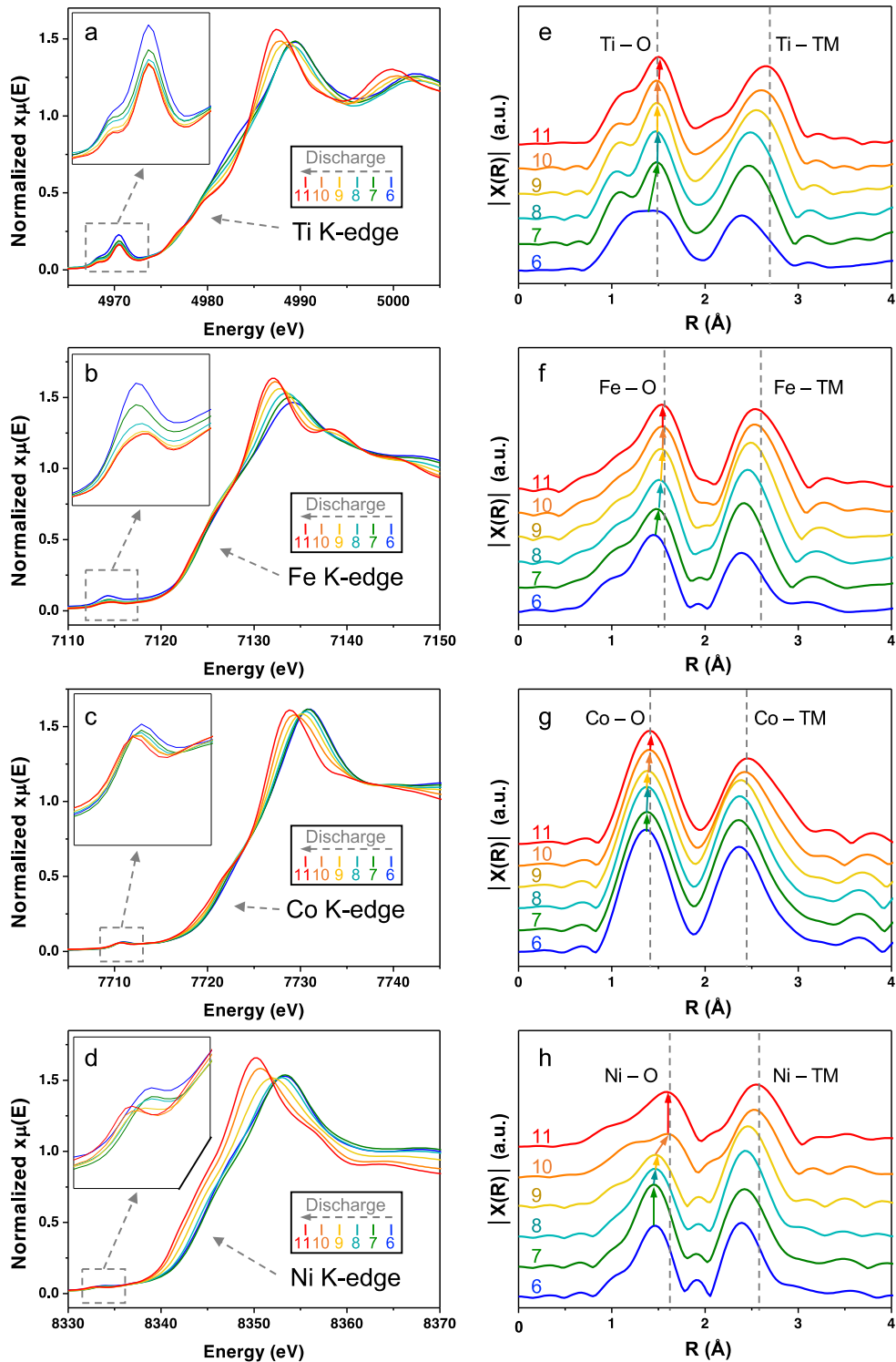


Figure S6. *Ex situ* XAS for the quaternary transition metals upon discharging. XANES for (a) Ti, (b) Fe, (c) Co, and (d) Ni and EXAFS for (e) Ti, (f) Fe, (g) Co, and (h) Ni. Samples 6, 7, 8, 9, 10, and 11 are prepared by electrochemical sodiation into NaTFCN, in which the capacities are 0, 34, 70, 105, 133, and 159 mAh g⁻¹, respectively.

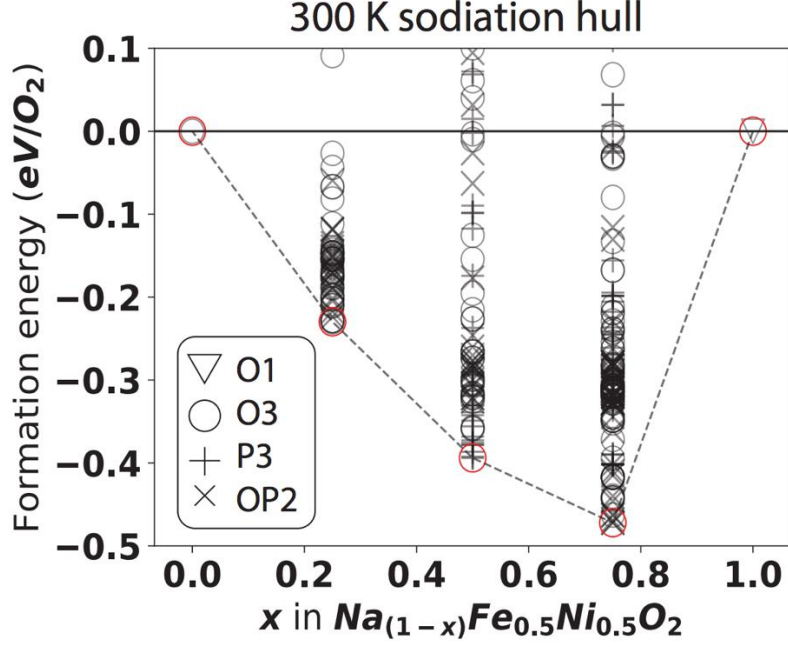


Figure S7. The 300 K formation energy hull when considering a simple ideal-solution-like approximation of Na configurational entropy arising from disorder over prismatic and octahedral sites.

We approximate the Gibbs free energy G , considering only Na configurational entropy, as:

$$G = H - TS \approx H - TS_{Config} = H_{DFT} - T(k_B \ln \omega)$$

where H_{DFT} is DFT-calculated enthalpy and S_{Config} is configurational entropy of Na. ω is the occupational degeneracy, which can be approximated in a combinatorial way by

$$\omega = \frac{N!}{(X_{Na}N_{Na})!(X_{Vacancy}N_{Vacancy})!}$$

Here, N is total number of sites, X_{Na} and N_{Na} are the mole fraction and mole number of Na and $X_{Vacancy}$ and $N_{Vacancy}$ are the mole fraction and mole number of vacancy where $X_{Na} + X_{Vacancy} = 1$.

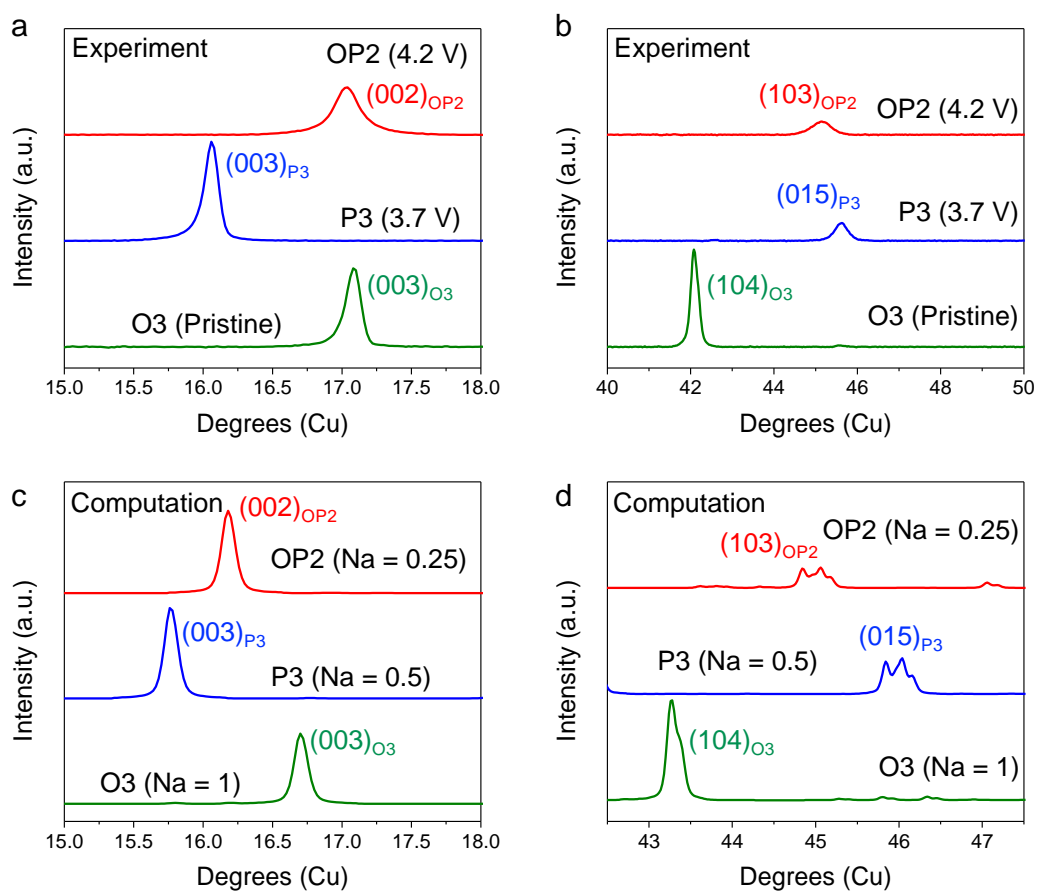


Figure S8. Comparison between (a-b) *ex situ* XRD for Na_{1-x}Ti_{0.25}Fe_{0.25}Co_{0.25}Ni_{0.25}O₂ and (c-d) peak simulation for O3, P3, and OP2 structures of Na_{1-x}Fe_{0.5}Ni_{0.5}O₂ obtained from DFT

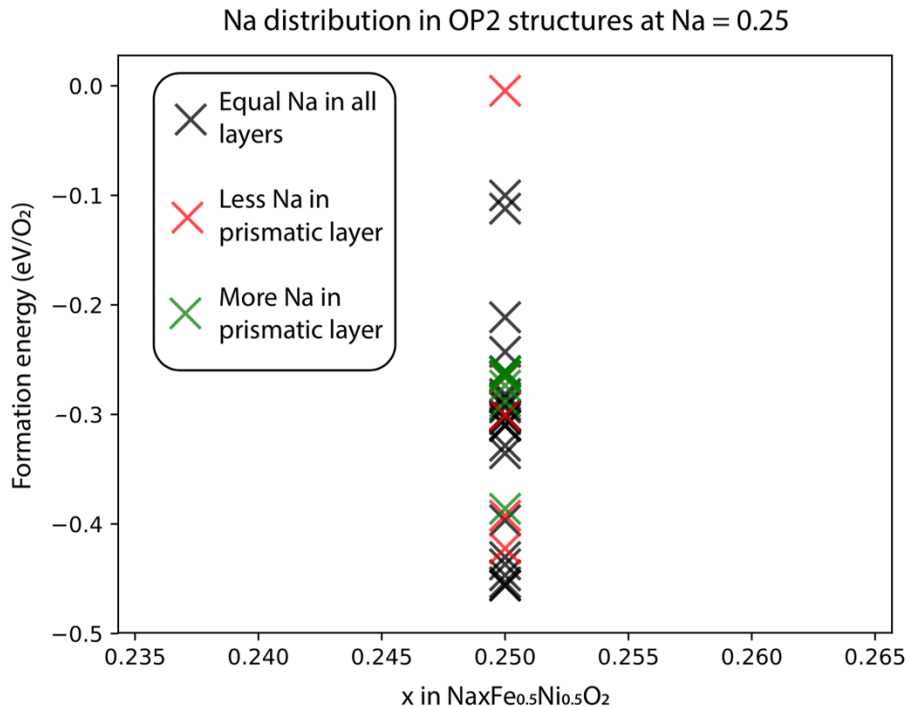


Figure S9. The formation energy of the OP2 structure ($\text{Na} = 0.25$) with respect to Na distribution (i.e., the Na occupancies in the O and P layers)

Description S9.

We separately explore Na-Na, TM-TM, and Na-O-TM interactions in NaTMO_2 as possible reasons for OP2 formation. Na-Na interactions at $\text{Na} = 0.25$ are not likely to be the factor to stabilize OP2- $\text{Na}_{0.25}\text{TMO}_2$. Our DFT results indicate that the Na occupancy is equal in the O and P layers at the OP2 ground state ($\text{Na} = 0.25$), as well as in all competing structures up to 40 meV/ O_2 above the hull (**Figure S9**). This suggests, unsurprisingly, that the Na-Na inter-slab interactions in the O and P layers in OP2 are weak. TM-TM interactions cannot lead to stabilization of OP2 as no long-range or short-range TM ordering is observed in neutron Bragg diffraction (Figure 1). Therefore, we consider that the OP2 stabilization must be associated with Na-O-TM interactions.

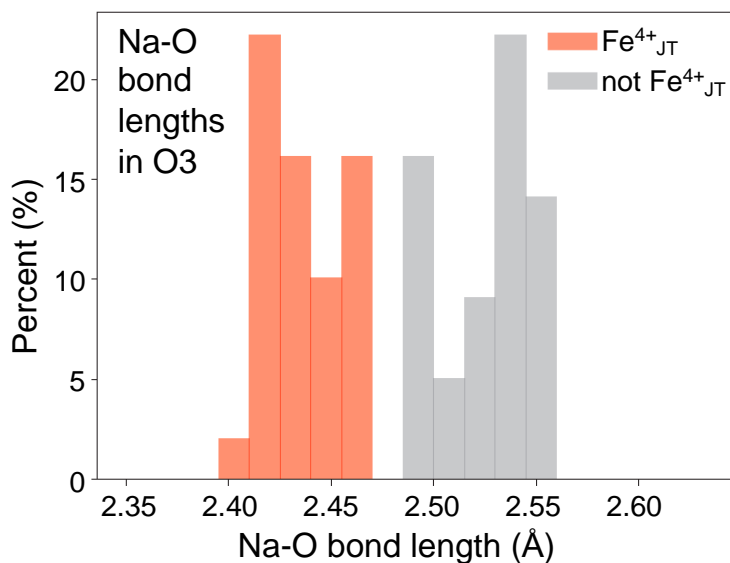


Figure S10. The normed distribution of Na-O bond lengths for all O3 structures which are less than 50 meV/O₂ above the hull at Na = 0.25. Red indicates connectivity of the O anion (in the Na-O bond) to the long axis of the Jahn-Teller (JT) Fe⁴⁺ ion while grey indicates an alternate connection (e.g. short axis of the Jahn-Teller-active Fe⁴⁺ ion, or any bond with Ni³⁺ or Ni⁴⁺).

Figure S10 shows how the JT Fe⁴⁺ ion also accommodates a shorter Na-O bond in O3 structures. Only O3 and OP2 structures are within 50 meV/O₂ above the hull, so together Figure S10 and Figure 6a summarize how the Na-O bond lengths connected to Fe⁴⁺_{JT} are shorter than bond lengths not connected to Fe⁴⁺_{JT}.

Description S10. Gagné and Hawthorne [Acta Crystallogr. B, 72, 4 (2016)] calculated an optimal Na⁺-O²⁻ bond length of 2.441 Å in NaO₆-type environments using experimental data from 920 six-fold coordination polyhedra, for a total of Na⁺-O²⁻ 5520 bonds. All crystallographic data, published after 1975, were measured at ambient conditions, had no Na disorder, and had a reasonable fit with the structural refinement R₁ < 0.06. It is evident from Gagné and Hawthorne that the six-fold NaO₆ coordination is most likely to accommodate a bond length of 2.441 Å in ambient conditions, a value which we find is shorter than many Na-O bonds at high desodiation.

We hypothesize that more optimized Na-O bonds, i.e. shorter Na-O bonds, are promoted directly by the long axial bonds of the Fe⁴⁺ Jahn Teller ions and refer to this coupling as a “Na-O-Fe⁴⁺_{JT}” connection.