Supporting Information

Enhanced Oxygen Redox Reversibility and Capacity Retention of Titanium-Substituted $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ in Sodium-Ion Batteries

Stephanie F. Linnell,^{a, b} Eun Jeong Kim,^{a, b} Yong-Seok Choi,^{b, c, d} Moritz Hirsbrunner,^e Saki Imada,^f Atin Pramanik,^a Aida Fuente Cuesta,^a David Miller,^a Edoardo Fusco,^a Bela E. Bode,^a John T. S. Irvine,^{a, b} Laurent C. Duda,^e David Scanlon,^{b, c, d} A. Robert Armstrong^{*, a, b}

^aSchool of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, United Kingdom

^bThe Faraday Institution, Quad One, Harwell Science and Innovation Campus, Didcot, OX11 ORA, United Kingdom

^cDepartment of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, UK

^dThomas Young Centre, University College London, Gower Street, London WC1E 6BT, UK

^eDepartment of Physics and Astronomy, Division of Molecular and Condensed Matter Physics, Uppsala University, Uppsala, S-75120, Sweden

^fFaculty of Electrical Engineering and Electronics, Kyoto Institute of Technology, Sakyo, Kyoto 606-8585, Japan

Corresponding Author

*Email : ara@st-andrews.ac.uk

1. Supplemental Experimental Procedures

1.1. Synthesis and characterisation

 $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ was synthesised using a solid-state method.¹ Stoichiometric amounts of sodium carbonate (Na_2CO_3 , Fischer Chemistry, \geq 99.5%), manganese(II) carbonate ($MnCO_3$, Aldrich, \geq 99.9%) and titanium oxide (TiO_2 , anatase Aldrich, 99.9%) were ball-milled at 300 rpm for 1 h and pressed into pellets. These were heated to 600 °C at a rate of 5 °C min⁻¹ for 4 h under oxygen and cooled to 50 °C at a rate of 5 °C min⁻¹. For comparison, $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ was prepared using the same method. The as-synthesised materials were stored and handled in an argon filled glovebox.

Laboratory powder X-ray diffraction (PXRD) data for as-synthesised $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ and $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ were collected using a PANalytical Empyrean diffractometer with a Ge (110) monochromator with Cu radiation ($\lambda_{Cu-K\alpha 1} = 1.5406$ Å) and X'celerator RTMS detector. PXRD patterns were collected over 12 h per scan, in the 2 θ range 10 - 80 ° with a step size of 0.0170 ° and 4117 number of steps and a time per step of 10.60 s. Powdered samples were loaded into a zero-background silicon sample holder in an argon filled glovebox covered with a Kapton film to protect the powdered samples during data acquisition and PXRD patterns were collected in Bragg-Brentano geometry. In addition, as-synthesised $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ was loaded in a 0.5 mm glass capillary and synchrotron powder X-ray diffraction data were obtained using the I11 diffractometer at the Diamond Light Source, UK (wavelength 0.826579(5) Å). Diffraction data were analysed using the Rietveld method using Topas Academic V6.² A JEOL JSM-5600 SEM fitted with a tungsten filament electron source and a secondary electron detector were used to examine the morphology of the as-synthesised materials. Energy dispersive X-ray spectroscopy (EDS) analysis were recorded on as-synthesised $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ using a JSM IT200 SEM equipped with a Jeol DrySD EDS detector.

1.2. Electrochemical testing and ex situ characterisation

To evaluate the electrochemical properties of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ and $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$, positive electrodes were prepared by mixing 75 wt% of the active material, with 15 wt% super C65 carbon and 10 wt% Solef binder (modified polyvinylidene fluoride, PVDF) in n-methyl-2-polyvinylidene which were cast onto aluminium foil, giving typical cast electrode loadings of 2.6 mg cm⁻³. Electrodes were prepared in air within 6 h and once dry, punched into 13 mm diameter discs and dried at 80 °C under vacuum overnight. CR2325 coin cells were assembled in an argon filled glovebox made up of a positive disk electrode, sodium metal as a counter/reference electrode, separated by a glass fibre separator (Whatman, GF/F) soaked in electrolyte (1M NaPF₆ in ethylene carbonate/diethyl carbonate (1:1 v/v%), Kishida). Electrochemical measurements were collected in a temperature-controlled environment at 30 °C using a Biologic BCS-805 or Maccor series 4200 battery cycler.

For ex-situ PXRD characterisation, 80 wt% of active material Na_{4/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂ was mixed with 20 wt% super C65 carbon, with no binder and Swagelok type cells were assembled as described above using typical powder electrode loadings of 29 mg cm⁻². Cells were cycled galvanostatically at 10 mA g⁻¹ using a Biologic Mac Pile II system at 30 °C. Positive electrodes were recovered after cycling in an argon filled glovebox, washed with dimethyl carbonate (DMC, Sigma Aldrich, ≥99%) three times and dried under vacuum at room temperature. Laboratory PXRD patterns were collected on a PANanalytical Empyrean diffractometer, using MoK $\alpha_{1,2}$ radiation ($\lambda = 0.7107$ Å) with a Zr β -filter and X'celerator detector. Data were collected at room temperature in the 2 θ range, 5.0 – 40.0 ° over 24 h per scan with a step size of 0.0084 °, in 0.7 mm glass capillaries prepared in an argon filled glovebox. Diffraction data were analysed using the Rietveld method using Topas Academic V6.²

For soft X-ray absorption spectroscopy (SXAS) measurements, CR2325 coin cells were assembled as described above, except that Solupor membranes were used, soaked with electrolyte and cells cycled at 10 mA g⁻¹. Electrodes were recovered, washed with DMC three times, and dried under vacuum. Spectra were collected at the C-branch of beamline BL27SU at Spring 8 in Japan.³ SXAS spectra at the Mn and Ti L-edges and O K-edge, the partial fluorescence yield (PFY) and total electron yield (TEY) signals were measured simultaneously at a resolution of about 0.1 eV. PFY was detected using an energy dispersive soft X-ray analyser and TEY was recorded using the sample drain current detected by a pico-ammeter. A linear background was removed by performing a linear fit to the region before the respective absorption edge and subtracting it from the spectrum. Further normalisation was carried out by setting the low energy region before any absorption peaks to zero and the post-edge region after any absorption features to unity.

For electron paramagnetic resonance (EPR) measurements, 80 wt% of active material was mixed with 20 wt% super C65 carbon, and Swagelok type cells were assembled and cycled as described above. The powdered electrodes were extracted, washed with DMC three times and dried under vacuum at room temperature for 1 h. The powdered samples were loaded under argon into quartz EPR tubes and sealed using silicone rubber. EPR measurements were collected at room temperature on the same day the electrodes were prepared. To study their structural stability, EPR measurements were collected on the same samples after an additional five days. EPR spectra were acquired using an X-band (9.9 GHz) Bruker EMX 10/12 spectrometer equipped with an ELEXSYS super-high-sensitivity probehead (Bruker ER4122SHQE). Microwave power and modulation amplitude were set to 0.2 mW and 2 G, respectively. The conversion time and time constant were set to 40.00 ms and 40.96 ms,

respectively. EPR spectra were collected with a total field sweep of 5000 G. The spectra were normalised based on the weight of sample used and the field axis was corrected against a DPPH standard sample (g = 2.0036).

Ex situ Raman spectroscopy measurements were performed with a Renishaw inVia Qontor confocal Raman microscope using a 532 nm laser and 1800 l mm⁻¹ grating from 100 to 1900 cm⁻¹. Pellet electrodes containing 80 wt% of $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$, 10 wt% super C65 carbon and 10 wt% polyvinylidene fluoride were prepared and dried at 80 °C under vacuum overnight. CR2325 coin cells were assembled as described above, except Celgard replaced the glass fibre separator. The pellet electrodes were recovered from disassembled cells in an argon filled glovebox, washed with DMC three times, and dried under vacuum at room temperature for 1 h. Electrodes were loaded into an airtight optical Raman test cell (ECC-Opto-Gas, EL-Cell) inside an argon filled glovebox to avoid air exposure. Static scan measurements were collected using a 50× objective, 5% laser power, and an exposure time of 1 second with 10-30 accumulations per measurement. The pristine sample and its mixture with C65 were analysed both in and out of the optical Raman test cell to observe the contributions from the El-Cell holder and separator. The Raman spectra were collected in at least three different locations per sample to ensure the measurements were reproducible. Wire 5.5 software (Renishaw) was used to remove cosmic rays and correct the baseline of the spectra.

2. Density functional theory calculations

All the calculations performed in this work employed density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package code.^{4,5} Interactions between core and valence electrons were described using the projector augmented wave (PAW) method.⁶ Geometry optimisations for all structures were carried out using the PBEsol functional,^{7,8} a variation of the Perdew-Burke Ernzerhof (PBE)⁹ generalised-gradient approximation (GGA) functional revised for solids. The electron configurations Na ($3s^1$), Mn ($3p^63d^54s^2$), Ti ($3d^24s^2$), and O ($2s^22p^4$) were treated as the valence electrons. Convergence to plane wave energy was checked, with a cut-off of 450 eV found to be sufficient to converge the total energy to within 0.01 eV atom⁻¹. Brillouin zones for all compounds were sampled such that the k-points were converged in an accuracy of the total energy in 0.001 eV atom⁻¹. To correct the self-interaction error inherent to the strongly correlated Mn *d* orbitals, PBEsol+U method,^{10,11} where the U value of 3.9 eV was applied for Mn *d* orbitals was used. The magnetic arrangement of Mn was set to be ferromagnetic because it was found to be the most stable one among all possible symmetrically unique magnetic arrangements.

To predict the solubility limit of Ti in $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$, the primitive cells of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ ($P^{\overline{1}}$) and $Na_{4/7}[\Box_{1/7}Ti_{6/7}]O_2$ ($P2_1/m$) were first retrieved from the Inorganic Crystal Structure Database (ICSD),¹² and the geometries were then optimised using the PBEsol+U method (see Tables S2 and S3 for the optimised structures). The optimised structures were then expanded into supercells with four formula units (48 atoms). To minimise the interatomic interactions with their corresponding periodic images, supercells close to simple cubic were generated using Atomic Simulation Environment.¹³ The transformation matrices for generating the supercells of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ (P_{NMO}) and $Na_{4/7}[\Box_{1/7}Ti_{6/7}]O_2$ (P_{NTO}) are given in Equation 1.

$$P_{NMO} = \begin{bmatrix} 1 & 0 & 1 \\ 0 & 1 & 1 \\ 0 & 0 & 2 \end{bmatrix}, P_{NTO} = \begin{bmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$
(1)

Atomic configurations after Ti-substitution were then generated by substituting Mn (or Ti) to the target Ti composition x of $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$, followed by DFT geometry optimisation. The total energies and degeneracy of optimised supercells were then used to calculate mixing enthalpy, entropy, and Ti solubility within the generalised quasi-chemical approximation (GQCA).¹⁴ See the Supporting Information, Sections 3.1, 3.2 and 3.3 for details.

From the optimised primitive Na_{4/7}[$\Box_{1/7}$ Mn_{6/7}]O₂ and Na_{4/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, the structures with differing Na contents during cycling were modelled to predict the theoretical voltage profiles of Na_x[$\Box_{1/7}$ Mn_{6/7}]O₂ and Na_x[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂. The partially desodiated structures with 0.0 < *x* < 4/7 were generated by creating Na vacancies, whereas those with 4/7 < *x* < 6/7 were constructed by adding additional Na atoms in the interstitial sites. In this calculation, all atomic arrangements arising from symmetry unique Na vacancy and interstitial sites were considered, where interstitial sites are predicted from primitive Na_{4/7}[$\Box_{1/7}$ Mn_{6/7}]O₂ using the Voronoi tessellation methods¹⁵ and subsequent DFT geometric optimisations. The predicted stable Na interstitial sites and their Wyckoff positions are 1*h* (0.5,0.5,0.5), 2*i* (0.20,0.70,0.74), 2*i* (0.09,0.61,0.14), and 1*f* (0.5,1.0,0.5). Depending on the atomic arrangements of Na vacancies and interstitials, 23 and 111 different structures were generated for Na_x[$\Box_{1/7}$ Mn_{6/7}]O₂ and Na_x[$\Box_{1/7}$ Mn_{5/7}]O₂, respectively. The subsequent geometry optimisations of the constructed structures provide total energies, the values of which were then used to predict theoretical voltage profiles as follows.

Theoretical voltages were calculated from the difference in DFT total energies of cathode structures before and after sodiation, the details of which can be found elsewhere.^{16,17} The discharge process of $Na_x[\Box_{1/7}Mn_{6/7}]O_2$ and $Na_x[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ with the intercalation of Δx amount of Na are expressed in Equation 2.

$$Na_{x}[\Box_{1/7}Ti_{y}Mn_{6/7-y}]O_{2} + \Delta xNa^{+} + \Delta xe^{-} \rightarrow Na_{x+\Delta x}[\Box_{1/7}Ti_{y}Mn_{6/7-y}]O_{2}$$
(2)

Where the Ti content, y, is 0 and 1/7 for Na_{4/7}[$\Box_{1/7}$ Mn_{6/7}]O₂ and Na_{4/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, respectively. The theoretical voltage (V) for Equation 2 can then be predicted using the total energies of Na_x[$\Box_{1/7}$ Ti_yMn_{6/7-x}]O₂ $(E_{Na_x}[\Box_{1/7}Ti_yMn_{6/7-y}]O_2)$, Na_{x+ $\Delta x}[<math>\Box_{1/7}$ Ti_yMn_{6/7-x}]O₂ $(E_{Na_x + \Delta x}[\Box_{1/7}Ti_yMn_{6/7-y}]O_2)$, and Na (E_{Na}) as given in Equation 3.</sub>

$$V = (E_{Na_{x}}[\Box_{1/7}Ti_{y}Mn_{6/7-y}]o_{2} + \Delta x E_{Na} - E_{Na_{x} + \Delta x}[\Box_{1/7}Ti_{y}Mn_{6/7-y}]o_{2}/\Delta x$$
(3)

Here, the Na_x[$\Box_{1/7}$ Ti_yMn_{6/7-y}]O₂ and Na_{x+Δx}[$\Box_{1/7}$ Ti_yMn_{6/7-y}]O₂, determine the end points of theoretical voltage plateaux and are two adjacent ground state phases that can be predicted from the convex hull diagrams of the formation energies. For this reason, we calculated the formation energies of all constructed model structures and then plotted the formation energy convex hull diagrams of Na_x[$\Box_{1/7}$ Mn_{6/7}]O₂ and Na_x[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂ (Figure 8 (a)). The predicted ground state structures have chemical formulae of [$\Box_{1/7}$ Mn_{6/7}]O₂, Na_{1/7}[$\Box_{1/7}$ Mn_{6/7}]O₂, Na_{1/7}[$\Box_{1/7}$ Mn_{6/7}]O₂, Na_{1/7}[$\Box_{1/7}$ Mn_{6/7}]O₂, and Na_{6/7}[$\Box_{1/7}$ Mn_{6/7}]O₂, and Na_{6/7}[$\Box_{1/7}$ Mn_{6/7}]O₂, for Na_x[$\Box_{1/7}$ Mn_{6/7}]O₂, Na_{1/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, Na_{1/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, Na_{3/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, and Na_{6/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, Na_{3/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, Na_{4/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, Na_{2/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, Na_{3/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, and Na_{6/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, Na_{3/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, Na_{4/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, and Na_{6/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, Na_{3/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, Na_{4/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂, and Na_{6/7}[$\Box_{1/7}$ Ti_{1/7}Mn_{5/7}]O₂. Among all atomic arrangements for each chemical formula, we then screened out ones that can format room temperature. This was done by selecting structures with total energy close to the ground state structure by less than 0.0259 eV/atom, *i.e.*, thermal vibration energy at room temperature. Theoretical voltages were then calculated from all possible pairs of structures in the selected group of structures.

3. Additional experimental results



Figure S1. (a) Laboratory powder X-ray data for as-synthesised $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ (black solid line) and $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ (blue solid line). (b) SEM micrograph of as-synthesised $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$.

Na₄/7[□ _{1/7} Ti _{1/7} Mn _{5/7}]O ₂									
	R_{exp} = 2.35%, R_{wp} = 6.30%, R_p = 4.55%								
	Lattice parameters Space group P^{1} a = 6.5719(10) Å, b = 6.9370(11) Å, c = 7.5319(9) Å								
	C	α = 106.63(1)°, β =	106.49(2)°, γ= 11	1.35(1)° <i>, V</i> = 275.	95(10) Å ³				
Atom	Wyckoff Symbol	x/a	y/b	z/c	Occupancy	Biso			
Mn1/Ti1	2 <i>i</i>	0.0608(10)	0.0728(13)	0.2377(10)	0.83/0.17	0.3			
Mn2/Ti2	2 <i>i</i>	0.3279(12)	0.3568(13)	0.0671(13)	0.83/0.17	0.3			
Mn3/Ti3	2 <i>i</i>	0.2246(10)	0.2244(11)	0.6412(12)	0.83/0.17	0.3			
Na1	2 <i>i</i>	0.238(2)	0.715(3)	0.501(3)	1	1.5			
Na2	2 <i>i</i>	0.309(3)	0.850(2)	0.068(2)	1	1.5			
01	2 <i>i</i>	0.381(4)	0.222(4)	0.270(4)	1	0.6			
02	2 <i>i</i>	0.705(4)	0.939(5)	0.170(4)	1	0.6			
03	2 <i>i</i>	0.020(4)	0.193(4)	0.016(4)	1	0.6			
04	2 <i>i</i>	0.130(4)	0.333(4)	0.463(4)	1	0.6			
05	2 <i>i</i>	0.711(4)	0.493(4)	0.112(4)	1	0.6			
06	2 <i>i</i>	0.122(3)	0.957(4)	0.411(4)	1	0.6			
07	2 <i>i</i>	0.429(3)	0.601(4)	0.294(4)	1	0.6			

Table S1. Rietveld refinement results of as-synthesised $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$.

Atom	Wyckoff Symbol	x/a	y/b	z/c	Occupancy	Biso
Mn1/Ti1	2i	0.0608(10)	0.0728(13)	0.2377(10)	0.83/0.17	0.3
Mn2/Ti2	2i	0.3279(12)	0.3568(13)	0.0671(13)	0.83/0.17	0.3
Mn3/Ti3	2 <i>i</i>	0.2246(10)	0.2244(11)	0.6412(12)	0.83/0.17	0.3
Na1	2i	0.238(2)	0.715(3)	0.501(3)	1	1.5
Na2	2i	0.309(3)	0.850(2)	0.068(2)	1	1.5
01	2 <i>i</i>	0.381(4)	0.222(4)	0.270(4)	1	0.6
02	2 <i>i</i>	0.705(4)	0.939(5)	0.170(4)	1	0.6
03	2i	0.020(4)	0.193(4)	0.016(4)	1	0.6
04	2 <i>i</i>	0.130(4)	0.333(4)	0.463(4)	1	0.6
05	2i	0.711(4)	0.493(4)	0.112(4)	1	0.6
06	2 <i>i</i>	0.122(3)	0.957(4)	0.411(4)	1	0.6
07	2 <i>i</i>	0.429(3)	0.601(4)	0.294(4)	1	0.6

3.1. Simulation of preferred Ti sites

In order to establish if Ti has a preferred position out of the three Mn sites in $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$, the total energies of $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ with Ti positioned on each of the three Mn sites were calculated. In this calculation a $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ supercell with four formula units (see Figure S2) is used so that calculated total energies are less affected by Ti atoms across periodic boundaries, while allowing the effect of long-range ordering of Ti atoms.

Figure S2 (b) and (c) show the calculated total energies after substituting one and two Mn of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ supercell with Ti, respectively. It is noted that, for both $Na_{4/7}[\Box_{1/7}Ti_{1/14}Mn_{11/14}]O_2$ and $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$, the position of Ti is less likely to influence the total energy of structures: the most unstable atomic configuration of $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ has a relative total energy of 2.65×10⁻³ eV/atom, which is an order of magnitude lower than the thermal vibration energy at room temperature (0.0259 eV). In this regard, Ti atoms can occupy any one of the three symmetrically unique Mn sites of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$, as shown in Figure S2 (a).



Figure S2. Energy change after adding Ti on Mn sites of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$, (a) primitive and supercell model structures constructed to test the preferential Ti sites in Mn sites of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$. Symmetrically unique three Mn sites are denoted as numbers in (a). Relative total energies of (b) $Na_{4/7}[\Box_{1/7}Ti_{1/14}Mn_{11/14}]O_2$ and (c) $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$, when a single and two Mn of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ supercells are substituted with Ti, respectively.



Figure S3. Laboratory X-ray diffraction pattern of the as-prepared $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ (black solid line) and $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ (blue solid line), showing the (001) diffraction peak which corresponds to the to the interlayer distance between the transition metal oxide layers.

3.2. Calculation of mixing enthalpy and entropy for Ti solubility calculations

Once Ti is added to $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$, the resultant $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ can have two different crystal structures: one with space group P^{1} for Mn-rich condition with *x* close to 0.0, or another with $P2_1/m$ for Ti-rich condition with *x* close to 6/7. To predict the maximum amount of Ti that can be miscible to the structure with P^{1} symmetry, the energy of mixing should be calculated under the consideration of the P^{1} and $P2_1/m$ structures. For this reason, we first optimised the $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ (P^{1}) and $Na_{4/7}[\Box_{1/7}Ti_{6/7}]O_2$ ($P2_1/m$) structural models that correspond to the two end points (x = 0.0 and x = 6/7) of the alloy composition (Tables S2 and S3). The lattice parameters of both structures are in good agreement with the experimental values.

Table S2. Unit cell parameters of optimised structures of fully sodiated $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ and $Na_{4/7}[\Box_{1/7}Ti_{6/7}]O_2$ relaxed using PBEsol functionals.

	Lattice parameters/ Å			Lattice angles		
	a/ Å	<i>b/</i> Å	c/ Å	$lpha$ / $^{\circ}$	6/ °	۲/ °
	Na₄/⁊[□ _{1/7} Mn _{6/7}]O ₂					
Present study	6.5534	6.7618	7.5415	105.1795	107.7200	110.6309
Experiment ¹	6.5921(34)	6.8916(34)	7.5071(30)	105.022(46)	107.543(39)	111.651(37)
Na₄/⁊[□ _{1/7} Ti _{6/7}]O ₂						
Present study	8.4570	3.8040	9.0921	90.00	101.6879	90.00
Experiment ²	8.5647	3.7982	9.1226	90.00	101.6042	90.00

Possible atomic configurations under intermediate compositions of 0.0 < x < 6/7 were then modelled by generating two supercell structures of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ ($P^{\overline{1}}$) and $Na_{4/7}[\Box_{1/7}Ti_{6/7}]O_2$ ($P2_1/m$) with four formula units, and the number of transition metal elements (*i.e.*, Mn and Ti) were adjusted to the desired Ti composition. In this model the full range of symmetrically inequivalent atomic arrangements were considered, resulting in a total of 1738 structures for 13 different Ti compositions for $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ (see Table S4).

Table S3. Fractional coordinates of symmetry unique atomic sites in conventional $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ and $Na_{4/7}[\Box_{1/7}Ti_{6/7}]O_2$ structures relaxed using PBEsol functionals. Wyckoff position and the volumes of MnO_6 and TiO_6 octahedra are also included for reference.

Element	Fract	tional coordina	ates	Wyckoff Octahed			
	x/ a	y/ b	<i>z/</i> c	symbol	volume/ Å ³		
Na₄/⁊[□ _{1/7} Mn _{6/7}]O ₂							
Na(1)	0.2585	0.6839	0.4905	2 <i>i</i>			
Na(2)	0.3388	0.8240	0.0743	2 <i>i</i>			
Mn(3)	0.0768	0.0763	0.2196	2 <i>i</i>	9.1535		
Mn(4)	0.3575	0.3604	0.0805	2 <i>i</i>	9.1938		
Mn(5)	0.2202	0.2190	0.6409	2 <i>i</i>	9.1995		
O(6)	0.3904	0.1952	0.2396	2 <i>i</i>			
O(7)	0.2639	0.0869	0.8421	2 <i>i</i>			
O(8)	0.0256	0.2072	0.0234	2 <i>i</i>			
O(9)	0.1275	0.3179	0.4386	2 <i>i</i>			
O(10)	0.6921	0.5098	0.1299	2 <i>i</i>			
O(11)	0.1266	0.9414	0.4118	2 <i>i</i>			
O(12)	0.4493	0.6434	0.2834	2 <i>i</i>			
		Na _{4/7} [□ _{1/7} Ti _{6/7}]O ₂				
Na(1)	0.7500	0.0029	0.6605	2 <i>e</i>			
Na(2)	0.7500	0.8161	0.0798	2 <i>e</i>			
Ti(3)	0.7500	0.4706	0.7786	2 <i>e</i>	9.8974		
Ti(4)	0.7500	0.2487	0.1794	2 <i>e</i>	10.1164		
Ti(5)	0.7500	0.3535	0.4844	2 <i>e</i>	9.9507		
O(6)	0.7500	0.5856	0.5434	2 <i>e</i>			
O(7)	0.7500	0.7001	0.8152	2 <i>e</i>			
O(8)	0.7500	0.4837	0.2552	2 <i>e</i>			
O(9)	0.7500	0.1690	0.4096	2 <i>e</i>			
O(10)	0.7500	0.0485	0.1535	2 <i>e</i>			
O(11)	0.2500	0.7215	0.3103	2 <i>e</i>			
O(12)	0.2500	0.6496	0.0349	2 <i>e</i>			

Figure S4 (a, b) show the calculated energy profile of $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ with respect to Ti composition across the range of Ti compositions for $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$, $P^{\bar{1}}$ symmetry has lower total energies than $P2_1/m$ symmetry, except $Na_{4/7}[\Box_{1/7}Ti_{6/7}]O_2$ where $P2_1/m$ is more stable by 0.13 meV atom⁻¹ (Figure S4 (a)). This indicates that, $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ tends to adopt $P^{\bar{1}}$ structure for most of the Ti compositions and thus, the mixing enthalpy and entropy of $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ is mostly influenced by the total energies of $P^{\bar{1}}$ structure.

Close examination on the total and mixing energies reveals that P^{1} structures have smaller energy spread than $P2_{1}/m$. Such small energy spread is mainly attributed to the small volume difference in MnO₆ octahedra of P^{1} structure (Figure S4 (c) and Table S3): when examining Na_{4/7}[$\Box_{1/7}$ Mn_{6/7}]O₂ (P^{1}), the volume of MnO₆ octahedra differs by only 0.5%, whereas that of TiO₆ in Na_{4/7}[$\Box_{1/7}$ Ti_{6/7}]O₂

 $(P2_1/m)$ displays a greater volume difference of up to 2.2%. Hence, even though Ti can be doped in three symmetrically unique Mn sites, the resultant P^1 structure, and its total energy, are similar regardless of the Ti position (see the small spread in the unit cell volumes of P^1 in Figure S4 (d)).

The small energy difference between Ti (or Mn) configurations of P^1 structure can cause the mixing entropy to be less dependent on temperature, which will be quantitatively assessed within the generalised quasi-chemical approximation (GQCA)¹⁸ in the following.



Figure S4. Changes in (a) total energy and (b) mixing energy of all $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ supercells with respect to Ti composition x, calculated for two different crystal symmetry of $P\overline{1}$ and $P2_1/m$. (c) Symmetrically unique Mn (Ti) sites of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ ($Na_{4/7}[\Box_{1/7}Ti_{6/7}]O_2$) and their corresponding octahedral volumes of MnO_6 (TiO₆). (d) Unit cell volumes of all $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ supercells plotted in the full compositional range.

Based on the calculated total energies in Figure S4, the variation in the enthalpy of mixing ($\Delta U_{Na_{4/7}}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$) of $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ was calculated under the assumption that the crystal symmetry of $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ to be P^1 for x < 6/7 and $P2_1/m$ for x = 6/7. This was attained by comparing the total energies $\binom{E_{Na_{4/7}}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2}{D_1/7}$ of intermediate structures with those (E_{NMO} and E_{NTO}) of the two pure structures of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ (P^1) and $Na_{4/7}[\Box_{1/7}Ti_{6/7}]O_2(P2_1/m)$ according to Equation S4.

$$\Delta U_{Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2} = E_{Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2} - (3-x)E_{NMO} - xE_{NTO}$$
(4)

Table S4. Number of symmetrically unique configurations for differing Ti compositions of $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$. Two possible atomic structures with crystal symmetry of P^{1} and $P2_1/m$ are considered. Number of Ti atoms (N_{Ti}) in the supercell structures of $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ are denoted for reference.

N _{Ti}	<i>x</i> Ti in Na₄/⁊[□ _{1/7} Ti _x Mn _{6/7-x}]O ₂	P $^{ar{1}}$ symmetry	P2 ₁ /m symmetry
0	0	1	1
1	0.25	3	3
2	0.5	21	15
3	0.75	55	37
4	1	135	84
5	1.25	198	120
6	1.5	246	146
7	1.75	198	120
8	2	135	84
9	2.25	55	37
10	2.5	21	15
11	2.75	3	3
12	3	1	1
Total		1072	666

The thermodynamic properties of the solid solution were then determined using the GQCA method,¹⁸ which is proven to be effective in predicting thermodynamics of solid-solution alloys where the long-range order is less important.^{19,20} By incorporating the total energy and the degeneracy of atomic configurations into a statistical mechanical mean field model, this method predicts the internal energy, ΔU and the configurational entropy, ΔS with respect to the alloy composition and temperature.

At 300, 800, 1400 and 1600 K, the calculated enthalpy of mixing of the solid solution can be well represented as the regular solution expression of $\Omega x(1 - x)$, which can be best fit with $\Omega = 0.028$ (eV atom⁻¹) at room temperature (Figure S5 (a)). As can be seen in Figure S5 (b), the variation in the entropy of mixing of the alloy is close to the ideal solution expression of $-k_B[xlnx + (1-x)ln(1-x)]$. The entropy changes with respect to temperature are negligibly small, which is attributed to the small energetic changes of $P^{\overline{1}}$ symmetry structure with respect to the Ti configuration (Figure S4).



Figure S5. (a) Enthalpy and (b) entropy of mixing as functions of the $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ alloy composition and temperature, predicted within the generalised quasi-chemical approximation. Both energy values are obtained under the assumption that the P^1 symmetry structure is stable for all composition range except x = 6/7, according to Figure S4 (a).

By comparing the calculated mixing enthalpy and entropy, one can derive the Helmholtz free energy of mixing according to Equation 5.

$$\Delta F(x,T) = \Delta U(x,T) - T\Delta S(x,T)$$
(5)

For each temperature, the common-tangent construction of the calculated ΔF give rise to two binodal compositions, whereas alloy compositions where the second derivative of ΔF corresponds to the spinodal points.

The temperature-composition diagram of the alloy can then be constructed by plotting all binodal and spinodal points along composition and temperatures. The above procedures of predicting thermodynamic properties of $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ were done by employing GQCA alloy Python codes available from https://github.com/WMD-group/GQCA_alloys. The detailed explanation of the obtained Helmholtz free energy and temperature-composition diagram are described in Figure S6.

3.3. Calculated Ti solubility of Na_{4/7}[$\Box_{1/7}$ Mn_{6/7}]O₂

Whilst increasing the amount of a dopant may result in enhanced electrochemical performance, adding too much of a dopant can cause phase separation and negatively affect the performance. Therefore, to take full advantage of dopants, it is important to predict the maximum amount of dopants that can dissolve in the parent structure, *i.e.*, solubility limit.

For this purpose, we employed a mean field statistical mechanical model, called generalised quasi-chemical approximation (GQCA)¹⁸ to predict the solubility limit of Ti dopants on $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2(P^{1})$ cathodes (see Figure S4 and Figure S5 for the detailed calculation procedures). This model is especially suitable for solid solutions where the long-range order is less important.

Figure S6 shows the calculated Helmholtz free energy of mixing of $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ at different temperatures. The results show that, at room temperature, none of the Ti dopants are soluble in $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ ($P^{\bar{1}}$), as all values are positive and local minima are not found for all composition range. As the temperature increases, the free energy of mixing becomes negative for small amounts of Ti and, at the same time, common tangent plane can be plotted near local minima. This indicates the presence of binodal decomposition, which allows the Ti doping in $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ up to this alloy composition.

To quantitatively estimate the maximum Ti dopant composition for $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$, the temperature-composition phase diagram is plotted from the calculated Helmholtz free energy (Figure S6 (b)). The critical temperature of $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$, *i.e.*, temperature above when solid solution is stable for any Ti composition, is 1533 K. In the synthesis temperature of 873K used in this study, maximum of 0.54 of Ti contents (*x*) is expected to be miscible to $P^{\overline{1}}$ structure. In this regard, 5 mol% Ti-substitution of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ is an ideal composition that is expected to maximise the effect of Ti dopants on the electrochemical performances of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$.



Figure S6. (a) Helmholtz free energy calculated as functions of alloy composition of $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ and temperature, predicted using the generalised quasi-chemical approximation. (b) Predicted phase diagram of the $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ alloy above 300 K. The blue and pink area are the binodal and spinodal decomposition ranges, respectively, whereas the white area marks the fully miscible range. Synthesis temperature (T) and corresponding maximum Ti composition (x) of metastable $Na_{4/7}[\Box_{1/7}Ti_xMn_{6/7-x}]O_2$ are denoted by red dotted lines.

Na _{4/7} [□ _{1/7} Ti _{1/7} Mn _{5/7}]O ₂ charged to 4.4 V						
	R _{exp} : 3.06%, R _{wp} : 4.13%					
	Lattice paran	neters P3 Space	e group R3 <i>m a</i>	= 2.8489(3) Å, c	: = 16.637(4) Å	
Atom	Wyckoff symbol	x/a	y/b	z/c	Occupancy	Biso
Mn1/Ti1	3 <i>a</i>	0	0	0	0.714/0.143	0.3
Na1	3 <i>a</i>	0	0	0.1604(7)	0.40(2)	1.2
01	3 <i>a</i>	0	0	0.4036(19)	1	0.5
02	3 <i>a</i>	0	0	0.5946(18)	1	0.5

Table S5. Rietveld refinement results for $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ charged to 4.4 V.



Figure S7. Electronic structure changes of $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ during charge and discharge. (a) Ex situ soft X-ray absorption spectra for O K-edge in partial fluorescence mode. (b) First-cycle charge-discharge load curve and the points indicate the states of charge and discharge at which ex situ measurements were collected. The integrated intensity of the pre-edge feature (526-532.5 eV) for the O K-edge SXAS, relative to the pristine phase.



Figure S8. (a) EPR spectra of pristine $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ and ex-situ electrodes of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ cycled between 3.0 – 4.4 V at 10 mA g⁻¹, mixed with conductive carbon C65 additive. EPR spectra were collected on the same day after cycling ceased and were normalised based on the mass of the sample. The sharp, intense peak is assigned to conductive carbon C65 additive. (b) The corresponding galvanostatic charge/discharge profile with the voltages highlighted where the ex-situ EPR measurements were conducted.



Figure S9. (a) Ex-situ EPR spectra for $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ electrode charged to 4.4 V collected on the same day and then again 5 days after the cycling had ceased. (b) Ex-situ EPR spectra for $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ electrode charged to 4.4 V collected on the same day and then again 5 days after the cycling had ceased. EPR spectra were normalised based on the mass of the samples. The sharp, intense peak is assigned to conductive carbon C65 additive.



Figure S10. (a) Raman spectra of pristine $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ and pristine $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ mixed with C65 carbon, collected in and out of the EL-Cell holder. Spectrum show bands at ~640 cm⁻¹ and a broad shoulder at ~582 cm⁻¹ which likely correspond to the O-TM-O bending and TM-O stretching modes (TM = Mn, Ti), respectively. The $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ mixed with C65 samples also show bands at ~1346 and ~1598 cm⁻¹ attributed to the D and G bands. The orange region highlights contributions from the EL-Cell holder and separator. (b) Ex situ Raman spectra of $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ electrodes at different states of charge and discharge, showing the pristine material mixed with C65 (black line), after charge to 4.1 V (red line), charge to 4.4 V (blue line), discharge to 4.1 V (green) and discharge to 3.0 V (pink line), collected in the EL-Cell holder.

3.4. Calculated voltage profiles before and after Ti-substitution

Table S6. Unit cell parameters and fractional coordinates of primitive $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ structure with the most stable Ti and
Na arrangements.

Na₄/⁊[□ _{1/7} Mn _{6/7}]O₂							
Lattice parameters Space group $P^{\overline{1}} a = 6.9180$ Å, $b = 6.3466$ Å, $c = 7.8024$ Å							
	<i>α</i> = 99.3	3170 ° <i>, θ</i> = 112.5313 °	, γ = 109.4087 °				
Element		Fractional coordinates	5	Wyckoff			
Element	x/ a	y/ b	z/ c	positions			
Na(1)	0.5000	0.5000	0.5000	2 <i>i</i>			
Na(2)	0.5000	0.0000	0.5000	2 <i>i</i>			
Na(3)	0.2156	0.7005	0.6310	2 <i>i</i>			
Na(4)	0.3158	0.8224	0.0585	2 <i>i</i>			
Mn(5)	0.0734	0.0669	0.2148	2 <i>i</i>			
Mn(6)	0.3584	0.3629	0.0743	2 <i>i</i>			
Mn(7)	0.2077	0.2163	0.6435	2 <i>i</i>			
O(8)	0.3862	0.1805	0.2521	2 <i>i</i>			
O(9)	0.2540	0.0715	0.8563	2 <i>i</i>			
O(10)	0.0362	0.2159	0.0127	2 <i>i</i>			
O(11)	0.1317	0.3231	0.4187	2 <i>i</i>			
O(12)	0.6694	0.4719	0.1180	2 <i>i</i>			
O(13)	0.1137	0.9050	0.4021	2 <i>i</i>			
O(14)	0.4642	0.6509	0.2699	2i			

Table S7. Unit cell parameters and fractional coordinates of primitive $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ structure with the most stable Ti and Na arrangements.

Na₄/7[□1/7Ti1/7Mn5/7]O2

Lattice parameters Space group $P^{\overline{1}} a = 6.8693$ Å, b = 6.4012 Å, c = 7.8609 Å

α = 99.2604 °, β = 112.1145 °, γ = 109.1791 °

Flomont		Fractional coordinates	5	Wyckoff
Element	x/ a	y/ b	z/ c	positions
Na(1)	0.5018	0.5031	0.5056	1 <i>a</i>
Na(2)	0.9203	0.4296	0.7913	1 <i>a</i>
Na(3)	0.2321	0.7150	0.6011	1 <i>a</i>
Na(4)	0.7695	0.2783	0.3689	1 <i>a</i>
Na(5)	0.3415	0.8400	0.0866	1 <i>a</i>
Na(6)	0.6502	0.1482	0.9377	1 <i>a</i>
Ti(7)	0.0816	0.0761	0.2317	1 <i>a</i>
Mn(8)	0.9272	0.9294	0.7885	1 <i>a</i>
Mn(9)	0.3558	0.3616	0.0730	1 <i>a</i>
Mn(10)	0.6414	0.6411	0.9323	1 <i>a</i>
Mn(11)	0.2165	0.2135	0.6502	1 <i>a</i>
Mn(12)	0.7839	0.7766	0.3586	1 <i>a</i>
O(13)	0.3851	0.1871	0.2479	1 <i>a</i>
O(14)	0.6185	0.8143	0.7565	1 <i>a</i>
O(15)	0.2579	0.0719	0.8573	1 <i>a</i>
O(16)	0.7356	0.9245	0.1458	1 <i>a</i>
O(17)	0.0255	0.2141	0.0020	1 <i>a</i>
O(18)	0.9629	0.7753	0.9850	1 <i>a</i>
O(19)	0.1324	0.3290	0.4296	1 <i>a</i>
O(20)	0.8735	0.6707	0.5888	1 <i>a</i>
O(21)	0.6698	0.4717	0.1202	1 <i>a</i>
O(22)	0.3223	0.5287	0.8844	1 <i>a</i>
O(23)	0.1052	0.9009	0.4017	1 <i>a</i>
O(24)	0.8940	0.0911	0.6024	1 <i>a</i>
O(25)	0.4570	0.6350	0.2685	1 <i>a</i>
O(26)	0.5486	0.3607	0.7424	1 <i>a</i>

Na₄/7[□_{1/7}Mn_{6/7}]O₂ Na_{4/7}[□_{1/7}Ti_{1/7}Mn_{5/7}]O₂ Ti in Mn(4) Ti in Mn(3) Ti in Mn(5) Phase Madelung potential (V) O1 O₂ O₃ O_4 O_5 O_6 Na4/7[01/7Mn6/7]O2 25.38 26.98 Ti in Mn(3) 25.31 25.45 25.42 24.83 25.20 25.40 Ti in Mn(4) 25.06 25.62 25.43 25.13 25.15 25.08 Ti in Mn(5) 25.11 25.52 25.15 24.74 25.46 25.52

3.5. Interpretation on the increased voltages after Ti-substitution

Figure S11. Madelung potentials calculated for oxygen atoms adjacent to unoccupied Mn sites of $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ and $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$. Symmetrically equivalent oxygen atoms are denoted by the same number. Oxygen atoms with low Madelung potentials are highlighted by yellow.



Figure S12. The Bader charge difference of individual Mn and O atoms of $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$ with three different Ti arrangements, which were calculated by subtracting the Bader charges of atoms in pristine $Na_{4/7}[\Box_{1/7}Mn_{6/7}]O_2$ from those in $Na_{4/7}[\Box_{1/7}Ti_{1/7}Mn_{5/7}]O_2$. The charges accumulated more than 0.05 after Ti-substitution are highlighted by blue to better visualise charge localisation and associated bond ionicity.

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