Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2022

# Na<sub>2.4</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> anionic redox cathode material for sodium-ion batteries- a combined experimental and theoretical approach to elucidate its charge storage mechanism

Cindy Soares<sup>1,#</sup>, Begoña Silván<sup>1,3,#</sup>, Yong-Seok Choi<sup>2,3,4,#</sup>, Veronica Celorrio<sup>5</sup>, Valerie R. Seymour<sup>1,3</sup>, Giannantonio Cibin<sup>5</sup>, John M. Griffin<sup>1,3</sup>, David O. Scanlon<sup>2,3,4,5</sup> and Nuria Tapia-Ruiz<sup>1,3,\*</sup>

<sup>1</sup>Department of Chemistry, Lancaster University, Lancaster, LA1 4YB, UK

<sup>2</sup>Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

<sup>3</sup>The Faraday Institution, Quad One, Harwell Science and Innovation Campus, Didcot OX11 0RA, UK

<sup>4</sup>Thomas Young Centre, University College London, Gower Street, London WC1E 6BT, UK

<sup>5</sup>Diamond Light Source Ltd., Diamond House, Harwell Science and Innovation Campus, Didcot OX11 0DE, UK

<sup>#</sup>Contributed equally to the work

\*corresponding author: n.tapiaruiz@lancaster.ac.uk

# Methods

Experimental details for GITT measurements	4
Computational details for the construction of model structures	5
Computational details for the theoretical voltage calculations	6
Discussion on the structural changes after AI substitution	7

# List of Tables

Table S1	8
Table S2	9
Table S3	10
Table S4	11
Table S5	

# List of Figures

Figure S1	
Figure S2.	14
Figure S3	15
Figure S4	16
Figure S5	17
Figure S6	18
Figure S7	19
Figure S8	20
Figure S9	21
Figure S10.	22
Figure S11	23
Figure S12	24
Figure S13.	25
Figure S14	26
Figure S15	27
Figure S16	
Figure S17	29
Figure S18	
Figure S19	31
Figure S20	32
Figure S21	
Figure S22	34
Figure S23	35
Figure S24	
Figure S25.	
Figure S26.	

Figure S27	39
Figure S28	40
Figure S29	41
Figure S30.	
Figure S31	43

erences
---------

# Methods

# **Experimental details for GITT measurements**

GITT analysis was carried out to determine the sodium-ion diffusion coefficient of Na<sub>2.4</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>,  $D_{Na^+}$ , according to Fick's laws of diffusion through the following equation: [1,2]

$$D = \frac{4}{\pi\tau} \left(\frac{m_b V_M}{M_B S}\right)^2 \left(\frac{\Delta E_s}{\Delta E_t}\right)^2 \tag{S1}$$

Where  $\tau$  is the time interval during current flux,  $m_b = 3$  mg is the mass of the component,  $V_M = 169.81$  cm<sup>3</sup> mol<sup>-1</sup> is the molecular volume,  $M_B = 320.812$  g mol<sup>-1</sup> is the molecular weight of the compound (estimated from XRD data) and *S* is the area of the sample-electrolyte interphase. In this case, the surface has been estimated assuming perfect spherical particles with an average size determined from SEM images, S = 123.73 cm<sup>2</sup>.  $\Delta E_s$  is the change in the equilibrium voltage, and  $\Delta E_t$  is the change of the cell voltage during the current pulse, neglecting the ohmic (iR) drop (see Figure S13).

#### Computational details for the construction of model structures

The PBEsol functional [3], a variation of the Perdew-Burke-Ernzerhof (PBE) [4] generalisedgradient approximation (GGA) functional revised for solids, was used to find optimized geometries of partially and fully sodiated Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>. Standard density functional calculations, however, are incapable of correctly describing the strongly correlated Mn *d* orbitals, owing to the self-interaction error inherent to such functionals. This is typically the case for materials containing strongly localized orbitals, such as transition metal d states or rare-earth f states. To resolve the poor description of these orbitals, the +U correction has been applied on GGA functionals for a variety of materials. In this calculation, we used the PBEsol+U [5,6] method, where a U value of 3.9 eV was used to correct the interactions of Mn d-electrons, to optimize the primitive cell of Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> retrieved from the Inorganic Crystal Structure Database (ICSD) [7]. The magnetic arrangement of Mn was set to be ferromagnetic since it was found to be the most stable one among all possible symmetrically unique magnetic arrangements (Figure S1). The optimized Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> structure was then expanded into a supercell with ten formula units (120 atoms), to construct partially sodiated Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> structures. To minimize the interatomic interactions with their corresponding periodic images, the Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> supercell was generated by introducing a transformation

matrix  $P = \begin{bmatrix} -1 & -1 & 1 \\ 1 & 0 & 2 \end{bmatrix}$  that renders the shape of the supercell to be close to a simple cubic cell [8]. From the resultant cubic-like Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> supercell, the partially sodiated Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> structures were generated by adjusting the number of Na atoms and substituting Mn with Al atoms (Figure S2). However, unlike Na-poor structures (Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> with Al atoms (Figure S2). However, unlike Na-poor structures (Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> with x  $\leq$  2.0) that can be readily modelled by creating Na vacancies and Al<sub>Mn</sub> antisites, the construction of Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> with x > 2.0 cannot be realised without understanding the interstitial sites where excess Na atoms can intercalate. For this reason, we first predicted 12 Na interstitial sites in the primitive Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> structure, using the Voronoi tessellation methods [9], followed by performing a screening with DFT geometric optimizations. This yields four symmetry unique stable interstitial sites, where the Wyckoff

positions of these sites correspond to 1h (0.5,0.5,0.5), 2i (0.20,0.70,0.74), 2i (0.09,0.61,0.14), and 1f (0.5,1.0,0.5). Depending on the atomic arrangements of Na interstitial/vacancy and Al<sub>Mn</sub> antisites, numerous structures can be generated for Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>. Among those arrangements, we selected the most stable atomic configuration for each Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> or Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> structure, which results in 11 Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> (x = 2.0, 1.6, 1.2, 1.0, 0.8, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1) and 16 Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> structures (x = 2.4, 2.3, 2.2, 2.1, 2.0, 1.6, 1.4, 1.2, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2, and 0.1). This was done in three steps: 1) Calculation of the electrostatic energy using the Ewald summation method for all possible symmetrically

unique atomic configurations, 2) DFT geometry optimizations of the five lowest electrostatic energy structures with PBEsol+U, and 3) Selection of the most stable configurations by comparing the DFT total energies of the structures calculated in 2). All DFT geometry optimizations of  $Na_xMn_3O_7$  and  $Na_xAl_{0.4}Mn_{2.6}O_7$  structures were carried out until the forces on all atoms become less than 0.01 eV<sup>-1</sup>. The cell parameters of the optimized structures in this study are listed in Table S1. All structures to reproduce the results discussed in this study can be found in the data repository at https://doi.org/10.5281/zenodo.5787489

#### Computational details for the theoretical voltage calculations

Theoretical voltages were calculated from the difference in DFT total energies of cathode structures before and after sodiation. The discharge process of Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> involving Na intercalation by an  $\Delta x$  amount can be expressed as:

$$Na_{x}Al_{y}Mn_{3-y}O_{7} + \Delta x Na^{+} + \Delta x e^{-} \rightarrow Na_{x+\Delta x}Al_{y}Mn_{3-y}O_{7}$$
(S2)

Where AI content (*y*) is 0 and 0.4 for Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>2.4</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> cathodes, respectively. The theoretical voltage (*V*) for Eq. S2 can then be predicted using the total energies of Na<sub>x</sub>Al<sub>y</sub>Mn<sub>3-y</sub>O<sub>7</sub> ( $E_{Na_xAl_yMn_{3-y}O_7}$ ), Na<sub>x+Δx</sub>Al<sub>y</sub>Mn<sub>3-y</sub>O<sub>7</sub> ( $E_{Na_x+Ax}Al_yMn_{3-y}O_7$ ), and Na ( $E_{Na}$ ):

$$V = (E_{Na_x A l_y M n_{3-y} O_7} + \Delta x E_{Na} - E_{Na_{x+\Delta x} A l_y M n_{3-y} O_7}) / \Delta x$$
(S3)

Here,  $Na_xAl_yMn_{3-y}O_7$  and  $Na_{x+\Delta x}Al_yMn_{3-y}O_7$ , of which Na contents determine the endpoints of theoretical voltage plateaus, are two adjacent ground state phases that can be predicted from the convex hull diagrams of the formation energies. The details of the method can be found elsewhere [10,11]. For this reason, we calculated the formation energies of all constructed model structures and then plotted the formation energy convex hull diagrams of Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> (Figure S3). The predicted ground state structures are Na<sub>0.1</sub>Mn<sub>3</sub>O<sub>7</sub>, NaMn<sub>3</sub>O<sub>7</sub>, Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub>, and Na<sub>3</sub>Mn<sub>3</sub>O<sub>7</sub> for the Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> cathode, and Na<sub>0.1</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>, Na<sub>0.7</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>, Na<sub>1.4</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>, Na<sub>2</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>, and Na<sub>2.4</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>

To roughly predict the discharge voltage plateaus in the  $2.0 \le x \le 3.0$  range of Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub>, we modelled Na<sub>2.5</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>3</sub>Mn<sub>3</sub>O<sub>7</sub> by adding one and two extra Na atoms to the predicted interstitial sites of primitive Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub>, followed by DFT geometric optimizations. Among all possible atomic arrangements of Na interstitials, we used the most stable one to calculate the voltage plateau.

#### Discussion on the structural changes after AI substitution

The most direct consequence of AI substitution on layered transition metal oxides is the shortening of bonds between transition metal (TM) and oxygen. Under octahedral coordination, the AI-O bond length is relatively shorter than that of Mn-O [12], which causes the overall length of bonds in the TM layer to be reduced after AI substitution. In this context, we first investigated whether AI substitution can change the TM size in Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> and, in turn, alter the shape of the Na<sup>+</sup> ion diffusion pathways. For this purpose, we estimated the octahedra volumes in the constructed supercells of Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> (Figure S11). Overall, octahedra volumes decrease when lowering the Na content as desodiation oxidizes oxygen and reduces its ionic radius. Further examination of octahedra volumes reveals that, for the same Na content, AI-substituted supercells have relatively smaller octahedral volumes, showing the shrinkage of the TM layer after AI substitution. This shrinkage of the TM layer is equivalent to the shortening of diffusion pathways along the in-plane direction, as quantified by the decrease in cross-sectional area of the TMO<sub>6</sub> octahedra (Figure 11b). As a result, the bond shortening effect from AI<sup>3+</sup> ions facilitates Na<sup>+</sup> ion diffusion, by reducing the in-plane diffusion distances.

Another important effect of AI substitution is increasing the number of localized holes on nonbonding oxygen atoms of the TM layer. Compared to Mn<sup>4+</sup>, Al<sup>3+</sup> has a lower oxidation state and thus, to satisfy the charge balance of a compound, generates extra holes on a cathode under the same Na content. For instance, compared to pristine Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> where all oxygen atoms are in (2-) oxidation state, the Na<sub>2</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> cathode has partially oxidized oxygen atoms, as revealed by localized holes of its partial charge density (Figures S12a and S12b). These extra holes on non-bonding oxygen atoms repel nearby Na<sup>+</sup> ions and, in turn, widen the interlayer space between TM layers. This is especially the case when there is a large amount of Na<sup>+</sup> ions that repel electron holes, as it can be shown from the widened interlayer space of Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> supercells when *x* is greater than 0.7 (Figure S12c). Considering that Na content varies from 0.4 to 3 during cycling (see Figure 4c in the manuscript), this suggests that Al-substituted compounds have a greater interlayer spacing during cycling.

# List of tables

**Table S1.** List of unit cell parameters of Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> structures relaxed using PBEsol and HSE06 functionals. *a*, *b*, and *c* lattice parameters are given in Å, whereas  $\alpha$ ,  $\beta$ , and  $\gamma$  angles are given in degrees (°). All supercell structures were transformed into primitive ones for a better comparison with pristine Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub>.

Na <sub>x</sub> Mn₃O	7						
Phase		а	b	С	α	β	γ
x = 2.0	HSE06	6.77733	6.75603	7.64072	103.0508	109.9334	111.0403
	PBEsol	6.63626	6.83558	7.56920	105.3968	107.3517	111.2885
	Experiment [13]	6.5921(34)	6.8916(34)	7.5071(30)	105.022(46)	107.543(39)	111.651(37)
x = 1.6	PBEsol	6.53901	6.89293	7.57044	105.2713	107.5410	111.4646
x = 1.2	PBEsol	6.49227	6.87603	7.55720	103.6343	109.4874	111.3187
x = 1.0	HSE06	6.58901	6.90947	7.60827	100.4594	113.1645	110.9254
	PBEsol	6.55827	6.83486	7.51020	101.4537	111.9576	111.4832
x = 0.8	PBEsol	6.54185	6.87781	7.50581	101.7086	111.5290	111.7448
x = 0.6	PBEsol	6.53624	6.91366	7.50772	102.1666	110.8863	111.9511
x = 0.5	PBEsol	6.44802	6.99210	7.52746	105.1050	107.9244	111.9172
x = 0.4	PBEsol	6.43831	6.93839	7.51348	104.2955	108.7172	111.6449
x = 0.3	PBEsol	6.45894	6.85962	7.51342	102.7880	110.3275	111.2505
x = 0.2	PBEsol	6.26508	6.84646	7.52312	106.7875	106.6523	110.0928
x = 0.1	PBEsol	5.90978	6.50593	7.53054	104.3256	105.5894	111.2997
Na <sub>x</sub> Al <sub>0.4</sub> N	In <sub>2.6</sub> O <sub>7</sub>	-	-	-	-	-	-
Phase		а	b	С	α	β	γ
x = 2.4	HSE06	6.45731	7.03594	7.61736	105.2204	107.8233	111.4732
	PBEsol	6.45731	7.03594	7.61736	105.2204	107.8233	111.4732
	Experiment	6.585(2)	6.950(2)	7.586(2)	105.20(2)	107.33(2)	110.88(3)
x = 2.3	PBEsol	6.54239	6.95519	7.61446	106.1328	106.8716	111.4323
x = 2.2	PBEsol	6.59848	6.91980	7.60729	107.1621	105.7452	111.5287
x = 2.1	PBEsol	6.61172	6.88273	7.59460	107.7603	105.2172	111.5310
x = 2.0	PBEsol	6.67013	6.81046	7.57913	108.9198	104.1222	111.4929
x = 1.6	PBEsol	6.52128	6.92271	7.54788	107.4843	105.0742	111.8614
x = 1.4	HSE06	6.61299	6.91122	7.61474	106.6269	106.1193	111.5257
	PBEsol	6.51455	6.91210	7.51535	106.1942	106.5347	111.9492
x = 1.2	PBEsol	6.54048	6.93690	7.51910	102.6252	110.4572	112.0545
x = 1.0	PBEsol	6.59450	6.79931	7.50280	101.2450	112.2007	111.5569
x = 0.8	PBEsol	6.57411	6.87866	7.50472	102.3654	110.6731	112.1551
x = 0.7	PBEsol	6.58618	6.82254	7.50710	101.8168	111.4703	111.7692
x = 0.6	PBEsol	6.61256	6.74355	7.51500	101.4407	111.8499	111.5021
x = 0.5	PBEsol	6.44802	6.99210	7.52746	105.1050	107.9244	111.9172
x = 0.4	PBEsol	6.34489	6.78764	7.55854	103.8378	109.8516	110.4351
x = 0.3	PBEsol	6.40578	6.77773	7.54894	103.9049	109.6610	110.5932
x = 0.2	PBEsol	6.22438	6.84097	7.53199	104.7119	109.2913	109.8229
x = 0.1	PBEsol	5.42407	6.65887	7.55243	119.7708	94.7115	103.6044

**R**<sub>p</sub> **R**<sub>wp</sub> SG a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å<sup>3</sup>)  $\chi^2$ (%) (%) Pristine  $P\overline{1}$ 6.578(8) 6.98(1) 7.542(8) 106.1(2) 107.62(3) 22.7 109.9(3) 281.3(1) 3.81 16.6 Ch-4.7  $P\overline{1}$ 6.996(2) 7.586(3) 6.821(3) 104.9(1) 107.4(1) 112.4(2) 289.7(2) 2.32 21.7 14.4 v  $P\overline{1}$ 7.10(2) 7.70(2) 112.7(4) 294.1(3) Disch-6.78(2) 105.5(3) 107.4(3) 1.64 12.6 17.4 1.5 V Pbma 9.10(2) 26.36(8) 2.84(1) 90 90 90 681.0(5)

**Table S2.** Summary of structural data obtained by indexing X-ray diffraction data shown inFigure S19 using the Le Bail method.

**Table S3.** Local bonding environments of all O sites in  $Na_2Mn_3O_7$  and  $Na_{2.4}Al_{0.4}Mn_{2.6}O_7$  and their Madelung potentials. Coordination numbers and average distances were determined from atoms adjacent to O atoms by less than 3.0 Å.

				Coordination number			verage dis	Madelung		
		O-Na	O-Mn	O-Al	0-0	O-Na	O-Mn	O-AI	0-0	potential (V)
	O1	2	2	0	7	2.34	1.87	-	2.76	25.25
No.Mp.O-	O2	1	2	0	7	2.22	1.85	-	2.75	24.88
Na2WI11307	O3	1	3	0	9	2.28	1.95	-	2.77	29.07
	O4	2	3	0	9	2.54	1.96	-	2.73	29.55
	O1	2	2	0	7	2.36	1.86	-	2.76	25.16
	O2	3	2	0	7	2.43	1.89	-	2.76	25.88
	O3	3	1	1	7	2.31	1.87	1.88	2.75	23.93
	O4	1	2	1	9	2.26	1.94	1.91	2.69	27.42
Na2.4A10.4WIN2.6U7	O5	2	2	1	9	2.44	1.94	1.96	2.71	27.39
	O6	1	3	0	9	2.27	1.95	-	2.73	29.58
	07	2	3	0	9	2.56	1.97	-	2.72	29.14
	O8	3	3	0	9	2.45	1.97	-	2.72	29.86

**Table S4.** Local bonding environments of all Mn sites in  $Na_2Mn_3O_7$  and  $Na_{2.4}Al_{0.4}Mn_{2.6}O_7$  and their Madelung potentials. Coordination numbers and average distances were determined from atoms adjacent to Mn atoms by less than 3.3 Å.

		Coordination number				Average distance (Å)				Madelung	
		Mn-Na	Mn-Mn	Mn-Al	Mn-O	Mn-Na	Mn-Mn	Mn-Al	Mn-O	potential (V)	
	Mn1	2	5	0	6	3.20	2.92	-	1.93	-83.36	
Na <sub>2</sub> Mn <sub>3</sub> O <sub>7</sub>	Mn2	2	5	0	6	3.21	2.91	-	1.91	-82.85	
	Mn3	1	5	0	6	3.27	2.91	-	1.93	-83.10	
	Mn1	2	4	1	7	3.02	2.89	2.96	2.12	-83.42	
	Mn2	2	5	0	6	3.08	2.92	-	1.93	-81.4	
	Mn3	2	5	0	6	3.1	2.92	-	1.93	-82.17	
	Mn4	2	5	0	6	3.15	2.91	-	1.93	-82.8	
	Mn5	2	4	1	6	3.1	2.9	2.93	1.93	-83.46	
No. Ale Mp. O	Mn6	2	4	1	6	3.08	2.9	2.93	1.93	-82.98	
Na2.4A10.4W112.6U7	Mn7	2	4	1	6	3.07	2.91	2.91	1.93	-81.72	
	Mn8	0	4	1	6	-	2.89	2.94	1.93	-84.22	
	Mn9	1	4	1	7	2.92	2.88	2.92	2.12	-83.85	
	Mn10	4	4	1	6	3.15	2.94	2.86	1.93	-81.58	
	Mn11	2	3	2	6	3.03	2.94	2.85	1.94	-83.76	
	Mn12	1	5	0	6	2.89	2.93	-	1.93	-80.48	

SOC (V)	Mn spe	ecies composit	ion (%)	Average Mn	-	. 2
	Mn <sup>2+</sup>	Mn <sup>3+</sup>	Mn <sup>4+</sup>	oxidation state	Rfactor	Λ
Pristine	$0.0 \pm 0.0$	70.1 ± 6.0	29.9 ± 2.3	3.3 ± 0.4	0.009	0.002
3.3	3.5 ± 2.5	96.5 ± 1.4	0.0 ± 0.0	3.0 ± 0.1	0.007	0.002
4.2	0.0 ± 0.0	37.5 ± 1.7	62.5 ± 3.3	3.6 ± 0.3	0.006	0.001
4.7	$0.0 \pm 0.0$	25.3 ± 1.8	74.7 ± 3.3	3.7 ± 0.3	0.006	0.001
4.2	$0.0 \pm 0.0$	38.9 ± 2.3	61.1 ± 3.7	3.6 ± 0.3	0.010	0.002
2.8	$0.0 \pm 0.0$	36.3 ± 1.8	63.7 ± 2.8	3.6 ± 0.2	0.006	0.001
1.5	53.3 ± 2.4	0.0 ± 5.5	46.7 ± 7.6	2.9 ± 0.7	0.015	0.002

**Table S5.** Linear combination fit analysis results for Na<sub>2.4</sub>Mn<sub>2.6</sub>Al<sub>0.4</sub>O<sub>7</sub> XANES spectra at different states of charge and discharge.

# **List of Figures**



**Figure S1.** (a) List of symmetrically unique magnetic arrangements of Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub>. (b) Comparison in total energy of Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> calculated with different magnetic arrangements and pseudopotentials. Ferromagnetic and antiferromagnetic arrangements are denoted by blue and green boxes, respectively. The symmetrically unique magnetic arrangements are obtained using the magnetic structure analyzer contained in Pymatgen [9].



**Figure S2.** Schematic procedure of the modeling methodology of Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> structures employed in the present work. The transformation matrix for generating cubic-like supercells was obtained using an algorithm for finding optimal supercell shapes [8], implemented in an atomic simulation environment [14]. When enumerating all possible atomic arrangements of Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>, symmetrically inequivalent configurations were removed to reduce the overall computational cost, the algorithm of which is described by Morgan *et al.* [15]. Electrostatic energies of structures were evaluated by the Ewald summation method contained in Pymatgen [9].



**Figure S3.** Convex hull diagrams of sodiation/desodiation reactions calculated for (a) Na<sub>x</sub>Mn<sub>3</sub>O<sub>7</sub> and (b) Na<sub>x</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>. Stable ground state structures are denoted by empty circles and used to plot theoretical voltage profiles.



**Figure S4.** XRD pattern and Le Bail refinement of Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub>. Pink circles are the experimental results, grey line is the simulated pattern, blue line is the difference between experimental and simulated patterns and grey tick marks correspond to calculated Bragg diffractions.



**Figure S5.**  $Na_{2.4}AI_{0.4}Mn_{2.6}O_7$  powder XRD data collected in a flat holder (black line) and a spinning capillary (green line) and shown as a function of reciprocal space. Peak intensities are normalised to the (-101) diffraction peak (located at 1.1 Å<sup>-1</sup>). Peak broadening in the spinning capillary data is attributed to the short sample-detector distance in the diffractometer used for data collection.



Figure S6. EDS spectrum corresponding to the elemental mapping shown in Figure 1c.



**Figure S7**. <sup>23</sup>Na MAS NMR spectra (MAS 20 kHz, 9.4 T) of (a)  $Na_2Mn_3O_7$ ; and (b)  $Na_{2.4}Al_{0.4}Mn_{2.6}O_7$  pristine samples. Asterisks denote the positions of resonances discussed in the manuscript.



**Figure S8.** <sup>23</sup>Na MAS spectra (9.4 T) recorded at MAS rates of 20, 28, and 30 kHz for Na<sub>2.4</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>. Dashed lines identify locations of isotropic peaks, identified from comparison of spectra recorded at different MAS rates and using Dmfit software [16] to fit the experimental spectra.



**Figure S9.** <sup>23</sup>Na static and 20 kHz MAS spectra (9.4 T) of (a)  $Na_2Mn_3O_7$  and (b)  $Na_{2.4}Al_{0.4}Mn_{2.6}O_7$ . NAMO and NMO samples. The static spectrum for  $Na_{2.4}Al_{0.4}Mn_{2.6}O_7$  shows two main regions of intensity centred at ~1000 and ~300 ppm.



**Figure S10.** Normalised Mn K-edge XANES spectra of Na<sub>2.4</sub>Mn<sub>2.6</sub>Al<sub>0.4</sub>O<sub>7</sub> at different states of (a) charge and (b) discharge. (c) Summary of the Mn<sup>3+</sup> and Mn<sup>4+</sup> ion ratios at different states of charge. These data show that the pristine electrode has a composition of around 70% of Mn<sup>3+</sup> and 30% of Mn<sup>4+</sup> ions. This is in good agreement with CV and galvanostatic data (Figure 3), where the Mn<sup>3+/4+</sup> oxidation reaction is observed during the first cycle. Upon charge to 4.2 V, Mn<sup>3+</sup> ions will oxidise to Mn<sup>4+</sup> ions and thus, the % of Mn<sup>4+</sup> ions will increase *cf.* % Mn<sup>3+</sup> ions. At 4.7 V, the % Mn<sup>4+</sup> ions will decrease *cf.* to that found at 4.2 V due to oxygen loss and subsequent reduction to Mn<sup>3+</sup> ions. As expected, when discharging to 1.5 V, that is, below the Mn<sup>4+/3+</sup> reduction potential, Mn is reduced to  $\approx$  3+.



**Figure S11.** Changes in average (a) octahedra volumes and (b) cross-sectional area (a) of TMO<sub>6</sub> octahedra calculated for  $Na_xMn_3O_7$  and  $Na_xAl_{0.4}Mn_{2.6}O_7$  supercells, with respect to their Na contents. *a* values were estimated by averaging the cross-sectional area of octahedra parallel to TM layers, as shown in the inset. All structures are obtained after DFT geometric optimization using PBEsol functional.



**Figure S12.** (a) Projected density of states of  $Na_{2.0}AI_{0.4}Mn_{2.6}O_7$  supercells and (b) corresponding partial charge densities (yellow isosurfaces), calculated from excess hole states formed by  $AI^{3+}$  ion substitution. Hole states are highlighted by red dashed lines in (a). Na layers are omitted for better visualization in (b). Changes in the (c) interlayer spacing, *d*, between TM layers of  $Na_xMn_3O_7$  and  $Na_xAI_{0.4}Mn_{2.6}O_7$  supercells, with respect to their Na content. The *d* values were measured from the distance between TMs perpendicular to TM layers, as shown in the insets.



**Figure S13.** (a) Voltage profile during GITT measurement. (b) Zoomed in area of GITT data shown in (a) that indicates iR drop,  $\Delta E_t$  and  $\Delta E_s$  in a selected charge step.



**Figure S14.** Sodium-ion diffusion coefficient in Na<sub>2.4</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>, *D*, as a function of voltage during the first charge-discharge cycle. Solid black and red triangles correspond to the diffusion coefficient calculated using the active material surface area (based on particle size), and open grey and orange triangles correspond to the values obtained using the electrode surface area ( $\pi$ r<sup>2</sup>). Dashed lines have been added at 10<sup>-11</sup> cm<sup>2</sup> s<sup>-1</sup> and 10<sup>-14</sup> cm<sup>2</sup> s<sup>-1</sup> as eye guides.



**Figure S15**. (a) CV curves of  $Na_2Mn_3O_7$  at a scan rate of 0.1 mV s<sup>-1</sup> in the voltage range 1.5 -4.7 V vs  $Na^+/Na$ . (b) Galvanostatic charge-discharge voltage profiles in the voltage range 1.5 -4.7 V vs  $Na^+/Na$  at C/20 (8 mA g<sup>-1</sup>) for cycles 1 and 2. (c) Discharge capacity (solid squares) and Coulombic Efficiency (open circles) as a function of cycle number in the voltage range 1.5 - 4.7 V vs.  $Na^+/Na$  at a current density of C/20 (8 mA g<sup>-1</sup>). (d) Rate capability tests in the voltage range of 1.5-4.7 V vs  $Na^+/Na$  using current densities ranging from C/20 to 5C.



**Figure S16.**  $Na_{2.4}Al_{0.4}Mn_{2.6}O_7$  voltage profiles at the 5<sup>th</sup> cycle at C/20, C/10, C/5, C/2, 1C and 5C rates, extracted from the rate capability test data shown in Figure 3d. The voltage profile of C/20 after cycling (dashed lines) corresponds to the first cycle.



**Figure S17.** Nyquist plots of  $Na_{2.4}Al_{0.4}Mn_{2.6}O_7$  (blue) and  $Na_2Mn_3O_7$  (red) at selected states of charge: (a) pristine state, (b) charge to 4.7 V, (c) discharge to 1.5 V, and (d) 100th discharge cycle.



**Figure S18.** Equivalent electric circuits used to fit EIS data shown in Figure S17. Both equivalent circuits are derived from the modified Randles equivalent circuit [17]. EIS data collected in a three-electrode cell were fit with the equivalent circuit from (a), which contains a resistance ( $R_s$ ) corresponding to the electrolyte, cell components and connections, and a single semicircle ( $R_{CT}||Q_{CT}$ ), corresponding to charge transfer resistance. EIS data collected in a coin-cell were fit with the equivalent circuit from (b), consisting of cell resistance ( $R_s$ ), a semicircle related to the anode side ( $R_a||Q_a$ ), and a semicircle corresponding to charge transfer resistance resistance ( $R_{CT}||Q_{CT}$ ).



**Figure S19.** *Ex situ* XRD data of  $Na_{2.4}Al_{0.4}Mn_{2.6}O_7$  pristine (black), charged to 4.7 V (red) and discharged to 1.5V (blue) electrodes.



**Figure S20**. Le Bail fit on XRD data of the Na<sub>2.4</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> electrode discharged to 1.5V, showing two phases with  $P\overline{1}$  and P b m a space groups, based on Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> and Na<sub>0.44</sub>MnO<sub>2</sub> reported structures [18].



**Figure S21**. *Ex situ* <sup>23</sup>Na Hahn echo MAS NMR spectra (30 kHz MAS, 9.4 T) collected for Na<sub>2.4</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub> electrode materials at different states of charge: (a) OCV, (b) 4.3 V, (c) 4.7 V and (d) 1.5 V. \* Shaded areas show peaks discussed in the text. The different colours of shading, with asterisk markers, indicate isotropic peaks present in the initial phase (red and grey); and additional peaks that are observed upon charging (blue). At the MAS rate of 30 kHz the isotropic peak at ~330 ppm is largely obscured by a spinning sideband of the isotropic peak at ~0 ppm.



**Figure S22**. *Ex situ* <sup>23</sup>Na Hahn echo MAS NMR spectra (30 kHz MAS, 9.4 T for collected for Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> electrode materials at different points along the electrochemical charge/discharge cycle, (a) OCV, (b) 4.3 V, (c) 4.7 V and (d) 1.5 V. \* Shaded areas show peaks discussed in the text. The different colours of shading, with asterisk markers, indicate isotropic peaks present in the initial phase (red and grey); and additional peaks that are observed upon charging (blue).



Figure S23. Projected density of states of (a) Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> and (b) Na<sub>2.4</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>.



**Figure S24.** Projected density of states of O sites in (a)  $Na_2Mn_3O_7$  and (b)  $Na_{2.4}Al_{0.4}Mn_{2.6}O_7$ . The indices of O sites were determined by their local bonding environments, which are listed in Table S3.



**Figure S25.** Projected density of states plotted for  $Na_2Mn_3O_7$  with differing Na vacancy sites. The Na vacancy and associated electron removal cause the formation of hole bands in ~ 2.0 eV above the Fermi level. The insets show the partial charge densities (blue isosurfaces) calculated for the hole bands, showing the localized hole states near the Na vacancy.



**Figure S26.** Projected density of states plotted for  $Na_{2.4}AI_{0.4}Mn_{2.6}O_7$  with differing Na vacancy sites. The Na vacancy and associated electron removal cause the formation of hole bands in ~ 1.5 eV above the Fermi level. The insets show the partial charge densities (blue isosurfaces) calculated for the hole bands, showing the localized hole states near the Na vacancy.



NaMn<sub>3</sub>O<sub>7</sub>

 $Na_2Mn_3O_7$ 



 $Na_{1.4}AI_{0.4}Mn_{2.6}O_7$ 

 $Na_{2.4}AI_{0.4}Mn_{2.6}O_{7}$ 

**Figure S27.** Distributions of O-O bond lengths near unoccupied Mn sites of TM layers before and after the desodiation of (a) Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub> and (b) Na<sub>2.4</sub>Al<sub>0.4</sub>Mn<sub>2.6</sub>O<sub>7</sub>. Contracted O-O bonds are highlighted in blue. The excess holes formed near O-O bonds are denoted by yellow isosurfaces and superimposed on the figures.



**Figure S28.** Atomic structures of NaMn<sub>3</sub>O<sub>7</sub> (a) before and (b) after the formation of an O<sub>2</sub> dimer nearby a partially oxidized O<sup>n-</sup> at non-bonding oxygen sites. Partially oxidized O<sup>n-</sup> are denoted by yellow spheres, and oxygen atoms participating in O<sub>2</sub> dimer formation are highlighted by square dashed boxes. (c) Energy profiles of the O-O dimerization calculated from the reaction pathway between (a) and (b). Empty spheres in the graph indicate the intermediate images used for the energy barrier calculation. The initial energy before the formation of the O<sub>2</sub> dimer is set to 0 eV as a reference point. Note that two adjacent oxygen atoms of O<sup>2-</sup> (red) and O<sup>n-</sup> (yellow) are bonded to each other to form a thermodynamically more stable structure, i.e., O<sub>2</sub> dimer (red spheres).



**Figure S29.** (a-d) The local structures of  $Na_2Mn_3O_7$  after the formation of an O vacancy in (a) O1, (b) O2, (c) O3, and (d) O4. Mn atoms reduced by excess electrons are highlighted in red and blue. (e-h) Projected density of states of Mn atoms before ( $Mn_{host}$ ) and after (Mn1, Mn2, and Mn3) the formation of O vacancies in (e) O1, (f) O2, (g) O3, and (h) O4 of  $Na_2Mn_3O_7$ . See Table S3 and S4 for the details of individual O and Mn sites.



**Figure S30.** (a-h) Local structures of  $Na_{2.4}Al_{0.4}Mn_{2.6}O_7$  after the formation of an O vacancy in (a) O1, (b) O2, (c) O3, and (d) O4. Mn atoms reduced by excess electrons are highlighted in red and blue. (e-h) Projected density of states of Mn atoms before (Mn<sub>host</sub>) and after (Mn1, Mn2, and Mn3) the formation of O vacancies in (e) O1, (f) O2, (g) O3, and (h) O4 of Na<sub>2</sub>Mn<sub>3</sub>O<sub>7</sub>. See Table S3 and S4 for the details of individual O and Mn sites.



**Figure S31.** (a-h) Projected density of states of Mn atoms before ( $Mn_{host}$ ) and after (Mn1, Mn2, Mn5, Mn10, and Mn12) the formation of O vacancies in (a) O1, (b) O2, (c) O3, (d) O4, (e) O5, (f) O6, (g) O7, and (h) O8 of  $Na_{2.4}Al_{0.4}Mn_{2.6}O_7$ . See Table S3 and S4 for the details of individual O and Mn sites.

## References

- Y. Zhu and C. Wang, "Galvanostatic intermittent titration technique for phasetransformation electrodes," *J. Phys. Chem. C*, vol. 114, no. 6, pp. 2830–2841, 2010, doi: 10.1021/jp9113333.
- W. Weppner and R. A. Huggins, "Determination of the Kinetic Parameters of Mixed-Conducting Electrodes and Application to the System Li3Sb," *J. Electrochem. Soc.*, vol. 124, no. 10, pp. 1569–1578, 1977, doi: 10.1149/1.2133112.
- J. P. Perdew *et al.*, "Restoring the density-gradient expansion for exchange in solids and surfaces," *Phys. Rev. Lett.*, vol. 100, no. 13, 2008, doi: 10.1103/PhysRevLett.100.136406.
- J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.*, vol. 77, no. 18, pp. 3865–3868, 1996, doi: 10.1103/PhysRevLett.77.3865.
- [5] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, "First-principles calculations of the electronic structure and spectra of strongly correlated systems: The LDA + U method," *J. Phys. Condens. Matter*, vol. 9, no. 4, pp. 767–808, 1997, doi: 10.1088/0953-8984/9/4/002.
- V. I. Anisimov, J. Zaanen, and O. K. Andersen, "Band theory and Mott insulators: Hubbard U instead of Stoner I," *Phys. Rev. B*, vol. 44, no. 3, pp. 943–954, 1991, doi: 10.1103/PhysRevB.44.943.
- [7] A. Belkly, M. Helderman, V. L. Karen, and P. Ulkch, "New developments in the Inorganic Crystal Structure Database (ICSD): Accessibility in support of materials research and design," *Acta Crystallogr. Sect. B Struct. Sci.*, vol. 58, no. 3 PART 1, pp. 364–369, 2002, doi: 10.1107/S0108768102006948.
- [8] P. Erhart, B. Sadigh, A. Schleife, and D. Åberg, "First-principles study of codoping in lanthanum bromide," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 91, no. 16, p. 165206, Apr. 2015, doi: 10.1103/PhysRevB.91.165206.
- [9] S. P. Ong *et al.*, "Python Materials Genomics (pymatgen): A robust, open-source python library for materials analysis," *Comput. Mater. Sci.*, vol. 68, pp. 314–319, 2013, doi: 10.1016/j.commatsci.2012.10.028.
- [10] A. S. Dalton, A. A. Belak, and A. Van Der Ven, "Thermodynamics of lithium in TiO 2(B) from first principles," *Chem. Mater.*, vol. 24, no. 9, pp. 1568–1574, May 2012,

doi: 10.1021/CM203283V.

- [11] C. Ling and F. Mizuno, "Capture lithium in αmnO 2: Insights from first principles," *Chem. Mater.*, vol. 24, no. 20, pp. 3943–3951, Oct. 2012, doi: 10.1021/CM302347J.
- T. N. Stokes, G. D. Bromiley, G. D. Gatta, N. Rotiroti, N. J. Potts, and K. Saunders,
  "Cation distribution and valence in synthetic Al–Mn–O and Fe–Mn–O spinels under varying conditions," *Mineral. Mag.*, vol. 82, no. 4, pp. 975–992, Aug. 2018, doi: 10.1180/MGM.2018.109.
- B. Song *et al.*, "Understanding the Low-Voltage Hysteresis of Anionic Redox in Na2Mn3O7," *Chem. Mater.*, vol. 31, no. 10, pp. 3756–3765, 2019, doi: 10.1021/acs.chemmater.9b00772.
- [14] A. Hjorth Larsen *et al.*, "The atomic simulation environment A Python library for working with atoms," *Journal of Physics Condensed Matter*, vol. 29, no. 27. 2017, doi: 10.1088/1361-648X/aa680e.
- [15] B. J. Morgan, "bsym: A basic symmetry module," *J. Open Source Softw.*, vol. 2, no. 16, p. 370, 2017, doi: 10.21105/joss.00370.
- [16] D. Massiot *et al.*, "Modelling one- and two-dimensional solid-state NMR spectra," Magn. Reson. Chem., vol. 40, no. 1, pp. 70–76, Jan. 2002, doi: 10.1002/MRC.984.
- [17] J. E. B. Randles, "Kinetics of rapid electrode reactions," *Discuss. Faraday Soc.*, vol. 1, pp. 11–19, Jan. 1947, doi: 10.1039/DF9470100011.
- [18] N. Muralidharan and K. Nallathamby, "Strategy to Qualify Layered Family Na2Mn3O7Anode for Use in Sodium-Ion Batteries," *Energy and Fuels*, vol. 35, no. 14, pp. 11545–11550, Jul. 2021, doi: 10.1021/ACS.ENERGYFUELS.1C01080.