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# Unlocking anionic redox activity in O3-type sodium 3d layered oxides via Li substitution

Qing Wang<sup>1,2,3</sup>, Sathiya Mariyappan<sup>1,4</sup>, Gwenaëlle Rousse<sup>1,2,4</sup>, Anatoly V. Morozov<sup>5</sup>, Benjamin Porcheron<sup>6</sup>, Rémi Dedryvère<sup>4,7</sup>, Jinpeng Wu<sup>8</sup>, Wanli Yang<sup>8</sup>, Leiting Zhang<sup>9</sup>, Mohamed Chakir<sup>3</sup>, Maxim Avdeev<sup>10,11</sup>, Michaël Deschamps<sup>6</sup>, Young-Sang Yu<sup>8</sup>, Jordi Cabana<sup>12</sup>, Marie-Liesse Doublet<sup>4,13</sup>, Artem M. Abakumov<sup>5</sup>, and Jean-Marie Tarascon<sup>1,2,4,\*</sup>

<sup>1</sup>*Chimie du Solide-Energie, UMR 8260, Collège de France, 75231 Paris Cedex 05, France*

<sup>2</sup>*Sorbonne Université, 4 Place Jussieu, 75005, Paris, France*

<sup>3</sup>*Renault, Technocentre, 1 avenue du Golf, 78288 Guyancourt, France*

<sup>4</sup>*Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France*

<sup>5</sup>*Center for Energy Science and Technology, Skolkovo Institute of Science and Technology, Nobel str. 3, 143026 Moscow, Russia*

<sup>6</sup>*CNRS, CEMHTI UPR3079, Université d'Orléans, 1D avenue de la recherche scientifique, 45071 Orléans Cedex 2, France*

<sup>7</sup>*IPREM-UMR 5254 CNRS, Université de Pau et des Pays de l'Adour, Hélioparc, 2 Avenue Pierre Angot, 64053 Pau Cedex 9, France*

<sup>8</sup>*Advanced Light Source, Lawrence Berkeley National Laboratory, One Cyclotron Road, Berkeley, CA 94720, USA*

<sup>9</sup>*Electrochemistry Laboratory, Paul Scherrer Institute, Forschungsstrasse 111, 5232, Villigen PSI, Switzerland*

<sup>10</sup>*School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia*

<sup>11</sup>*Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia*

<sup>12</sup>*University of Illinois at Chicago, Department of Chemistry, Chicago Illinois 60607, United States*

<sup>13</sup>*ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier, France.*

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\*Corresponding author: jean-marie.tarascon@college-de-france.fr

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## Abstract

Sodium ion batteries, because of their sustainability attributes, could be an attractive alternative to Li-ion technology for specific applications. However, it remains challenging to design high energy density and moisture stable Na-based positive electrodes by implementing the anionic redox process that has recently boosted the capacity of Li-rich layered oxides. Here, we report the first anionic-redox active O3-NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> phase obtained through a ceramic process by carefully controlling the delicate balance between synthesis conditions and stoichiometry. It shows a sustained reversible capacity of 190 mAh g<sup>-1</sup> by redox processes on oxygen and manganese ions as deduced by combined HAXPES and mRIXS spectroscopy techniques. Remarkably, unlike any other anionic-redox layered oxides so far

1 reported, O3-NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> electrodes do not show voltage fade upon cycling. This finding  
2 is due to switching from the interlayer to intralayer migration of the Mn cations promoted by  
3 Li<sup>+</sup> displacement towards the alkali layer upon first Na<sup>+</sup> de-insertion. Another practical asset  
4 of this material stems from its moisture stability, hence facilitating its handling and electrode  
5 processing. Besides providing insightful fundamental findings pertaining to anion redox, this  
6 work offers future directions towards designing high energy density electrodes for advanced  
7 Na-ion batteries.

## 8 **Introduction**

9 Rechargeable lithium ion batteries have empowered the success of consumer devices, and are  
10 continuing to conquer the market of electric vehicles.<sup>1</sup> Despite the foreseeable dominance of  
11 Li-ion technology within the near future, there is a rising demand for cost-effective and more  
12 sustainable cathode materials for large-scale energy storage. The Na-ion technology, the  
13 working principle of which mimics Li-ion batteries, offers an alternative to fill this gap,  
14 provided improvements are made in terms of energy density.<sup>2,3</sup> Inspired by the discovery of  
15 anionic redox in Li-rich oxides with subsequent increase in the material capacity,<sup>4-6</sup> great  
16 efforts have been devoted to the design of Na-rich layered oxides (Na(Na<sub>y</sub>M<sub>1-y</sub>)O<sub>2</sub>, 0 < y < 1,  
17 M = transition metal cation(s)). Commonly, anionic redox in layered oxides is triggered by  
18 the introduction of alkali metals into the MO<sub>2</sub><sup>δ-</sup> layer that generates oxygen lone pairs  
19 associated with oxygen non-bonding 2p-states in the electronic structure.<sup>7,8</sup> However,  
20 implementing this strategy to Na layered oxides is not simple owing to the size mismatch  
21 between NaO<sub>6</sub> and MO<sub>6</sub> octahedra. Hence, Na-rich layered oxides with the O3-type structure  
22 were successfully prepared with either larger and more covalent 4d and/or 5d metals (Ru, Ir,  
23 etc.).<sup>9-13</sup> But with 3d metals, anionic redox is solely reported with non-stoichiometric P2/P3-  
24 type Na<sub>x</sub>A<sub>y</sub>M<sub>1-y</sub>O<sub>2</sub> (0 < x < 1, y < 1) phases where the non-bonding O 2p orbitals are made  
25 available by increasing the O/M ratio compared to LiMO<sub>2</sub> using Li<sup>+</sup> / Mg<sup>2+</sup> / Zn<sup>2+</sup> or  
26 vacancies as the A cation instead of Na<sup>+</sup>.<sup>14-20</sup> However, practical wise P2/P3 phases fall short  
27 in achieving high energy density target, because of their Na deficiency.<sup>21</sup> Hence, the standing  
28 challenge resides in the synthesis of anionic-redox active sodium layered oxides consisting of  
29 3d transition metals while having full sodium stoichiometry (Na(A,M)O<sub>2</sub> with Na/(A,M) = 1).

30 Several attempts to increase the Na content have invariably led to anionic redox  
31 inactive O3-type structures which are thermodynamically favored against the P2 structure  
32 when Na/(A,M) ratio approaches 1.<sup>22</sup> This failure is most probably due to synthesis  
33 difficulties in achieving the proper targeted composition.<sup>23-25</sup> Combining the proper Li

1 content to trigger anionic redox with full Na occupancy has even been predicted by DFT and  
2 confirmed experimentally since the authors synthesized P2-Na<sub>0.75</sub>Li<sub>0.25</sub>Mn<sub>0.75</sub>O<sub>2</sub> and not  
3 NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> as they wished.<sup>26</sup>

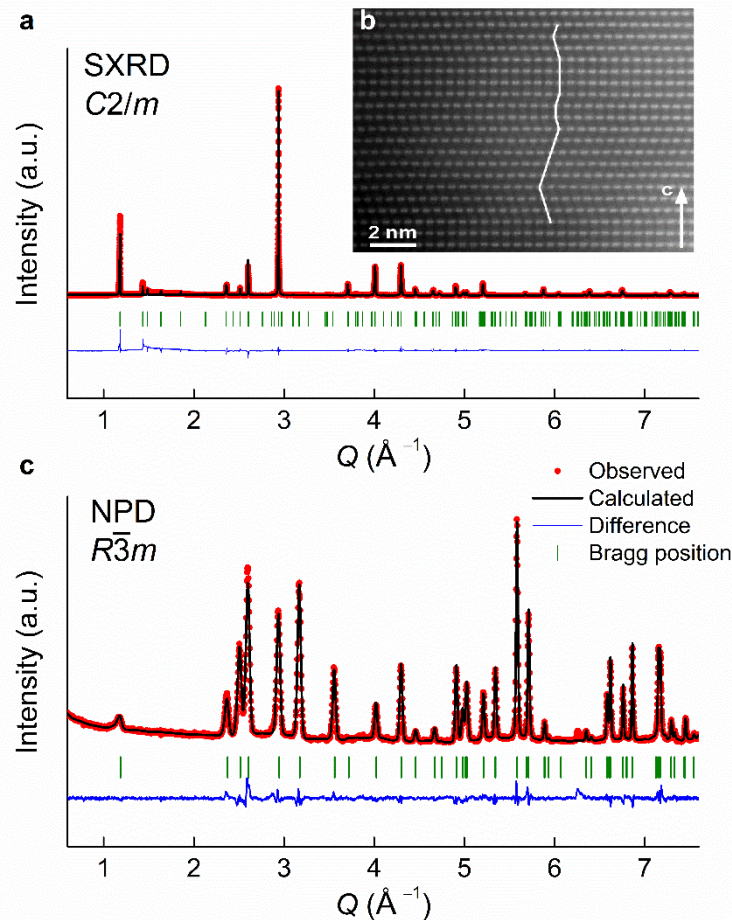
4 Following our early study on stabilizing the NaLi<sub>1/3</sub>Ir<sub>2/3</sub>O<sub>2</sub> phase,<sup>27</sup> we herein explore the  
5 delicate Na-Li composition balance in the NaLi<sub>y</sub>Mn<sub>1-y</sub>O<sub>2</sub> phase to stabilize anionic-redox  
6 active O3 structure with full Na content and successfully synthesized a new NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>  
7 phase. It delivers an abnormally high first charge capacity of ~ 250 mAh g<sup>-1</sup> with reversible  
8 capacity of ~190 mAh g<sup>-1</sup> while showing neither voltage fade nor reactivity against moisture,  
9 both of which are serious assets practical-wise.

#### 10 ***Identifying structure and composition of NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>***

11 A survey of various key parameters (Li/Mn ratio, nature of precursors, annealing temperature,  
12 flushing gases) was conducted and the results are cumulated in Supplementary Fig. 1–3 with  
13 the optimized synthesis condition explained in experimental section. Single phase was solely  
14 obtained for the composition NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> by heating a ball-milled mixture of Na<sub>2</sub>O<sub>2</sub>, Li<sub>2</sub>O,  
15 and Mn<sub>2</sub>O<sub>3</sub> at 700 °C in a tubular furnace, where the tube was flushed with argon before  
16 calcination. The X-ray powder diffraction (XRD) pattern of the as-synthesized material was  
17 fitted in an O3-type structure with minute amounts of an impurity phase (Supporting Fig. 1  
18 and 4). Interestingly, by soaking the sample into distilled water, the impurity phase was  
19 washed away while leaving the O3 phase intact, hence indicating its stability against moisture  
20 (Supplementary Fig. 4 and 5). This water-washed material with a Na<sub>0.97</sub>Li<sub>0.32</sub>Mn<sub>0.68</sub>O<sub>2</sub>  
21 composition deduced from inductively coupled plasma (ICP) analysis was further used for all  
22 studies and hereafter referred to as “Na<sub>1</sub>Li<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>” for simplicity purpose.

23 Figure 1a shows the synchrotron XRD (SXRD) pattern of the water-washed material. It can  
24 be refined using two models, both suitable for describing an O3 structure: either in the  $R\bar{3}m$   
25 space group with the lattice parameters  $a = 2.92441(1)$  Å,  $c = 15.96473(9)$  Å (Supplementary  
26 Fig. 6, Supplementary Table 1), or in the  $C2/m$  space group with  $a = 5.05911(5)$  Å,  $b =$   
27  $8.77505(6)$  Å,  $c = 5.58491(5)$  Å, and  $\beta = 107.6217(5)^\circ$  (Fig. 1a, Supplementary Table 2). The  
28 latter indexes the superstructure reflections between 5–10°  $2\theta$  (Supplementary Fig. 6) that  
29 were not taken into account using the  $R\bar{3}m$  space group and allows to describe the  
30 [Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> honeycomb-ordered layers. In this model, Na is distributed in the interlayer  
31 space on two Wyckoff sites,  $2c$  and  $4h$ . The superstructure reflections shows asymmetric  
32 broadening and reduced intensities that arise from copious stacking faults as we deduced from  
33 simulated X-ray diffraction patterns (Supplementary Fig. 7), with these faults propagating

1 along the  $c$  axis,<sup>9,11</sup> as evidenced by  $[\bar{1}10]$  HAADF-STEM image (Fig. 1b) and corresponding  
 2 SAED pattern (Supplementary Fig. 7). Both SXRD and STEM support the structure model  
 3 where Na takes up octahedral sites in between the  $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  slabs while Li and Mn form  
 4 a “honeycomb” ordering within the  $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  slabs. Lastly the neutron powder  
 5 diffraction (NPD) was also collected for the pristine phase (Fig.1c, Supplementary Table 3)  
 6 and alike XRD it is consistent with the target composition as deduced by the Rietveld  
 7 refinement.



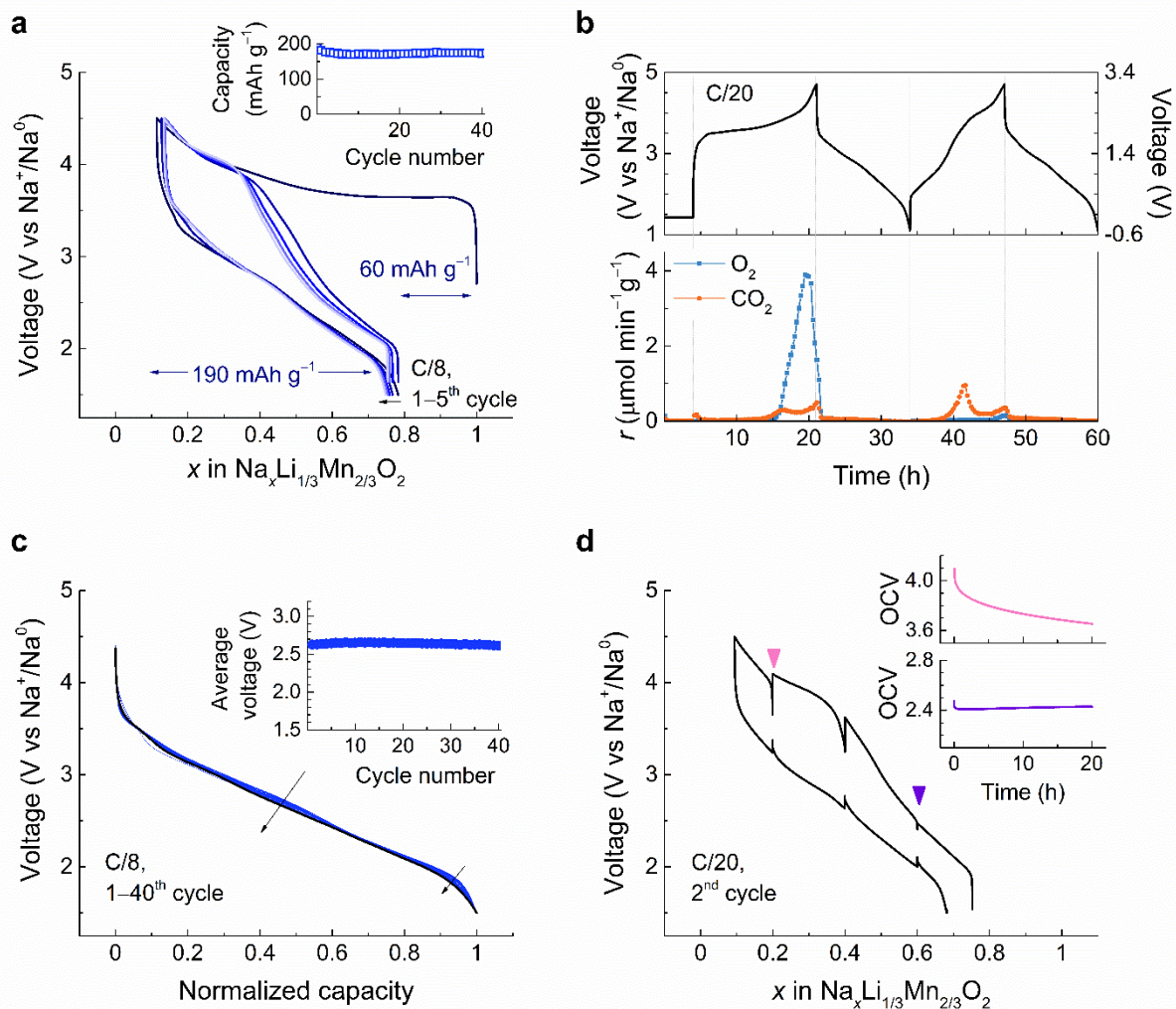
8  
 9 **Fig. 1 Structure of the water-washed pristine material.** **a**, Rietveld refinement of the  
 10 SXRD pattern in  $C2/m$  space group ( $O3$ -type) of  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  after being washed in  $\text{H}_2\text{O}$ .  
 11 The red dots, black, and blue lines and green tick bars represent the observed, calculated,  
 12 difference patterns and Bragg positions, respectively. **b**,  $[\bar{1}10]$  HAADF-STEM image of  
 13 pristine  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  (indexes refer to the  $R\bar{3}m$  cell). The periodicity along the stacking  
 14 direction of the “honeycomb”  $\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_2$  layers is frequently violated by stacking faults  
 15 appearing as lateral shifts of the layers (traced with the white line). **c**, Rietveld refinement of  
 16 the NPD pattern of  $\text{H}_2\text{O}$ -washed  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  sample. The  $R\bar{3}m$  space group was chosen  
 17 instead of  $C2/m$  to fit the neutron pattern due to the bare visibility of superstructure peaks  
 18 from the  $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  honeycomb ordering. As the coherent neutron scattering lengths for  
 19 Mn and Li differ only by a factor of 2 ( $b(\text{Mn}) = -0.37$  fm versus  $b(\text{Li}) = -0.19$  fm) as  
 20 compared to a factor of 8 for XRD ( $Z(\text{Mn}) = 25$  versus  $Z(\text{Li}) = 3$ ), superstructure peaks

1 associated with the honeycomb ordering are barely visible in the NPD pattern than in XRD,  
2 and even more attenuated in presence of stacking faults.

### 3 ***Electrochemical properties of NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>***

4 The electrochemical properties of NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> were examined versus metallic Na within  
5 the voltage range of 1.5–4.5 V at the rate of C/8 (1C = 285 mAh g<sup>-1</sup>) in Swagelok-type cells  
6 (Fig. 2). Upon oxidation, the voltage rapidly reaches a plateau at around 3.6 V followed by a  
7 sloping region to reach the “Na<sub>0.09</sub>Li<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>” composition at 4.5 V. The subsequent  
8 discharge profile evolves into a nearly S-shape curve, which persists upon repeated cycles,  
9 indicating an electrochemically driven structural transformation during the first charge. Out of  
10 0.9 Na<sup>+</sup> that can be removed during the first charge, solely 0.67 Na<sup>+</sup> is reinserted on the  
11 following discharge without any loss of Li from the structure as deduced from inductively  
12 coupled plasma-optical emission spectrometry (ICP-OES) measurements performed on the  
13 fully charged and discharged samples (Supplementary Fig. 8). This leads to a reversible  
14 capacity of ~190 mAh g<sup>-1</sup> which is stable upon continuous cycling, retaining 90% of the initial  
15 capacity after 40 cycles (Fig. 2a, inset). Similar behavior with charge activation and S-shaped  
16 curve evolution is usually observed for numerous anionic redox compounds<sup>28</sup> which  
17 occasionally show O<sub>2</sub> release. To check this possibility, we carried out pressure test and  
18 online electrochemical mass spectrometry (OEMS) (Fig. 2b, Supplementary Fig. 9). Both  
19 techniques confirm gas release in the first charge which is predominantly O<sub>2</sub> with the onset at  
20 ~0.58 Na<sup>+</sup> removal (*ca.* 3.8 V *vs.* Na<sup>+</sup>/Na<sup>0</sup>) as shown by OEMS data in Fig. 2b. For precise  
21 quantification, the OEMS analyses were carried out using Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (NVP) as counter  
22 electrode instead of sodium metal which itself generates gases by reactions with the  
23 electrolyte. Correspondingly, the amount of O<sub>2</sub> release in the first cycle equals to 757.4 μmol  
24 g<sup>-1</sup> (equivalent to 80 mAh g<sup>-1</sup> charge capacity, Fig. 2b), yielding the material composition  
25 Na<sub>~0.09</sub>Li<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>1.86</sub> at the end of charge, whereas almost no O<sub>2</sub> release (less than 1%) is  
26 observed in the second charge. This irreversible O<sub>2</sub> release explains part of the first cycle  
27 irreversible capacity, and is likely rooted in the number of hole per oxygen (h<sup>0</sup>) generated  
28 upon charge since this parameter was recently proposed as a good indicator of the  
29 reversibility of the anionic process.<sup>8</sup> Lastly, the CO<sub>2</sub> evolution observed through both cycles,  
30 as already being noticed with other layered oxides, is most likely linked with the  
31 decomposition of residual carbonates<sup>29</sup> on the material surface and/or from the oxidative  
32 decomposition of the electrolyte.<sup>30</sup> Through parallel measurements (Supplementary Fig.9)<sup>31</sup>  
33 we could conclude that the occurrence of CO<sub>2</sub> through the second cycling is likely associated

1 with the presence of  $H^+$  generated by electrolyte decomposition as previously reported<sup>32</sup>,  
 2 which cannot be reduced using an NVP anode as opposed to a hard carbon or Na anode.  
 3 Altogether, the cycling profile and the  $O_2$  gas release in the first cycle are reminiscent of Li-  
 4 rich layered oxide. However, a striking difference emerges with the neatly superposition of  
 5 the discharge curves upon cycling (Fig. 2c). This indicates the absence of noticeable voltage  
 6 fade in  $NaLi_{1/3}Mn_{2/3}O_2$  that we further confirmed by plotting the average discharge voltage  
 7 for the first 40 cycles that remains constant (Fig. 2c, inset). Interestingly, such a feature is not  
 8 mirrored in charge, which shows a gradual evolution in the shape of the charge curve on  
 9 repeated cycling (Supplementary Fig. 10).



10

11 **Figure 2 Electrochemical behavior of  $NaLi_{1/3}Mn_{2/3}O_2$ .** **a**, Voltage profile of first five galvanostatic  
 12 cycles (dark to light blue) of  $NaLi_{1/3}Mn_{2/3}O_2$  against metallic sodium at C/8 rate between 1.5–4.5 V.  
 13 Inset shows the capacity retention over 40 cycles. **b**, OEMS gas analysis during the first and second  
 14 cycles of  $NaLi_{1/3}Mn_{2/3}O_2$  cycled versus  $Na_3V_2(PO_4)_3$  between  $-0.5$ – $3.1$  V (right axis), which is  
 15 converted to  $1.2$ – $4.7$  V vs  $Na^+/Na^0$  (left axis) as presented in the upper panel. Gas evolution rates  
 16 ( $\mu\text{mol}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$ ) were monitored for  $O_2$  ( $m/z = 32$ ) and  $CO_2$  ( $m/z = 44$ ) as shown in the bottom panel  
 17 and the amount of  $O_2$  release in the first cycle equals to  $757.4 \mu\text{mol g}^{-1}$  (equivalent to  $80 \text{ mAh g}^{-1}$



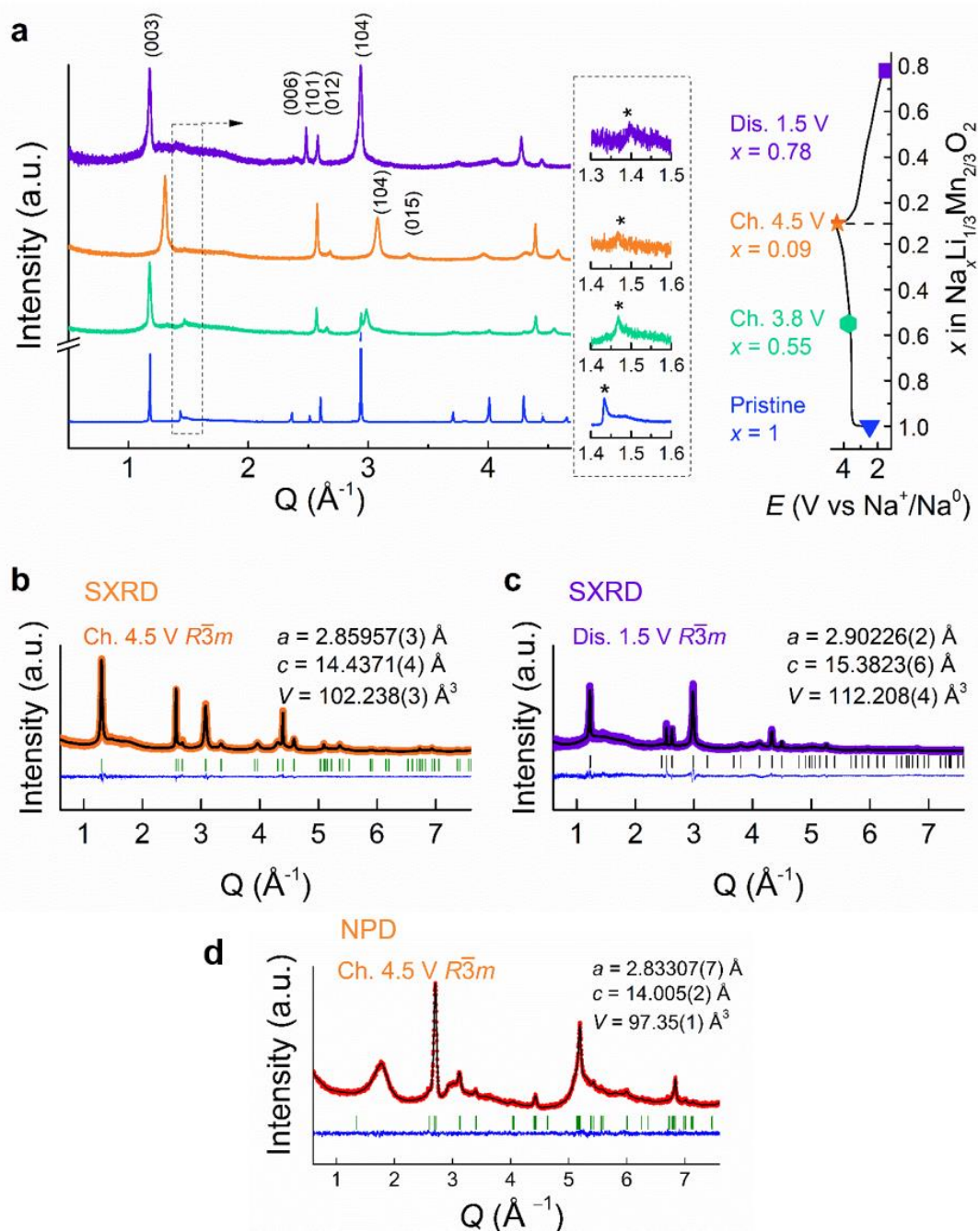
1 charge capacity). **c**, Normalized discharge curves of the  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2/\text{Na}$  half cell data shown in Fig.  
2 2a for 40 cycles. Inset shows the average discharge voltage calculated by dividing the specific energy  
3 by capacity omitting the  $iR$  drop upon cycling. **d**, GITT measurements conducted on the second cycle  
4 at a current rate of  $C/20$ , with a 20-hour relaxation period for every 4 hours ( $0.2 \text{ Na}^+$  exchange). Inset  
5 shows OCV evolution during 20 hours' relaxation at weakly and highly charged states.

6 To understand the asymmetric behavior between charge/discharge, we followed the variation  
7 of equilibrium potential process by galvanostatic intermittent titration technique (GITT). The  
8 GITT voltage profile for the second cycle (Fig. 2d) shows a large voltage gap ( $300 \sim 500 \text{ mV}$ )  
9 between OCVs at charge vs. discharge despite very long rest periods of 20 hours. This  
10 suggests that the hysteresis is of thermodynamic nature. The comparison between the GITT  
11 measurements and a cell cycling at  $C/50$  rate (Supplementary Fig. 11) also suggests slow  
12 equilibration dynamics. To better understand the hysteresis, we progressively opened the  
13 charge window with each cycle by increasing the upper cut-off voltage (Supplementary Fig.  
14 12). Charge profiles are identical but discharge profiles drop gradually upon reaching the high  
15 voltage redox process ( $> 3.3 \text{ V}$ ) with simultaneous rapid growth of the overpotential,  
16 therefore pointing that the hysteresis is triggered towards the last 50% of charge. Moreover,  
17 the magnification of the voltage relation profile for weakly and highly charged states (arrows  
18 in Fig.2d) shows two different time of equilibrium. The voltage of the highly charged state  
19 (top insert in Fig.2d) did not fully relax even for rest period close to one day, hence indicating  
20 a process with a large time constant. This contrasts with the small time constant observed for  
21 the low voltage charge state (bottom insert in Fig.2d) and equally for various discharge  
22 voltage states.

23 The origin of such a difference was explored experimentally through *operando* XRD  
24 on  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2/\text{Na}$  half cell. The cell was cycled at a  $C/20$  rate and XRD patterns were  
25 collected for every change in sodium stoichiometry of 0.05 (Supplementary Fig. 13). Our data  
26 reveal several electrochemically driven biphasic and solid solution regions. Initially, a  
27 biphasic process is observed with the appearance of a new phase O3 (II) having an increased  $c$   
28 lattice parameter ( $\sim 5.64 \text{ \AA}$ ) compared to the pristine O3 (I) phase ( $\sim 5.58 \text{ \AA}$ ). Further pursuing  
29 the desodiation leads to a narrow solid solution through which the  $c$  lattice parameter initially  
30 contracts prior to decrease rapidly, once the  $\text{O}_2$  evolution potential is reached, leading to the  
31 O3(III) phase at the very end of charge. An in-depth exploration of the crystal structure  
32 evolution in different states of charge and discharge was undertaken using synchrotron XRD  
33 (Fig. 3). Rietveld refinements (Supplementary Table 4–5) show that all patterns (middle, end  
34 of charge and discharge) can be indexed with O3 ( $R\bar{3}m$ ) structures that solely differ in lattice  
35 parameters while containing copious amount of micro-strain. Note that we did not use the

1  $C2/m$  space group to refine the patterns, because the  $[Li_{1/3}Mn_{2/3}]O_2$  honeycomb superstructure  
2 reflections are barely visible and no splitting resulting from a monoclinic distortion is  
3 observed. We therefore conclude that the O3-P3 phase transition, very frequently reported  
4 upon removal of  $Na^+$  in O3 sodium layered oxide is not observed with  $NaLi_{1/3}Mn_{2/3}O_2$ . This  
5 suggests the absence of Na-vacancy ordering in  $Na_{1-x}Li_{1/3}Mn_{2/3}O_2$  that is usually proposed as  
6 the origin of the O3-P3 phase transition<sup>22</sup> in Na-based layered oxides.

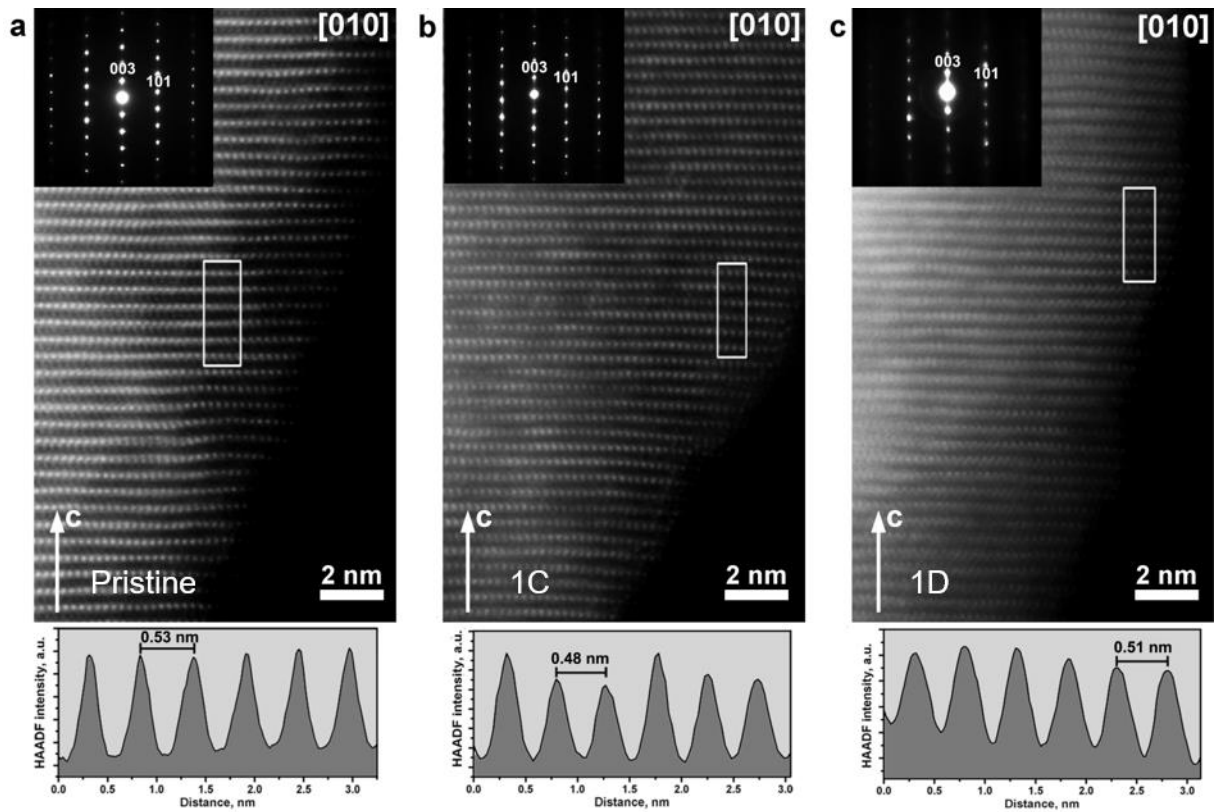
7         Turning to oxygen deficiency, two models with and without oxygen vacancies (as  
8 deduced by OEMS) were tried for the fully charged  $Na_{0.09}Li_{1/3}Mn_{2/3}O_2$  sample but both giving  
9 refinements of comparable quality preventing reliable assignment (Supplementary Fig.14). In  
10 contrast, models having Mn placed in either octahedral or tetrahedral sites within the Na  
11 interlayer spaces deteriorate the refinement with respect to the one having Mn solely located  
12 in the transition metal layers (Supplementary Fig.15), hence suggesting the absence of  
13 manganese migration to the alkali layer. This was confirmed by refining the NPD pattern  
14 collected for the fully charged sample of which the best fit was obtained with Mn in the metal  
15 layers together with all the Li and remaining Na atoms being in the alkali layers so that the  
16 resulting chemical formula can be written as  $[Na_{0.09}Li_{1/3}]_{interlayer}[(\square_{cat})_{1/3}Mn_{2/3}]_{metal}O_{1.86}$  (Fig.3d,  
17 Supplementary Table 6). Lastly, it is of paramount importance to note, that the peaks in  
18 SXRD corresponding to the honeycomb superstructure largely reduce in intensity through the  
19 first charge and discharge processes. Such disappearance of superstructure peaks can be either  
20 associated with the collapse of the honeycomb ordering due to metal ion migration within the  
21 metal layers or with an increased amount of stacking faults that reduce the long range  
22 ordering.



1  
 2 **Fig. 3 Structural evolution in the first cycle.** **a**, (left) SXR D patterns of pristine (blue), *ex*  
 3 *situ* samples stopped at mid-charge (green), end of charge (orange) and end of discharge (purple) of  
 4 the initial cycle. Zoomed view of superstructure peaks (marked by asterisks) together with the *ex*  
 5 *situ* points on the electrochemistry curve are illustrated on the right. **b**, **c**, Rietveld refinement of the  
 6 SXR D patterns of the fully charged and fully discharged samples, respectively. All the SXR D were  
 7 indexed in  $R\bar{3}m$  space group (O3 structure) having the lattice parameters,  $a = 2.92441(1) \text{ \AA}$ ,  $c =$   
 8  $15.96473(9) \text{ \AA}$ ,  $V = 118.241(1) \text{ \AA}^3$  for pristine;  $a = 2.86135(6) \text{ \AA}$ ,  $c = 16.067(1) \text{ \AA}$ ,  $V = 113.922(9)$   
 9  $\text{ \AA}^3$  as the major phase for the mid-charged  $\text{Na}_{0.45}\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_2$ ;  $a = 2.85957(3) \text{ \AA}$ ,  $c = 14.4371(4)$   
 10  $\text{ \AA}$ ,  $V = 102.238(3) \text{ \AA}^3$  for the fully charged  $\text{Na}_{0.09}\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_{1.86}$ ; and  $a = 2.90226(2) \text{ \AA}$ ,  $c = 15.3823(6)$   
 11  $\text{ \AA}$ ,  $V = 112.208(4) \text{ \AA}^3$  for the fully discharged  $\text{Na}_{0.78}\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_{1.86}$ . **d**, Rietveld refinement of the NPD  
 12 pattern of the fully charged sample in  $R\bar{3}m$  space group (O3 structure) with  $a = 2.83307(7) \text{ \AA}$  and  $c =$   
 13  $14.005(2) \text{ \AA}$ ,  $V = 97.35(1) \text{ \AA}^3$ . The oxygen content was fixed to 1.86 per formula unit, and different  
 14 structural models were tested that differ in the Mn, Li and Na distribution in the metal layer and/or

1 interlayer sites. The best fit was obtained with Mn in the metal layers, and interlayers accommodating  
2 all Li atoms and remaining Na, so that the resulting chemical formula can be written as  
3  $[\text{Li}_{1/3}\text{Na}_{0.09}]_{\text{interlayer}}[(\square_{\text{cat}})_{1/3}\text{Mn}_{2/3}]_{\text{metal}}\text{O}_{1.86}$  (see Supplementary Table 6 for more details).

4 High angle annular dark field scanning transmission electron microscopy (HAADF-  
5 STEM) was next used to grasp further insights into local structure of  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  upon  
6  $\text{Na}^+$  removal and uptake. Our data confirms the presence of O3-type layered structure for the  
7 pristine sample that is maintained in the samples charged to 4.5 V and discharged to 1.5 V, as  
8 evidenced by the [010] SAED patterns in Fig. 4. The [010] HAADF-STEM images also  
9 confirm the O3-type stacking demonstrating the lateral displacement of the  $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$   
10 layers by 1/3 of the distance between two neighboring dots denoting the Mn columns (Fig. 4).  
11 No additional intensity was observed between the  $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  layers in the HAADF  
12 intensity profiles (except of very faint dots of the Na columns barely visible at the thicker part  
13 of the pristine  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  crystallite (Fig. 4a, left)) that agrees well with the absence of  
14 Mn migration to the Na sites in the charged 4.5 V and discharged to 1.5 V states, as deduced  
15 from SXRD. After charge and discharge for 10 cycles, the O3 structure remained  
16 (Supplementary Fig.16). The reflections in the SAED patterns are very broad and streaked  
17 with diffuse intensity along the  $c^*$  axis, which is not surprising given the enormous  
18 anisotropic broadening observed from SXRD (Supplementary Fig.17). HAADF-STEM  
19 images show that the reflection broadening and diffuse intensity originate from pronounced  
20 local structure distortions, where the  $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  layers become wavy, demonstrating  
21 strong local variations of the interlayer distance. The HAADF-STEM images of the sample  
22 after 10 cycles show that Mn migration to the interlayer space occurs only at the top surface  
23 areas, and not in the more bulky parts. Another feature is the significant suppression of the  
24 honeycomb ordering visible in both SAED pattern and the HAADF-STEM image  
25 (Supplementary Fig.16). Overall, combined SXRD and TEM results unambiguously confirm  
26 the absence of out-of-plane Mn migration in  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  with therefore signs of in-plane  
27 migration increasing with cycling.



1

2 **Fig. 4. Structural analysis by microscopy.** [010] HAADF-STEM images and corresponding HAADF  
 3 intensity profiles across the  $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  layers in the outlined rectangular areas for (a) pristine, (b)  
 4 charged to 4.5 V and (c) discharged to 1.5 V  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$ . Corresponding [010] SAED patterns are  
 5 given in the insets; the patterns are indexed as the  $\text{O}3 \bar{R}3m$  phase. The peaks in the HAADF intensity  
 6 profiles correspond to the Mn columns solely at the  $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  layers, whereas absence of the  
 7 intensity between the peaks indicates no Mn migration into the Na layers.

8 In absence of  $\text{Li}^+$  loss from the structure, as deduced from ICP-OES, a legitimate  
 9 question regards its structural role through the Na (de)insertion process. To evaluate its  
 10 impact, both  $^6\text{Li}$  and  $^{23}\text{Na}$  Nuclear Magnetic Resonance (NMR) spectra were recorded on  $\text{Na}_{1-x}\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_2$   
 11 at various states of charge and discharge (Fig. 5). Both  $^6\text{Li}$  (Fig.5C) and  $^{23}\text{Na}$   
 12 (Fig.5D) spectra show two signals for the pristine material with in each case a nearly 1 to 2  
 13 balance. The doublet for Na is consistent with the  $C2/m$  structure having two different sites  
 14 ( $2c$  and  $4h$ ) for  $\text{Na}^+$  (Fig. 5B). The large shift to  $\sim 1400$  ppm in the  $^6\text{Li}$  Lorentzian line is  
 15 indicative of the presence of lithium in transition metal  $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  layer<sup>33</sup>. Moreover, the  
 16 two slightly different environments causing two lines at 1400 and 1450 ppm most likely arise  
 17 from the difference in Li position due to the frequent violation of periodicity along the  
 18 stacking direction of the honeycomb TM layers (see Fig.1b, Supplementary Fig.7). Upon  
 19 charging, this signal (blue) progressively disappears to the expense of a new one (green) with  
 20 a significantly different chemical shift centered around  $\sim 700$  ppm that becomes unique for the  
 21 fully charged sample. In light of previous studies, this new signal is assigned to  $\text{Li}^+$  ions

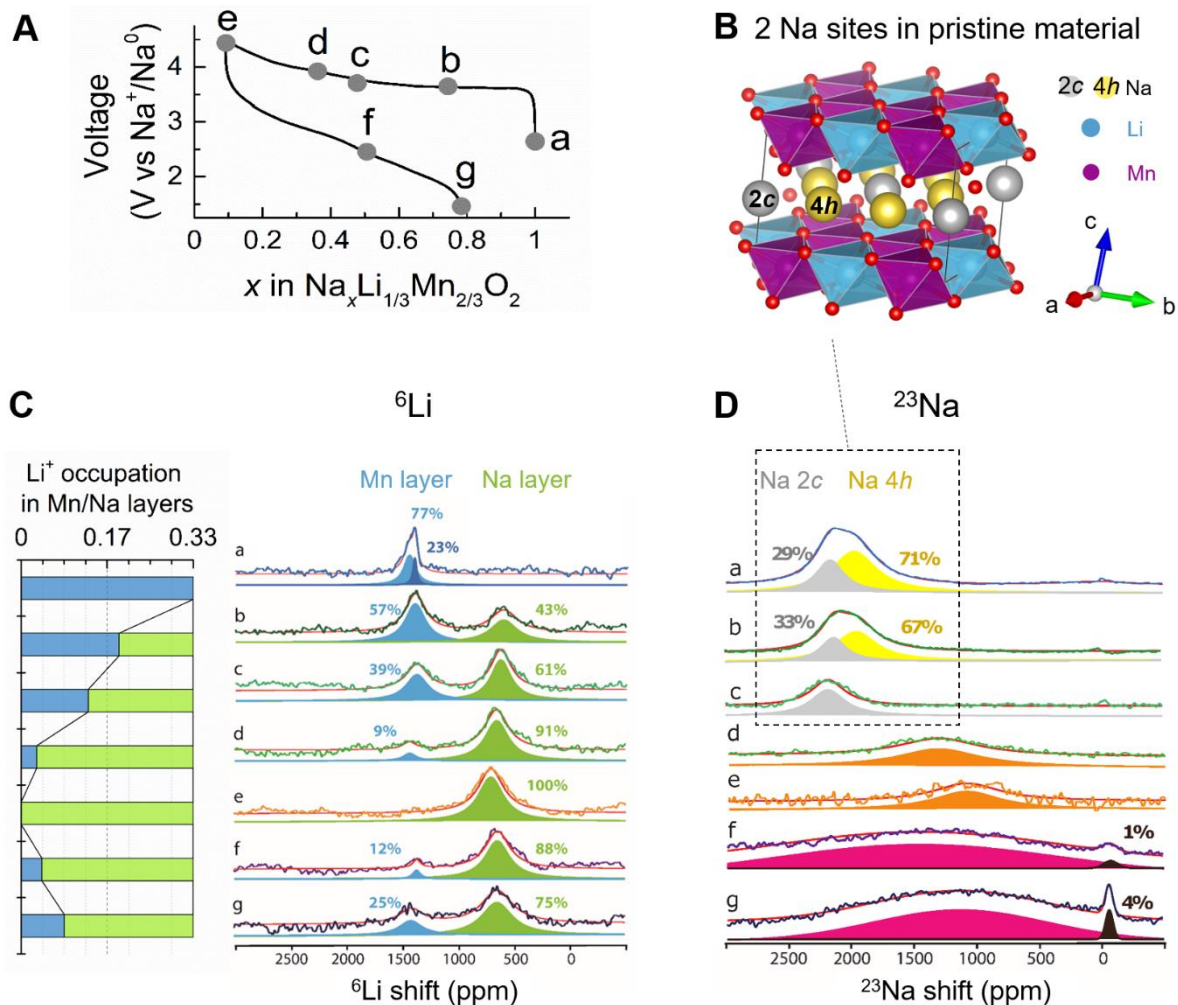
1 sitting in octahedral coordination within the alkali metal layers,<sup>34,35</sup> in full agreement with the  
2 NPD data (Fig.3d, Supplementary Table 6). An additional feature is the partial irreversibility  
3 of this Li-site migration upon discharge since the peak at 700 ppm remains large (75% of the  
4 total) for the fully discharged sample (spectrum g in Fig. 5C). The irreversible migration of  
5 lithium is likely responsible for the wavy nature of the  $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  layers and the strong  
6 local variations of the interlayer distances observed by HAADF-STEM. Lastly, the integration  
7 of the  $^6\text{Li}$  signal through the process remains constant further confirming that no Li is lost (as  
8 seen from ICP-OES measurements in Supplementary Fig. 8) and all  $^6\text{Li}$  spins are detected by  
9 NMR. This is in contrast to previous studies, where a similar behavior of lithium was  
10 observed but lithium loss could not be prevented.<sup>36,37</sup>

11 The  $^{23}\text{Na}$  NMR spectra upon charging first show the progressive disappearance of the  
12 1980 ppm shift (yellow) to the benefit of the 2170 ppm one (grey) implying that the  $\text{Na}^+$  ions  
13 are initially removed from the  $4h$  position. This signal becomes unique, showing an almost  
14 single Na environment after removal of 0.55  $\text{Na}^+$  corresponding to the  $2c$  positions (spectrum  
15 c in Fig. 5D), indicative of a reorganization of Na sub-lattice associated to the early Li  
16 displacement. Afterwards, there is a dramatic change in the sodium environment and the  
17 signal is now shifted to lower chemical shifts (1300 ppm) and much broadened (800 ppm vs  
18 250-500 ppm), signifying an increase in the local disorder around the remaining sodium ions,  
19 which amount to nearly  $\sim 0.09$  Na per formula unit in the fully charged sample. The origin of  
20 such disorder is most likely linked to the onset of  $\text{O}_2$  release, which starts between points c  
21 and d in Fig.5A according to the OEMS measurement. Moreover, the existence of a very  
22 broad peak is also compatible with the slow  $\text{Na}^+$  dynamics which prevents the averaging of  
23 the shift, and may explain the hysteresis observed in GITT measurements at high potential.  
24 Upon discharge, the initial signals are not recovered since the reinsertion of  $\text{Na}^+$  leads to a  
25 very broad ( $> 1300$  ppm) Gaussian distribution of environments, indicative of the persistence  
26 of a massive structural disorder resulting from a broader distribution of Na-O-Mn angles  
27 which govern the NMR shifts<sup>37</sup>. Note that the  $^{23}\text{Na}$  NMR spectrum for a subsequently  
28 recharged sample (Supplementary Fig.18) shows a broad line, centered at a lower shift of 910  
29 ppm, but with a width of 650 ppm that is solely half as wide as at the end of the first charge,  
30 indicating that, somehow, some local order is restored during the second cycle.

31 Consistently, similar broad  $^{23}\text{Na}$  NMR signals were previously reported for the fully  
32  $\text{Na}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$  phase with disordered Na occupation.<sup>38</sup> Thus, this scenario could in fact  
33 explain the difference in cycling curve between first charge-discharge and also the absence

1 O3 to P3 phase transition (*operando* XRD in Supplementary Fig.13) since the irreversibly  
 2 migrated lithium may arrest the long range zig-zag ordering of Na and vacancy which is  
 3 required to stabilize the P3 phase<sup>22</sup>.

4 Altogether, NMR results show that upon Na<sup>+</sup> removal, Na<sub>1-x</sub>Li<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> undergoes a  
 5 partially irreversible migration of Li<sup>+</sup> to the Na layers that creates cation vacancies and  
 6 disorder within the [Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> layers. Due to such an intense modification of the structure,  
 7 some of the Na<sup>+</sup> cannot any longer fully return to their initial sites as some of them are  
 8 irreversibly occupied by 0.25 lithium ions per unit formula (explaining the irreversible loss of  
 9 0.23 Na during the first charge/discharge cycle). Therefore, they will occupy sites having  
 10 changed coordination, explaining the broadened spectra.



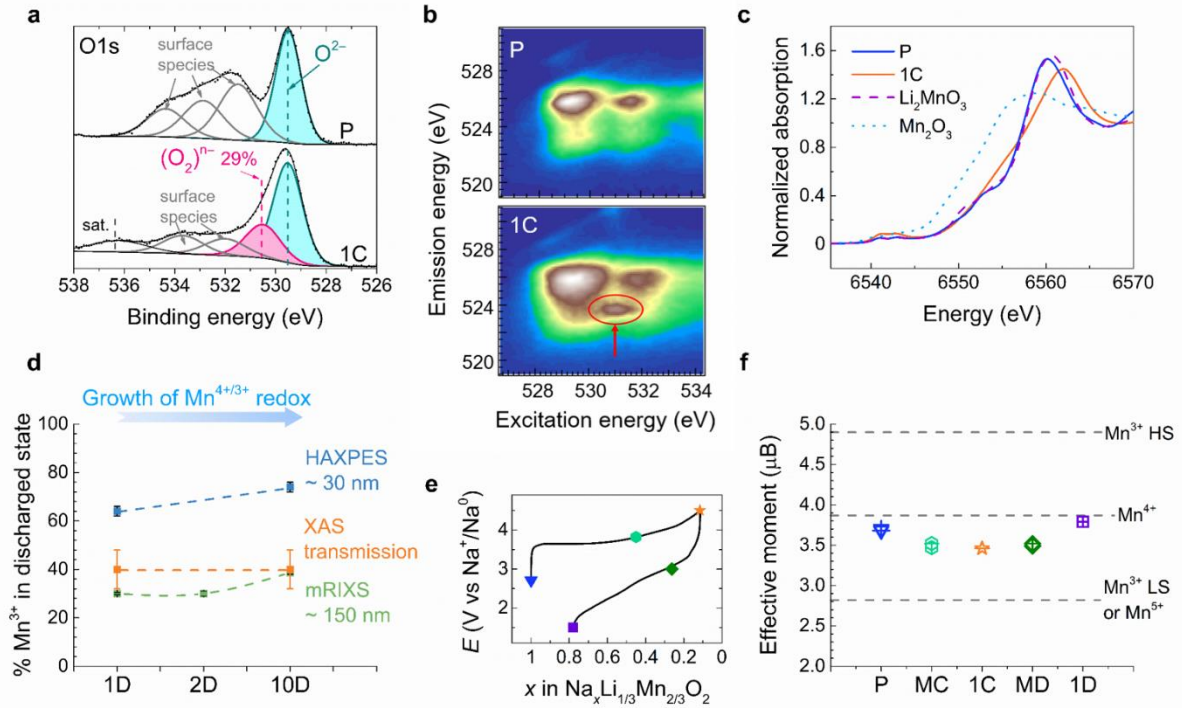
11

12 **Fig. 5** <sup>6</sup>Li and <sup>23</sup>Na MAS NMR spectroscopy results. **A**, First-cycle charge-discharge voltage profile  
 13 with points indicating states of charge/ discharge at which the *ex situ* samples were extracted. **B**,  
 14 Crystal structure of the pristine NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> (space group *C2/m*) showing two Wyckoff sites (*2c*  
 15 and *4h*) for Na<sup>+</sup>. **C**, <sup>6</sup>Li MAS NMR spectra showing two types of peaks corresponding to the isotropic  
 16 shifts for Li in the [Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> layers (blue) and alkali layers (green). Li<sup>+</sup> population in both

1 environments are compared in stacked bar chart on the left as guide to the eye. **D**,  $^{23}\text{Na}$  MAS NMR  
2 results showing peak shifts and broadening. The two  $\text{Na}^+$  signals in the pristine material can be  
3 understood by the two distinct crystal sites shown in figure panel B (see text). The two sharp peaks at  
4 nearly 0 ppm in f and g are due to trace amounts of remaining Na salt from the electrolyte that left  
5 unwashed.

6 Next we interrogate the nature of the electrochemically driven redox processes and  
7 their interplay with local structural changes in  $\text{Na}_{1-x}\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_2$ . Complementary *operando*  
8 X-ray Absorption (XAS), *ex situ* Hard X-ray Photoelectron Spectroscopy (HAXPES) and  
9 mapping of Resonant Inelastic X-ray Scattering (mRIXS) were used to probe the sample at  
10 various depths (particles are of  $> 0.5 \mu\text{m}$  size as seen by SEM, Supplementary Fig. 19).  
11 During the first charge (Fig. 6, a–c) all the techniques show features related solely to oxygen  
12 oxidation. The  $\text{O}1s$  HAXPES spectra (Fig. 6a, Supplementary Fig. 20, 21, left) of the pristine  
13 and fully charged samples differ by the appearance of a new peak at binding energy ( $BE$ ) of  
14 530.5 eV for the fully oxidized sample that corresponds, in light of previous reports,<sup>39</sup> to  
15 oxidized lattice oxygen  $\text{O}^{n-}$  ( $n < 2$ ). This oxygen activity is unambiguously confirmed by the  
16 appearance of a new feature in mRIXS (outlined by an ellipse in Fig. 6b), at an excitation and  
17 emission energy of 531.0 eV and 523.7 eV, respectively, that is characteristic of  $\text{O}^{n-}$  species.<sup>40</sup>  
18 This feature disappears and reappears on subsequent charge-discharge confirming the  
19 reversibility of the anionic redox process (Supplementary Fig. 22). Turning to the outcome of  
20  $\text{Mn}^{4+}$  during the first oxidation process,  $\text{Mn}2p$  HAXPES (Supplementary Fig. 20, 21, right),  
21  $\text{Mn} L_3$  mRIXS (Supplementary Fig. 23, 24), *ex situ* and *operando* XAS on Mn K edge  
22 (Supplementary Fig. 25, 26) indicate that  $\text{Mn}^{4+}$  is redox inactive on first charge since there is  
23 no evolution in the Mn oxidation state in neither of the techniques between pristine and fully  
24 charged sample.





1

2 **Fig.6 Charge compensation mechanism in  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$ .** **a**, *ex situ* HAXPES ( $h\nu = 6900$  eV) O1s  
3 spectra of pristine (P) and charged to 4.5 V samples (1C). **b**, *ex situ* O K-edge mRIXS spectra of  
4 pristine (P) and sample charged to 4.5 V (1C). Red arrows and circles at 531.0 eV excitation energy  
5 and 523.7 eV emission energy indicate the oxidized oxygen feature at charged state. **c**, Mn K-edge  
6 XANES spectra of pristine (blue solid) and sample charged to 4.5 V (orange solid), compared to  
7 references of  $\text{Mn}^{4+}$  (purple dashed) and  $\text{Mn}^{3+}$  (cyan dotted). **d**, Concentration of  $\text{Mn}^{3+}$  species derived  
8 from *ex situ* HAXPES, mRIXS and XAS in the 1<sup>st</sup>, 2<sup>nd</sup>, and 10<sup>th</sup> discharged 1.5 V samples. **e**, First  
9 cycle charge-discharge curve with points indicating the state of charge/ discharge at which *ex situ*  
10 samples for magnetic measurements were extracted from. **f**, Effective magnetic moment deduced from  
11 magnetic susceptibility measurements. P, MC, 1C, MD and 1D represents pristine, mid-charge, first  
12 charge, mid-discharge and first discharge samples, respectively. Dashed lines indicate theoretical  
13 values of spin-only effective magnetic moments of Mn at different oxidation states and spin states.

14 On discharge, all the techniques converge in showing conjointly a nearly reversible  
15 oxygen redox process together with a varying degree of reduction from  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$   
16 (Supplementary Fig. 20–26). However, they show discrepancies in quantifying the amount of  
17  $\text{Mn}^{3+}$  (Fig. 6d). For instance, HAXPES, which is mainly a surface technique (~30 nm in  
18 depth), indicates nearly 60% of  $\text{Mn}^{3+}$  in the fully discharged sample as opposed to solely ~30 %  
19 with mRIXS, which has a probe depth of ~150 nm, compared to a total thickness of the  
20 cathode of ~40  $\mu\text{m}$ .

21 A comprehensive view of the electrode ensemble can be acquired from XAS  
22 measurements at the Mn K-edge, which was collected in transmission geometry. Despite the  
23 clear trend of Mn reduction as the edge shift to lower energies in discharge (Supplementary  
24 Fig. 25, 26), quantification via linear combination fits of references, as performed for Mn  $L_3$

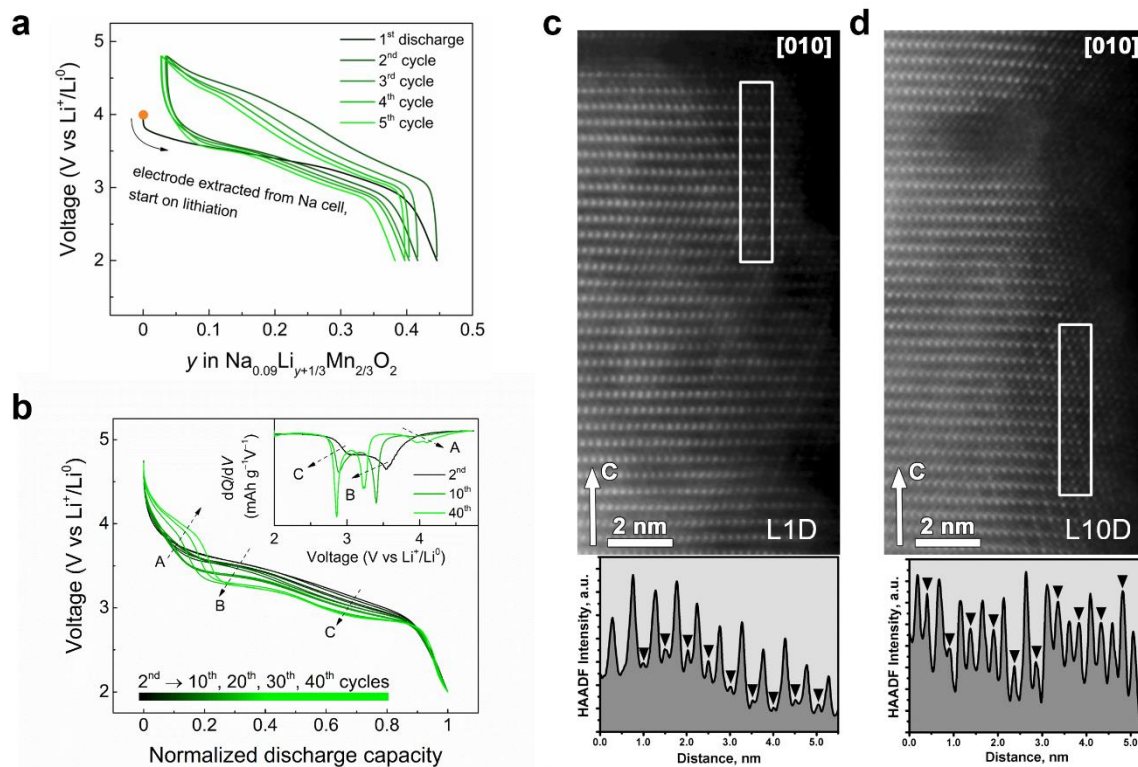
1 mRIXS, was not possible because the position and shape of the Mn spectra at K-edge heavily  
2 depend on both formal oxidation state and coordination environment of Mn.<sup>41</sup> To account for  
3 variations in line shape introduced by changes in coordination environment, the spectra were  
4 analyzed following the integration method proposed by Dau et al.<sup>42</sup> Such approach rendered  
5 an approximate average oxidation state of ~3.6+ for the discharged (1D) sample  
6 (Supplementary Fig. 25b), consistent with the quantification from Mn L<sub>3</sub> mRIXS  
7 (Supplementary Fig. 24, Figure 6d). It is worth noting that we found the linear fit in this  
8 method is still rather sensitive to the choice of reference spectra, leading to a larger  
9 uncertainty than with other methods. The difference between HAXPES and the mRIXS and  
10 XAS results could be ascribed to differentiated surface reactivity worth exploring in future  
11 work, but, in all, it is clear that partial reduction of Mn<sup>4+</sup> into Mn<sup>3+</sup> occurred during the first  
12 discharge, reminiscent to the behavior of the parent Li<sub>2</sub>MnO<sub>3</sub>.<sup>43</sup> However, the degree of Mn  
13 reduction was lower than expected from the measured capacities, pointing to complex charge  
14 compensation. Lastly, independent of the spectroscopy employed, the changes in Mn spectra  
15 were reproduced upon extensive cycling, proving that Mn redox couple was activated after  
16 the first charge (Supplementary Fig. 21, 24, 25).

17 Alternatively, *ex situ* magnetic susceptibility measurements from 2 to 400 K carried out on  
18 the samples at various states of charge and discharge (Fig. 6e) (Supplementary Fig. 27,  
19 Supplementary Table 7) confirm the presence of Mn<sup>4+</sup> with a magnetic moment close to the  
20 expected value in the pristine material ( $\mu_{\text{eff}} \sim 3.7 \mu\text{B}$  vs. 3.9, Fig6f) and displaying a valley-  
21 like variation upon cycling. Such a mirror variation in charge/charge is surprising  
22 considering that the partial reduction of Mn<sup>4+</sup> → Mn<sup>3+</sup> should lead to an increase of  $\mu_{\text{eff}}$ . Given  
23 the significant amount of Mn<sup>3+</sup> determined by spectroscopy, the small increase of  $\mu_{\text{eff}}$  in the  
24 discharge sample compared to the pristine one (3.79 vs. 3.7  $\mu\text{B}$ ,) strongly suggests charge  
25 transfer between Mn and O during oxidation. This indirectly supports the participation of  
26 anions in the redox activity of NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>, as corroborated by our recent theoretical  
27 calculations on Na<sub>2/3</sub>[Mg<sub>1/3</sub>Mn<sub>2/3</sub>]<sub>2</sub><sup>44</sup> showing that the coupling unpaired electrons on both Mn  
28 and O the decreases the total magnetization of the cell. However, it is beyond the scope of this  
29 paper to quantitatively decouple the Mn from the O contribution for  $\mu_{\text{eff}}$  values, whose  
30 robustness is ensured by having duplicated twice our measurements on different samples.

31 Overall, we report a novel anionic redox active O3 NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> layered phase vs. Na  
32 showing no voltage fade and oxygen redox not associated with 3d metal migration to the  
33 alkali layer, unlike most Li-rich layered oxides. Moreover, it turns out that NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> is

1 an ideal model compound to clarify the key role of the alkali metal in Li(Na)-rich layered  
2 oxides with respect to both voltage fade and 3d cation migration owing to its versatility to  
3 intercalate Na and Li as shown next. A nearly Na-free electrode,  $\text{Na}_{0.09}\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_{1.86}$ , was  
4 recovered and washed from a  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2/\text{Na}$  Swagelok cell that was fully charged to 4.5  
5 V, prior to be used in a new Swagelok with Li metal as a negative electrode and 1M  $\text{LiPF}_6$  in  
6 EC-DMC (v/v = 50/50, LP30) as electrolyte. The voltage profile for the  $\text{Na}_{0.09}\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_2/\text{Li}$   
7 cell (Fig. 7a) shows the reversible uptake of 0.4  $\text{Li}^+$  per formula unit together with good  
8 capacity retention upon cycling, yet accompanied by large voltage decay. From combined  
9 coulombic titration and ICP analysis, the chemical composition of the fully discharged sample  
10 was identified as  $\text{Na}_{0.09}\text{Li}_{0.73}\text{Mn}_{2/3}\text{O}_2$ .

11 Evidence for Mn migration upon Li insertion in this material was obtained by TEM. The [010]  
12 HAADF-STEM images and corresponding HAADF intensity profiles across the  
13  $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  layers are reported after one (Fig. 7c) and ten (Fig. 7d) charge-discharge cycles  
14 in Li-ion half cells. The outlined rectangular areas reveal the Mn cation migrations that are  
15 enhanced with cycling. The peaks in the HAADF intensity profiles (bottom) correspond to  
16 the Mn columns at the  $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  layers, whereas the intensity between the peaks (marked  
17 with black arrowheads) indicates the migration of the Mn cations into the interlayer space.  
18 Note that the Mn migration is more pronounced in the sample after 10 cycles which indicates  
19 only partially irreversible character of this migration. This drastically contrasts with similar  
20 images taken on the material cycled vs. Na in Na-based electrolytes where no Mn migration  
21 towards the alkali layer can be spotted.



1  
 2 **Fig. 7 Voltage fade and cation migration in Li half cells.** **a**, First five cycles of voltage-composition  
 3 profiles of the desodiated  $\text{Na}_{0.09}\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_{1.86}$  cycled in Li half cells with LP30 electrolyte. **b**,  
 4 normalized discharge curves of the same cell for 40 cycles with  $dQ/dV$  of selected cycles, showing the  
 5 evolution of low voltage redox process and voltage fade upon cycling in the Li cell. The actual  
 6 discharge profile before normalization is given in Supplementary Fig. 28. [010] HAADF-STEM  
 7 images and corresponding HAADF intensity profiles show increasing cation migration from the **c**, 1<sup>st</sup>  
 8 discharged to **d**, 10<sup>th</sup> discharged sample in the Li cell.

## 9 Discussion

10 Altogether, the electrochemical activity of Na (Li) in the alkali-rich  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  phase  
 11 provides valuable information for clarifying the complex interplay between anionic redox,  
 12 cationic migration, voltage hysteresis and voltage fade in layered 3d transition metal oxides. It  
 13 now pertains to confront these findings with existing literature data to move one-step forward  
 14 in the general understanding of the anionic redox mechanism.

15 Among the Na-based anionic redox active layered compounds so far reported, O3-  
 16  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  is the one that shows the lowest oxygen redox potential ( $\sim 3.6$  V vs  $\text{Na}^+/\text{Na}$ ).  
 17 To rationalize this finding DFT calculations were performed on the  $C2/m$  structural model of  
 18 multiple variations of partially charged O3- $\text{Na}_x\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_2$  structures with the  $\text{Li}^+/\text{Na}^+$   
 19 cations distributed over three crystallographic positions  $2b$  (Mn layer) and  $4h$ ,  $2c$  (alkali layer).  
 20 Up to the removal of  $1/3$   $\text{Na}^+$ , all O3 configurations with partial or total Li migration to the  
 21 alkali layer, namely  $\text{Li}(\text{M}+\text{A})$  or  $\text{Li}(\text{A})$  are significantly destabilized against those having Li

1 in the Mn layer, namely Li(M). This energy penalty for Li migration to the alkali layer is  
2 removed upon further Na<sup>+</sup> extraction as Li(M+A) and Li(A) configurations become as stable  
3 or more stable than Li(M) configurations at Na concentration  $x_{\text{Na}} = 1/3$  and  $1/6$ , respectively.  
4 (Supplementary Table 8). Remarkably, the Mn<sup>4+</sup> (0.54 Å) migration to the alkali layer is  
5 energetically prevented due to a significant destabilization of the MnO<sub>6</sub> octahedron that would  
6 display much too long Mn-O bonds when sitting in the alkali layer (2.2 Å) compared to the  
7 metallic layer (1.9 Å). This thermodynamic preference for Li migration is likely related to the  
8 well-known interlayer electrostatic instability of layered oxides at low alkali-content and is  
9 here activated once the Na/Li concentration ratio reaches 1 in Na<sub>x</sub>(Li<sub>1/3</sub>Mn<sub>2/3</sub>)O<sub>2</sub>. This ratio  
10 therefore sets the critical Na concentration below which Li rather than Na should dominate  
11 the crystallographic features of the O3 phase. Accordingly, Li migration at  $x_{\text{Na}} \leq 1/3$  comes  
12 along with a significant contraction of the *c* lattice parameter, which obviously affects the  
13 kinetics of Na<sup>+</sup> diffusion for further de-sodiation. Altogether, these results allow reconciling  
14 the XRD, NMR and electrochemical data and help in rationalizing the role of Na on the  
15 stabilization of the O3 phase.

16 Upon Na removal, a biphasic process occurs between  $x_{\text{Na}} = 1$  and  $x_{\text{Na}} \sim 2/3$  for which the  
17 computed average potential (3.5 V) is in fair agreement with experiments (Supplementary  
18 Table 8). The end-member Na<sub>2/3</sub>[Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> phase of this biphasic process displays an  
19 increased *c* lattice parameter compared to the pristine phase, fully consistent with the O3(II)  
20 phase identified by *operando* XRD (Supplementary Fig.13) at the very beginning of charge.  
21 Removing more sodium from the structure leads to Na<sub>1/3</sub>[Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> or Na<sub>1/6</sub>[Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub>  
22 phases having Li in the alkali layer and contracted *c* lattice parameters, consistent with the  
23 less chemically shifted <sup>6</sup>Li NMR signal observed in Fig.5C and the crystallographic features  
24 of O3(II) just before the onset of O<sub>2</sub> release (Supplementary Table 8). Interestingly, further  
25 Na<sup>+</sup> removal from the Li-migrated O3(II) phase (Supplementary Fig.13) should be kinetically  
26 hindered by the size-constrained alkali interlayer, hence leading to the voltage polarization  
27 observed in the galvanostatic curve of Fig.2 along the second process. We believe this kinetic  
28 limitation of Na-ion diffusion in the structure most likely prevents the Na-ordering required  
29 for the O3 to P3 transition. Moreover, it is at this stage of the Na removal process, when  
30 nearly all Li has moved to the alkali layers (as deduced from <sup>6</sup>Li NMR) that O<sub>2</sub> release is  
31 triggered. This observation is not fortuitous since Li migration to the alkali layer implies that  
32 some oxygen atoms become less electrostatically bonded to the structural network due to  
33 cationic vacancies in their local environment and therefore more prone to oxidation.

1 Noteworthy, the presence of Li vacancies in the metallic layer may also favor Mn/Li<sub>vac</sub>  
2 disorder in the metallic layer, as observed in the synchrotron XRD and TEM data. While no  
3 evidence of ribbon ordering<sup>14</sup> was found in the XRD patterns of the charged sample, the  
4 Mn/Li<sub>vac</sub> disorder is predicted to be thermodynamically achievable at low Na content ( $x_{\text{Na}} =$   
5  $1/6$ ) which should prevent Li<sup>+</sup> ions from moving back to the metallic layer in discharge  
6 (Supplementary Table 9). Obviously, towards the very end of charge ( $x_{\text{Na}} < 1/6$ ), the phases  
7 determined by DFT calculations without considering O<sub>2</sub> release may no longer be  
8 representative of the experimental ones. Therefore, a thorough analysis of O-defective phases  
9 that enlists, besides O- and Na-vacancies, the migration of Mn within the metallic layer,  
10 would be required to get more insights into the impact of these structural modifications on  
11 further cycling.

12 Another intriguing question regards whether the O<sub>2</sub> release leads to oxygen vacancies or  
13 material densification, which has so far been associated solely to the migration of the  
14 transition metal cations into the alkali metal layers in the Li-rich layered oxides. In  
15 NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> such interlayer migration can safely be excluded based on the XRD and TEM  
16 structure analysis. First-principles DFT calculations confirm this point by showing that Mn  
17 migration from the metallic to the alkali layer is thermodynamically less favored (by at least  
18 200-300 meV/Mn, Supplementary Table 9) when the alkali layer contains Na compared to Li,  
19 even at low sodium content. This suggests that the presence of Na<sup>+</sup> ions in the alkali layer,  
20 even in small amount, imposes much too large interlayer spacing (large  $c$  parameter) to  
21 stabilize Mn<sup>4+</sup> in the octahedral site. Moreover, we could also compute with DFT the  
22 variation of the  $c$  parameter from the fully sodiated Na[Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> phase to the desodiated  
23 Na<sub>0.125</sub>[Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> one which nicely follows the experimental data reported from XRD  
24 analysis in Fig.3a only when Li migration is considered in the partially desodiated  
25 Na<sub>1/3</sub>[Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> phase (Supplementary Table 8). In contrast, the  $c$ -parameter for pure-Li  
26 phases is systematically smaller by at least 1.5 Å, which again confirms the greater ability of  
27 Li-based phases to stabilize the Mn cations in the interlayer space. Interestingly, O<sub>3</sub>-  
28 Na<sub>0.09</sub>Li<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> on Li-insertion behaves similarly to the pure Li-phases, as Li<sup>+</sup> occupies  
29 positions in both alkali and metallic layers.

30 Consequently, we could hastily eliminate the densification hypothesis prior to realizing that  
31 Mn migration within the metal layers could be an alternative way to trigger densification. The  
32 complete migration of Li<sup>+</sup> cations from the [Li<sub>1/3</sub>Mn<sub>2/3</sub>]O<sub>2</sub> layer to the alkali layer on the first  
33 charge leaves cationic vacancies ( $\square_{\text{cat}}$ ), and, taking into account oxygen release at high voltage,

1 the chemical formula for the fully charged state can be represented as  
2  $\text{Na}_{0.09}\text{Li}_{1/3}[(\square_{\text{cat}})_{1/3}\text{Mn}_{2/3}]\text{O}_{1.86}$ . Realization of oxygen deficiency through anion vacancies should  
3 lower the coordination number of Mn below six, but Mn K-edge XANES spectra and EXAFS  
4 reveal octahedral Mn coordination at all states of charge. Thus the oxygen vacancies must be  
5 eliminated by migration from bulk to the surface with subsequent annihilation and the  
6 increasing Mn/O ratio is accommodated by intralayer  $\text{Mn}^{4+}$  cation migration to vacant cation  
7 sites  $\square_{\text{cat}}$ . The chemical formula at full charge can be recast as  $\text{Na}_{0.09}\text{Li}_{0.36}[(\square_{\text{cat}})_{0.28}\text{Mn}_{0.72}]\text{O}_2$ .  
8 Disrupting the 1:2 ( $\square_{\text{cat}}$ ):Mn ratio should suppress the honeycomb cation ordering and  
9 promote stochastic arrangement of  $\text{Mn}^{4+}$  and cation vacancies in the densified  
10  $[(\square_{\text{cat}})_{0.28}\text{Mn}_{0.72}]\text{O}_2$  layers, as indicated by vanishing intensity of the honeycomb superlattice  
11 reflections in the SXRD patterns (Fig. 3a) and confirmed by DFT calculations  
12 (Supplementary Table 9)

13 Our study also showed that discharging of the  $\text{O3-Na}_{0.09}\text{Li}_{1/3}\text{Mn}_{2/3}\text{O}_{1.86}$  material either in Na-  
14 ion or in Li-ion cells promote intralayer and interlayer cation migration, respectively,  
15 therefore comforting the robustness of the interplay between cationic migration and voltage  
16 fade early proposed.<sup>45</sup> The  $\text{O3-NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  phase exemplifies very clearly that if the  
17 densification after first oxygen release occurs through the intralayer transition metal cation  
18 migration, the material demonstrates virtually no voltage fade, whereas switching to the  
19 interlayer migration mode (e.g., cycling vs.  $\text{Li}^+/\text{Li}^0$ ) readily introduces voltage fade. Therefore,  
20 a new way to mitigate voltage fade could consist in promoting the intralayer migration of  
21 transition metal by controlling, via chemical composition, the structural location of vacancies  
22 formed by alkali cation de-insertion with respect to the onset of oxygen release. The benefit  
23 associated to the absence of voltage fade for  $\text{O3-NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  is however tarnished by the  
24 fact that the Na uptake-removal in this phase comes with a large voltage hysteresis. Numerous  
25 explanations enlisting either reformation/breaking of O-O dimers<sup>46</sup>, cationic-anionic redox  
26 inversion induced by small charge-transfer bandgap<sup>47</sup> or sluggish structural rearrangements<sup>48</sup>  
27 have so far been proposed to account for such hysteresis with the most favored one being  
28 interlayer transition metal migration during the first oxidation.<sup>49-51</sup> We could hypothesize that  
29 the hysteresis observed in  $\text{O3-NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  is also due to intralayer Mn migration, but  
30 further in depth investigation is needed. If true, the voltage hysteresis might appear as  
31 unavoidable consequence of the  $\text{O}_2$  loss at the first “activation” charge to high voltage, which  
32 is also responsible for most of the irreversibility obtained during the first cycle.

1 To conclude, we have reported the Na-rich  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  phase having an O3-type structure  
2 and showing highly reversible de-insertion/ insertion of  $\sim 0.7$  Na via combined cationic and  
3 anionic redox processes. At a fundamental level, with this material we could consolidate the  
4 established link between cation migration and voltage fade, demonstrating that the voltage  
5 fade can be arrested by switching migration of the transition metal to an intralayer mode  
6 through displacement the  $\text{Li}^+$  cations from the  $[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  layers to the alkali layers on the  
7 first charge. At a practical level, O3- $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  offers positive attributes such as a  
8 reversible capacity of  $190 \text{ mAh g}^{-1}$  associated with a good capacity retention and no  
9 discernable voltage fade while showing robust water stability, which is rare for stoichiometric  
10 Na-based layered compounds representing a serious asset for the future applications.  
11 Therefore, as the remaining voltage hysteresis in this material still stands as a roadblock, we  
12 are trying to solve via the injection of a robust ordering scheme within the transition metal  
13 layer. We hope these findings pave the way towards the design of novel moisture stable  
14 anionic redox active O3-type Na phases having large capacity and minimized voltage fade  
15 and hysteresis for the next generation of advanced Na-ion batteries.

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## 1 **Author contributions**

2 Q.W, S.M. and J.-M.T. conceived the idea and designed the experiments. M.D. and B.P.  
3 performed NMR measurements. J.C./Y.-S.Y., R.D. and J.W./W.Y. performed and interpreted  
4 the XANES/EXAFS, HXAPES and mRIXS measurements. M.A. collected the NPD data,  
5 G.R. analyzed and interpreted the SXRD and NPD patterns and performed the magnetic  
6 measurements while A.V. M and A. A collected and interpreted all the microscopy data.  
7 Lastly, L. Z. performed the OEMS measurements and M.C. supervised the project. M-L.D  
8 performed the theoretical calculations and contributed to the overall interpretation of the  
9 results. J.-M.T, A.A, S.M and Q.W. wrote the paper, with contributions from all authors.

## 10 **Competing interests**

11 The authors declare no competing interest. The material O<sub>3</sub>-Na(Li<sub>1/3</sub>Mn<sub>2/3</sub>)O<sub>2</sub> is patented with  
12 patent application number B19-5233FR.

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## 1 **Methods**

2 **Synthesis.** 415 mg of Na<sub>2</sub>O<sub>2</sub> (Alfa Aesar, 95%), 53 mg of Li<sub>2</sub>O (Alfa Aesar, 99.5%) and 560  
3 mg of Mn<sub>2</sub>O<sub>3</sub> (Sigma Aldrich, 99%) were thoroughly mixed in a mortar prior to be placed in  
4 an alumina boat. The boat was placed in a quartz tube of 62 cm length and 32 mm diameter  
5 that was placed in a tubular furnace (type carbolite) having a 30 cm heating zone. After  
6 placing the sample, the alumina tube was flushed with argon for 45 minutes with an Ar flow  
7 of 50mL/ min. Then, the argon flow was stopped and the sample was heated to 700 °C for 8h  
8 and then cooled down to room temperature. The as-synthesized material was soaked in  
9 distilled water (100 mg/10 mL H<sub>2</sub>O) while sonicating for 30 minutes followed by drying at  
10 80 °C under vacuum overnight.

11 **Electrochemical characterization.** Electrochemical characterization was carried out in  
12 Swagelok-type cells versus metallic Na, with 1 M NaPF<sub>6</sub> (Stella Chemifa) dissolved in  
13 propylene carbonate (PC) as electrolyte, and Whatman GF/D borosilicate glass fiber  
14 membrane as separator. The cathode material was used in form of self-standing film electrode  
15 comprising 76 wt% active material, 20 wt% carbon Super P (Csp) and 4 wt%  
16 polytetrafluoroethylene (PTFE). Typical loading of cathode active materials was around 5  
17 mg/cm<sup>2</sup>. All cells were assembled in an Ar-filled glovebox and were cycled in galvanostatic  
18 mode at current rates ranging from C/8 to C/20 (1 Na<sup>+</sup> exchanged in 8 to 20 hours).  
19 Galvanostatic intermittent titration technique (GITT) measurement was performed in the  
20 second cycle of NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>/Na cells at 25 °C with steps of 0.2 Na<sup>+</sup> exchange and OCV  
21 period of 20 h.

22 For cycling versus metallic Li, a nearly Na-free electrode, Na<sub>0.09</sub>Li<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub> was recovered  
23 and washed from a NaLi<sub>1/3</sub>Mn<sub>2/3</sub>O<sub>2</sub>/Na Swagelok cell that was fully charged to 4.5 V vs  
24 Na<sup>+</sup>/Na<sup>0</sup>, prior to being used in a new Swagelok with Li metal as a negative electrode and 1M  
25 LiPF<sub>6</sub> in EC-DMC (v/v = 50/50) as electrolyte. The Li cells are also cycled at current rates  
26 ranging from C/8 to C/20 at 25 °C.

27 To prepare *ex situ* samples for characterization, the cathode consisted of either PTFE film  
28 (XAS, mRIXS) as described before, or a powder composite of active material mixed with  
29 15–25 wt% Csp (SXR, TEM, NMR, HAXPES, SQUID, ICP). *Ex situ* samples were  
30 extracted from the cycled cells in an Ar-filled glovebox and washed in anhydrous dimethyl  
31 carbonate (DMC) for five times before sealing and transferring under Ar.

1 **Gas analysis.** For pressure analysis and OEMS measurements, we employed  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  as  
2 counter electrode to avoid gas generation from side reactions with common anode materials  
3 such as Na and hard carbon. The  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$  and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  (NVP) were used both in  
4 form of self-standing electrode (76% active material, 20% Csp, 4% PTFE). One piece of  
5 GF/D glass fiber was used as separator. In-house pressure cells or OEMS cells were  
6 assembled in an Ar-filled glovebox and then cycled at C/20 current rate (0.05  $\text{Na}^+$  exchange/h  
7 for  $\text{NaLi}_{1/3}\text{Mn}_{2/3}\text{O}_2$ ) with 150  $\mu\text{L}$  of electrolyte (1 M  $\text{NaPF}_6$  dissolved in PC) and cut-off  
8 potentials of  $-0.5$ – $3.1$  V vs. NVP. The OEMS and pressure cell setup was described  
9 elsewhere.<sup>52,53</sup> For OEMS, gaseous products were collected and analyzed by LabView  
10 program.

11 **XRD.** XRD patterns were performed on pristine samples using a BRUKER D8 Advance  
12 diffractometer equipped with Cu  $\text{K}\alpha$  radiation source ( $\lambda \text{K}\alpha_1 = 1.54056 \text{ \AA}$ ,  $\lambda \text{K}\alpha_2 = 1.54439$   
13  $\text{ \AA}$ ). *Operando* XRD was carried out on the same diffractometer in an electrochemical cell  
14 equipped with a Be window. SXRD was performed on pristine and *ex situ* powders at the 11-  
15 BM beamline (Advanced Photon Source, Argonne National Laboratory). Rietveld refinement  
16 on the XRD patterns were conducted using FullProf Suite.<sup>54</sup> Simulation of stacking faults in  
17 the pristine sample was done with the FAULTS software available in the FullProf Suite.<sup>55</sup>

18 **TEM.** The samples were prepared by crushing the crystals with an agate mortar and pestle in  
19 dimethyl carbonate and depositing drops of suspension onto a carbon film supported by a  
20 copper grid. Samples for TEM were stored and prepared in an Ar-filled glovebox. A special  
21 Gatan vacuum transfer holder was used for analyses and transportation of the samples from  
22 the Ar-filled glovebox to the TEM column to prevent the interaction with air. Selected area  
23 electron diffraction (SAED) patterns and high resolution high angle annular dark field  
24 scanning transmission electron microscopy (HAADF-STEM) images were acquired on a  
25 probe aberration-corrected FEI Titan Themis Z transmission electron microscope operated at  
26 200 kV.

27 **NPD.** Neutron diffraction data were collected at the ECHIDNA high-resolution powder  
28 diffractometer at the OPAL research facility (Lucas Heights, Australia).<sup>56</sup> Three samples were  
29 filled into thin-wall vanadium containers with the wall thickness (150  $\mu\text{m}$ ) and 10 mm in  
30 diameter and sealed under argon with indium metal wire. The data collection was performed  
31 at ambient temperature in Debye-Scherrer geometry under constant spinning. Monochromatic  
32 neutrons were obtained at (533) reflection of composite vertically focusing Ge



1 monochromator at  $140^\circ$  take-off angle. Wavelength  $\lambda = 1.622043(15) \text{ \AA}$  was determined  
2 using the full-profile refinement of  $\text{LaB}_6$  reference from NIST. Diffraction data were obtained  
3 in the  $2\theta$  range (4-164 deg) using 25 resolution steps of the 2D multidetector consisting of  
4 128  $^3\text{He}$  vertically positionally sensitive tubes. The exposure time was 9 h per dataset and  
5 equal for the samples studied. All patterns were refined by Rietveld method using the FullProf  
6 suite.<sup>57</sup>

7 **ICP.** ICP was performed to determine the elemental compositions of the material before and  
8 after  $\text{H}_2\text{O}$  treatment and electrochemical cycling with a ThermoFisher iCAP 6000 device. All  
9 powders were first digested in aqua regia, followed by a filtering process for the cycled  
10 samples to remove the conductive carbon in the composite electrodes.

11 **NMR.** Solid-state NMR experiments were performed on a 4.7 T Avance III HD Bruker NMR  
12 spectrometer (200 MHz for  $^1\text{H}$ , 29.4 MHz for  $^6\text{Li}$  and 52.9 MHz for  $^{23}\text{Na}$ ), using a 1.3 mm  
13 MAS probe spinning at 62.5 kHz under pure nitrogen gas. Without temperature regulation,  
14 the temperature inside the rotor is expected to be around  $50^\circ\text{C}$ .

15 All experiments were recorded with a rotor-synchronized Hahn echo sequence. For the  $^6\text{Li}$   
16 spectra, the  $90^\circ$  pulse was set to  $1.11 \mu\text{s}$  and the chemical shift was referenced with liquid  
17  $^6\text{LiCl}$  in water (corresponding to a 225 kHz  $B_1$  field strength). For  $^{23}\text{Na}$  spectra, the Hahn  
18 echo was recorded with a  $45^\circ-\tau-90^\circ-\tau$  sequence to account for the quadrupolar effect, using  
19 a  $1.47 \mu\text{s}$  long, low power  $45^\circ$  radiofrequency pulse (corresponding to a 85 kHz  $B_1$  field  
20 strength). To ensure optimal detection of the signals affected by quadrupolar broadening,  
21 several experiments were performed with RF powers ranging between 50 and 5W, and the RF  
22 power was set at 12.5W to avoid any loss of signal. Moreover, to ensure proper detection and  
23 phasing of the broad signal for discharged samples and avoid baseline distortion issues, a full  
24 echo signal was also acquired after a first evolution delay of 16 rotor periods<sup>58</sup>. The resulting  
25 full echo signal has the same lineshape as the conventional Hahn echo signal after proper  
26 phasing, thereby confirming the first results. All  $T_1$  relaxation times were measured in the  $500$   
27  $\mu\text{s} - 10 \text{ ms}$  range, and therefore, all spectra were recorded with a 50 ms recycling delay  
28 ensuring full recovery of the magnetization. No spinning sideband were detected in our  
29 experiments thanks to the low-field/high spinning speed combination.

30 The 1.3 mm zirconia rotor were filled inside a glove box under argon, and the rotor was  
31 weighted before and after the filling procedure to obtain the sample mass (around 2.7 to  
32 4.6 mg). Depending upon the sensitivity of the experiments, the total number of recorded

1 transients varied between 32'768 and 1'403'472 and MAS was performed under dry N<sub>2</sub> gas.  
2 The spectra were deconvoluted with dmfit.<sup>59</sup> Special care was taken to measure NMR spectra  
3 on fresh samples with as little contact as possible with residual moisture in the glove box or in  
4 the NMR spectrometer. Contact with moisture results in the quick evolution of the NMR  
5 spectra, with sharper peaks appearing in the 0-300 ppm range in <sup>23</sup>Na NMR spectra, as  
6 noticed previously<sup>37</sup>.

7 **HAXPES.** HAXPES measurements were performed at the GALAXIES beamline of  
8 synchrotron SOLEIL (France),<sup>60</sup> using photon excitation energy of  $h\nu = 6900$  eV obtained  
9 from the third-order reflections of the Si(111) crystal monochromator. Photoelectrons were  
10 analyzed by a SCIENTA EW4000 spectrometer, and the obtained energy resolution from the  
11 Au Fermi edge was 0.14 eV for 6900 eV photon energy. No charge neutralization was used  
12 and the analysis chamber was under high vacuum of  $\sim 10^{-11}$  bar during the measurements.

13 **mRIXS.** mRIXS was measured in the iRIXS endstation at Beamline 8.0.1 of Advanced Light  
14 Source, Lawrence Berkeley Lab.<sup>61</sup> Further experimental details are exhibited in  
15 supplementary note 1.

16 **XAS.** *Ex situ* and *operando* XAS measurements at the Mn K-edge were performed in  
17 transmission mode at the ROCK beamline<sup>62</sup> of synchrotron SOLEIL (France). Further details  
18 of the experiments and data analyses are included in supplementary note 2.

19 **Magnetic measurements.** Susceptibility measurements were conducted in zero field cooling  
20 (ZFC) mode using a SQUID XL magnetometer (Quantum design), under applied magnetic  
21 fields of 1 T in temperature range of 2–400 K. The powder samples were sealed in quartz  
22 tubes under vacuum to avoid any contact with air. A small piece of cotton is used to prevent  
23 the motion of the powders along the quartz tube. Both the quartz tube and cotton are found to  
24 be transparent to magnetic measurements.

25 **DFT.** Spin-polarized density functional theory (DFT) calculations were performed using the  
26 plane-wave density functional theory VASP (Vienna Ab initio Simulation Package) code<sup>63,64</sup>  
27 within the generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE) to describe  
28 electron exchange and correlation.<sup>65</sup>

29 The rotationally invariant Dudarev method (DFT+U)<sup>66</sup> was used to correct the self-interaction  
30 error of conventional DFT for correlated d-electrons with  $U_{\text{eff}} = 4$  eV for Mn. Various Li/Na  
31 configurations were tested with alkali lying in the *2b*, *2c* or *4h* Wyckoff positions of the *C2/m*

1 model structure. Mn migration was investigated in  $2\times 1\times 1$  super-cells (8 Mn per cell). All  
2 atom coordinates and lattice parameters were fully relaxed using conjugate gradient energy  
3 minimization until the forces acting on each atom were less than  $5.10^{-3}$  eV  $\text{\AA}^2$ . A plane-wave  
4 cutoff of 600 eV was used to define the basis set, with well-converged k-point sampling for  
5 each compound. Both ferromagnetic and antiferromagnetic arrangements were considered in  
6 the calculation, the former leading generally to slightly more stable structures within one or  
7 two  $k_{\text{B}}T$  (room temperature activation energy  $\sim 25$  meV). Madelung potentials were computed  
8 using home-made code.