

SUPPORTING INFORMATION

Stacking Faults in an O2-type Cobalt-Free Lithium-Rich Layered Oxide: Mechanisms of the Ion Exchange Reaction and Lithium Electrochemical (De)Intercalation

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**Structural parameters determined for Retveld refined for the P2-
Na_{0.7}[Li_{0.14}Ni_{0.14}Mn_{0.72}]O₂ phase**

Space Group: $P6_3$						
Cell parameters: a = 4.969(8) Å, c = 11.139(3) (Å)						
Position	x	y	z	Atom	Occupancy	Biso
Mn1	0	0	0.022(9)	Mn ⁴⁺	1	0.55
Mn2	2/3	1/3	0.024(2)	Mn ⁴⁺	1	0.55
M	1/3	2/3	0.020(6)	Mn ⁴⁺	0.16	0.55
				Ni ²⁺	0.42	0.55
				Li ⁺	0.42	0.55
O1	0.332(7)	0.014(2)	-0.378(6)	O ²⁻	1	0.80
O2	0.636(1)	-0.006(5)	0.441(2)	O ²⁻	1	0.80
Na1	0	0	0.278(1)	Na ⁺	0.20(1)	0.71
Na2	0.393(6)	0.040(4)	0.285(1)	Na ⁺	0.34(1)	0.71
Na3	1/3	2/3	0.283(7)	Na ⁺	0.26(7)	0.71
Na4	2/3	1/3	0.305(5)	Na ⁺	0.12(9)	0.71

Monitoring the ion-exchange reaction by variable X-ray diffraction

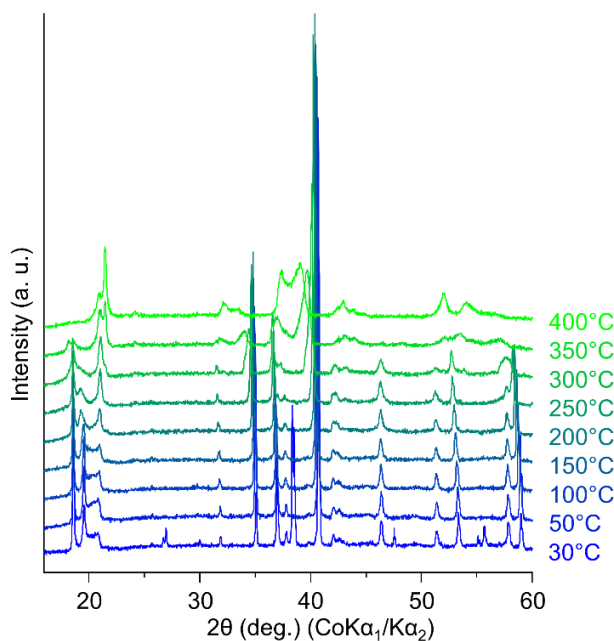


Figure S1. Variable temperature X-ray diffraction patterns recorded in a helium flow during (a) the ion exchange reaction between 1 mole of $\text{P2-Na}_{0.7}[\text{Li}_{0.14}\text{Ni}_{0.14}\text{Mn}_{0.72}]\text{O}_2$ and 1.5 mole of LiCl .

Simulation of the X-ray diffraction pattern of the $\text{O2-Li}_{0.84}\text{Ni}_{0.14}\text{Mn}_{0.72}\text{O}_2$ phase

In order to explain the origin of the anisotropic broadening of the diffraction peaks of the phase $\text{O2-Li}_{0.84}\text{Ni}_{0.14}\text{Mn}_{0.72}\text{O}_2$, we considered the presence of stacking faults along the c axis of this layered structure. These stacking faults are created when the $(\text{Li},\text{Ni},\text{Mn})\text{O}_2$ layers glide during the ion exchange reaction. We considered the different gliding directions of the $(\text{Li},\text{Ni},\text{Mn})\text{O}_2$ layers with respect to each other that occurred during the ion-exchange in order to transform prismatic sites occupied by sodium ions into octahedral sites occupied by lithium ions. In a first step, for the sake of simplification, we considered homogeneous $(\text{Li},\text{Ni},\text{Mn})\text{O}_2$ layers with no cation ordering

between the large and small cations. The octahedral sites of the (Li,Ni,Mn)O₂ layers are therefore occupied at 14% by lithium, 14% by nickel and 72% by manganese.

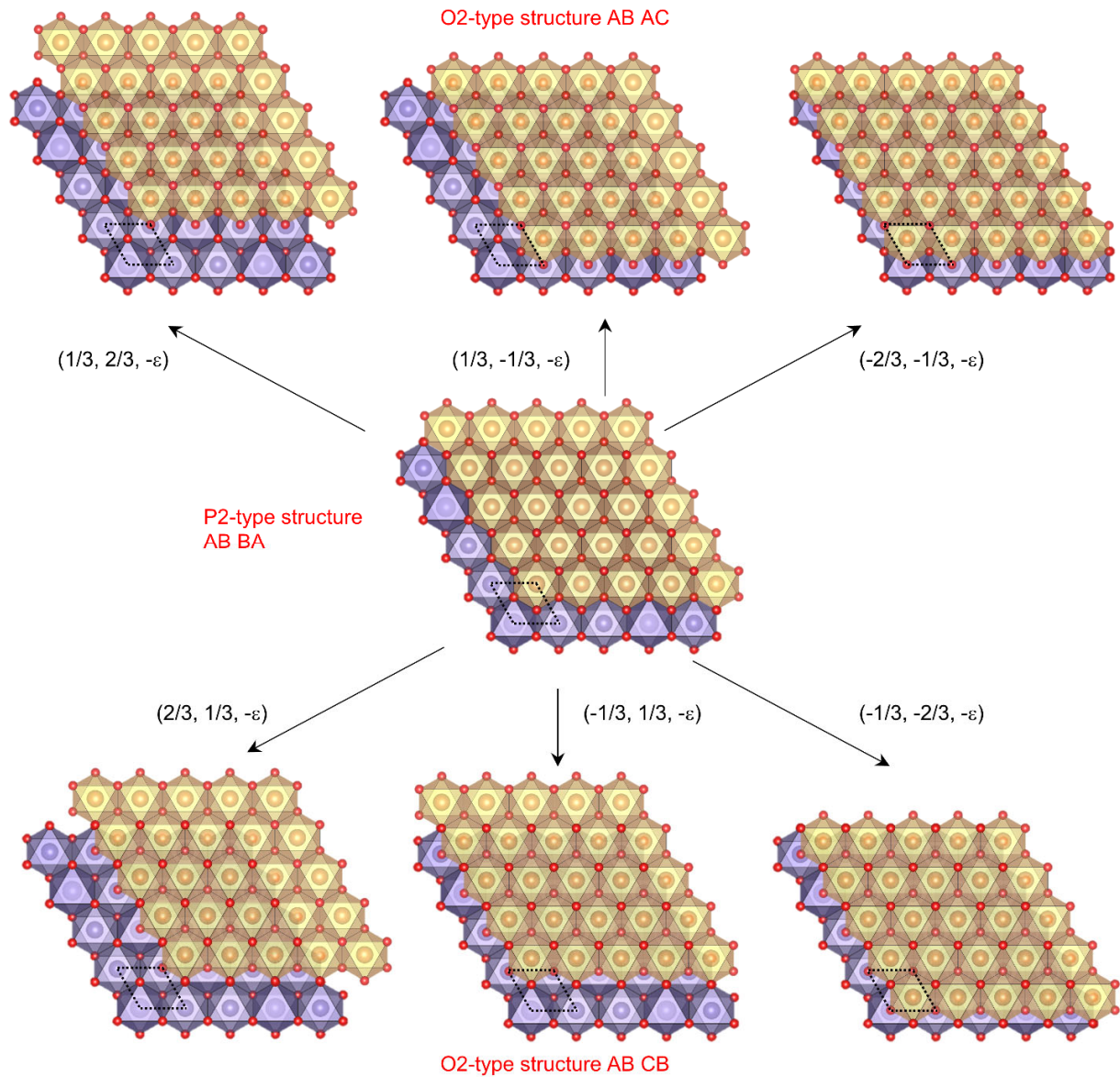


Figure S2. Projection of two (Li,Ni,Mn)O₂ layers made of (Li,Ni,Mn)O₆ octahedra (purple and yellow octahedra) in a P2-type structure (center) and after the gliding of one of them along the 6 different possible vectors. The limits of the unit cell are shown with the dashed black line. The lithium ions of the interlayer space are not represented here.

In the sodium P2-phase, the oxygen packing is (AB)(BA)(AB)(BA)... The two letters in brackets indicate the positions of the two successive layers of oxygen atoms forming the (Li,Ni,Mn)O₂ layers. We are now interested in the relative gliding of a layer (BA) with respect to the layer (AB) occurring during the ion-exchange. The layer (BA) can glide along 6 directions in the (a,b) plane which are shown in Figure S2. A first set of three directions leads to the formation of a O2-type structure where the new oxygen packing is (AB)(CB). The second set of three directions also leads to the formation of a O2-type structure but in which the oxygen layers are now (AB)(AC). For a perfect O2-type structure (AB)(CB)(AB)(CB)... to grow, exactly one layer (Li,Ni,Mn)O₂ out of two must glide according to the vectors $(1/3, 2/3, -\varepsilon)$ or $(1/3, -1/3, -\varepsilon)$ or $(-2/3, -1/3, -\varepsilon)$, where ε represents the small translation along the c-axis which allows modeling the shorter interlayer distance in the O2-type structure than that in the P2-type structure. Similarly, for a perfect O2-type structure (AB)(AC)(AB)(AC)... to grow, exactly one layer (Li,Ni,Mn)O₂ out of two must glide according to the vectors $(2/3, 1/3, -\varepsilon)$ or $(-1/3, 1/3, -\varepsilon)$ or $(-1/3, -2/3, -\varepsilon)$. In reality, each layer can glide randomly along the 6 different directions and the structure of the O2-phase is much more complicated than a perfect stacking layers according to the sequence (AB)(CB)(AB)(CB)... or (AB)(AC)(AB)(AC)....

To describe the structure of the phase, it appeared that 12 different (Li,Ni,Mn)O₂ layers were necessary in order to describe all the possibilities of stacking. The possible stacking sequences of the layers are represented in two tree-structures shown in Figure S3. The position of the cations (lithium ions in the interlayer space and lithium, nickel and manganese ions in the (Li,Ni,Mn)O₂ layers) has been indicated by lowercase letters. It then appears clearly that the layer **a**(AB) is different from the layer **c**(AB) (where the lowercase letters **a** and **c** represent the position in the

plane (a,b) of the lithium ions of the interlayer space) as the lithium occupies a different position in the interlayer space preceding the oxygen layer A.

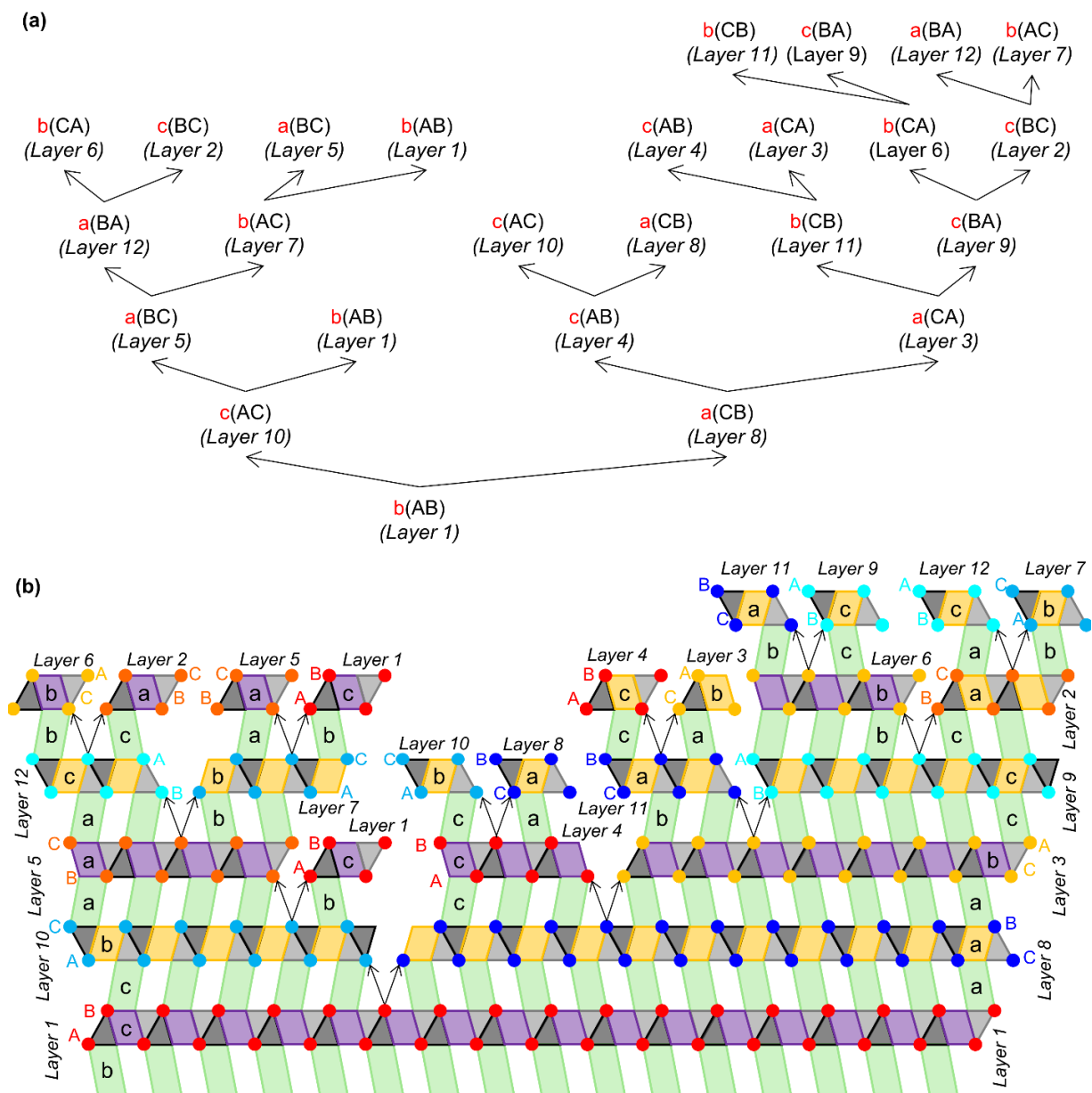


Figure S3. Tree-structures representing the different possible stacking sequences present in the $\text{O}_2\text{-Li}_{0.84}\text{Ni}_{0.14}\text{Mn}_{0.72}\text{O}_2$ phase. In (b), the tree-structure is presented as a projection of the structure of the different layers along the vector (1,-1,0): colored spheres (yellow, orange, red and different

shades of blue) represent oxygen atoms. Purple and yellow parallelograms represent (Li,Ni,Mn)O₆ octahedra and green parallelograms represent LiO₆ octahedra in the interlayer space. For simplicity, all octahedral sites possibly occupied by lithium ions have been represented by green parallelograms. However, only 70% of them are occupied. Capital letters (A, B and C) represent the three different positions that oxygen can occupy, whereas lowercase letters (a, b and c) represent the three different positions that cations can occupy.

To simulate the diffraction diagram, we therefore used the *Faults* program by considering the 12 layers shown in Figure S3. The number of layers can even be reduced to 4 layers, some layers being equivalent by translation. The atomic parameters of the 4 different layers used in the *Faults* simulation are described in the tables from S2 to S5.

Table S2. Atomic parameters of the layer 1, layer 2 and layer 3 used in the *Faults* simulation. The cell parameters of these layers are $a = b = 2.837 \text{ \AA}$, $c = 4.824 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The atomic positions for Li, Ni and Mn are set by symmetry. “z” atomic position for oxygen and atomic displacement parameters B_{iso} are set to reasonable values.

Atom	x	y	z	B_{iso}	Occupancy
O1	2/3	1/3	0.20	0.8	1
Li1	0	0	0	0.5	0.14
Ni	0	0	0	0.5	0.14
Mn	0	0	0	0.5	0.72
O2	1/3	2/3	-0.20	0.8	1
Li2	2/3	1/3	-1/2	1.0	0.70

Table S3. Atomic parameters of the layer 4, layer 5 and layer 6 used in the *Faults* simulation. The cell parameters of these layers are $a = b = 2.837 \text{ \AA}$, $c = 4.824 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The atomic positions for Li, Ni and Mn are set by symmetry. “z” atomic position for oxygen and atomic displacement parameters B_{iso} are set to reasonable values.

Atom	x	y	z	B_{iso}	Occupancy
O1	2/3	1/3	0.20	0.8	1
Li1	0	0	0	0.5	0.14
Ni	0	0	0	0.5	0.14
Mn	0	0	0	0.5	0.72
O2	1/3	2/3	-0.20	0.8	1
Li2	0	0	-1/2	1.0	0.70

Table S4. Atomic parameters of the layer 7, layer 8 and layer 9 used in the *Faults* simulation. The cell parameters of these layers are $a = b = 2.837 \text{ \AA}$, $c = 4.824 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The atomic positions for Li, Ni and Mn are set by symmetry. “z” atomic position for oxygen and atomic displacement parameters B_{iso} are set to reasonable values.

Atom	x	y	z	B_{iso}	Occupancy
O1	0	0	0.20	0.8	1
Li1	2/3	1/3	0	0.5	0.14
Ni	2/3	1/3	0	0.5	0.14
Mn	2/3	1/3	0	0.5	0.72
O2	1/3	2/3	-0.20	0.8	1
Li2	2/3	1/3	-1/2	1.0	0.70

Table S5. Atomic parameters of the layer 10, layer 11 and layer 12 used in the *Faults* simulation. The cell parameters of these layers are $a = b = 2.837 \text{ \AA}$, $c = 4.824 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The atomic positions for Li, Ni and Mn are set by symmetry. “z” atomic position for oxygen and atomic displacement parameters B_{iso} are set to reasonable values.

Atom	x	y	z	B_{iso}	Occupancy
O1	0	0	0.20	0.8	1
Li1	2/3	1/3	0	0.5	0.14
Ni	2/3	1/3	0	0.5	0.14
Mn	2/3	1/3	0	0.5	0.72
O2	1/3	2/3	-0.20	0.8	1
Li2	0	0	-1/2	1.0	0.70

To build the structure of the $\text{O2-Li}_{0.84}\text{Ni}_{0.14}\text{Mn}_{0.72}\text{O}_2$ phase, successive layers are stacked on top of each other along the c -axis with some probability. For example, only layers **a**(CB) (layer 8) and **c**(AC) (layer 10) can stack on the layer **b**(AB) (layer 1). The probability that the layer **a**(CB) (layer 8) stacks on the layer **b**(AB) (layer 1), $\alpha_{1 \rightarrow 8}$, is therefore related to the probability that the layer **c**(AC) (layer 10) stacks on the layer **b**(AB) (layer 1), $\alpha_{1 \rightarrow 10}$, by the relation:

$$\alpha_{1 \rightarrow 8} + \alpha_{1 \rightarrow 10} = 1$$

Some layers being equivalent to each other, the probabilities can be simplified:

- $\alpha_{1 \rightarrow 10} = \alpha_{2 \rightarrow 12} = \alpha_{3 \rightarrow 11} = \alpha_{10 \rightarrow 1} = \alpha_{11 \rightarrow 3} = \alpha_{12 \rightarrow 2}$
- $\alpha_{1 \rightarrow 8} = \alpha_{2 \rightarrow 7} = \alpha_{3 \rightarrow 9} = \alpha_{10 \rightarrow 5} = \alpha_{11 \rightarrow 4} = \alpha_{12 \rightarrow 6} = 1 - \alpha_{1 \rightarrow 10}$
- $\alpha_{4 \rightarrow 8} = \alpha_{5 \rightarrow 7} = \alpha_{6 \rightarrow 9} = \alpha_{10 \rightarrow 5} = \alpha_{8 \rightarrow 4} = \alpha_{9 \rightarrow 6}$
- $\alpha_{4 \rightarrow 10} = \alpha_{5 \rightarrow 12} = \alpha_{6 \rightarrow 11} = \alpha_{7 \rightarrow 1} = \alpha_{8 \rightarrow 3} = \alpha_{9 \rightarrow 2} = 1 - \alpha_{4 \rightarrow 8}$

and the values of only two probabilities, $\alpha_{1\rightarrow 10}$ and $\alpha_{4\rightarrow 8}$, were changed during the *Faults* simulations. Many sets of values from $\alpha_{1\rightarrow 10}$ and $\alpha_{4\rightarrow 8}$ were tested in order to best simulate the X-ray diffraction pattern of the O2 phase. The best simulation was obtained for the combination $\alpha_{1\rightarrow 10} = 0.6$ and $\alpha_{4\rightarrow 8} = 0.65$.

In a second step, the cation ordering between large cations (Li^+ and Ni^{2+}) and small cations (Mn^{4+}) in the $(\text{Li,Ni,Mn})\text{O}_2$ layers was considered. In Figure S4, it clearly appears that the three translations which enabled the stacking of the **c**(AC) layer on top of the **b**(Ab) layer are no longer equivalent (top of Figure S4), just like the three translations which made it possible to stack the **a**(CB) layer on the **b**(AB) layer are no longer either (bottom of Figure S4). Therefore, a new unit cell and new layers have been defined in the input file of the *Faults* program. The unit cell has been enlarged by a factor of $\sqrt{3}$ along *a* and *b*. This unit cell contains three positions in the $(\text{Li,Ni,Mn})\text{O}_2$ layers which are occupied by the three cations, two positions are occupied at 100% by manganese and the last one is occupied by lithium and nickel at 42% and by manganese at 16% in order to respect the stoichiometry of the O2 phase. The layer **b**(AB) used in the 12-layer simulation then gives rise to three layers, **b**(AB)₁, **b**(AB)₂ and **b**(AB)₃, which differ from each other, not by the position of the oxygen atoms, but by the cation ordering in the $(\text{Li,Ni,Mn})\text{O}_2$ layers. The atomic parameters of these 3 different layers used in the *Faults* simulation are described in the tables from S6 to S9.

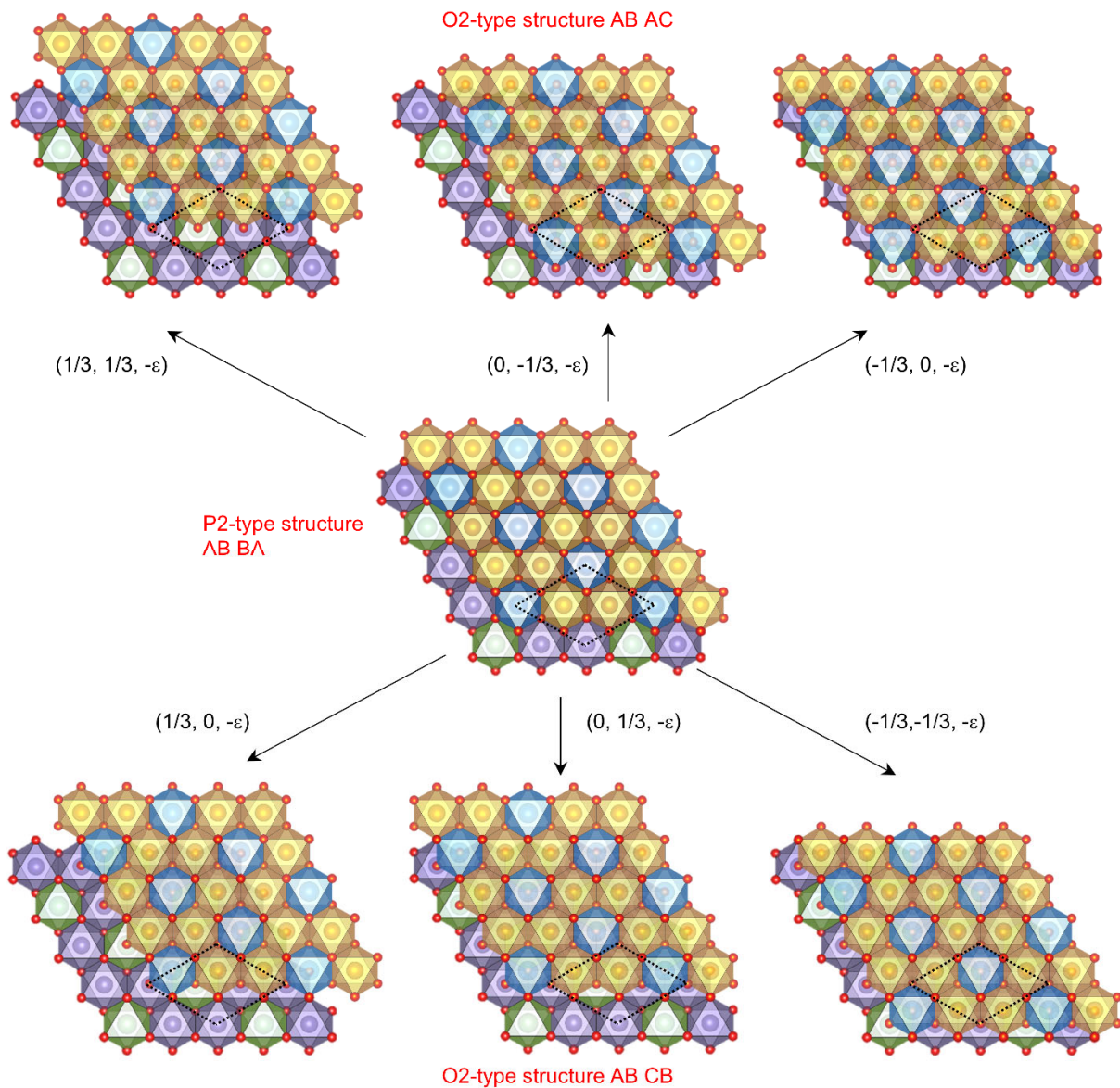


Figure S4. Projection of two (Li,Ni,Mn)O₂ layers made of (Li,Ni,Mn)O₆ octahedra (green and blue octahedra) and MnO₆ octahedra (purple and yellow octahedra) in a P2-type structure (center) and after the gliding of one of them along the 6 different possible vectors. The limits of the unit cell are shown with the dashed black line. The lithium ions of the interlayer space are not represented here.

Table S6. Atomic parameters of the $b(\text{AB})_1$ used in the *Faults* simulation. The cell parameters of these layers are $a = b = 4.914 \text{ \AA}$, $c = 4.824 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The atomic positions for Li, Ni and Mn are set by symmetry. “z” atomic position for oxygen and atomic displacement parameters B_{iso} are set to reasonable values.

Atom	x	y	z	B_{iso}	Occupancy
O1	1/3	0	0.20	0.8	1
O2	0	1/3	0.20	0.8	1
O3	2/3	2/3	0.20	0.8	1
Li1	0	0	0	0.5	0.42
Ni1	0	0	0	0.5	0.42
Mn1	0	0	0	0.5	0.16
Mn2	2/3	1/3	0	0.5	1
Mn3	1/3	2/3	0	0.5	1
O4	2/3	0	-0.20	0.8	1
O5	0	2/3	-0.20	0.8	1
O6	1/3	1/3	-0.20	0.8	1
Li2	1/3	0	-1/2	1.0	0.70
Li3	0	1/3	-1/2	1.0	0.70
Li4	2/3	2/3	-1/2	1.0	0.70

Table S7. Atomic parameters of the $b(\text{AB})_2$ used in the *Faults* simulation. The cell parameters of these layers are $a = b = 4.914 \text{ \AA}$, $c = 4.824 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The atomic positions for Li, Ni and Mn are set by symmetry. “z” atomic position for oxygen and atomic displacement parameters B_{iso} are set to reasonable values.

Atom	x	y	z	Biso	Occupancy
O1	1/3	0	0.20	0.8	1
O2	0	1/3	0.20	0.8	1
O3	2/3	2/3	0.20	0.8	1
Li1	2/3	1/3	0	0.5	0.42
Ni1	2/3	1/3	0	0.5	0.42
Mn1	2/3	1/3	0	0.5	0.16
Mn2	0	0	0	0.5	1
Mn3	1/3	2/3	0	0.5	1
O4	2/3	0	-0.20	0.8	1
O5	0	2/3	-0.20	0.8	1
O6	1/3	1/3	-0.20	0.8	1
Li2	1/3	0	-1/2	1.0	0.70
Li3	0	1/3	-1/2	1.0	0.70
Li4	2/3	2/3	-1/2	1.0	0.70

Table S8. Atomic parameters of the $b(AB)_2$ used in the *Faults* simulation. The cell parameters of these layers are $a = b = 4.914 \text{ \AA}$, $c = 4.824 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The atomic positions for Li, Ni and Mn are set by symmetry. “z” atomic position for oxygen and atomic displacement parameters B_{iso} are set to reasonable values.

Atom	x	y	z	Biso	Occupancy
O1	1/3	0	0.20	0.8	1
O2	0	1/3	0.20	0.8	1
O3	2/3	2/3	0.20	0.8	1
Li1	1/3	2/3	0	0.5	0.42
Ni1	1/3	2/3	0	0.5	0.42
Mn1	1/3	2/3	0	0.5	0.16
Mn2	2/3	1/3	0	0.5	1
Mn3	0	0	0	0.5	1
O4	2/3	0	-0.20	0.8	1
O5	0	2/3	-0.20	0.8	1
O6	1/3	1/3	-0.20	0.8	1
Li2	1/3	0	-1/2	1.0	0.70
Li3	0	1/3	-1/2	1.0	0.70
Li4	2/3	2/3	-1/2	1.0	0.70

Finally, each of the 12 layers used in the 12-layer simulation generates 3 layers with a different arrangement of Li^+ , Ni^{2+} and Mn^{4+} ions and the new simulation was then based on the stacking of 36 distinct layers. As in the 12-layer model, only a few transitions from one layer to another are possible in the 36-layer model. For example, only $a(\text{CB})$ and $c(\text{AC})$ layers can stack on a $b(\text{AB})$ layer in the 12-layer model. It is then the same in the model with 36 layers, only the layers $a(\text{CB})_1$,

$a(\text{CB})_2$, $a(\text{CB})_3$ and $c(\text{AC})_1$, $c(\text{AC})_2$, $c(\text{AC})_3$ can stack on the layer $b(\text{AB})_1$. These same 6 layers can also be stacked on $b(\text{AB})_2$ or $b(\text{AB})_3$.

The results of the 12-layer model allowed us to conclude on the stacking of the oxygen layers, we therefore considered that the sum of the probabilities of stacking from the $b(\text{AB})_1$ layer to $a(\text{CB})_1$, $a(\text{CB})_2$, and $a(\text{CB})_3$ is equal to the transition probability from the $b(\text{AB})$ layer to $a(\text{CB})$ in the 12-layer model. We still had to determine if the probability of transition from the $b(\text{AB})_1$ layer to $a(\text{CB})_1$ was different from that of $b(\text{AB})_1$ layer to $a(\text{CB})_2$ or from that $b(\text{AB})_1$ layer to $a(\text{CB})_3$. None of the three transitions seemed more favorable to us than the other two. The probabilities of the transitions from the $b(\text{AB})_1$ layer to $a(\text{CB})_1$, from the $b(\text{AB})_1$ layer to $a(\text{CB})_2$ and from the $b(\text{AB})_1$ layer to $a(\text{CB})_3$ were therefore set at $1/3$ each. The reasoning presented above was applied to all the layers generated by the enlargement of the unit cell used in the *Faults* simulation and the diagram simulated thanks to this 36-layer model is presented in Figure 5 of the main manuscript.

Electrochemical tests

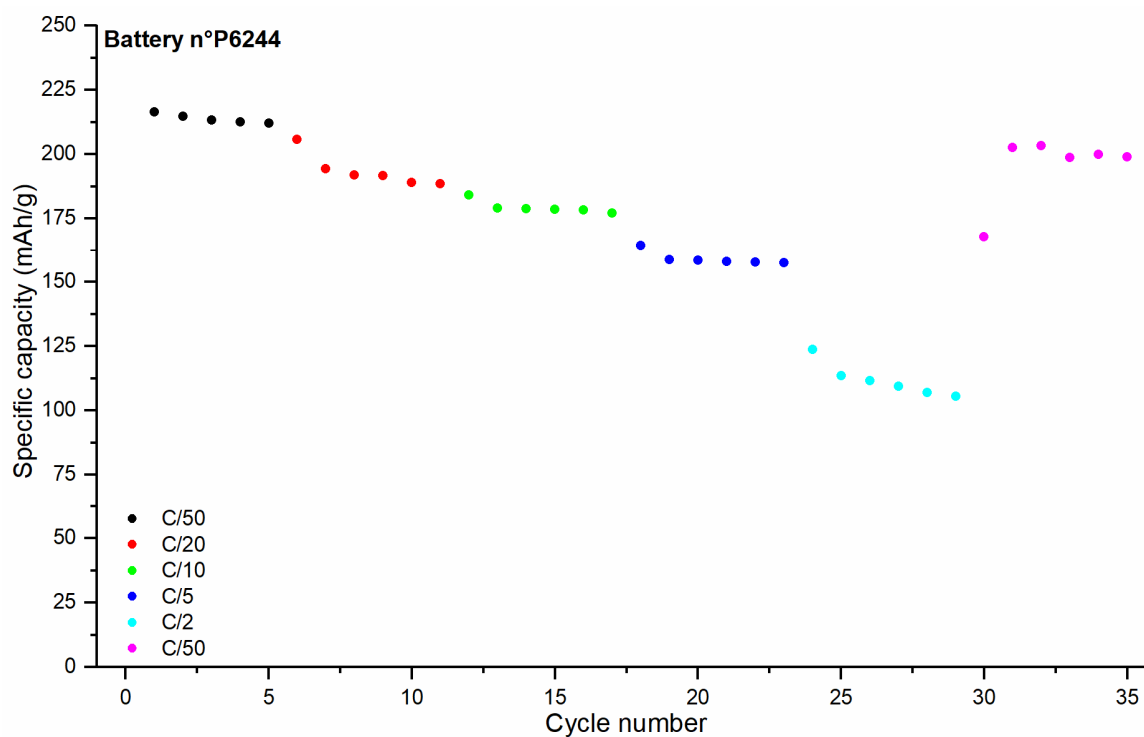


Figure S5. C-rate test realized with a lithium battery cell using the $\text{O2-Li}_{0.84}\text{Ni}_{0.14}\text{Mn}_{0.72}\text{O}_2$ phase at the positive electrode. Discharge specific capacities are reported.

Operando X-ray absorption spectroscopy

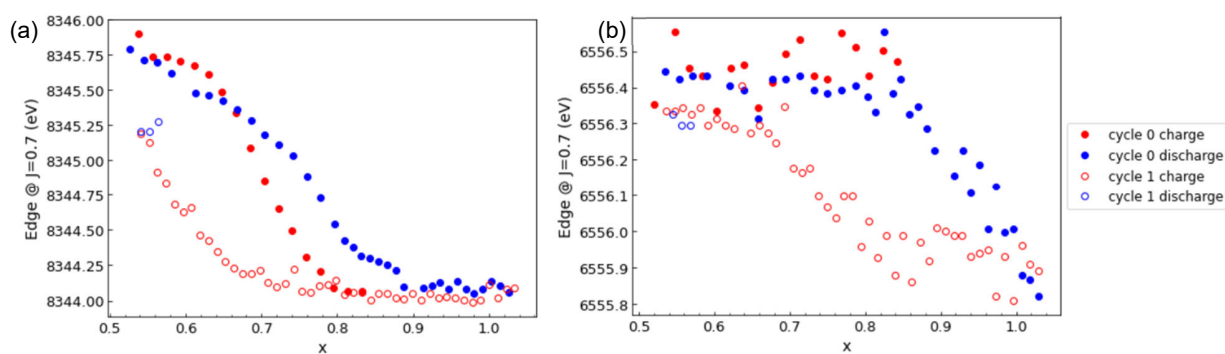


Figure S6. Variation in the energy position of (a) Ni K-edge and (b) Mn K-edge XAS spectra recorded during the operando X-ray absorption spectroscopy experiment at intensity 0.7 as a function of Li content over the two cycles