On the reversibility of transition metal migration and its impact on the performance in layered oxides for sodium-ion batteries: NaFeO₂ as a case study.

Supplementary information

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Table S1. Structural parameters and reliability factors from Rietveld refinements of pristine NaFeO₂ powder (Fig. 1a).

Space group: $R\overline{3}m$ a = b = 3.02262(6) Å c = 16.0916(5) Å $B_{cm} = 1.7 \text{ Å}^2$	$\chi^2 = 1.83$ $R_B = 5.31$ $R_f = 5.12$
$B_{ov} = 1.7 \text{ Å}^2$	$n_f = 0.12$

Atom	Wyckoff		Coordinates	Occupancy	р (Å2)		
Atom	wyckon	х	У	z	Occupancy	D (A)	
Na	3a	0	0	0	0.98(4)	1.6	
Fe	3b	0	0	0.5	1	0.9	
0	6c	0	0	0.234(5)	1	1.2	

Table S2. Synthesis method and size of NaFeO₂ in the literature.

Reference	Na precursor	Fe precursor	Heating Temp.	dwell time	Average particle size
Kikkawa et al. Mat. Res. Bull. 20:373, 1895	Na ₂ O ₂	Fe ₂ O ₃	500°C	48h	-
Takeda et al. Mat. Res.Bull. 29(6):659, 1994	Na ₂ O ₂	Fe ₃ O ₄	600-700°C	12h	-
Blesa et al. Solid State Ionics 126:81, 1999	Na ₂ O ₂	Fe ₂ O ₃	500°C		-
McQueen et al. Phys. Rev. B 76:024420, 2007	Na ₂ O ₂	Fe ₂ O ₃	500°C + 700°C	2h + 48h	-
Yabuuchi et al. Electrochemistry 80(10):716, 2012	Na ₂ O ₂	Fe ₃ O ₄	650°C	12h	-
Terada et al. Phys. Rev. B 89:184421 (2014)	Na ₂ CO ₃	Fe ₃ O ₄	-	24h	-
Lee et al. Chem. Mater. 27:6755, 2015	Na ₂ O ₂	Fe ₃ O ₄	650°C	12h	-
Kataska at al Electrophim Asta 182,871 2015	Na ₂ O ₂	Fe ₃ O ₄	630°C	10h	2-10 µm
	Na ₂ O ₂	nano-Fe ₃ O ₄	630°C	10h	1-2 µm
Hwang et al. Mater. Lett. 206:100,2016	Na ₂ O ₂	Fe ₃ O ₄	650°C	12h	0.9-5 µm
This work	Na ₂ CO ₃	Fe ₃ O ₄	650°C	15h	250 nm

Table S3. Cell parameters of Le Bail refinements shown in Fig. S9.

Refinement	Phase	Space	Cell parameters					
		group	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)
(a) O3 + P3	03	R-3m	2.95(1)	2.95(1)	16.32(4)	90	90	120
	Р3	R-3m	2.96(4)	2.96(4)	16.75(2)	90	90	120
(b) O3 + P'3	03	R-3m	2.95(1)	2.95(1)	16.33(5)	90	90	120
	P'3	C 2/m	5.26(2)	2.97(1)	5.89(2)	90	108.7(1)	90

Table S4. Angle depending factors that affects experimental intensity by which the experimental XRD patterns have been corrected before calculating Fe migration. Attenuation coefficient values have been estimated using NIST online tool (<u>https://www.nist.gov/pml/x-ray-mass-attenuation-coefficients</u>) and Debye Waller factors have been calculated from Rietveld refinements of pristine powder samples (see Fig. 1a and Table S1 for example measured with Cu tube source).

Factor	Formula	
Be window attenuation	$\exp\left[-\mu_{Be}\frac{2d_{Be}}{\sin\theta}\right]$	μ : attenuation coefficient $\mu_{Be}(Co) = 253.45m^{-1}$ $\mu_{Be}(Cu) = 158.92m^{-1}$ d:Be thickness $d_{Be} = 250 \times 10^{-6}m$
Al foil attenuation	$\exp\left[-\mu_{Al}\frac{2d_{Al}}{\sin\theta}\right]$	μ : attenuation coefficient $\begin{array}{l} \mu_{Al}(Co)=20196m^{-1}\\ \mu_{Al}(Cu)=13600m^{-1}\\ d: \text{Al thickness}\\ d_{Al}=6\times10^{-6}m \end{array}$
Polarization	$1 + \cos^2 2\theta$	
Irradiated volume change	$\frac{1}{\sin 2\theta}$	
Powder ring distribution factor	$\frac{1}{\sin \theta}$	
Thermal factor	$\left(\exp\left[-\frac{B\sin^2\theta}{\lambda}\right]\right)^2$	B: Debye Waller temperature factor $B(Co) = 1.8 \text{ Å}^2$ $B(Cu) = 1.7 \text{ Å}^2$ λ : wavelength $\lambda_{Co} = 1.78897\text{ Å}$ $\lambda_{Cu} = 1.54053\text{ Å}$



Figure S1. Discharge capacity vs. cycle number (markers) and coulombic efficiency (line) of NaFeO₂ at (a) C/10 with V = 3.5-2.5 V voltage range and (b) 1C with different voltage windows, labeled in the figure.



Figure S2. First cycle (voltage vs. Na content) for cells charged up to 3.5 V, 4.0 V and 4.5 V.



Figure S3. Example of the fitting used to calculate de values of R_1 , R_2 and R_3 in Fig. 3. Contributions from each part of the circuit are shown in different colors. Equivalent circuit is shown in the inset.



Figure S4. Voltage (blue line) and current (red line) of a cell discharged and hold at 1.5V for 10 h and left at OCV for 10 h.



Figure S5. PITT measurement of NaFeO₂ at different voltage windows. Voltage, current and sodium content are presented as a function of time. Black circles correspond to the point where eq. 2 was applied.



Figure S6. Diffusion coefficient of NaFeO₂ calculated from the current relaxations during the PITT titration steps (triangles) and from EIS measurements (yellow stars) during charge in the region where the charge transfer resistance was low enough to observe the mass diffusion regime.



Figure S7. 2D data plots operando HRXRD data recorded in Australian synchrotron together with voltage profile. Measurements were carried out in a modified coin cell, using Kapton covered holes, in transmission mode. No shift of reflected peaks is observed.



Figure S8. Le Bail refinements of one every 10 patterns *cell* 1 (Fig. 5) using $R\overline{3}m$ space group, and reflections have been indexed with *hkl* label. Shaded areas correspond to contributions for in-situ cell components, which have been considered as constant background for the refinements.



Figure S9. 10 hours ex situ XRD pattern (red circles) of an electrode charged to 3.6V fitted with different space groups. Le Bail refinements (black line) have been done with (a) O3 and P3 (R-3m) space groups and (b) O3 and P'3 (R-3m and C 2/m) space groups, including Al foil and Be window from in situ cell. Bragg reflection positions are shown with marks in black (O3), red (P3 and P'3 in (a) and (b) respectively), green (Al foil) and blue (Be window). Intensity ratio between reflections (003) and (104) in R-3m space groups, shown in the insets, indicates that the secondary phase appearing is most likely a P3 phase. Moreover, reflections at 46.9° and 51.5°, shown in arrows in Fig. (b) indicate that appearing P3 phase has a monoclinic distortion. Structural parameters can be found in Table S3.



Figure S10. Structural models (top panel) and XRD simulations (bottom panel), using the Fullprof software suite,² of O3, P3 (R-3m space group) and P'3 (C 2/m space group) phases using cell parameters from Table S3, Na occupation x = 0.5 and no iron migration z = 0. Discontinuous lines: uncorrected results from the simulation. Plain lines: simulation results after correction by the factors presented in table S4 in order to be compared to experimental data.



Figure S11. XRD patterns of charged NaFeO₂ to 4V. (a) Simulated pattern for Na_{0.25}FeO₂, without Fe migration; (b) simulated pattern for (Na_{0.2}Fe_{tet 0.3}) Fe_{0.7}O₂ with 30% of migrated Fe to tetrahedral sites as estimated in Fig. 6; (c) *operando* XRD pattern at 4.0V from cell 1; (d) *in-situ* HRXDR pattern of cell 3 charged in CCCV mode to 4V followed by a long OCV relaxation. Cell components are shown with * for sodium, # for aluminium foil and + for beryllium.

Simulation method:

The amplitude S_{hkl} of the diffracted X-ray beam is the sum of the amplitudes scattered from single atoms:¹

$$S_{hkl} = \sum_{i} f_{i} \exp(-2\pi i \, \boldsymbol{h} \cdot \boldsymbol{r}_{i}) \tag{S1}$$

Where *h*, *k* and *l* stand for Miller indices of the *hkl* reflection, f_j the atomic form factor, **h** the scattering vector and r_j atomic coordinates of the jth atom.

Considering the atomic positions in the NaFeO₂ structure, where $r_1 = (0,0,0)$ for Na in the interlayer and $r_2 = (0,0,0.5)$ for Fe in the FeO₂ layers, and considering the amplitude of the (003) reflection, atoms in the Na site or tetrahedral site ($r_{tet} = (0,0,5/8)$) of the interlayer will contribute positively while atoms in the Fe site in the FeO₂ layers will contribute negatively. For a given composition with *x* atoms of Na and *z* TM atoms migrated into the Na sites or tetrahedral sites of the interlayer, corresponding to the formula (Na_xFe_z)Fe_{1-z}O₂, with x + z ≤ 1, the amplitude of the (003) reflection can be described as follows

$$S_{003} = x f_{Na} + z f_{TM} - (1 - z) f_{TM} + \sum f_0 \exp(-2\pi i \, \boldsymbol{h} \cdot \boldsymbol{r}_j) = x f_{Na} + 2z f_{TM} - f_{TM} + \sum f_0 \exp(-2\pi i \, \boldsymbol{h} \cdot \boldsymbol{r}_j)$$
(S2)

Taking into account that the O atoms contribution does not depend on x nor z, it can be considered constant (K). The intensity, which is proportional to the square of the scattered amplitude, can be simplified as:

$$I \propto (S_{hkl})^2 \propto (x f_{Na} + 2z f_{TM} - f_{TM} + K)^2$$
 (S3)

From this equation it can be concluded that intensity can be described as a two-variable function (Na content x and migrated Fe content z), both of them as a 2^{nd} order polynomial.



Figure S12. Intensity of the reflection (003) of the simulated patterns, as a function of the content z of migrated Fe for different Na contents x (a, d), as function of the Na content x for different amounts z of migrated Fe (b, e), and as function of the interlayer distance d for z = 0 and two different sodium contents x. In all cases the intensity has been normalized by I_0 , the intensity simulated with x = 1, z = 0 and d = 5.37 Å, which corresponds to the pristine NaFeO₂ phase. The simulation has been run considering the migration of Fe to the Na sites (a-c) and tetrahedral sites (d-f).

The dots presented in figures S12a-c present the result of the simulations of the evolution of the intensity of the (003) reflexion of the O3 structure of $(Na_xFe_z)Fe_{1-z}O_2$ performed using the Fullprof software suite,² for different values of x, z,

and interlayer distance d. The curves presented in Figure S12a,b and S12d,e are the best fit of equation S3 to the result of the simulations (dots). Finally, the influence of the interlayer distance d on the intensity, represented in Figure S12c and f, has been adequately fitted as a linear dependency. As a result of this parametrization of the simulations, the following dependency of the intensity of the (003) reflection on x, y and d has been established for Fe migration into tetrahedral sites (S4) and Na sites (S5):

$$\frac{I(x,z,d)}{I_0(x_0,z_0,d_0)} = ((2.517 - 1.867x + 0.349x^2) + z(-10.402 + 3.846x - 0.0134x^2) + z^2(10.781 + 0.0213x - 0.0306x^2))(1 - 0.260(d - d_0))$$
(S4)

$$\frac{I(x,z,d)}{I_0(x_0,z_0,d_0)} = ((2.517 - 1.867x + 0.349x^2) + z(-8.225 + 2.894x + 0.0129x^2) + z^2(6.722 + 0.019x - 0.032x^2))(1 - 0.260(d - d_0))$$
(S5)

where $x_0 = 1, z_0 = 0$ and d = 5.37 Å are the parameters corresponding to the pristine NaFeO₂ phase.

The dashed lines of Figures 6c and 8b, which correspond to the normalized intensity variation of reflection (003) without Fe migration, have been obtained using equation (S4) with z=0 and deducing the values of x and d from the analysis of the experimental data. The amount z of migrated Fe has been obtained by solving equation (S4) or (S5) for each experimental data point, supposing it exclusively migrates into tetrahedral sites or Na sites, respectively, with the values of I/I_0 , x and d determined from the analysis of the experimental data.

To calculate I/I_0 from the experimental XRD patterns of the operando measurements of Figures 5 and 7, the intensity in the 20 angle ranges 15°-18° and 18°-21° respectively was integrated after constant background subtraction and correction by the angle dependent intensity affecting factors gathered in table S4. The sodium content x was deduced from the chronoamperometric curves recorded during the operando measurements of Figures 5 and 7, and the interlayer distance d, presented in Figure 6c, was deduced from the position of the (003) reflection deduced from the LeBail refinement of Figure S8. Note that the angular range of intensity integration has been chosen so that the contribution from both O3 and P'3 phases is summed-up. This allows compensating the intensity loss of the (003) O3 reflection due to the onset of the O3 to P'3 phase transition for compositions in the range 0.7 < x < 0.6, and hence avoiding any bias that it may have on the estimated amount of migrated Fe.



Figure S13. Simulation of diffractions (006), (101) and (012) for Na_{0.6}FeO₂ and 40% of iron migrated to Na or octahedral sites (oct.) and tetrahedral sites (tetr.) in Na planes in different proportions.



Figure S14. Comparison of calculated migrated iron considering it exclusively migrated to Na sites (open green circles) or tetrahedral sites (plain green circles) for *cell 1* (a,b) and *cell 2* (c) versus time.



Figure S15. X-ray scattering intensity measured *in-situ* at charged state (CCCV charge to 4 V) in the same *cell 3* with different equipment and acquisition times, shown at the vicinity of the (003) reflection versus scattering vector Q after background subtraction and shifted by a constant value for more clarity. Red line: 2h measurements using a lab-scale diffractometer ($\lambda = 0.1789$ Å, CICe). Green line: sum of 33 successive measurements (2h each for a total of 66h) using the same lab-scale diffractometer ($\lambda = 0.1789$ Å, CICe). Blue line: measurement performed at ALBA synchrotron recorded for 30 seconds ($\lambda = 0.8257$ Å), two days after the previous lab scale measurement.



Figure S16. *Ex-situ* XRD measurement of an electrode charged to 4.5 V, with contributions from the cell shaded in grey, (a) and (b) for selected Q range and (c) in the whole measured range. In the inset the low angle area is shown, were an additional peak is observed near $2\theta = 24^{\circ}$ suggesting the "X" phase that appear at the end of charge is not a layered phase.

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