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Rate-dependent structure-electrochemistry relationships and origins of capacity fading in P2-type $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ †

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Sodium transition metal oxides with layered structures have generated significant research interest as promising cathode materials for use in ambient temperature sodium-ion batteries. In this study, the structure and magnetic properties of P2- $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ are investigated, in tandem with *operando* diffraction studies to resolve the structural changes taking place in the material when subject to variable current cycling in the range 1.5–4.2 V vs. Na^+/Na^0 . Complementary diffraction studies are used to provide insight into the mechanism of sodium de-intercalation in P2- $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ at low rates, as well as high current densities up to 1 C, enabled by the excellent time resolution allowed by high intensity synchrotron radiation. The structural evolution is found to differ markedly depending on the applied current density which illustrates the need to perform such structural studies under various applied current rates to better understand processes taking place in the electrode. The results obtained shed new light on the reaction mechanism of P2-type layered oxides and provide insight into some of the causes for their capacity fading.

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1. Introduction

The successful commercialisation of various positive electrode materials with layered structures for use in lithium-ion batteries (LIBs) has proven that intercalation materials exhibiting

these structures can offer high energy density, good capacities and long cycle life.^{1–5} A good understanding of the reaction pathways and structural evolution during cycling has proven key to overcoming issues with cycle life due to structural degradation after repeated (de-)intercalation reactions and therefore to avoid unfavourable reactions taking place.^{6–8} Sodium-ion batteries (SIBs) present a more economical and sustainable alternative to LIBs and there has similarly been significant interest in developing sodium transition metal oxide materials with layered structures for use in high-performance SIBs.^{9–11} Although SIBs will struggle to match the energy densities offered by LIBs, it is expected they would be favourable for use in larger-scale energy storage systems to support renewable energy sources where capacity per unit mass or volume is less of a concern.^{9,12,13}

A variety of different promising positive electrode materials have been reported for SIBs including layered transition metal oxides,^{10,14–18} polyanionic compounds such as sodium vanadium phosphates or fluorophosphates,^{19–22} Prussian blue analogues,^{23,24} and organic compounds.^{25–27} Among these candidates, the layered transition metal oxides, with formula Na_xTMO_2 (where TM is typically a transition metal or combination of transition metals), appear most promising in terms of performance and continue to generate significant interest from researchers.^{28–30} Materials in this system adopt

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numerous polytypes with different stacking arrangements of the metal–oxygen layers. These are typically denoted as P-type or O-type corresponding to whether Na^+ is situated in a prismatic or octahedral coordination environment, respectively. The P2 (ABBA stacking), P3 (ABBCCA stacking) and O3 (ABCABC) polytype notation was first proposed by Delmas.³¹ Layered sodium metal oxides tend to exhibit limited cycling performance due to unfavourable structural changes such as transition metal (TM) migration, Na site ordering, and Jahn–Teller collective ordering, which occur as sodium is (de-)intercalated within the structure.^{32–34} As a consequence, significant research is devoted to the understanding of the structural evolution occurring in this class of materials in order to further improve their performance in SIBs.³⁵ In P2-type materials sodium diffusion is more favourable than in O type phases, which gives rise to superior rate capability of the former compared to O3-type oxides.^{36–38} It is also known that O3 phases are less stable at high state of charge, inducing poorer reversibility and faster capacity fading upon cycling.^{39,40} This is believed to be related to TM migration to the tetrahedral vacancies in the Na interlayers, which is expected to be more pronounced for an O-type phase than P-type phase.^{41–45} In fact, the migration of TM ions in O-type phases is one of the main contributors to the poor capacity retention of these materials.⁴⁶ Previous studies suggest that the P-type materials are not prone to TM migration, and thus when cycled to higher states of charge these materials will deliver a higher reversible capacity.^{45,47,48}

Several ternary transition metal layered oxides have been investigated for SIBs including NaCoO_2 , NaNiO_2 , NaFeO_2 , and NaMnO_2 , which have similar high theoretical capacities of 243, 235, 241, and 243 mA h g^{-1} respectively, assuming reversible extraction of 1 Na. However, in practice these materials are reported to exhibit significantly lower reversible capacities of 70, 123, 80 and 197 mA h g^{-1} , respectively.^{49–53} In these materials, the extraction of Na^+ is associated with several structural transitions, some of which may be irreversible, leading to poor cycling stability and limited reversible capacities.^{54,55} These properties have, until now, limited their implementation in commercial SIBs as energy storage devices, and researchers continue to identify new, more complex quaternary or quinary Na_xTMO_2 compounds, with several elements occupying the transition metal site, in order to manipulate the redox behaviour and structural stability of the electrode material and alleviate the issues mentioned above.^{53,56,57}

In particular, Mn- or Fe-based oxides have attracted significant research interest as they offer high capacities as well as high natural abundance and non-toxicity of the resources.^{58–64} The O3-type NaFeO_2 end member presents poor reversibility when de-sodiated to $x(\text{Na}) < 0.5$ (charged to >3.6 V), but reversible capacity can be improved by cycling in a narrower window of 2.5–3.4 V vs. Na^+/Na^0 (or until $x(\text{Na}) \approx 2/3$), albeit with a relatively low capacity of 80 mA h g^{-1} .^{51,65} The $\text{Na}_{2/3}\text{Fe}_{1/2}\text{Mn}_{1/2}\text{O}_2$ composition was first reported by Yabuuchi *et al.* and the P2-type and O3-type materials were found to deliver capacities of 190 mA h g^{-1} and 111 mA h g^{-1} respectively when cycled from

1.5–4.3 V vs. Na^+/Na^0 . Various stoichiometries of $\text{Na}_x[\text{Fe}_y\text{Mn}_{1-y}]\text{O}_2$ have since been reported.^{40,66–69} However, the 3d transition metal ions Mn^{III} and Fe^{IV} both elicit Jahn–Teller distortion effects in octahedral coordination environments, which can have a strong influence on Na^+ mobility within the structure.^{70–72} The synthesis and characterisation of both P2-type and O3-type $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ have also been reported and direct comparisons made between the two materials.^{68,73} Interestingly, despite differing initial capacities, both materials exhibited a reversible capacity of 122 mA h g^{-1} after 10 cycles which remained stable to the 15th cycle. Compared to $\text{Mn}^{\text{III/IV}}$, the $\text{Fe}^{\text{III/IV}}$ redox couple offers a higher working voltage, improving energy density, and also enhanced Na diffusion through the Jahn–Teller activity of Fe^{IV} .⁷³ Thus, the combination of these elements in appropriate ratios could give rise to a co-operative Jahn–Teller distortion, enabling greater reversible capacities to be achieved.^{74,75}

In this study, P2-type $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ is investigated first through the combination of X-ray and neutron diffraction to obtain a precise depiction of the initial structure. The structural evolution of this material during cycling is then studied using *operando* X-ray diffraction by incorporating these materials into electrodes for SIBs. Synchrotron radiation enables excellent time resolution and angular resolution to precisely model the structural changes taking place in the electrode material in real-time.^{76–78} The significant influence of current density on the observed reaction mechanisms has also been previously highlighted in studies regarding a variety of cathode materials.^{79–83} The material studied herein was subjected to cycling at low and at relatively high rates of up to 1 C over an extended voltage window of 1.5–4.2 V vs. Na^+/Na^0 to investigate the structural stability and structure-dependent rate capability of these materials. The results obtained shed new light on the reaction mechanism of P2-type layered oxides, providing insight into some of the causes for their capacity fading.

2. Experimental

P2-type $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ (hereafter denoted P2-NFMO) was synthesized by the ceramic method as previously reported.^{73,84} In summary, a stoichiometric mixture of Na_2CO_3 , Fe_2O_3 , and Mn_2O_3 was ground in a planetary ball mill for 1 hour at 250 rpm with 12 mm diameter zirconia balls (1 : 20 sample : balls weight ratio) and pressed into pellets. Then, the pellets were fired at 1000 °C for 12 hours under O_2 flow with 1 bar of pressure, followed by slow cooling.

Synchrotron X-ray diffraction (SXRD) data were collected at the materials science and powder diffraction (MSPD) beamline⁸⁵ (ALBA Synchrotron, Barcelona, Spain). Data were collected in transmission geometry at a wavelength of $\lambda = 0.82589$ Å determined using the NIST 640d Silicon standard reference material.⁸⁶ Prior to the *operando* experiment, SXRD data were collected from the as-synthesised powder which was packed into a glass capillary of outer diameter 0.5 mm.



Neutron diffraction (ND) data were collected using ECHIDNA, the high-resolution powder diffractometer at the open-pool Australian light-water (OPAL) reactor, Sydney, Australia.⁸⁷ Data suitable for structural characterization were collected at a wavelength of $\lambda \approx 1.6217$ Å. The as-synthesised powder was packed into a vanadium can of 9 mm diameter for data collection at temperatures ranging from 1.5 to 300 K. Diffraction patterns were collected in the angular range $6^\circ < 2\theta < 164^\circ$.

Magnetic measurements have been carried out using a quantum design physical properties measurement system (PPMS), equipped with an AC measurement system (ACMS) option. The zero-field cooled (ZFC) susceptibility measurements have been performed while heating from 2.5 to 300 K in an AC magnetic field of 10 Oe at a frequency of 1000 Hz, allowing the temperature to stabilize for each point. The field cooled (FC) susceptibility measurements have been performed in a similar manner to the ZFC measurements, cooling to 2.5 K under an applied DC magnetic field of 0.1 T followed by the procedure for the ZFC. The M(H) curves have been measured at constant temperature (2.5 K) with an applied external DC field ranging from -9 to 9 T. The samples have been measured in mildly packed powder form placed inside an airtight sample holder, surrounded by a pure He atmosphere. To avoid any exposure to moisture or air, the sample was loaded into the sample holder in an argon glove box and transferred to the PPMS sample chamber in an airtight container.

For *operando* electrochemical characterisation, the P2-NFMO active material was prepared into a positive electrode by mixing with Ketjen carbon black at the weight ratio of 80 : 20. The electrode is then incorporated into a custom-designed *in situ* cell equipped with beryllium (Be) window.⁸⁸ The cell features Be windows, and a thin Al sheet is used to cover the positive electrode window, onto which 100–150 mg of electrode material is dispersed. This is followed by 2 sheets of glass-fibre separator and 1 M NaPF₆ in ethylene carbonate : dimethyl carbonate (EC : DMC 1 : 1 wt%) electrolyte solution, before closing the cell with a Na metal counter electrode and stainless steel current collector.

Operando X-ray diffraction (XRD) data at slow rates were collected in reflection geometry using a lab-scale Bruker D8 Advance diffractometer equipped with a Cu anode ($\lambda_{\text{CuK}\alpha} = 1.5418$ Å) and a LinxEye 1D detector. Slow-rate cycling was undertaken over a voltage window of 1.5–4.2 V vs. Na⁺/Na⁰ at C/20 (1 C was defined as 260 mA g⁻¹), using a biologic potentiostat. Diffraction patterns were collected in the angular range $15^\circ < 2\theta < 50^\circ$ with an acquisition time of 30 minutes. *Operando* SXR data during cycling was collected using the same cell was used described above, but equipped with a Be window to allow collection in transmission geometry.⁸⁹ The cell was cycled while collecting data with 40 seconds exposures in the angular range $0.3^\circ < 2\theta < 42^\circ$. The cell was subjected to variable current cycling (C/10–1 C) over a voltage window of 1.5–4.2 V vs. Na⁺/Na⁰ using a biologic potentiostat.

Processing, visualization and analysis of *operando* diffraction patterns was undertaken using the large array manipulation program (LAMP).⁹⁰ Le Bail refinements were performed using the FullProf software suite.⁹¹ Rietveld refinements were performed using GSAS-II,⁹² and further details about the refined parameters and constraints are provided below and in the results and discussion section. Crystal structure illustrations were rendered using VESTA.⁹³ Ionic form factors were chosen for all sites in the structural models refined against SXR and ND. It should be noted that during the *operando* experiment, each diffraction pattern contains contributions (peaks, background, self-attenuation) from the electrode materials as well as electrochemically inactive phases such as the cell casing and current collectors. The *operando* data collected from the lab diffractometer were analysed using the Le Bail method, while the synchrotron data were analysed using Rietveld refinement as the significantly higher intensity and angular resolution enable more precise resolution of peaks from the active material. For sequential Rietveld refinements, the structural parameters of the electrochemically inactive phases were determined from the first dataset and then fixed. The peak profile functions, atomic parameters (including atomic coordinates, atomic occupancies, and atomic displacement parameters (ADPs)) of inactive phases and the background profile were also fixed to those obtained from the first dataset. The structural parameters of the active material allowed to refine include the lattice parameters and scale factors of each observed phase. For the P2 phase, the site occupancy factors (SOFs) of the sodium sites and positional parameter of the oxygen site (z_{O}) were also allowed to refine.

3. Results and discussion

3.1 Structural characterisation

The fitting profiles resulting from Rietveld refinement of structural models against SXR and ND patterns collected from P2-NFMO are shown in Fig. 1, and the corresponding refined structural parameters are detailed in Tables 1 and 2 respectively. The material adopts a structure with $P6_3/mmc$ symmetry and was determined to have lattice parameters of $a = 2.9408(1)$ Å and $c = 11.1811(2)$ Å from the SXR data. The P2-type structure contains two sodium sites, where the Na(1) site face shares and the Na(2) site edge shares with transition metal octahedra. The Na(1) and Na(2) sites are refined to have SOFs of 0.223(6) and 0.439(1), respectively, reaching a total Na amount per formula unit of 0.662(8), in good agreement with the target stoichiometry. Fe₂O₃ is also identified as minor impurity phase with a refined weight fraction of 5.9(2) wt%. Closer inspection of the $10^\circ < 2\theta < 20^\circ$ region of the SXR pattern reveals the presence of an additional reflection at $2\theta \approx 11^\circ$ ($d \approx 4.4$ Å), which can be attributed to presence of $\sqrt{3}a \times \sqrt{3}a$ -type in-plane Na-vacancy ordering.^{94–97} A supercell model, involving both Fe^{III}/Mn^{IV} and Na/vacancy ordering, has been predicted for P2-NFMO based on theoretical calculations.⁶⁸ Several supercell models were trialled to account for



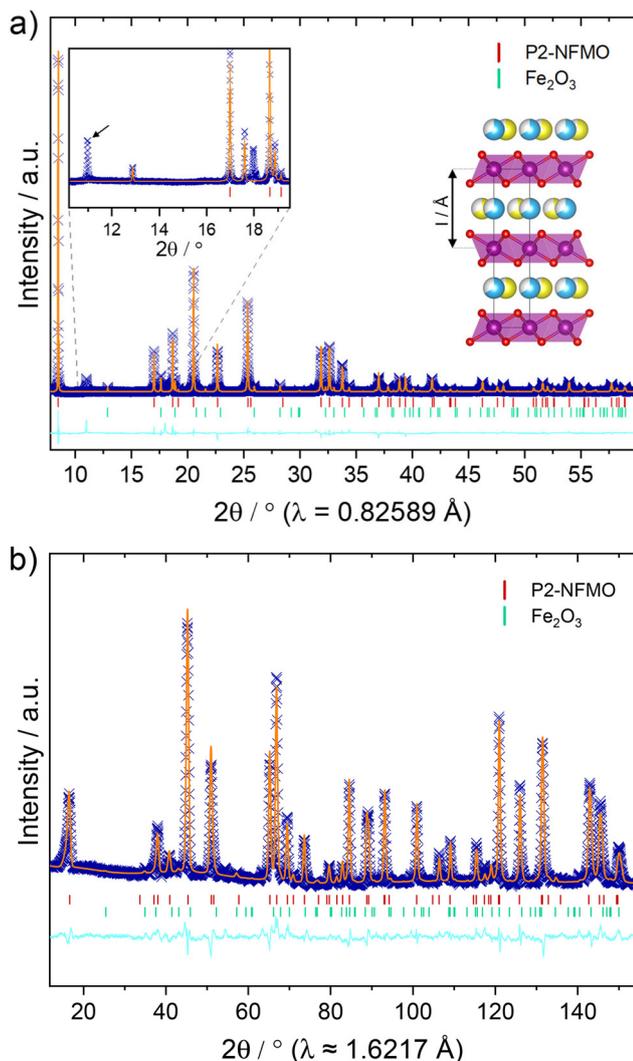


Fig. 1 Rietveld refinement profile of (a) SXR D data and (b) ND data collected from P2-NFMO. The diffraction data is represented as blue crosses, the calculated model in orange, and the difference profile is shown in cyan. The inset of figure (a) highlights the region $10.2^\circ < 2\theta < 19.5^\circ$. The arrow indicates the position of the superstructure reflection which was ascribed to Na vacancy ordering ($2\theta = 10.972^\circ$). The illustration of the P2-type unit cell shows the partially occupied Na sites, Na (1) in blue and Na(2) in yellow, while the transition metal octahedra are shown in magenta. The interlayer distance, labelled and referred to as ' l ' in throughout the text, is defined as the distance between the sites of adjacent transition metal layers.

Table 1 Refined structural parameters of P2-NFMO determined from SXR D data shown in Fig. 1a. SOF: site occupancy factor; U_{iso} : isotropic atomic thermal displacement (Debye–Waller factor)

Atom	x	y	z	SOF	$U_{\text{iso}}/\text{\AA}^2$
Na1	0	0	0.25	0.223(6)	0.0450(50)
Na2	0.6667	0.3333	0.25	0.439(1)	0.0104(28)
Mn	0	0	0	0.333	0.00116(20)
Fe	0	0	0	0.667	0.00116(20)
O	0.3333	0.6667	0.0829(4)	1.000	0.0030(11)

$R_w = 6.34\%$, space group = $P6_3/mmc$, $a = 2.9408(1) \text{ \AA}$, $c = 11.1811(2) \text{ \AA}$.

Table 2 Refined structural parameters of P2-NFMO determined from ND data shown in Fig. 1b

Atom	x	y	z	SOF	$U_{\text{iso}}/\text{\AA}^2$
Na1	0	0	0.25	0.136(7)	0.0080(37)
Na2	0.6667	0.3333	0.25	0.552(8)	0.0438(16)
Mn	0	0	0	0.379(3)	0.0056(5)
Fe	0	0	0	0.621(3)	0.0056(5)
O	0.3333	0.6667	0.0926(1)	1.000	0.0101(3)

$R_w = 4.61\%$, space group = $P6_3/mmc$, $a = 2.9432(1) \text{ \AA}$, $c = 11.1827(3) \text{ \AA}$.

the reflections observed here, see Fig. S1, S2 and Table S1 in the ESI.† Despite this, the supercell models adopting $P6_3$ symmetry still provided unsatisfactory fits (supercells #1–#3), especially due to the absence of additional superlattice reflections in the experimental SXR D data. A more satisfactory Le Bail fit was obtained using a Pm space group with a relative cell parameter of $5\sqrt{3}a_0$ (supercell #4 in ESI†).

The NPD data do not show any superstructure reflections, characteristic of honeycomb ordering on the transition metal sites, observed in, for instance in P2-type $\text{Na}_{2/3}\text{Mn}_{2/3}\text{Ni}_{1/2}\text{O}_2$, which results in symmetry lowering to the space group $P6_3$.^{98,99} This is not surprising since due to the close ionic radius of Mn^{IV} (0.53 Å) and Fe^{III} (0.645 Å),¹⁰⁰ also reducing the likelihood of Fe/Mn atomic ordering. Moreover, this also indicates that Na/vacancy ordering, evidenced by superstructure reflections in the SXR D data, is not driven by or coupled to Fe/Mn ordering in the TM layers. The NPD patterns collected above the Néel temperature ($T_N = 8 \text{ K}$, see Fig. S3†) of the material do not contain any extraneous reflections, see Fig. S8,† however the pattern collected at 3 K exhibits two new reflections at $d \approx 4.7 \text{ \AA}$ and 4.2 \AA which may be attributed to long-range magnetic ordering in the material.

3.2 Operando diffraction studies at low rates

The evolution of *operando* XRD data collected during cycling of P2-NFMO at $C/20$ is shown in Fig. 2. Due to the compromise between angular range and signal/noise ratio, the evolution of the superstructure peak was not observed here, however its evolution is resolved below in the SXR D data. Initially, Na is extracted from the initial P2 phase *via* a solid solution mechanism as evidenced from the monotonous shifting of the reflections and absence of any phase transitions (until $t \approx 5 \text{ h}$). This coincides with the shift of the $(00l)$ reflections to lower 2θ angles, indicating an expansion of the interlayer distance l , defined as the distance between transition metal sites along the c axis, as depicted in Fig. 1, from 5.63 Å to 5.70 Å. Meanwhile, the (100) peak shifts to higher 2θ angle, denoting in-plane compression of the a lattice parameter from 2.93 Å to 2.90 Å. These structural changes, common in layered oxides upon Na extraction, can be ascribed, respectively, to an increased electrostatic O–O repulsion between TM–O layers and a decreased TM–Na electrostatic repulsion within the layers.^{55,101–104}



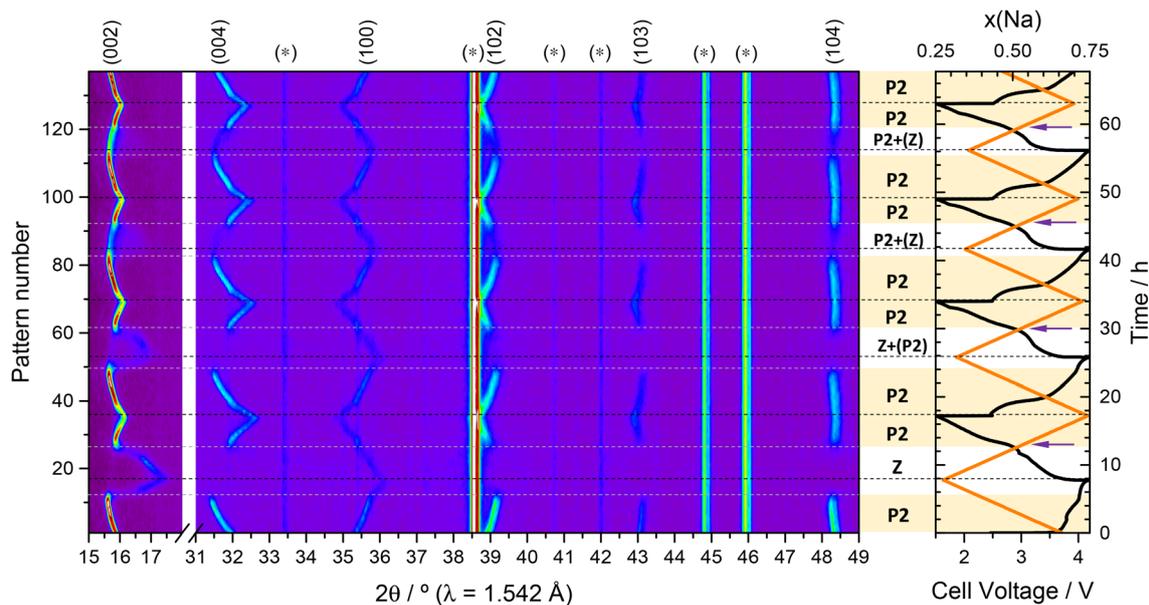


Fig. 2 Evolution of diffraction data collected during cycling of P2-NFMO at a rate of C/20. Right panel: evolution of the cell voltage (black line) and Na content $x(\text{Na})$ (orange line), together with shaded area indicating the domain of existence of the P2 and Z phases – when two phases coexist the phase in brackets is the minority phase; purple arrows indicate the voltage drop ascribed to transition from $\text{Fe}^{\text{III/IV}}$ to $\text{Mn}^{\text{III/IV}}$ redox activity. Left panel: contour plot of the XRD pattern evolution. The peaks are indexed according to the $P6_3/mmc$ space group.

As the cell reaches ≈ 4.0 V vs. Na^+/Na^0 ($x(\text{Na}) = 0.4$, $t = 5$ h), an abrupt shift in position of the (002) reflection from 15.60° to 16.65° is observed, see Fig. 3a, indicating collapse of the interlayer distance from $I = 5.70$ to 5.15 Å (see Fig. 3b). During this period the (100) reflection evolution does not seem to be as affected, demonstrating that the change is mainly on the interlayer distance. As can be seen in Fig. 3, this sudden phase transition toward a new phase with a more compact structure occurs through a biphasic transformation mechanism. Previous studies have attributed this to the appearance of Na-poor O-type interlayers within the initial P-type structure through a gliding of the TMO_6 oxide layers.^{40,73} If the resultant O–P stacking is ordered, the phase can be identified as OP4, while if the O–P stacking is aleatory, the phase is referred to as “Z”.^{105,106} The fact that only the (002) and (100) peaks of the newly formed phase are visible, with no appearance of any additional peaks, demonstrates that the stacking sequence of P and O interlayers follows a random pattern. The Le Bail refinements suggest that during this biphasic region the P2 phase presents a constant interlayer distance of 5.69 Å, see Fig. 3b and Fig. S4,[†] while that of the Z phase decreases from 5.35 Å to 5.25 Å, *i.e.*, showing some degree of solid solution. Note that the interlayer distance determined for the Z phase (Fig. 3b) corresponds to an average over the O and P interlayers. Since the interlayer distance is related to the repulsive electrostatic O–O interaction, it will be higher for the direct oxygen stacking of the P-type interlayers than for the shifted stacking of the O-type interlayers, leading to an average interlayer distance that will be shorter for the Z phase compared to the P2 phase at same Na content.⁴⁰ The changes in a are

however small during the $\text{P2} \rightarrow \text{Z}$ transformation, with very close values for the two separated phases, with a slight increase from 2.88 Å to 2.90 Å for the Z phase. Further Na extraction leads to a solid solution-type evolution of the Z phase, as indicated by the continuous shift of the peaks, see Fig. 2 and 3a, with the interlayer distance decreasing from $I = 5.25$ Å to 5.15 Å. At the same time, the in-plane parameter a evolves less drastically from 2.91 to 2.89 Å (see Fig. 3b).

At the end of the first charge cycle, when the $\text{P2} \rightarrow \text{Z}$ transition is complete, the (002) peak of the Z phase is broader compared to the initial P2 phase, $\text{FWHM}_Z \approx 0.3^\circ\text{--}0.6^\circ$ versus $\text{FWHM}_{\text{P2}} \approx 0.1^\circ$, see Fig. 3a. This indicates a partial loss of crystallinity, possibly due to inhomogeneous Na concentration combined with disorder in the O/P stacking sequence.¹⁰⁵ Since the reflections get sharper again upon discharge one can exclude a possible loss of integrity of the particles as source of this peak broadening.

At first glance the phase evolution of P2-NFMO on the first charge appears reversible during the following discharge. While reversibility of $\text{P2} \leftrightarrow \text{Z}$ or $\text{P2} \leftrightarrow \text{OP4}$ transitions has been previously observed in $\text{Na}_{2/3}\text{Ni}_{1/2}\text{Mn}_{1/2}\text{O}_2$ and $\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2$,¹⁰⁷ closer examination of the data presented here reveals several irregularities between charge and discharge. For instance, while the $\text{P2} \rightarrow \text{Z}$ transition occurs at $x(\text{Na}) \approx 0.35$ upon charge, the reverse transition $\text{Z} \rightarrow \text{P2}$ occurs at $x(\text{Na}) \approx 0.55$ upon discharge. The latter concentration corresponds to the onset of $\text{Mn}^{\text{IV} \rightarrow \text{III}}$ redox activity, as revealed by a drop in the voltage-composition curve (indicated by a purple arrow in the right panel of Fig. 2). Indeed, according to previous studies,^{68,73,99,108} the lower voltage plateau (typically



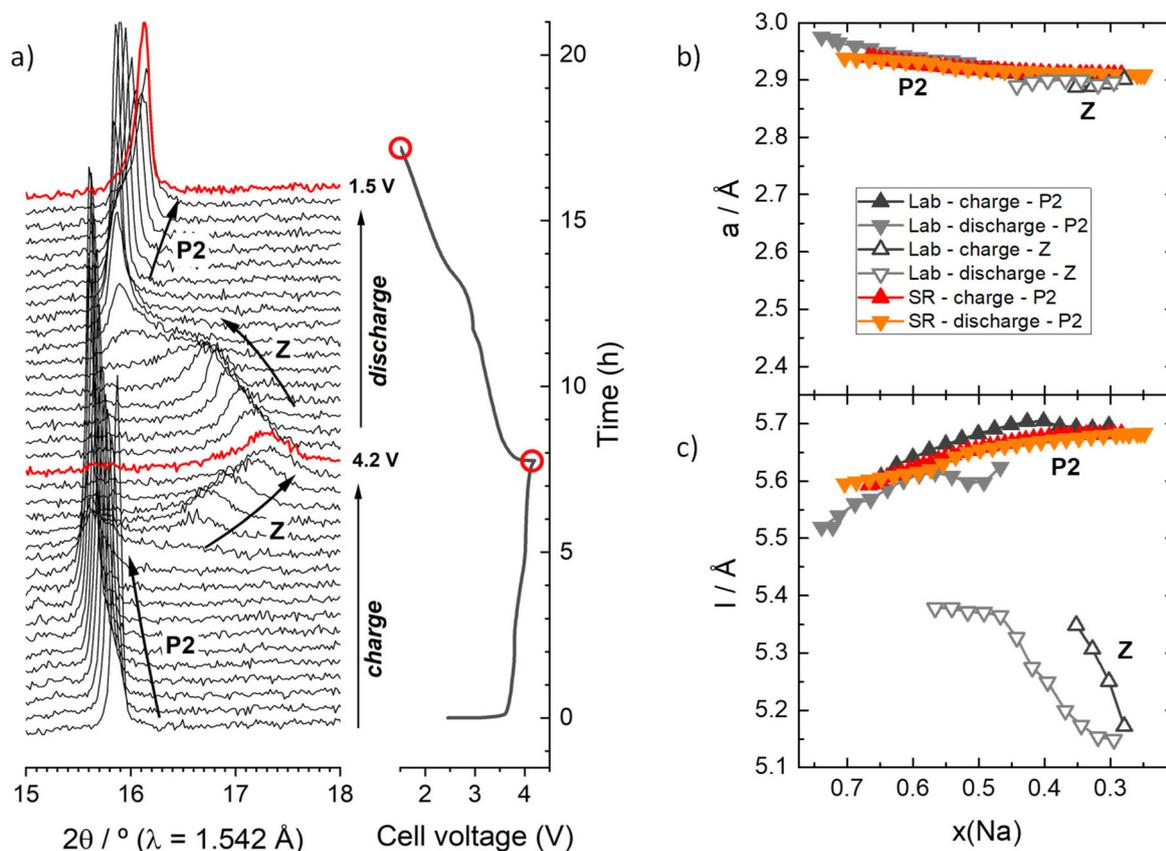


Fig. 3 (a) Stacked representation of the XRD patterns at the vicinity of the main interlayer peak (002) during the low-rate (C/20) lab-scale *operando* XRD measurements of P2-NFMO. (b) Evolution of the $P6_3/mmc$ unit cell parameter a and (c) interlayer distance l of P2-NFMO, determined from refinement of structural models against lab-scale XRD data ("Lab", black/grey dots, Le Bail refinement) and synchrotron XRD data ("SR", orange/red data points, Rietveld refinement). Up and down pointing triangles represent charge and discharge results, respectively. Sodium content $x(\text{Na})$ calculated from the measured charge delivered by the cell.

observed for $x > 2/3$) can be ascribed to $\text{Mn}^{\text{III/IV}}$ redox activity, while the higher voltage plateau (typically observed for $x < 2/3$) can be ascribed to the $\text{Fe}^{\text{III/IV}}$ redox activity. This means that most of the Na reinsertion (discharge) during the $\text{Fe}^{\text{IV/III}}$ reaction occurs within the Z phase, while it occurs predominantly within the P2 phase upon initial Na extraction (charge). It also suggests that the change from $\text{Fe}^{\text{IV/III}}$ to $\text{Mn}^{\text{IV/III}}$ redox activity might be what triggers the Z \rightarrow P2 transition upon Na reinsertion. The charge–discharge asymmetry of the transition can be also observed from the evolution of the cell parameters of the Z phase, as seen in Fig. 3b, which presents a clear hysteresis between charge and discharge, more pronounced than in the case of the P2 phase. Moreover, when the P2 phase reappears upon discharge near $x(\text{Na}) = 0.55$, its interlayer distance is slightly shorter than upon charge at the same Na composition: 5.70 Å upon charge compared to 5.63 Å upon discharge. Finally, the Z \rightarrow P2 transition upon discharge spans over a larger range of composition than the P2 \rightarrow Z reaction during charge.

This charge–discharge asymmetry of the structural evolution is associated with differing reaction pathways which differ in their kinetics. This is also in agreement with the

more pronounced slope of the voltage–composition profile upon discharge compared to the charge (see Fig. 2). Indeed, as can be seen in Fig. 3a, the peaks are broader during the P2 solid solution upon discharge compared to the charge ($\text{FWHM}_{002}(\text{charge}) \approx 0.10^\circ$ vs. $\text{FWHM}_{002}(\text{discharge}) \approx 0.14^\circ$). This is indicative of a less homogeneous Na concentration, or microstructural changes such as O-type stacking faults inherited from the Z phase during the P2 \rightarrow Z transition.¹⁰⁵ Inhomogeneous Na concentration could be a consequence of sluggish kinetics, while the presence of O-type interlayers could be responsible for the kinetic degradation. Furthermore, in addition to the poorer diffusion of Na^+ in O-type interlayers compared to P-type, previous studies suggest that O-type interlayers could be prone to Fe migration,^{44,105} which is not energetically favourable in a P-type structure.^{44,45} Therefore, discharge is likely to be more sluggish than charge in this material and this asymmetry is likely to affect subsequent cycles. Degraded electrochemical performance is to be expected when too much alkali metal is extracted upon charge from an O-type-stacking component in phases such as Z or OP.^{109,110}

At the end of the discharge, the interlayer distance of the P2 phase is shorter than that of the initial P2 phase, as the



contribution of the $\text{Mn}^{\text{IV/III}}$ reaction allows a higher Na concentration ($x(\text{Na}) = 0.72$) to be reached compared to the as-synthesized composition ($x(\text{Na}) \approx 2/3$), although full sodiation is not achieved. The incomplete sodiation can be correlated to the fact the P2 to O2 transition, commonly observed in P2 phases near complete sodiation,¹⁰⁷ is not observed in the *operando* study. This is likely due to sluggish kinetics, as consequence of the irreversible structural degradation and/or asymmetric charge-discharge structural evolution mentioned above.

The irregularity between charge and discharge of the P2-phase and Z-phase concentration domains is in fact observed at all cycles, see Fig. 2. Likewise, during all cycles, the Z \rightarrow P2 transition upon discharge occurs at the vicinity of the drop in the voltage-composition curve indicating change from the Fe^{IV} to $\text{Mn}^{\text{IV/III}}$ reaction, confirming the correlation between the two phenomena. Fig. 4 shows XRD patterns collected at the charged state of the first four cycles and reveals that while the P2 \rightarrow Z transition appears nearly complete at the end of the first cycle, it becomes less pronounced in the subsequent cycles and is no longer observed after the fourth charge cycle. Concomitantly, the amplitude of the change in $x(\text{Na})$, shown in the right panel of Fig. 2, also decreases progressively.

To better understand the link between the observed phase transitions, Na content in the structure, and redox activity, Fig. 5a shows the differential capacity curve (dx/dE) of P2-NFMO. Three processes can be observed during charge: a

broad peak at low voltage, which can be ascribed to the $\text{Mn}^{\text{III/IV}}$ redox activity, and two overlapping peaks at higher voltage which are ascribed to the $\text{Fe}^{\text{III/IV}}$ redox activity. A local minimum, indicated by the purple arrows, corresponds to the composition $x(\text{Na}) \approx 2/3$ ($\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$), which is ascribed to the transition from $\text{Fe}^{\text{III/IV}}$ to $\text{Mn}^{\text{III/IV}}$ redox activity. The $\text{Fe}^{\text{III/IV}}$ peak appearing at lower voltage is broad, while the one observed at higher voltage is sharp, as shown in Fig. 5a. According to the phase sequence observed in Fig. 2, these peaks in the dx/dE curve can be ascribed to the P2 solid solution and the P2 \rightarrow Z transition, respectively. Upon discharge (cathodic $\text{Fe}^{\text{IV/III}}$ activity), these two peaks are inverted, with the sharp peak observed at lower voltage, suggesting that Na is first extracted from the Z phase before the Z \rightarrow P2 transition occurs. This agrees with what was concluded from the *operando* XRD analysis. As can be seen from Fig. 5b, while the average voltage of the P2 \leftrightarrow Z reaction remains constant with the number of cycles at $\langle E \rangle \approx 3.58 \pm 0.01$ V vs. Na^+/Na^0 , the related voltage hysteresis ΔE between Na insertion and extraction evolves within the range 0.79–0.98 V. ΔE first decreases from 0.9 to 0.79 V from cycle 1 to 2, and it continuously increases from cycle 2 (0.79 V vs. Na^+/Na^0) to cycle 4 (0.98 V vs. Na^+/Na^0). Because this reaction is very close to the cut-off voltage of 4.2 V vs. Na^+/Na^0 , this increasing over polarization is possibly the reason why the Na concentration domain over which the Z phase is observed progressively shrinks upon cycling. This results in a decrease of the capacity related to the $\text{Fe}^{\text{III/IV}}$ reaction, see Fig. 5c, while that of the $\text{Mn}^{\text{III/IV}}$ reaction remains constant, leading to an overall capacity fading, as indicated by the progressive decrease of the amplitude of the Na concentration change in Fig. 2 (right panel). It should be noted that the loss of capacity for $\text{Fe}^{\text{III/IV}}$ reaction from the 1st to 2nd cycle is partially compensated by additional capacity provided by $\text{Mn}^{\text{III/IV}}$ during the first discharge, leading to an overall coulombic efficiency that is higher (90%) than the 67% that would be expected taking into account the initial stoichiometry, $x(\text{Na}) = 0.67$.

Interestingly, upon discharge, the XRD patterns recorded in the vicinity of the Fe to Mn redox activity transition, see Fig. 6, are all identical to each other in terms of peak position and peak width, but broader than that of the pristine material. This indicates that, although irreversible microstructural changes occur during the first cycle, the fading of the Fe redox activity observed for the next cycles is not related to any further detectable structural or microstructural degradation. Hence, the short term capacity loss of this material can be ascribed essentially to increasing overpotential or large voltage hysteresis of the P2 \leftrightarrow Z transition during the Fe redox process. The detrimental effect of phase transitions involving layers gliding for electrochemical performance has been already pointed out in this family of materials.^{105,111} This is however a surprising result as Jahn–Teller distortion induced by Mn^{III} is expected to influence the redox activity and hence the structure, by inducing lattice strain and reducing Na ion mobility, and therefore is the main factor affecting cyclability in Mn-rich transition metal layered oxides.^{71,112–114} However,

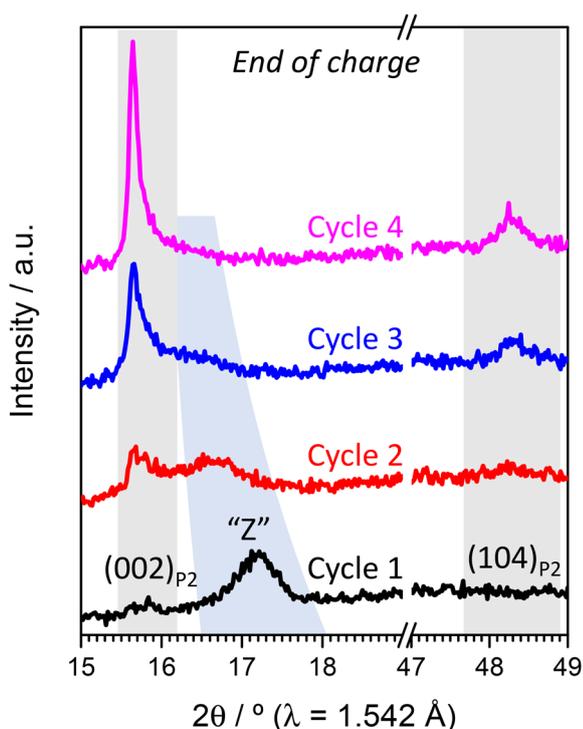


Fig. 4 *Operando* XRD patterns of P2-NFMO collected at the charged state during cycles 1 to 4. The shaded 2θ regions highlight the evolution of reflections originating from the P2-type and Z structures.



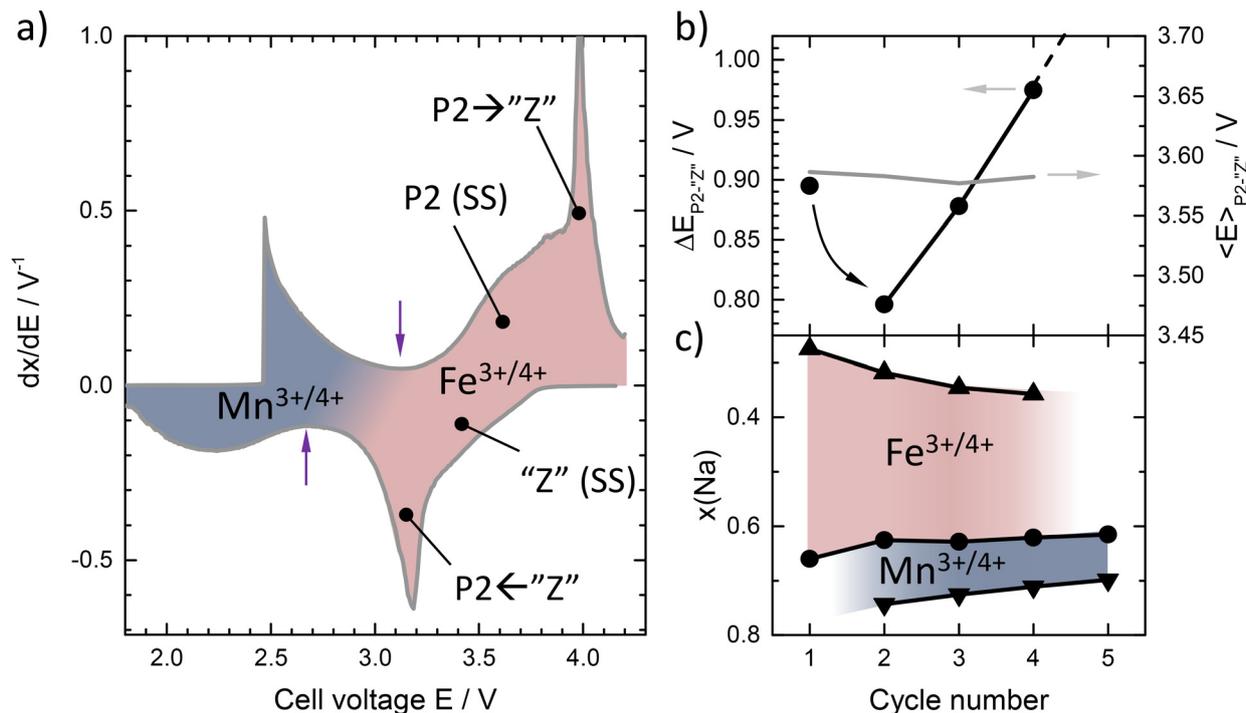


Fig. 5 (a) Example of differential voltage-composition curve recorded at C/20 (second cycle) (b) Left axis: polarization between charge and discharge for the P2-Z reaction, determined as the difference in position of the peak ascribed to the P2-Z transition in the differential voltage-composition curve; Right axis: observed voltage of the P2-Z reaction, calculated as the average between charge and discharge of P2-Z peak position in the derivative voltage-composition curves. (c) Attribution of capacity (sodium content determined by electrochemistry) to Fe and Mn redox with successive cycles; upward triangles refer to end of charge, downward triangles refer to the end of previous discharge, and circle symbols correspond to the transition from Mn to Fe redox, as indicated by the purple arrow upon charge in panel (a).

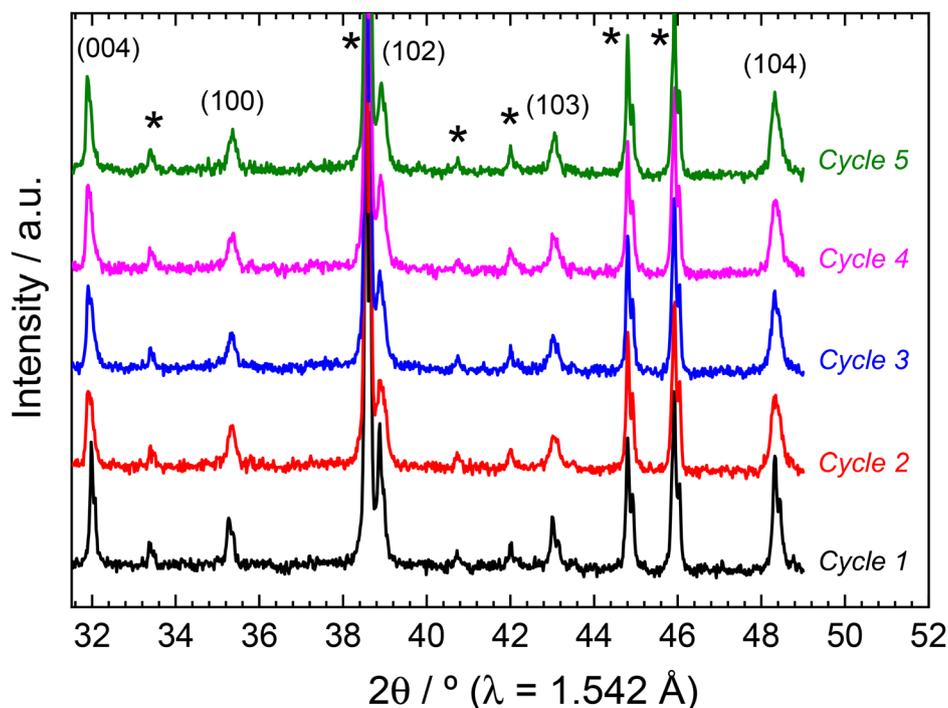


Fig. 6 Selected lab-scale XRD patterns collected during discharge of P2-NFMO at C/20 recorded at cell voltage $E \approx 2.7$ V, coinciding with the transition from Fe to Mn redox activity ($x(Na) \approx 2/3$). The peaks of the P2 phase are indexed according to the $P6_3/mmc$ space group. Peaks indicated by an (*) are due to inactive cell components.



the observations presented here suggest that the onset of Fe redox activity contributes more strongly to initial capacity fading as it is most prominently observed during the initial cycles, coinciding with the P2 → Z transition. This transition may also involve the migration of Fe ions to the Na layer, which once migrated reduce the decay contribution from this transition during long-term cycling.^{115,116} Meanwhile, the Jahn–Teller activity of Mn^{III} contributes more strongly to the long-term cycling stability of the material.^{117,118}

3.3 Operando diffraction studies at higher rates

Fig. 7 shows the evolution of the *operando* synchrotron SXR data over time, correlated with the recorded cell voltage during variable current cycling ranging from C/10 to 1 C. The evolution of the reflections is very similar to that of the lab-scale *operando* XRD experiment. During charge, de-sodiation, the (002) and (004) reflections are again observed to move to lower angles, which correspond to an expansion of the lattice along the *c*-axis as sodium is removed. During discharge, the reflections also return to their original positions. The (100) and (102) reflections meanwhile are found to behave inversely but exhibit the same reversibility, which can be related to the inverse evolution of the *a* and *c* parameters during de-sodiation, see Fig. 8b. As the applied current increases, the capacity delivered by the cell decreases, and as expected a lower magnitude of structural expansion is observed with each cycle. The capacity decreases from 136 mA h g⁻¹ at C/6 to 107 mA h g⁻¹ at C/2. During high rate cycling at 1 C, the capacity drop is more severe, reducing successively over each cycle from 71 mA h g⁻¹ to 42 mA h g⁻¹, as depicted in Fig. S4.†

The results of peak fitting to the superstructure reflection at $2\theta \approx 11^\circ$ ($d \approx 4.4 \text{ \AA}$) is presented in Fig. 9. The superstructure reflection is observed to initially move to higher angles before diminishing in intensity by $\approx 40\%$ at the end of the first charge cycle (see Fig. 7c). The fact that the superstructure reflection has retained $\approx 60\%$ of its original intensity when the sodium content in the electrode is at a minimum demonstrates that the Na/vacancy ordering remains during the whole charge process. Beyond the end of the first charge and during all the following cycles, the intensity of the superstructure reflection remains constant, independent of the charge–discharge sequence and on Na content as well as lattice parameters of the P2 phase. This could indicate that part of the Na remains trapped in the structure in a persistent Na-vacancy ordering, and that the Na that reinserts into the structure is likely to be more disordered. From the comparison of these observations with the refined structural parameters of P2-NFMO during cycling, see Fig. 8, it can be observed that the intensity of the superstructure reflection drops when the occupancy of the Na(1) starts to decrease, at $t \approx 2 \text{ h}$, while the occupancy of the Na(2) starts to decrease from the beginning of the charge. This suggests that the Na/vacancy ordering maybe related to the Na(1) site. Interestingly, the Na(2) site is less occupied at the end of the first charge at C/6 than the Na(1) site.

The P2 → Z transition observed at the end of charge during the *operando* lab-scale XRD (Fig. 3a), and associated with a shrinking of the *c* parameter, is not observed in the SXR after increasing the current density to C/10, compared to the C/20 rate used for lab-scale measurement. The higher rate used may

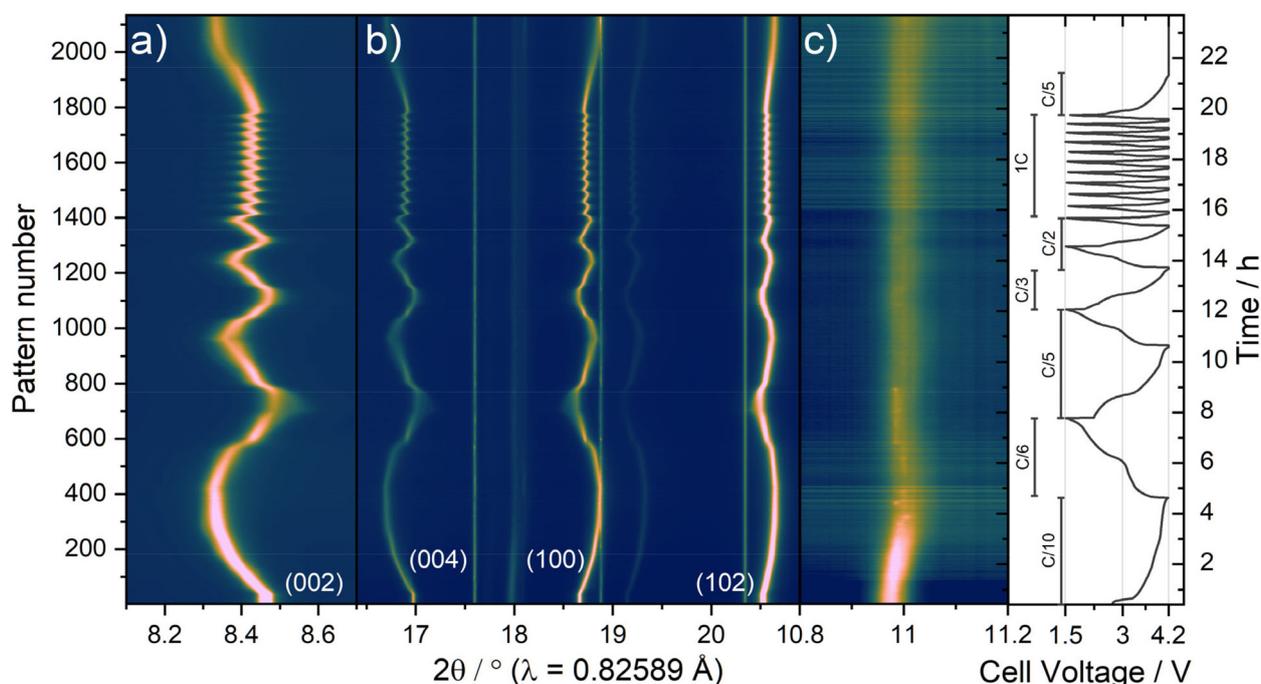


Fig. 7 The evolution of selected reflections during variable current cycling of the P2-NFMO. (a) (002), (b) (004), (100) and (102) (c) 'ordering' reflection. An overview of the full angular range is shown in Fig. S6.†



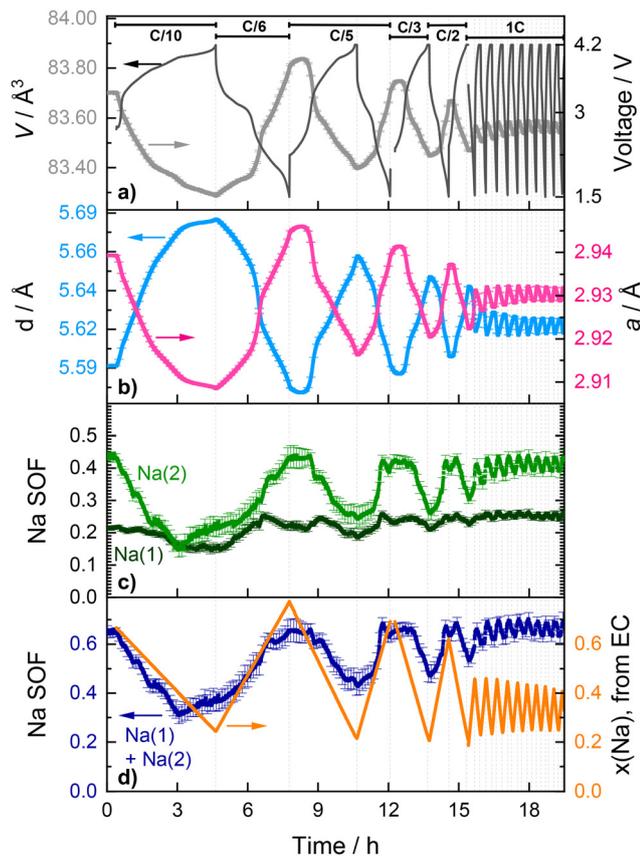


Fig. 8 Refined structural parameters of the P2 phase determined from sequential Rietveld refinement of the *operando* SXR data. (a) Unit cell volume (left axis) and cell voltage (right axis). (b) Interlayer distance l and in plane distance a . (c) Na occupancy in the two Na sites Na(1) and Na(2). (d) Total Na occupancy Na(1) + Na(2) from Rietveld and calculated Na content $x(\text{Na})$ in the electrode from electrochemical measurement (assuming an initial stoichiometry $x(\text{Na}) = 0.67$). Evolution of the a and c lattice parameters is shown in Fig. S6.†

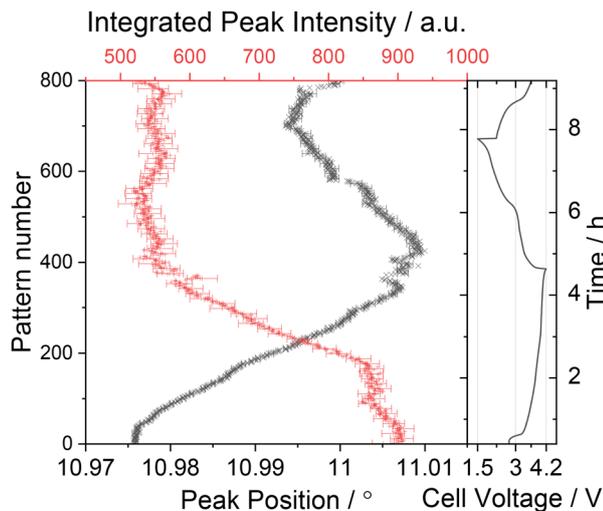


Fig. 9 Integrated peak intensity and peak position of the superstructure reflection shown in Fig. 7c over the first 800 datasets (first charge-discharge cycle).

induce larger overpotentials, causing the cell to reach the cut-off voltage of 4.2 V before the level of de-sodiation is sufficient to observe the P2 \leftrightarrow Z transition. Nonetheless, there are indirect indications that the transition might actually occur, or be very close to being initiated: (i) at the discharged state there is some evidence of a secondary phase which correlates to the stabilisation of the lattice parameters and sodium occupancy as shown in Fig. 8. (ii) Towards the end of the first discharge, $t \approx 6.7$ h, a subtle fluctuation in the symmetry and intensity of 002 reflection is observed, see Fig. 7a, which coincides with a change in the slope of the electrochemical curve and a change in the rate of lattice parameter evolution. This behaviour has been previously observed in studies of P2-type materials, and may be attributed to an inhomogeneous transition rate within the electrode.^{67,119} As the current rate is increased, these features are smoothed out, which is consistent with the assumption that the appearance of the P2 \rightarrow Z transition may be either rate dependent or dependent on the amount of sodium transferred to/from the electrode.

During the *operando* experiment the current density was increased successively with each cycle from C/6 to 1 C to investigate the higher rate behaviour of this material. Upon the 1st discharge at C/6 the c lattice parameter is found to reduce from 11.365(3) Å ($I = 5.683$ Å, 4.2 V vs. Na⁺/Na⁰) to 11.153(3) Å ($I = 5.577$ Å, 1.5 V vs. Na⁺/Na⁰), but returns to only 11.323(3) Å ($I = 5.662$ Å) upon the cell being recharged to 4.2 V vs. Na⁺/Na⁰ at C/3, see Fig. 8. At the highest current density of 1 C, the c lattice parameter is found to vary between ≈ 11.23 Å and ≈ 11.25 Å ($I \approx 5.615$ Å and ≈ 5.625 Å) at the discharged and charged states respectively. Similarly, the atomic parameters exhibit less variation with increasing current density, in agreement with the reduced capacities observed at higher current, see Fig. S5.† The largest change in sodium content is observed during the first cycle at C/10–C/6, where it reduces from an initial value of 0.658(3) to 0.309(16) upon de-sodiation. When subsequently discharging at a higher current density of C/3 the total sodium content returns to a value of 0.658(8). Although there seems to be a good qualitative agreement between the refined Na occupancies and the sodium content estimated from electrochemical control, they progressively depart from each other while the rate increases. This could be due to inhomogeneous de-sodiation of the electrode at high current densities, as highlighted in Fig. 8c. Previous studies of Fe-substitution into Ni- and/or Mn-based sodium layered oxide materials have shown that the formation of the Z phase coincides with the onset of Fe redox activity,^{107,120} which is expected to occur at a potential of ≈ 4 V vs. Na⁺/Na on charge composition. This is consistent with the structural evolution observed here showing the onset of P2 $>$ Z transition in this voltage region in the low-rate experiment (Fig. 3a and 5), as discussed earlier. Indeed, as shown in Fig. 8, there is good agreement in the low-rate region, however during the high rate region, the total sodium content varies between only ≈ 0.63 and ≈ 0.69 . This is about one third of the Na concentration within the whole electrode, according to electrochemical control, which varies between ≈ 0.25 and ≈ 0.44 . In the lab-



experiment, evidence of an inhomogeneous Na distribution was identified and related to sluggish kinetics of Na diffusion after transition to the O-type structure, and additionally a more pronounced slope in the voltage profile upon discharge compared to charge, suggesting better kinetics upon sodiation than desodiation. This behaviour is observed again in the SXR D experiment, where the asymmetric (de-)sodiation kinetics become particularly prominent during the high-rate 1 C cycling. Better kinetics of the reverse sodiation reaction result in a gradual increase of the total refined sodium occupancy. The refined structural parameters, such as the a parameter and interlayer spacing d also show an asymmetric increase and decrease respectively to accommodate the increasing Na concentration in the structure. Further comparison with the data presented earlier in Fig. 3b and c, shows that the degree of reversibility of the structural changes occurring during the first cycle in the *operando* synchrotron SXR D experiment at C/10–C/6 is much higher than in the case of the lab-experiment at C/20. This further confirms that the P2 \rightarrow Z transition, which was not observed in the “more reversible” synchrotron experiment, is detrimental for the reversibility of the electrochemical process and hence the performance of the material. Furthermore, the fact that this detrimental P2 \rightarrow Z transition is prevented at higher rates explains the generally observed tendency of P2 layered oxides to present better cyclability as the rate increases.

4. Conclusions

P2-type $\text{Na}_{2/3}\text{Fe}_{2/3}\text{Mn}_{1/3}\text{O}_2$ has been successfully synthesized by the ceramic method, and its structure has been resolved by neutron and synchrotron X-ray powder diffraction. Neutron diffraction data confirm the absence of Fe–Mn ordering, while synchrotron diffraction data revealed Na-vacancy ordering as a superstructure peak observed at $d \approx 4.4 \text{ \AA}$. Insights into the relationship between electrochemical performance and structural evolution in P2-NFMO have been presented based on the results of two experimental protocols.

In the low-rate lab-scale experiment, a Z phase is observed to form in the second part of the charge as $x(\text{Na})$ reaches ≈ 0.4 . This Z phase consists of disordered O- and P-type interlayers. The P2 \rightarrow Z phase transition hence occurs through layer gliding, which leads to (over-)polarization in the electrochemical curve. This P2 \rightarrow Z transition is partially reversible upon discharge, but the reverse Z \rightarrow P2 transition does not occur until the drop in cell voltage at $x(\text{Na}) \approx 0.55$. The P2 \rightarrow Z and Z \rightarrow P2 transitions were shown to be directly related to the change from Mn to Fe redox activity, *i.e.*, the redox activity triggers the structural change and *vice versa*. In particular the P2 \rightarrow Z phase transition has an associated over-polarization and thus the compositional range at which the Z phase is observed on charge progressively reduces as the cycle number increases, with the P2 phase being the main phase during the entire fourth cycle. The presence of the Z phase and associated Fe redox activity are identified as the main causes of irreversible

capacity fading during the first cycles at C/20. The P2 \rightarrow Z transition must thus be avoided by reducing the charge voltage for improved cyclability. In the variable rate SXR D experiment, it was found that the two Na sites in the P2-type structure exhibit selective extraction, one of them presenting Na/Vac ordering which is preserved during cycling, which presumably assists in the stabilization of the P2 phase upon Na extraction. The results herein shed new light on the structural evolution and reaction mechanism of P2-type Fe-, Mn-based sodium layered oxides during (de-)sodiation at current densities relevant for practical application and provide new insight into the causes of capacity fading and how this can be alleviated.

Data availability

The data supporting this article have been included as part of the ESI.† Additionally, crystallographic data for structures refined against data presented in the article have been previously reported and deposited in the ICSD repository and can be obtained from Coll. Codes 252021.

Conflicts of interest

All authors declare they have no competing interests to disclose which could be perceived to influence the results and discussion reported in this paper.

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