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The Fe^{4+/3+} redox mechanism in NaFeO₂: A simultaneous *operando* Nuclear Resonance and X-ray Scattering study

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Abstract

Simultaneous *operando* Nuclear Forward Scattering and transmission X-ray diffraction and ^{57}Fe Mössbauer spectroscopy measurements were carried out in order to investigate the electrochemical mechanism of NaFeO_2 vs. Na metal using a specifically designed *in situ* cell. The obtained data were analysed using an alternative and innovative data analysis approach based on chemometric tools such as Principal Component Analysis (PCA) and Multivariate Curve Resolution - Alternating Least Squares (MCR-ALS). This approach, which allows the unbiased extraction of all possible information from the *operando* data, enabled the stepwise reconstruction of the independent "real" components permitting the description of the desodiation mechanism of NaFeO_2 . This wealth of information allows a clear description of the electrochemical reaction at the redox-active iron centres, and thus an improved comprehension of the cycling mechanisms of this material vs. sodium.

Keywords

Mössbauer spectroscopy, Chemometrics, MCR-ALS, Na-ion batteries, Nuclear Forward scattering, NaFeO_2

1 Introduction

Sodium ion batteries (SIB) are ideal for large-scale electrochemical storage which are not subject to weight or volume restrictions. Iron-based cathode materials are particularly interesting, since they fulfil both economical and ecological requirements [1]. In this regard, the layered transition metal oxide NaFeO_2 has received much interest since it was the first electrode material for SIB reversibly cycling on the $\text{Fe}^{3+/4+}$ redox couple [2]. Moreover, NaFeO_2 has the flattest and highest average working voltage of all single metal O3-type systems[3]. Unfortunately, its electrochemical performance deteriorates rapidly if more than

25 0.5 Na⁺ per formula unit are extracted due to irreversible structural changes which lead to
26 the disturbance of Na pathways caused by the migration of Fe into interslab spaces [4, 5].
27 Substituting Fe partially by other transition metals can suppress structural deterioration
28 and avoid Fe migration hence increasing overall capacity and cycling stability [6, 7].

29 Attempts to elucidate the reaction mechanism based on *ex situ* Mössbauer spectroscopy
30 suggest that sole Fe⁴⁺ formation cannot explain the overall capacity obtained and that
31 additional charge compensation contribution must be present [8]. As a possible explanation,
32 the contribution of both transition metal and oxygen to the charge compensation has been
33 lately proposed [9]. In their recent *in situ* XAS study, Susanto *et al.* highlighted that beyond
34 0.5 Na⁺ extraction the charge is predominantly provided by oxygen which is irreversibly
35 released when extracting more than 0.6 Na per formula unit [10]. In other studies based on
36 *ex situ* Mössbauer spectroscopy, it was revealed that Fe⁴⁺ formed during sodium/lithium
37 extraction is unstable and spontaneously reduces back to Fe³⁺ upon open circuit storage
38 [11, 12], underlining the importance of an *in situ* or *operando* based analytical approaches.

39 These observations demand for a thorough study of the evolution of the physico-chemical
40 properties of the iron centres under realistic cycling conditions in order to closely follow
41 the reaction mechanism and elucidate the working principle of the Fe⁴⁺/Fe³⁺ redox couple.
42 Such information can be obtained by several techniques such as X-ray absorption and ⁵⁷Fe
43 Mössbauer spectroscopy, which provide element-specific core resonance information about
44 the iron centres and can be easily applied under *in situ* conditions. On the other hand, the
45 high degree of long range order during the phase transition between increasingly desodiated
46 phases makes X-ray diffraction (XRD) a suitable technique to monitor the phase evolution
47 and lattice parameter change upon desodiation reaction.

48 In this work, we report the application of *operando* Nuclear Forward Scattering (NFS),
49 a spectroscopic technique based on the Mössbauer effect, to closely monitor the reaction
50 process of NaFeO₂ vs. sodium. NFS, applied here for the first time to the study of bat-
51 tery materials, benefits from the brilliance of 3rd generation synchrotron radiation sources

52 radiation sources, and therefore has the advantage of providing similar information but with
53 reduced collection times (here 7 minutes per spectrum), thus opening the application of the
54 Mössbauer effect to the study of faster reaction mechanisms than those measured conven-
55 tionally (several hours per spectrum for samples non-enriched in ^{57}Fe and large amount of
56 electrode materials).[13] Moreover, NFS allows working on samples with small sizes and is a
57 background free method, thus enabling the collection of data with very high signal-to-noise
58 ratios. Finally, in this experiment NFS could be coupled to *operando* transmission XRD,
59 which was measured in parallel on the same sample during the same electrochemical pro-
60 cesses. In this way, it was possible to measure simultaneously the evolution of both the
61 long-range order of the material and the local physico-chemical properties of the iron cen-
62 tres. To validate the approach, the results of NFS are closely compared to those obtained
63 by conventional lab-scale *operando* Mössbauer spectroscopy and X-ray diffraction applied on
64 the same system.

65 **2 Experimental**

66 **2.1 Material synthesis and electrode formulation**

67 The pristine NaFeO_2 powders used in this work were prepared starting from 260 mg of
68 Na_2CO_3 and 360 mg of a mixture of $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ isotopically enriched in ^{57}Fe (95
69 %). The two precursors were finely ground in a mortar for 10 minutes, and then annealed
70 in air at 600°C for 18 hours with a heating rate of 12°C h^{-1} . The phase purity of the
71 pristine material was checked by laboratory X-ray diffraction (Fig. S1 table S1). Due to
72 moisture sensitivity, the NaFeO_2 samples were stored and handled in a glovebox under inert
73 atmosphere.

74 Electrodes with approximate diameter of 12 mm were prepared as composite self-supported
75 pellets as previously described [14]. In short; electrodes were pasted on an aluminium foil
76 starting from a slurry containing 85 wt.% NaFeO_2 , 10 wt.% super-P carbon, 5 wt.% PVDF

77 (polyvinylidene fluoride) dissolved in NMP (1-methyl-2 pyrrolidinone). The electrode used
78 for the *operando* experiments contained $\approx 2 - 4 \text{ mg cm}^{-2}$ of NaFeO_2 .

79 **2.2 ^{57}Fe Mössbauer spectroscopy**

80 *Operando* ^{57}Fe Mössbauer spectra were measured with a source of $^{57}\text{Co}:\text{Rh}$ using a specially
81 designed electrochemical cell [15] during the first desodiation-sodiation and subsequent des-
82 odiation cycle. The measurements were performed with the source and sample at room
83 temperature with a triangular velocity waveform in the classical transmission geometry. A
84 $\text{NaI}(\text{Tl})$ scintillation detector was used for the detection of the γ -rays.

85 **2.3 Simultaneous Nuclear forward scattering and synchrotron X-** 86 **ray diffraction**

87 The *operando* NFS measurements were carried out at the nuclear resonance beamline ID18
88 of the European Synchrotron Radiation Facility.[16] Both the NFS and the XRD data were
89 measured at the nuclear resonance energy (*i.e.*, about 14.412 keV) [17] related to the first
90 excited state of ^{57}Fe . The NFS measurements utilised the time delayed nuclearly scattered
91 radiation, which was registered with a stack of 4 avalanche photodiode detectors [18]. The
92 time dependence of the NFS signal was detected between 15 and 160 ns after the arrival of
93 an X-ray pulse, which in the 16 bunch operating mode of ESRF arrives every 176 ns. In this
94 study each NFS spectrum was measured for about 7 minutes. Between two consecutive NFS
95 spectra, a transmission X-ray diffraction (XRD) pattern was collected using the prompt elec-
96 tronically scattered 14.412 keV radiation (corresponding to a wavelength of 0.860 Å), which
97 was registered using a MAXIPIX position sensitive detector [19]. Each XRD pattern was
98 measured for about 5 seconds.

99 2.4 Electrochemical cycling

100 Both Mössbauer spectroscopy and simultaneous NFS-XRD experiments were carried out
101 using a specifically designed *in situ* cell with two Be windows (with negligible Fe contami-
102 nation, checked beforehand by conventional Mössbauer spectroscopy) allowing experiments
103 in the transmission mode previously described elsewhere.[15] The cell was assembled in an
104 argon-filled glove-box with a NaFeO₂ positive electrode, a Whatman QM-A quartz fiber
105 separator and a sodium disc counter-electrode, using 1 M NaClO₄ in propylene carbonate
106 (PC) with addition of 5 % fluoroethylene carbonate (FEC) as the electrolyte. Galvanostatic
107 cycling with potential limitation was performed using a Biologic-VSP potentiostat at a C/n
108 rate (expressed as 1 mol of Na reacted in n hours per mole of NaFeO₂).

109 2.5 Chemometric data analysis

110 The complete *operando* Mössbauer spectroscopy, NFS and XRD datasets were analysed
111 by combining Principal Component Analysis (PCA) and Multivariate Curve Resolution-
112 Alternating Least Squares (MCR-ALS) analysis (more details about the application of these
113 methods to *operando* data are given in ref. [20] and, for this specific case, fig. S2). The
114 MCR-ALS analysis for Mössbauer data set was carried out with the following constraints:
115 non-negativity of the concentration of the components and closure (sum of the components
116 concentrations equal to 100%). For the MCR-ALS analysis of NFS the additional constrains
117 of unimodality, as well as the intensity of components 1, 2, 3, 4 were set to be 100% at
118 spectra #1, 15, 20 and 33, respectively. The reconstructed pure spectral components of
119 both techniques were subsequently fitted in a traditional way.

120 The components deriving from the analysis of the Mössbauer spectra were fitted with ap-
121 propriate combinations of Lorentzian lines using the computer program PC-Mos II computer.[21]
122 In this way, hyperfine parameters such as the isomer shift (δ), the electric quadrupole split-
123 ting (Δ), the full line width at half maximum (Γ) and the relative resonance areas (Area)
124 of the different spectral components were determined. The isomer shift scale is referred to

125 α -iron at room temperature. The components deriving from the analysis of the NFS spectra
126 where fitted using the software MOTIF.[22]

127 The same PCA + MCR-ALS procedure was applied to the XRD patterns collected to-
128 gether with NFS using the following constraints: non-negativity of the concentration and of
129 the intensity of the components, and closure (sum of the components concentrations equal
130 to 100%). The cells parameters of the four pure patterns obtained in this way were refined
131 using the Le Bail method (see SI for more information).[23]

132 **3 Results**

133 The results shown in the following of the article were obtained in two separate *operando* ex-
134 periments: a first conventional ^{57}Fe Mössbauer spectroscopy analysis, and a second synchrotron-
135 based simultaneous NFS and XRD study. The results of these investigations are reported in
136 the following sections and then critically discussed together.

137 **3.1 *Operando* Mössbauer Spectroscopy**

138 The evolution of *operando* ^{57}Fe Mössbauer spectra during first desodiation up to 3.5 V,
139 sodiation down to 2.0 V and subsequent desodiation up to 3.8 V of NaFeO_2 and corresponding
140 electrochemical signature are depicted in Fig. 1. PCA applied to the entire *operando* data
141 set indicates that it can be reproduced by 3 orthogonal vectors (see SI for more details).

142 The analysis of these data required three spectral components (see SI for more details)
143 thus excluding a biphasic reaction mechanism. Their concentration profile, see Fig. 2, reveals
144 that component 1 is dominant at the pristine state, then completely fades away during
145 electrochemical charge and reemerges at the end of discharge (EOD) to become primary
146 component again. This reflects the high reversibility of the reaction when the voltage cut-
147 off is limited to 3.5 V, as the pristine state is largely recovered after one complete cycle.
148 Component 3 is the majority component at the end of first and second charge (EOC) reaction

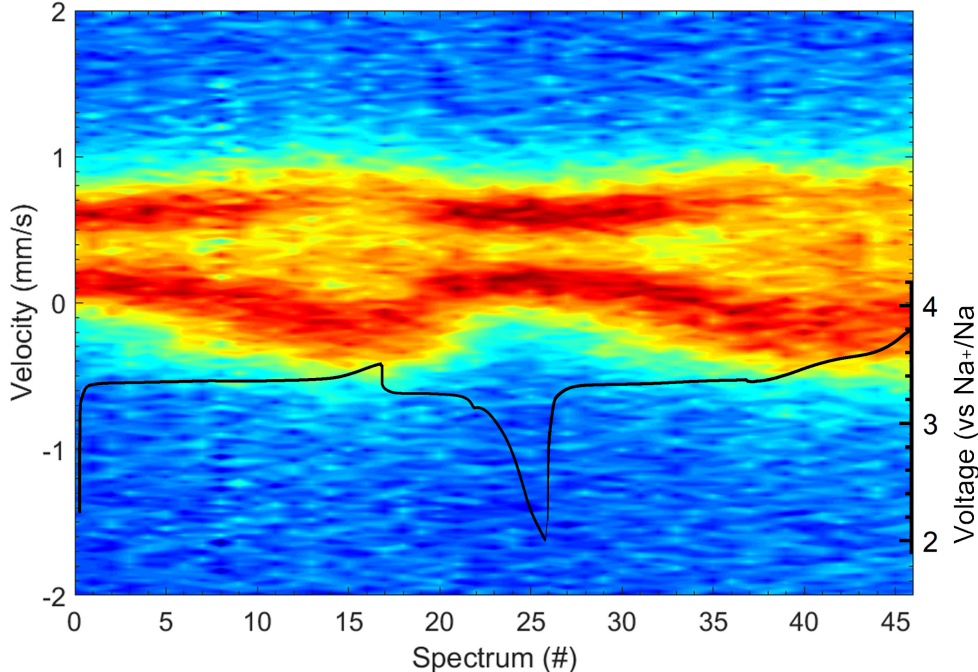


Figure 1: Evolution of *operando* ^{57}Fe Mössbauer spectra overlain with corresponding electrochemical cycling curve. First desodiation up to 3.5 V, sodiation and second desodiation reaction up to 3.8 V of NaFeO_2 vs. sodium.

149 (spectra #15 & #39). Interestingly, about halfway through each desodiation reaction step,
 150 component 2 culminates and then decreases again.

151 The three pure components obtained via MCR-ALS were fitted in the conventional way,
 152 the corresponding hyperfine parameters are reported in Tab. 1, and the fits are shown in Fig.
 153 3. Component 1 corresponds to the starting component and can be fitted in straightforward
 154 fashion using single species contribution of Fe(III) with a relatively narrow quadrupole split-
 155 ting Δ ($\approx 0.5 \text{ mm s}^{-1}$), well in line with literature values [2, 8]. Component 2 corresponds
 156 to the phase mix that is formed upon first and subsequent desodiation and consists of two
 157 species. Firstly, a majority of Fe(III) contribution with a larger quadrupole splitting (Δ)
 158 than observed in component 1. According to the bilinear nature of the MCR-ALS approach,
 159 this can be interpreted as either the formation of a new phase of Fe(III), or more likely a
 160 gradual increase of the Δ in the Fe(III) phase. Secondly, the apparition of a Fe(IV) minority
 161 species at significantly lower isomer shift (δ) is evinced. Component 3, which corresponds to

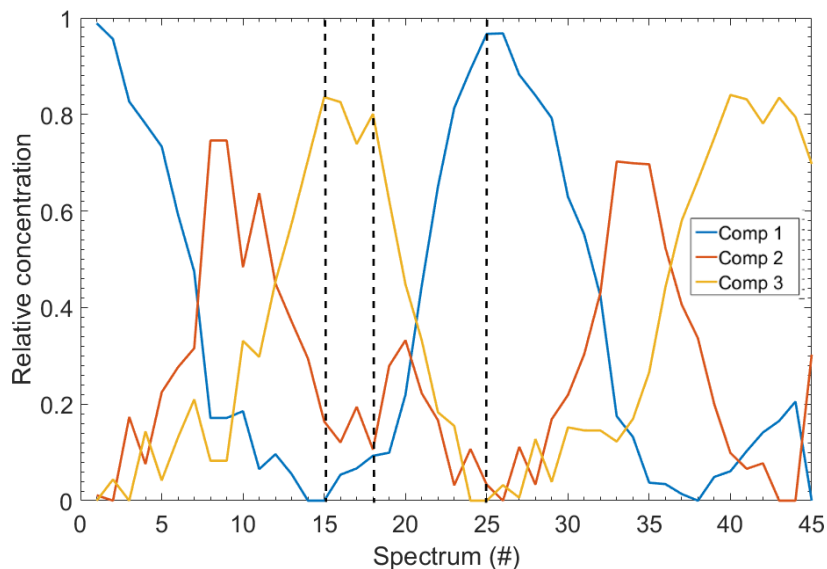


Figure 2: Concentration profile of MCR-ALS components during first 1.5 cycle of NaFeO_2 vs. Na . Dotted lines indicate end of charge (EOC) at #15, begin of discharge (sodiation) at #18 and end of discharge (EOD) at #25 followed by second charge (desodiation) up to 3.8 V.

162 the end of discharge, after completion of one electrochemical cycle can be fitted using same
 163 species as for component 2, however, with further increased quadrupole splitting Δ for both
 164 Fe(III) and Fe(IV) species. Such a strong increase in Δ was previously observed in *ex situ*
 165 Mössbauer studies and has been attributed to the distortion of the FeO_6 octahedra during
 166 desodiation [2, 11].

167 The gradual rise of the quadrupole splitting of the Fe(III) species and the simultaneous
 168 increase of the average oxidation state upon charge, and its reversion upon discharge are
 169 depicted in Fig. 4. It should be noted that quadrupole splitting of Fe(IV) species follows a
 170 similar trend as observed for Fe(III).

171 The evolution of the Mössbauer spectra beyond spectrum #38 is particularly interest-
 172 ing as they reflect the transformation of the cathode material upon oxidation above 3.5 V,
 173 surpassing the region of stable cycling $x \leq 0.5$. The electrochemical cycling curve reveals an
 174 additional plateau at ≈ 3.6 V followed by a steep slope. The chemometric analysis reveals
 175 that component 3 which reflects the formation of Fe(IV) is reaching its maximum at spectra
 176 #39. Interestingly, no further intensity increase of component 3 upon further forced oxida-

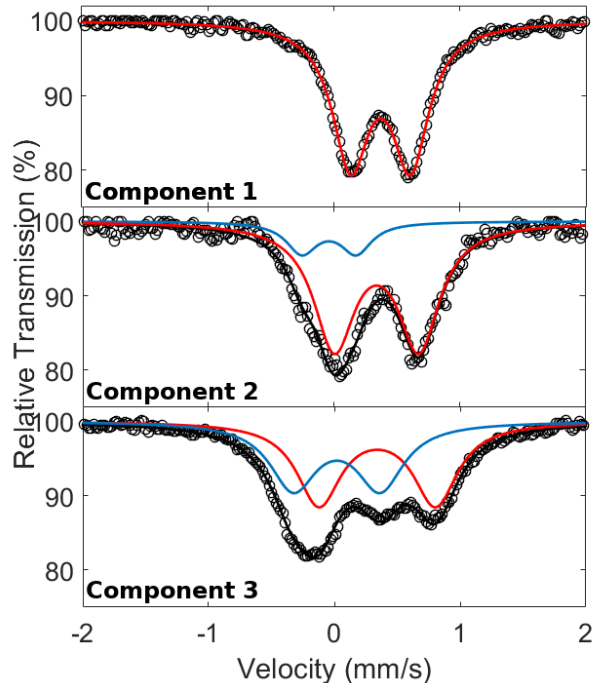


Figure 3: Mössbauer fits of pure components obtained via MCR-ALS for component 1 (pristine), component 2 (intermediate), and component 3 (EOC) in the top, centre, bottom, respectively.

177 tion is noticed. This suggests that the formation of Fe(IV) does not proceed beyond the 0.5
 178 sodiation threshold, which is also reflected by the stagnation (and even a slight decrease) of
 179 the average oxidation state in Fig. 4. We can therefore conclude that the capacity obtained
 180 beyond 3.5 V is not linked to the $\text{Fe}^{+3/+4}$ redox couple. These results comfort those of Su-
 181 santo *et al.*, who showed by *in situ* X-ray absorption spectroscopy that oxygen redox activity
 182 is responsible for charge compensation above 3.5 V, when more than 0.5 Na is extracted from
 183 the structure. They also suggested the formation of Fe_3O_4 caused by oxygen release at high
 184 voltage. In spite of a slight decrease of the average oxidation state, however, this observation
 185 could not be confirmed by our *in situ* data, since no clear formation of Fe(+II) species was
 186 detected.

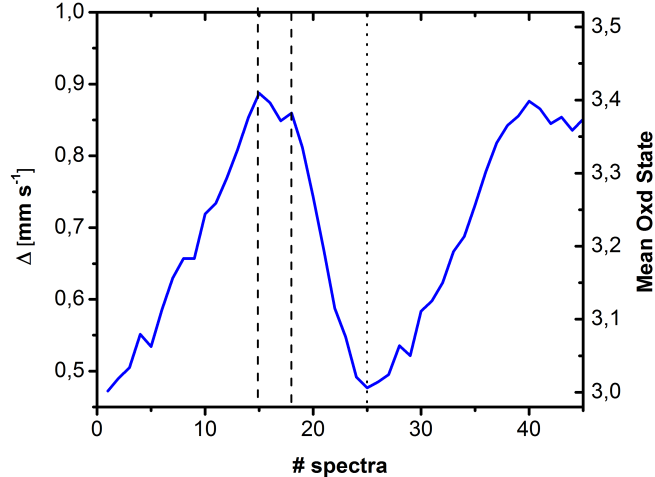


Figure 4: Evolution of Fe(III) quadrupole splitting (Δ) and Fe mean oxidation state during first 1.5 cycle of NaFeO_2 vs. Na. Dashed lines mark the end of first charge and the begin of first discharge at spectra # 15 and # 18 respectively. The dotted line at spectra # 25 indicates end of one complete electrochemical cycle.

187 3.2 Simultaneous Nuclear Forward Scattering and X-ray Diffraction 188 tion

189 *Operando* NFS spectra and XRD patterns were simultaneously collected during first charge
190 (desodiation) reaction up to 4.8 V, acquiring a total of 33 pairs of spectra and patterns
191 (Figure 5). The NFS and XRD data sets were analysed via the chemometric approach
192 implying PCA and MCR-ALS; in analogy with the analysis of the Mössbauer dataset (*vide*
193 *supra*).

194 In contrast to Mössbauer spectroscopy, four independent components were identified

Table 1: ^{57}Fe Mössbauer parameters of the components derived from the MCR-ALS analysis.

Component	Species	Δ [mm s $^{-1}$]	δ^* [mm s $^{-1}$]	Γ [mm s $^{-1}$]	Area [%]
MCR#1	Fe(III)	0.47(1)	0.37(1)	0.35(1)	100
MCR#2	Fe(III)	0.67(1)	0.34(1)	0.40(1)	84(1)
	Fe(IV)	0.43(1)	-0.04(1)	0.30**	16(1)
MCR#3	Fe(III)	0.93(1)	0.34(1)	0.43(1)	54(1)
	Fe(IV)	0.69(1)	0.02(1)	0.45(1)	46(1)

* Isomer shift values are given relative to α -Fe at RT.

** Values without errors were fixed during the fit.

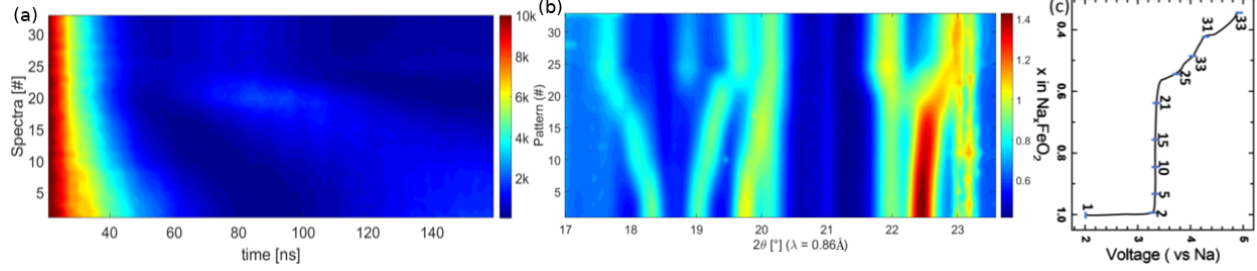


Figure 5: Evolution of (a) NFS spectra and (b) XRD pattern during first charge (desodiation) of NaFeO_2 up to 4.8 V vs. Na^+/Na . The NFS scattering intensity is plotted in logarithmic scale, the wavelength of angular scale is 0.86 \AA . Graph (c) shows the corresponding *operando* electrochemical signature with markers for consecutively numbered data acquisition points.

195 via principal component analysis for both NFS and XRD (see SI for more details). Their
 196 respective concentration profiles are depicted in Fig. 6.

197 Component 1 reflects the pristine state of the material, whereas component 4 represents
 198 the EOC state. Component 2, and 3 are intermediate compositions. The obtained pure
 199 NFS components, shown in Fig. 7, were fitted in the conventional manner as normal NFS
 200 spectra, and the corresponding hyperfine parameters are shown in Tab. 2.

Table 2: Iron NFS fitting parameters of the MCR-ALS components.

Component	Species	Δ [mm s^{-1}]	$\Delta(\delta)$ [mm s^{-1}] [*]	Γ [mm s^{-1}]	Angle [$^\circ$] ^{**}	Area [%]
MCR#1	Fe(III)	0.54(1)		0.35(2)	62.8(2)	100
MCR#2	Fe(III)	0.780(2)	0.415(8)	0.43 ^{***}	53.6(8)	82(2)
	Fe(IV)	0.50(4)		0.39 ^{***}		18(2)
MCR#3	Fe(III)	0.98(3)	0.36(3)	0.41(2)	58(2)	72(4)
	Fe(IV)	0.63(11)		0.44(3)		28(4)
MCR#4	Fe(III)	1.018(3)	0.328(2)	0.51(1)	60.0(5)	50(1)
	Fe(IV)	0.77(1)		0.39 ^{***}		50(1)

* Absolute value of difference in isomer shifts between two species.

** Angle refers to preferential orientation indicating texture effect.

*** Values without errors were fixed during the fit.

201 Component 1 can be fitted in a straight forward manner containing a single species with
 202 a quadrupole splitting (Δ) slightly higher than that observed by Mössbauer spectroscopy
 203 (MS) attributed to Fe(III), see Table 1. The other three NFS MCR components could be
 204 fitted only assuming the presence of two species with different isomer shifts. It must be

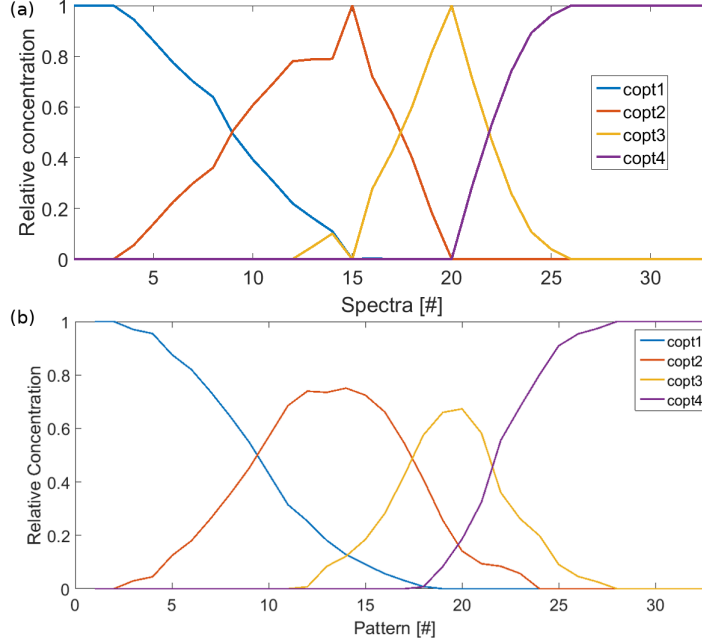


Figure 6: Concentration profile of (a) NFS and (b) XRD MCR-ALS components during first charge (desodiation) of NaFeO_2 vs. Na.

205 noted that, in contrast to MS, NFS features no reference for the isomer shift and thus only
 206 differences in isomer shift between components can be measured, but not the isomer shift
 207 itself with reference to, *e.g.*, the source or α -iron).[24].

208 Analogous to Mössbauer spectroscopy results, a continuous increase in quadrupole split-
 209 ting of both species upon desodiation reaction is observed. The reported absolute value
 210 of difference in isomer shift ($\Delta(\delta)$) of $\approx 0.4 \text{ mm s}^{-1}$ for component 2 and of 0.33 mm s^{-1}
 211 for component 4 are in good agreement with the differences in isomer shift of the spectral
 212 contributions of Fe(III) and Fe(IV) observed in the conventional Mössbauer spectra for the
 213 intermediate and the EOC components, which confirms the formation of Fe(IV) upon des-
 214 odiation. The concentration profile shows a flat plateau for the intensity of component 4
 215 (Figure 6) beyond spectrum #25, which coincides with a voltage above 3.5 V. This indicates
 216 that no significant changes occur to the iron doublets beyond this point. This observation is
 217 well in line with the findings of Mössbauer spectroscopy (*vide supra*) for the second charge
 218 reaction surpassing 3.5 V corresponding to spectrum $\geq \#35$.

219 For the linewidth (Γ) of pristine material (Component 1) a value of 0.35 is found which

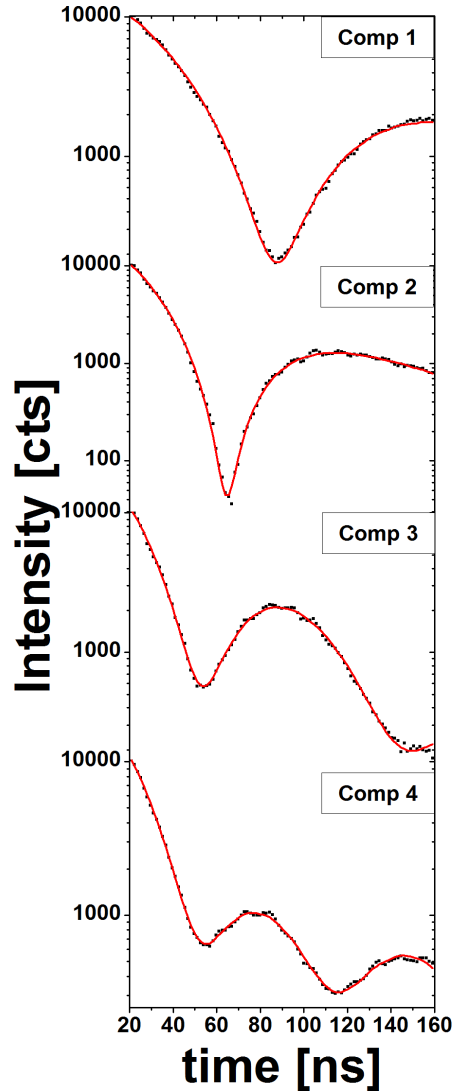


Figure 7: Fitted NFS MCR-ALS pure components during desodiation reaction of NaFeO_2 . Black points and red lines are the pure components and the fitted data respectively.

220 stems almost exclusively from the effective sample thickness. For the intermediate compo-
 221 nents 2 and 3 elevated (Γ) values of $\approx 0.4 \text{ mm s}^{-1}$ are obtained, well in agreement with
 222 component 2 of MS. At EOC, the Fe(III) contribution has a slightly higher linewidth com-
 223 pared to that observed by Mössbauer spectroscopy, which might be attributed to an in-
 224 creased disorder in the material causing a distribution of Fe(III) sites with slightly different
 225 quadrupole splittings. Nevertheless, these fitting parameters must be taken with care as
 226 linewidth strongly correlates with area weight and quadrupole splitting values.

227 For the angle parameter which expresses the preferential orientation effect in the material,

228 similar values are obtained for all components with the exception of component 2, suggesting
229 that upon desodiation the electric field gradient in the nascent phase containing Fe(IV) has
230 a slightly different preferential orientation from that of pristine NaFeO₂. As the reaction
231 continues this difference fades out.

232 The evolution of the simultaneously acquired *operando* synchrotron XRD patterns upon
233 desodiation of NaFeO₂ is also shown in Fig. 5(b). It depicts features at 18.31°, 19.03° and
234 19.06° corresponding to the (006), (101), (012) lattice planes of NaFeO₂, respectively. The
235 evolution of (003) plane XRD feature at low angle 9.12° is shown in Fig. S3.

236 Analogously to NFS and MS, the XRD dataset was analysed by the chemometric ap-
237 proach using PCA and MCR-ALS, which yield four pure components (shown in Fig. S4)
238 with the concentration profiles upon desodiation presented in Fig. 6(b). The concentration
239 profiles are almost identical to those of NFS in terms of occurrence and succession of pure
240 components. The four pure XRD patterns were refined using the Le Bail method (the refined
241 cell parameters are given in Tab. S2).

242 The first two components could be refined using the $R\bar{3}m$ space group ($O3$ -type), whereas
243 the last two had to be refined within the monoclinic $C2/m$ space group, designated as the
244 $O'3$ phase and typical of the partially desodiated Na_{0.5}FeO₂.^[2] The electrochemical process
245 seems to occur through a sequence of a monophasic-biphasic-monophasic regions. The first
246 two components, in fact, can be linearly combined to represent the first solid solution $O3$
247 domain, the first one representing pristine Na_{0.5}FeO₂ and the second one of the same structure
248 but with a decrease. The $O3 \rightarrow O'3$ transition is observed at about halfway through the
249 charge process, and is followed by a second solid solution $O'3$ domain which can be obtained
250 through the combination of components #3 and #4.

4 Discussion

The reversible extraction and insertion of Na from the NaFeO_2 was thoroughly monitored by *operando* Mössbauer spectroscopy and for the first charge by combined *operando* NFS-XRD. All these techniques go hand in hand, revealing the progressive oxidation of Fe(III) to Fe(IV) upon first charge. Moreover, the trend of increasing quadrupole splitting for the two iron species is mutually reflected by MS and NFS. This observation suggests an increasing distortion of the local iron environment upon extraction of sodium from the host structure. Analogously, the two techniques reflect that the electrochemical charge transfer above 3.5 V, revealed by their corresponding cycling curve, is not linked to the $\text{Fe}^{+3/+4}$ redox couple. Whether these irreversible oxidation reactions are linked to electrolyte degradation or anodic charge contribution, as recently proposed [10], cannot be answered with certainty based on our findings. Nevertheless, the formation of iron species with higher oxidation states can most certainly be excluded, in line with the findings of previous works. The increasing distortion upon oxidation is also reflected by the *operando* XRD pattern measured simultaneously with the NFS spectra. In this case, the process consists of a first solid solution domain, implying a slight decrease of the cell volume, followed by a biphasic $O3 \rightarrow O'3$ transition which occurs at about halfway through the extraction of the first 0.5 Na, *i.e.*, at a composition around $\text{Na}_{0.75}\text{FeO}_2$. This transition is followed by a further solid solution domain which ends with the extraction of 0.5 Na.

Interestingly, the application of chemometric tools to the two spectroscopic datasets leads to different number of principal components for describing the same oxidation process. The reason for this could be the more favourable signal-to-noise ratio of NFS technique compared to conventional lab-scale Mössbauer spectroscopy. Indeed, NFS data are intrinsically noise-free and do not suffer from the broadening of the experimental linewidth, which in conventional MS is the convolution of the linewidths of the source and of the absorber: in fact, the linewidth measured in NFS is that of the sample alone.

Consequently, to describe the gradual transformation of Fe(III) to Fe(IV) and their steady

278 increase in quadrupole splitting an additional component is needed for NFS data set. There-
279 fore, NFS allows an improved discrimination of unresolved superimposed quadrupole dou-
280 blets compared to conventional MS under similar experimental conditions.

281 Moreover, NFS allows for faster data collection and is particularly valuable when the
282 concentration of Mössbauer active nuclei is low, when the size of the sample is particularly
283 small (down to fractions of mm) or thin, and when the acquisition time is limited by the
284 experimental framework as it is usually the case for *operando* measurements [25]. The
285 collection of spectra in very short times permits capturing different instants of the reaction,
286 while Mössbauer spectroscopy, collected over longer times, produces less spectra averaged
287 over longer process fractions, and thus a lower resolution of the whole mechanism. The same
288 is true for XRD, which thanks to the intensity of the synchrotron source provides a very
289 good description of the redox process in relatively short measurement times.

290 In this regard the findings are well in line with our previous study on iron-based electrode
291 materials in which the use of synchrotron source allowed a noticeably reduced acquisition
292 time thanks to strongly reduced background noise compared to lab based source.[26]

293 5 Conclusion

294 In this paper, we show that Mössbauer spectroscopy and NFS are both suitable techniques
295 to follow closely the redox reaction at the iron centres during desodiation and sodiation of
296 NaFeO_2 . By applying a chemometric approach for data analysis, combining PCA with MCR-
297 ALS, it was shown that the oxidation reaction going along with the gradual extraction of
298 sodium from the host structure involves only Fe(III) and Fe(IV) species up to the extraction
299 of half of the sodium. After this point, the oxidation processes occurring at voltage above
300 3.5 V are not linked to the $\text{Fe}^{3+/4+}$ redox couple, in line with previous works suggesting the
301 presence of anionic redox activity during the second part of the process. Ancillary XRD
302 analyses, measured simultaneously with NFS, show that the redox reaction implies at least

303 three redox processes, *i.e.*, solid solution, biphasic and again solid solution. By comparing
304 conventional Mössbauer spectroscopy and synchrotron-based NFS results, it is demonstrated
305 here that the latter has greater accuracy for identifying characteristics of iron doublets.

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316 **Supporting Information Available**

317 Characterisation of pristine NaFeO₂; Principal Component Analysis of the *operando* Möss-
318 bauer spectroscopy, NFS and XRD data; *Operando* XRD data analysis.

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