## **Supporting Information**

## An in situ structural study on the synthesis and decomposition of LiNiO<sub>2</sub>

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"NiO" (mixture with LiOH in capillary)

 $R_{Bragg} = 3.54 \%$ 

S.G. : Fm-3m; Z = 4

	a = 4.134 V = 70.66	$\chi^2 = 9.94$					
	Atom	Wyckoff position	Atomic position			SOL	D
			x/a	y/b	z/c	30F	D <sub>iso</sub>
•	0	4b	0.5	0.5	0.5	1	0.60(2)
-	Ni	4a	0	0	0	0.78(6)	0.60(2)
	Li	4a	0	0	0	1-0.78(6)	0.60(2)

**Figure S1.** Top: On the left, Rietveld refinement of a synchrotron X-ray diffraction pattern of a mixture of Ni(OH)<sub>2</sub> + LiOH·H<sub>2</sub>O, pre-annealed at 350 °C for 12 h. The sample was measured in capillary on MSPD. On the right, comparison of synchrotron X-ray diffraction patterns of a pristine NiO obtained from Ni(OH)<sub>2</sub> (blue) and of "NiO" obtained from pre-annealing of the Ni(OH)<sub>2</sub> + LiOH·H<sub>2</sub>O mixture (red). Bottom: Table with refinement results for Li<sub>1-v</sub>Ni<sub>v</sub>O.



**Figure S2.** Picture of the sample environment allowing gas flow through a powder-filled capillary. The hot-blower heats the capillary from the top while the X-ray beam is orthogonal to the plane of the paper.



**Figure S3.** Top: Rietveld refinement of a synchrotron X-ray diffraction pattern of pristine LiNiO<sub>2</sub> prepared in BELLA and measured in capillary on MSPD. Bottom: Table with refinement results.



**Figure S4.** In situ synchrotron X-ray diffraction during synthesis of  $LiNiO_2$  from a mixture of  $Ni(OH)_2$  and  $LiOH \cdot H_2O$ . The contour plots (in the 2 $\theta$  region 12-18°) show the evolution of Bragg reflections with heating, divided in 5 main steps. The box above each contour plot shows the diffraction patterns taken at given times and represents horizontal cuts through the contour plot.

## Details on the Rietveld refinement.

Parameters during in situ synthesis experiment.

- Zero shift: Refined in the initial scan while keeping the unit cell parameters of LiOH and NiO fixed to values found from capillary measurement (Figure S1), then fixed throughout.
- Background: Taken point-by-point by hand to account for peculiar shape due to quartz glass contribution. Not refined afterwards. Only exception is at 66 minutes, when the background was observed to drift suddenly (likely due a small change in capillary filling after LiOH complete melting), so a new background point-by-point was taken. The shape of the background can be seen in Figure 4.
- Scale factors (thus phase fractions) between the different phases were always freely refined. Only exception is the NiO phase; when it reached a wt.-% < 5% (t = 120 min), it was subsequently set to zero to avoid software divergence and allow for single-phase sequential refinement of LiNiO<sub>2</sub> (wt.-% > 95%).
- Unit cell parameters of LiOH (*a*, *c*), NiO (*a*) and LNO (*a*, *c*) were always freely refined.
- For LiOH, z of oxygen was refined.
- For NiO, no fractional atomic coordinate can be refined due to the cubic symmetry. We refine the SOF of Ni constraining full site occupancy, such as Li<sub>1-y</sub>Ni<sub>y</sub>O. Detailed behavior is discussed in the main text.
- For each phase, isotropic Debye Waller factors are refined as a unique value for all atoms, B<sub>iso\_</sub>all, in order to reduce the amount of free parameters in the refinement. B<sub>iso\_</sub>all is fixed for phases with wt.-% < 10%. Typical values (Å<sup>2</sup>) found are 2.2 (25 °C) < B<sub>iso\_</sub>all(LiOH) < 3 (430 °C), 0.5 (25 °C) < B<sub>iso\_</sub>all(NiO) < 1.1 (700 °C) and 0.55 (25 °C) < B<sub>iso\_</sub>all(LiNiO<sub>2</sub>) < 1.5 (700 °C).</li>
- In LNO,  $z_{ox}$  is refined only when wt.-%<sub>LNO</sub> > 50% (strong overlap with NiO peaks). The site occupancy factors are instead only refined when the material becomes single phase.
- A Thompson-Cox-Hastings pseudo-Voigt (with axial divergence asymmetry) peak shape was used to model Bragg peaks (Npr = 7). In general, U, X, Y, GauSiz are refined to account for peak broadening. Since the instrumental peak broadening was obtained by measuring a NAC reference sample, V and W were held fixed. However, often only a subset of U, X, Y, GauSiz was necessary to account for the observed peak shapes, while still keeping the amount of refined parameters low.

As shown in **Figure 4**, LNO suffers from anisotropic peak broadening when crystallizing at low temperature, which is then relieved during the annealing. In principle, methods to account for it exist in Fullprof (size + strain broadening) and it would be possible to improve the fit by exploiting our understanding of the peculiar broadening rule selections (see main text and figure S6). However, due to the many coexisting phases and overlapping peaks of NiO and LNO at low T, and to the need to batch process most of the data, we preferred not to use any correction for anisotropic broadening. Although this clearly meant lower R<sub>bragg</sub> values obtained for LNO, it also allowed the number of refined parameter to remain reasonable and especially

to not artificially give an advantage (more available parameters) to the LNO phase during the NiO/LNO transformation.



**Figure S5.** Quality indicator  $\chi^2$  of the Rietveld fit and R<sub>bragg</sub> for each phase for the whole synthesis dataset. Smooth variations are mostly due to batch processing of the Rietveld fits, while jumps indicate that the input file for refinement was changed (for example adding or removing a phase), thus resulting in a discontinuous behavior.

## a) no size broadening



b) l = 2n+1 selective size broadening



**Figure S6.** Rietveld refinement of a synchrotron X-ray diffraction pattern of pristine LiNiO<sub>2</sub> synthesized in BELLA at 550°C for 12 h (rather than the typical 700 °C) and measured in capillary on MSPD. a) refinement performed with standard isotropic peak broadening (we use in Fullprof I.R.F. file + refinement of U, X, Y, GauSiz) b) refinement performed with anisotropic size broadening contribution with selective rule for (*hkl*) set to l = 2n+1, n = 0, 1, 2, ... (Size-Model = -2 in Fullprof). Note that many anisotropic size and/or strain broadening options implemented in Fullprof were tested to fit the diffraction data but all results in unsatisfactory fitting results.



**Figure S7.** Rietveld refinement of XRD data during *in situ* synthesis. Only one data point out of every 2 is shown for clarity. Evolution of crystalline phases (in wt.-%). In the left part, the temperature axis is used and time values are provided below. In the right part, the temperature is constant (annealing) and the time axis is used.



**Figure S8.** Total amount of Li and Ni obtained from Rietveld refinement of XRD data during *in situ* synthesis. The data points show the sum of the Li (and Ni) content in any phase. Ideally, 1.01 mol of Li and 1 mol of Ni is present in the powder mixture. The missing Li is calculated as 1.01-Li. Shaded areas represent error bars. The missing Li can be used to estimate the amount of liquid LiOH.



**Figure S9.** Evolution of  $z_{ox}$ , the fractional atomic coordinate z of oxygen in LiNiO<sub>2</sub>. The jump at 120 min is related to the disappearance of the cubic precursor phase, which was forced in the refinement when its wt.-% became <5%.



**Figure S10.** Top: Mol.-% of LNO as a function of time. The time axis is rescaled to set t = 0 at  $\vartheta$  = 350 °C, i.e., close to the beginning of LNO formation. Bottom: Plot of  $\ln(-\ln(1-Mol\%_{LNO}) vs \ln(t))$ . According to the Johnson-Mehl-Avrami-Kolmogorov, or JMAK, equation for solid-state phases transforming into one another at constant temperature, the above plot should be linear with slope *n* related qualitatively to the kind of nucleation + growth mechanism. We only fit the final region of the curve (region 4 in the paper), as it is the only region where the assumptions of the JMAK model are reasonably met. For n = 2, the growth would be bidimensional without nucleation.



**Figure S11.** Evolution of unit cell volume and *c*/*a* as a function of the off-stoichiometry *z*. Linear relationships are found.



**Figure S12.** a) Contour plot showing the Bragg peaks observed in the 5.5-9.5° 20 region and their evolution over time. Bragg peaks of LNO are not present in such range. Calculated Bragg peaks of  $Li_4SiO_4$  as obtained from ICSD-35169 ( $P2_1/m$ ) are reported (red line). b) wt.-% and unit cell volume of  $Li_4SiO_4$  from Rietveld refinement analysis. Only one data point out of every 3 is displayed for clarity.