SUPPLEMENTARY INFORMATION

From LiNiO₂ to Li₂NiO₃: synthesis, structures and electrochemical mechanisms in Li-rich nickel oxides

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Table S1. Site occupancies used to const	ruct the cation-disordered $Li_2NiO_{2.875}$ supercell.

Atoms	Wyckoff position	Occ	_
Ni	4g	0.75	
Li _{Ni}	4g	0.25	
Li	2b	0.5	
Ni _{li}	2b	0.5	
Li	2c	1	-
Ni _{Li}	2c	0	-
Li	4h	1	-
Ni _{Li}	4h	0	-
0	4i	0.875	-
0	8j	1	-

Supplementary note 1: FAULTS refinement.

The refinement of the diffraction data (XPRD and NPD) including stacking faults was done using the software FAULTS. All details about the unit cell and the layers used in the software can be found in ref. [1] and related supplementary material, where Li_2MnO_3 was investigated. Here the salient points are summarized:

- a cell as small as possible has to be used in FAULTS, and with the stacking direction perpendicular to the *ab* plane by default; hence, the unit cell used is redefined as a = b = 4.89323 Å, c = 4.69890 Å, $\alpha = \beta = 90^\circ$, $\gamma = 60.12^\circ$.
- within this cell, two types of layers are defined. Layer 1 (L1) constituted of the lithium atoms of the Li slabs (lithium layer), and layer 2 (L2) containing lithium, nickel and oxygen atoms (Ni_{2/3}Li_{1/3} layer).
- Stacking faults are generated using two extra layers in the model: layer 3 (L3) and layer 4 (L4) that are equivalent to L2 but that are stacked with different stacking vectors in order to introduce P and P' stacking faults. From layer 1, solely transitions to layers 2, 3 and 4 are possible and correspond to R, P and P' stacking, respectively. From layers 2, 3 and 4 there is a unique possible transition to layer 1. The ideal structure is hence built with a L1 → L2 → L1 stacking sequence.
- The initial atomic parameters used for the FAULTS refinement were adapted directly from the output values obtained from the "standard" Rietveld refinement done with Fullprof.
- The NPD data could be fitted simply by a single phase using FAULTS (plus the impurities). The XPRD data instead could not be fitted using a single phase, analogously to what has been reported for Li₂MnO₃ synthesized by MnO. In fact, in that case domains with regular stacking and faulted domains are identified, contributing to two distinct crystallographic phases. In NPD, the angular resolution is not sufficient to distinguish the two phases, which can instead be well separated by XPRD. To deal with this in FAULTS, the unfaulted structure is first obtained from the "standard" Fullprof refinement, and then treated as background with a scale factor while refining the faulted structure.
- For the NPD data, the following parameters were refined simultaneously: unit cell parameters a, c and γ, all refinable atomic positions, Ni/Li mixing in the sites belonging to the Ni_{2/3}Li_{1/3} layer, scale factor, stacking probabilities of layers L2, L3, L4. Debye-Waller factors were fixed to the values found by Rietveld refinement, but a common shift was allowed since FAULTS does not include the effect of absorption from the sample.
- For the XRPD data, the following parameters were refined simultaneously: unit cell parameters a, c and γ, Ni and O refinable atomic positions (not the Li ones due to its low scattering power), Ni/Li mixing in the sites belonging to the Ni_{2/3}Li_{1/3} layer, scale factor (of the main faulted phase and of the defect-free phase), stacking probabilities of layers L2, L3, L4. Debye-Waller factors were fixed to the values found by Rietveld refinement, but a common shift was allowed since FAULTS does not include the effect of absorption from the sample.

The initial structural parameters for the FAULTS refinement are reported in ref. [1] and related supplementary material, and we have used analogous parameters adapted to our Rietveld refinement results.

Likewise, we use the same definition to estimate the degree of defects: it was ranked from 0% (100% of ideal stacking and 0% of each stacking fault) to 100% (33% of each stacking possibility). The degree of defects is then obtained from the following formula: $3/2*[1-(L1\rightarrow L2)]*100$, $L1\rightarrow L2$ being the

probability for the ideal stacking transition, ranked from 1 (ideal structure) to 1/3 (fully defective structure). For the XPRD data treated as two-phase mixture, the formula above is normalized by the respective weight (area of the sub-pattern) of each phase in the refinement. Table S2 and S3 below reports the refined parameter during the FAULTS refinement.

Table S2. FAULTS refined parameters from NPD data.

a = b = 4 c = 4.699 γ = 59.76 V = 97.6 2V = 195	9034(2) 92(3) Å 52(2)° 1 Å ³ 5.22 Å ³	Å		R _P = 5. χ ² = 0.4 Ρ/Ρ΄fai	0737 1969 ults = Degr	ee of defects: 30%
		At	omic positi	on		
Atoms	Layer	x/a	y/b	z/c	B iso	Occup.
Li	L1	0	0	0	1.06	1
Li	L1	0.3474(4)	0.335(2)	0	1.06	0.99 Li, 0.01 Ni
Li	L1	0.6700(8)	0.671(3)	0	1.06	0.99 Li, 0.01 Ni
Ni	L2	0.311(1)	0.3130(5)	0	0.29	0.91(1) Ni, 0.09(1) Li
Ni	L2	0.638(2)	0.6391(4)	0	0.29	0.91(1) Ni, 0.09(1) Li
Li	L2	0	0	0	0.39	0.72(1) Li, 0.28(1) Ni
0	L2	0.323(2)	-0.017(2)	0.2271(9)	0.46	1
0	L2	0.6034(5)	-0.0332(5)	-0.2266(4)	0.46	1
0	L2	-0.0224(6)	0.3264(2)	-0.2268(1)	0.46	1
0	L2	0.329(1)	0.616(1)	-0.2219(3)	0.46	1
0	L2	0.6180(5)	0.3298(4)	0.2213(1)	0.46	1
0	L2	-0.0336(3)	0.6127(1)	0.2270(1)	0.46	1

Li₂NiO₃ FAULTS - Neutrons

a = b = 4.89323(2) Å	R_P = 8.8593
c = 4.69890(3) Å	χ^2 = 37.08
γ = 60.1200(7)°	P/P' faults in faulted phase: 31%
V = 97.553 Å ³	Phases ratio : Faulted 64.17% / Non Faulted 34.75%
2V = 195.106 Å ³	Degree of defects : 20%

Li₂NiO₃ FAULTS - synchrotron

Atoms	Lover	A	Atomic position		P	Occup. (faulted	Occup. (total, including
Atoms	Layer	x/a	y/b	z/c	D _{iso}	phase)	non faulted phase)
Li	L1	0	0	0	0.89	1	1
Li	L1	0.3333	0.3333	0	0.89	0.99 Li, 0.01 Ni	0.99 Li, 0.01 Ni
Li	L1	0.6667	0.6667	0	0.89	0.99 Li, 0.01 Ni	0.99 Li, 0.01 Ni
Ni	L2	0.3399(1)	0.3405(1)	0	0.18	0.90(1) Ni, 0.10(1) Li	0.85(1) Ni, 0.15(1) Li
Ni	L2	0.6609(1)	0.6610(1)	0	0.18	0.90(1) Ni, 0.10(1) Li	0.85(1) Ni, 0.15(1) Li
Li	L2	0	0	0	0.18	0.84(1) Li, 0.16(1) Ni	0.75(1) Li, 0.25(1) Ni
0	L2	0.3718(3)	-0.0005(5)	0.2259(3)	0.60	1	1
0	L2	0.6262(1)	0.0061(4)	-0.2300(1)	0.60	1	1
0	L2	-0.0031(3)	0.3726(1)	-0.2289(1)	0.60	1	1
0	L2	0.3688(3)	0.6315(3)	-0.2117(1)	0.60	1	1
0	L2	0.6255(1)	0.3759(1)	0.2055(1)	0.60	1	1
0	L2	0.0055(2)	0.6268(1)	0.22516(1)	0.60	1	1

Table S4. Data sources for Figure 3a.

Compound	ICSD codes	Additional comments / references
NIO	0000 01010 050010	
NIO	9866, 61318, 259812	
Ni(OH) ₂	169978, 109390	
Li ₂ NiO ₂	71421	
NiF ₂	73726, 9168	
LiNiO₂	174451, 248636, 78687	By XRD, the space group of LNO is <i>R</i> -3 <i>m</i> with 6 equivalent bonds (confirmed by our own work). By EXAFS/PDF and DFT, a local Jahn-Teller distortion is observed, with 2 long and 4 short bonds
		[2-6].
NaNiO ₂	85317, 154172	Cooperative JT distortion.
Na ₃ NiF ₆	26073	
AgNiO ₂	73974, 415451	
NiOOH	230448,	
PrNiO₃	69787	
NdNiO ₃	67725, 24875	
LaNiO₃	67717, 84933	
K ₂ NiF ₆	41416, 6046	
BaNiO ₃	266981, 264690, 175	
Li _{0.1} NiO ₂		H3 phase. Data confirmed by our own work and in [7, 8].
Li ₂ NiO ₃	29337	Data confirmed by our own work.

Atom	perfect Li ₂ NiO ₃	disordered	perfect	disordered
Ni	0.000	0,000	0.001	0.849
Ni	0.000	0.000	-0.016	0.010
Ni	0.000	0.000	0.001	-0.000
Ni	0.000	0.000	-0.016	-0.010
Ni	0.000	0.000	0.004	0.811
Ni		0.000	0.757	0.010
Ni		0.000	0.004	0.003
Ni		0.000	0.757	0.019
0	0.000	0.000	-0.001	0.015
0	0.000	0.000	0.001	-0.001
0	0.000	0.000	0.020	-0.001
0	0.000	0.000	-0.001	-0.001
0	0.000	0.000	0.001	-0.001
0	0.000	0.000	0.000	0.091
0	0.000	0.000	-0.036	-0.003
0	0.000	0.000	-0.001	-0.017
0	0.000	0.000	0.000	-0.005
0		0.000	0.002	-0.001
0		0.000	-0.009	-0.001
0		0.000	0.000	-0.016
0		0.000	-0.009	-0.006
0		0.000	0.000	-0.003
0		0.000	0.000	-0.003
0		0.000	-0.003	-0.040
0		0.000	-0.001	-0.002
0		0.000	0.203	-0.007
0		0.000	-0.007	-0.013
0		0.000	0.001	-0.002
0		0.000	-0.007	-0.004
0		0.000	0.000	0.151
0		0.000	-0.001	0.003
0		0.000	0.204	-0.003
0		0.000		

Table S5. Spin population present on each atom as obtained from the DFT computations (VASP).



Figure S1. Soft XAS spectra of the Ni L3 and L2 edges. Comparison of NiO reference (Ni^{2+}) in grey and $LiNiO_2$ detected in fluorescence yield (bulk, blue) and total electron yield (surface, red). All spectra are normalized in the same way as described in the methods section of the main text.



Figure S2. Rietveld refinement of the synchrotron XRPD pattern of $Li_{1+x}Ni_{1-x}O_2$ (x = 0). The material is indexed to a rhombohedral unit cell. A selective peak broadening according to I = 2n+1 is needed to fit the data, as described in [9] and related SI.

Table S6. Structural parameters obtained from Rietveld refinement of synchrotron XRPD data. Cationic sites are constrained to be full while allowing for Ni/Li site disorder. The overall Li/Ni ratio is fixed to the value of 1.04:1 found by ICP. Isotropic Debye-Waller factors (B_{iso}) were set equal for atoms occupying the same site.

	LiNiO ₂ (Li _{1.02} Ni _{0.98} O ₂)						
S.G.: <i>R</i> -3	3 <i>m</i> , Z = 6		sXRPD				
a = 2.87 c = 14.1 V = 101.	71(1) Å 614(5) Å 521(3) Å ³			$R_{Bragg} = 2.23$ $R_{wp} = 9.59 \%$ $\chi^2 = 7.00$		%	
Atom	Wyckoff	Ato	mic p	osition	505	P	
Atom	position	x/a	y/b	z/c	306	D _{iso}	
0	6c	0	0	0.2599(2)	1	0.80(5)	
Ni	3a	0	0	0	0.961(1)	0.41(1)	
Li	3a	0	0	0	0.039(1)	0.41(1)	
Li	3b	0.5	0.5	0.5	0.981(1)	1.0(-)	
Ni	3b	0.5	0.5	0.5	0.019(1)	1.0(-)	



Figure S3. Rietveld refinement of the synchrotron XRPD pattern of $Li_{1+x}Ni_{1-x}O_2$ (x = 0.1). The material is indexed to a rhombohedral unit cell, like the sample x = 0. A selective peak broadening according to l = 2n+1 is needed to fit the data, as described in [9] and related SI.

Table S7. Structural parameters obtained from Rietveld refinement of synchrotron XRPD data. Cationic sites are constrained to be full while allowing for Ni/Li site disorder. The overall Li/Ni ratio is fixed to the value of 1.12:0.9 found by ICP. Isotropic Debye-Waller factors (B_{iso}) were set equal for atoms occupying the same site.

	Li _{1.1} Ni _{0.9} O ₂ (Li _{1.11} Ni _{0.89} O ₂)						
S.G.: <i>R</i> -3 <i>m</i> , Z = 6					sXRPD		
a = 2.86 c = 14.1 V = 100.	= 2.8666(1) Å $R_{Bragg} = 2.13 \%$ = 14.1178(8) Å $R_{wp} = 12.9 \%$ $\chi^2 = 100.468(3) Å^3$ $\chi^2 = 16.8$			%			
Atom	Wyckoff	Atomic position			605	Р	
Atom	position	x/a	y/b	z/c	301	Diso	
0	6c	0	0	0.2598(3)	1	0.85(7)	
Ni	3a	0	0	0	0.876(1)	0.39(2)	
Li	3a	0	0	0	0.124(1)	0.39(2)	
Li	3b	0.5	0.5	0.5	0.986(1)	1.0(-)	
Ni	3b	0.5	0.5	0.5	0.014(1)	1.0(-)	



Figure S4. Rietveld refinement of the synchrotron XRPD pattern of $Li_{1+x}Ni_{1-x}O_2$ (x = 0.2). The material is indexed to a monoclinic unit cell, like the sample x = 0.33. Superstructure peaks due to stacking faults are shown in the inset.

Table S8. Structural parameters obtained from Rietveld refinement of synchrotron XRPD data. Cationic sites are constrained to be full while allowing for Ni/Li site disorder. Isotropic Debye-Waller factors (B_{iso}) were set equal for atoms occupying the same site.

	Li _{1.2} Ni _{0.8} O ₂ (Li _{1.22} Ni _{0.78} O ₂)	
S.G.: $C2/m$, $Z = 4$ a = 4.9653(4) Å b = 8.4844(6) Å c = 4.9852(5) Å $\beta = 109.417(6)^{\circ}$ V = 198.07(3) Å ³	sXRPD $R_{Bragg} = 8.49\%$ $R_{wp} = 23.6\%$ $\chi^{2} = 55.8$	

A t a ma a	Wyckoff	f Atomic position			0	P
Atoms	position	x/a	y/b	z/c	Ucc	B _{iso}
Ni	4g	0	0.167(1)	0	0.82(2)	0.57(4)
Li _{Ni}	4g	0	0.167(1)	0	0.18(2)	0.57(4)
Li	2b	0	0.5	0	0.42(2)	0.57(4)
Ni _{Li}	2b	0	0.5	0	0.58(2)	0.57(4)
Li	2c	0	0	0.5	0.98(2)	1.0(-)
Ni _{Li}	2c	0	0	0.5	0.02(2)	1.0(-)
Li	4h	0	0.69(-)	0.5	0.95(2)	1.0(-)
Ni _{Li}	4h	0	0.69(-)	0.5	0.05(2)	1.0(-)
0	4i	0.212(6) 0	0.218(8)	1(-)	0.6(2)
0	8j	0.257(4) 0.316(2)	0.221(4)	1(-)	0.6(2)



Figure S5. Voltage curves for a Li_2NiO_3 half-cell cycled at C/25 rate between 1.5 and 4.8 V vs Li^+/Li . The first (dashed black), second (dotted green), third (solid red) and tenth (solid grey) cycles are shown.



Figure S6. Voltage curves for Li_2NiO_3 half cells cycled at C/25 rate (for the preparation of ex situ samples). The cells were cycled to the cutoff voltages given in the figure legend (4.4, 4.65 and 4.8 V during charge, and 3.3 and 2 V during discharge (after an initial charge to 4.8 V)) and kept under potentiostatic conditions for 12 h.

Li2NiO3



Figure S7. Operando XRD during 3 cycles of a Li_2NiO_3 pouch half-cell cycled at C/25 rate. The XRD patterns are measured in transmission, with a counting time of 6 min each. The angular domain 8-9° includes the (001) reflection of Li_2NiO_3 . The other angular domains only show Al peaks from the pouch cell casing and current collector. At 28.6°, a periodic shift of the Al reflection indicates a change in cell thickness.



Figure S8. Electron diffraction pattern of Li_2NiO_3 in its pristine state (a), after 4 electrochemical cycles (b), after 100 cycles (c), and corresponding annular integrated profiles (d). The arrows indicate the reflections of the monoclinic lattice that are absent in the rock salt one.



Figure S9. Synchrotron XRPD of an ex situ sample prepared from Li_2NiO_3 after 100 cycles (in red), as in Figure 9. Other than the main peaks of a rock salt-like phase (red lines) and the extra narrow peaks due to the Al current collectors, broader bumps can be noticed in the background, whose angular positions match (see the blue lines) those of the reflections of a layered phase, $LiNiO_2$ -like (shown in blue), except for a shift indicating a different unit cell volume and hence a different Li/Ni ratio.



Figure S10. Rietveld refinement of the synchrotron XRD pattern collected on an ex situ cathode of a Li_2NiO_3 halfcell cycled at C/25 rate for 100 cycles.



Figure S11. XRD pattern of a rock salt $Li_yNi_{1-y}O$ structure simulated using VESTA. The amount of Li y on the cationic site 4a is varied in the simulation (y = 0, 0.25, 0.5, 0.75), and the strong effect on the intensity of the 111 reflection is shown. The patterns are normalized to the intensity of the 200 reflection.



Figure S12. Galvanostatic intermittent titration technique (GITT) curve of the rock salt-like CAM obtained after 122 galvanostatic cycles of the Li_2NiO_3 pristine material (cycling as in Figure 5). Charge and discharge pulses at a current rate of C/20 were set for 30 minutes, followed by 5 hours of relaxation. The voltage cutoff was 2.2 –

4.8 V. Li diffusivity values are provided, as derived from the classic GITT equation in [10] $(D_{Li^+} = \frac{4}{\pi \tau} \left(\frac{m_B V_M}{M_B A}\right)^2$

 $\left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2$).

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