Supplementary Information

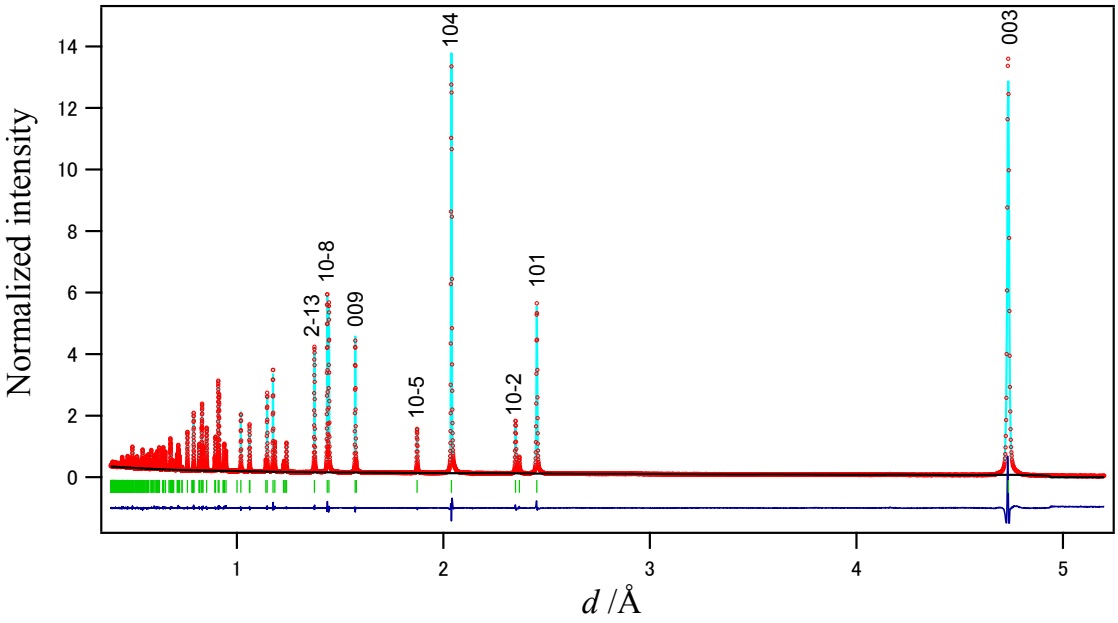
Synthesis of NMC precursors

Table 1: Precursor concentrations of used in the continuous hydrothermal synthesis of NMC precursors for solid-state lithiation.

Sample	$[Ni(NO_3)_2 \cdot 6H_2O]$ (M)	$[Mn(NO_3)_2 \cdot xH_2O]$ (M)	$[Co(NO_3)_2 \cdot 6H_2O]$ (M)	[KOH] (M)
NMC-811	0.4	0.3	0.2	1.0
NMC-622	0.05	0.1	0.15	1.0
NMC-433	0.05	0.1	0.15	1.0

NPD Rietveld refinement data of NMC-811, NMC-622 and NMC-433

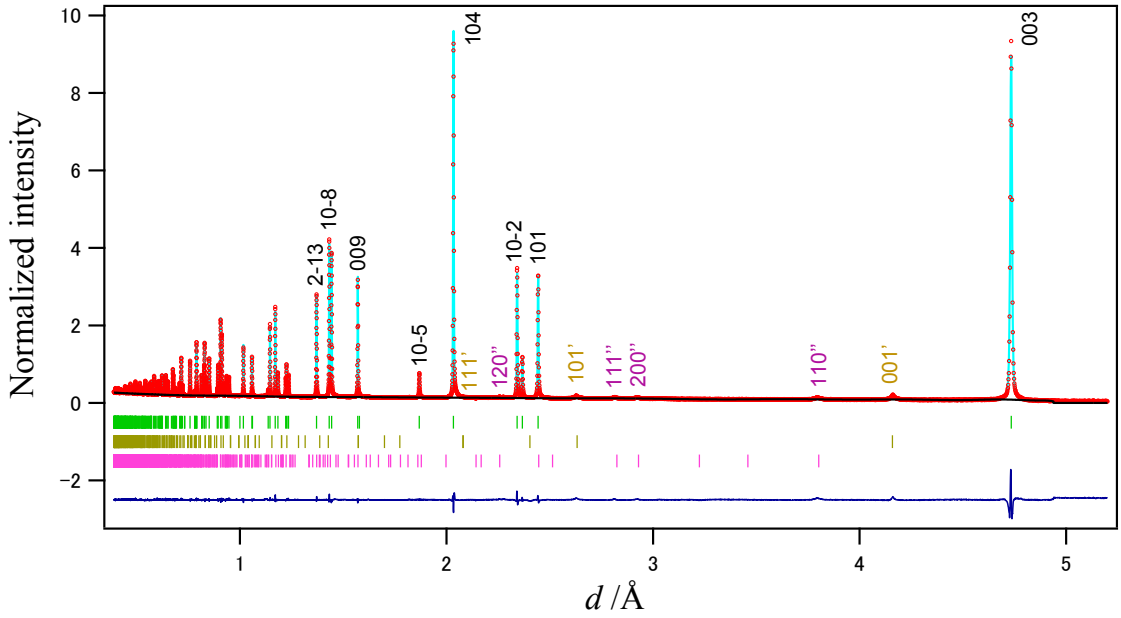
a) NMC-811



◦: Experimental data
-: Calculated data
| : Bragg-peak position (LiMO_2)
-: Difference between experimental and calculated data

	N-001					
	Occupancy	site	*x*	*y*	*z*	B_{iso}
Li1	0.8982(2)	3*b*	0	0	1/2	1.107(7)
Ni2	0.0317(2)	3*b*	0	0	1/2	1.107(7)
Co2	0.11	3*a*	0	0	0	0.3235(9)
Ni1	0.7659(1)	3*a*	0	0	0	0.3235(9)
Li2	0.0240(1)	3*a*	0	0	0	0.3235(9)
Mn1	0.1	3*a*	0	0	0	0.3235(9)
O1	1	6*c*	0	0	0.258872(4)	0.838(1)

b) NMC-622



◦: Experimental data
-: Calculated data
| : Bragg-peak position (LiMO_2)
| : Bragg-peak position (LiOH)
| : Bragg-peak position (Li_2O)
-: Difference between experimental and calculated data

	N-002					
	Occupancy	site	*x*	*y*	*z*	B_{iso}
Li1	0.9643(2)	3*b*	0	0	1/2	0.741(8)
Ni2	0.0356(2)	3*b*	0	0	1/2	0.741(8)
Co2	0.19	3*a*	0	0	0	0.330(1)
Ni1	0.5877(1)	3*a*	0	0	0	0.330(1)
Li2	0.0322(1)	3a	0	0	0	0.330(1)
Mn1	0.19	3*a*	0	0	0	0.330(1)
O1	1	6*c*	0	0	0.259105(4)	0.808(1)

Impurities:

1. LiOH
Space group:*P*4/*nmm*

a=*b*=3.4001(3) Å *c*=4.1597(9) Å

	LiOH					
	Occupancy	site	*x*	*y*	*z*	B_{iso}
Li	1	2*a*	0	0	0	1
H	1	2*c*	1/2	0	0.10(2)	1
O	1	2*c*	1/2	0	0.31(1)	1

2. Li_2O
Space group:*Pnnm*

a=5.8598(1) Å *b*= 4.8938(1) Å *c*=4.286(1) Å

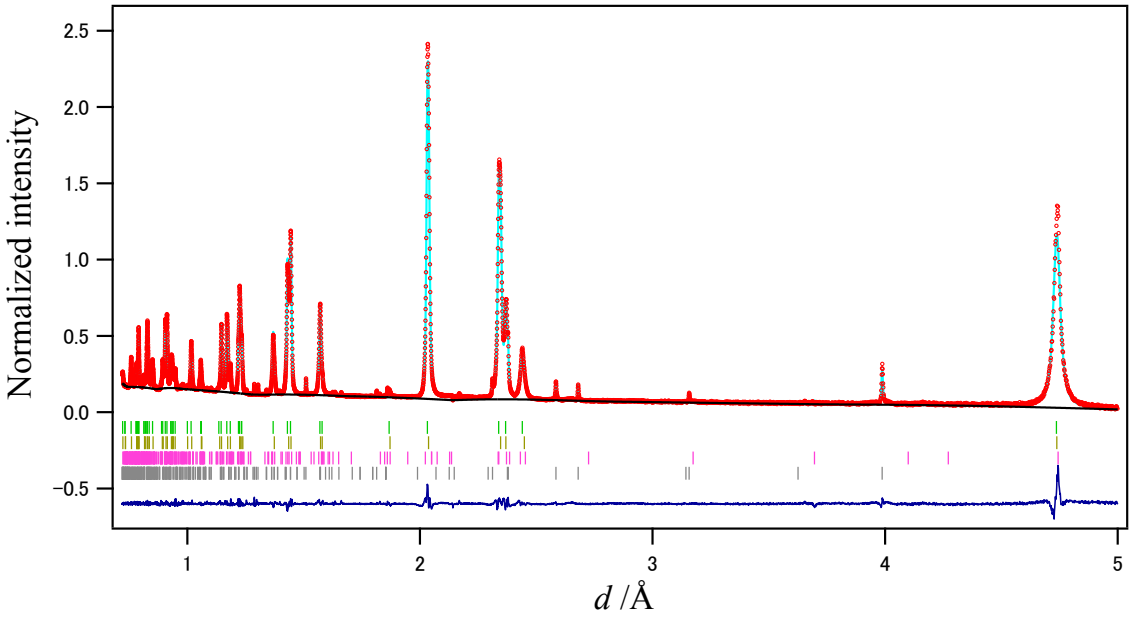
	Li_2O					
	Occupancy	site	*x*	*y*	*z*	B_{iso}
Li	1	2*a*	0	0	0	1
O	1	4*g*	0.212(1)	0.379(1)	0	1

Mass fraction of NMC-622:

Li*M*O_2: LiOH: Li_2O = 94.6% : 4.9% : 0.5%

c) NMC-433
Data: iMATERIA (DF mode), BS bank

Refinement: Model D



◦: Experimental data
-: Calculated data
| : Bragg-peak position (LiMO_2)
| : Bragg-peak position (LiMO_2)
| : Bragg-peak position (Li_2MnO_3)
| : Bragg-peak position (Pawley)
-: Difference between experimental and calculated data

	N-003_phase 1					
	Occupancy	site	*x*	*y*	*z*	B_{iso}
Li1	0.9579(9)	3*b*	0	0	1/2	0.87(5)
Ni2	0.0420(9)	3*b*	0	0	1/2	0.87(5)
Co2	0.25339	3*a*	0	0	0	0.46(2)
Ni1	0.433(1)	3*a*	0	0	0	0.46(2)
Li2	0.050(1)	3a	0	0	0	0.46(2)
Mn1	0.26244	3*a*	0	0	0	0.46(2)
O1	1	6*c*	0	0	0.25946(3)	0.56(1)

Sub-phases and impurities (?) of N003:

1. LiMO_2
Space group: *R*-3*m*

a=*b*= 2.87112(1) Å *c*= 14.2181(9) Å

	N-003_phase 2					
	Occupancy	site	*x*	*y*	*z*	B_{iso}
Li1	0.876(2)	3*b*	0	0	1/2	0.2(4)
Ni2	0.123(2)	3*b*	0	0	1/2	0.2(4)
Co2	0.25339	3*a*	0	0	0	0.33(8)
Ni1	0.255(3)	3*a*	0	0	0	0.33(8)
Li2	0.229(2)	3a	0	0	0	0.33(8)
Mn1	0.26244	3*a*	0	0	0	0.33(8)
O1	1	6*c*	0	0	0.25753(7)	1.26(4)

2. Li_2MnO_3
Space group: *C*2/*m*

a=4.971(2) Å *b*=8.5453(2) Å *c*=5.0466(2) Å *β*=109.923(3) °

	N-003_phase LiMnO3					
	Occupancy	site	*x*	*y*	*z*	B_{iso}
Li1	1	2*b*	0	1/2	0	0.9(2)
Li2	1	2c	0	0	1/2	0.9(2)
Li3	1	4*h*	0	0.621(2)	1/2	0.9(2)
Mn1	1	4*g*	0	0.111(3)	0	17.0(8)
O1	1	4*i*	0.104(1)	0	0.152(1)	2.7(1)
O2	1	8*j*	0.170(1)	0.3514(1)	0.154(1)	2.7(1)

3. Unknown
Used by Pawley method

Mass fraction of N003:

Li*M*O_2(main): Li*M*O_2(sub): Li_2MnO_3(sub): unknown = 58.5% : 33.4% : 7.8% : 0.3%

Crystallographic data of the main phases (N001-N003):

Samples	**N001**	**N002**	**N003**
Chemical formula	$LiNi_xMn_yCo_zO_2$ (x:y:z = 8:1:1)	$LiNi_xMn_yCo_zO_2$ (x:y:z = 6:2:2)	$LiNi_xMn_yCo_zO_2$ (x:y:z = 4:3:3)
Crystal system	Trigonal	Trigonal	Trigonal
Space group	*R* -3*m* (#166)	*R* -3*m* (#166)	*R* -3*m* (#166)
a (Å)	2.875386(1)	2.864772(1)	2.860223(9)
b (Å)	2.875386(1)	2.864772(1)	2.860223(9)
c (Å)	14.209716(8)	14.206010(8)	14.21263(9)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	120	120	120
V (Å^3)	101.744	100.96	100.69
Z	3	3	3
R_{wp} (%)	3.02	3.43	3.34
S^2	13.4	13.2	10.9