Supplementary Information

Real-time observations of lithium battery reactions—operando neutron diffraction analysis during practical operation

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Supplementary methods

Detection of lithium concentration in the cell

For the determination of lithium concentration, a custom designed 18650-type Li-ion rechargeable battery was used. The cell consists of $Li_x(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ cathode and graphite anode materials with 1 mol dm^{-3} $LiPF_6$ in a 3:7 mixture of ethylene carbonate and dimethyl carbonate as the electrolyte. Aluminium and copper foils are used as a current collector. The customized cell with a nominal capacity of 1,800 mAh was cycled at 0.18 A (theoretically equivalent to 0.1 C) in the CC/CV-charging and CC-discharging modes.

Supplementary Table S1 summarises the refinement results for the neutron diffraction experiments conducted at the 0.1 C rate. For the refinement of the cathode material, the thermal parameters *B* of the all sites were fixed, corresponding to the common values for the lithium metal oxides, $B_{Li} = 0.9$, $B_{Ni,Co,Mn} = 0.3$, $B_O = 0.5$, and $B_C = 0.3$[1,2]. Before the operando refinement of the NMC cathode, the Li/Ni mixing in the NMC cathode was refined using another cell with the same cell configuration. This refinement demonstrated no Li/Ni mixing in the NMC layered cathode. The site occupation parameters *g* were fixed at 0.333 and 1.0 for the transition metal and oxygen atoms, respectively. The lattice parameters of the *a* and *c* axes, the site occupation parameters of the lithium atoms on the 3*b* sites, and the fractional coordinate *z* of the oxygen atoms on the 6*c* sites (0, 0, *z*) were refined. For the refinement of the anode materials, only the lattice parameters and mass ratios of the two carbon materials were refined. The structural parameters of copper and aluminium as current collectors and α-type iron from the casing used the following respective models. For aluminium and copper: space group $Fm\bar{3}m$, with Al and Cu at 4a (0, 0, 0) sites[3,4]. For α-type iron: space group $Im\bar{3}m$, with Fe at 2a (0, 0, 0) sites[5]. The lattice parameters were only refined using the above models in the initial state of the cell, and were fixed in the subsequent refinements. The thermal parameters and site occupancies of these metal compounds were fixed as 0.5 and 1.0, respectively.

Supplementary Table S1. Rietveld refinement results for neutron diffraction patterns of 18650-type Li-ion cells in discharged states of (a) 0–61.7, (b) 61.7–123.3, (c) 123.3–185, (d) 185–246.7, (e) 246.7–308.3, (f) 308.3–370, (g) 370–431.7, (h) 555–616.7, (i) 616.7–678.3, (j) 678.3–740, (k) 740–801.7, and (l) 801.7–863.3 mAh.

a

Atom	Site	*g*	*x*	*y*	*z*	*B*/Å^2
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$						
Li(1)	3*b*	0.344(8)	0	0	1/2	0.9
Ni(1)	3*a*	0.333	0	0	0	0.3
Co(1)	3*a*	0.333	0	0	0	0.3
Mn(1)	3*a*	0.333	0	0	0	0.3
O(1)	6*c*	1	0	0	0.25912(9)	0.5
LiC_6						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	6*k*	1	0	0.333	1/2	0.3
LiC_{12}						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	12*n*	1	0	0.333	0.25	0.3

For $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Space group $R\bar{3}m$ (166), a = 2.81371(8) Å, c = 14.4890(10) Å, Phase fraction = 17.59%, R_B = 10.71%, R_F = 14.95%. For LiC_6: Space group *P6/mmm* (191), a = 4.31178(7) Å, c = 3.69571(18) Å, Phase fraction = 10.20%, R_B = 2.73%, R_F = 8.68%. For LiC_{12}: Space group *P6/mmm* (191), a = 4.29050(7) Å, c = 7.02506(8) Å, Phase fraction = 3.87%, R_B = 5.95%, R_F = 10.59%. R_{wp} = 1.70%, R_p = 1.26%, R_e = 0.36%, S (= R_{wp}/R_e) = 4.75.

B

Atom	Site	*g*	*x*	*y*	*z*	*B*/Å^2
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$						
Li(1)	3*b*	0.429(8)	0	0	1/2	0.9
Ni(1)	3*a*	0.333	0	0	0	0.3
Co(1)	3*a*	0.333	0	0	0	0.3
Mn(1)	3*a*	0.333	0	0	0	0.3
O(1)	6*c*	1	0	0	0.26073(7)	0.5
LiC_6						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	6*k*	1	0	0.333	1/2	0.3
LiC_{12}						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	12*n*	1	0	0.333	0.25	0.3

For $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Space group $R\bar{3}m$ (166), a = 2.81370(6) Å, c = 14.5047(10) Å, Phase fraction = 17.59%, R_B = 16.74%, R_F = 13.60%. For LiC_6: Space group *P6/mmm* (191), a = 4.31257(3) Å, c = 3.69373(7) Å, Phase fraction = 9.73%, R_B = 4.36%, R_F = 9.98%. For LiC_{12}: Space group *P6/mmm* (191), a = 4.28919(3) Å, c = 7.0376(3) Å, Phase fraction = 4.34%, R_B = 10.25%, R_F = 11.23%. R_{wp} = 1.78%, R_p = 1.36%, R_e = 0.36%, S = 4.95.

c

Atom	Site	*g*	*x*	*y*	*z*	*B*/Å^2
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$						
Li(1)	3*b*	0.373(9)	0	0	1/2	0.9
Ni(1)	3*a*	0.333	0	0	0	0.3
Co(1)	3*a*	0.333	0	0	0	0.3
Mn(1)	3*a*	0.333	0	0	0	0.3
O(1)	6*c*	1	0	0	0.26087(8)	0.5
LiC_6						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	6*k*	1	0	0.333	1/2	0.3
LiC_{12}						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	12*n*	1	0	0.333	0.25	0.3

For $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Space group $R\bar{3}m$ (166), a = 2.81401(6) Å, c = 14.5062(11) Å, Phase fraction = 17.59%, R_B = 9.10%, R_F = 14.65%. For LiC_6: Space group *P6/mmm* (191), a = 4.31173(7) Å, c = 3.69544(18) Å, Phase fraction = 9.05%, R_B = 3.74%, R_F = 7.04%. For LiC_{12}: Space group *P6/mmm* (191), a = 4.28813(6) Å, c = 7.0487(6) Å, Phase fraction = 5.02%, R_B = 6.51%, R_F = 10.63%. R_{wp} = 1.61%, R_p = 1.21%, R_e = 0.38%, S = 4.19.

d

Atom	Site	*g*	*x*	*y*	*z*	*B*/Å^2
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$						
Li(1)	3*b*	0.504(10)	0	0	1/2	0.9
Ni(1)	3*a*	0.333	0	0	0	0.3
Co(1)	3*a*	0.333	0	0	0	0.3
Mn(1)	3*a*	0.333	0	0	0	0.3
O(1)	6*c*	1	0	0	0.26013(7)	0.5
LiC_6						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	6*k*	1	0	0.333	1/2	0.3
LiC_{12}						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	12*n*	1	0	0.333	0.25	0.3

For $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Space group $R\bar{3}m$ (166), a = 2.81454(6) Å, c = 14.5046(10) Å, Phase fraction = 17.59%, R_B = 9.69%, R_F = 15.62%. For LiC_6: Space group *P6/mmm* (191), a = 4.31143(8) Å, c = 3.6955(2) Å, Phase fraction = 8.33%, R_B = 5.27%, R_F = 8.32%. For LiC_{12}: Space group *P6/mmm* (191), a = 4.28829(5) Å, c = 7.0378(5) Å, Phase fraction = 5.74%, R_B = 6.63%, R_F = 11.42%. R_{wp} = 1.65%, R_p = 1.23%, R_e = 0.36%, S = 4.54.

e

Atom	Site	*g*	*x*	*y*	*z*	*B*/Å^2
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$						
Li(1)	3*b*	0.432(8)	0	0	1/2	0.9
Ni(1)	3*a*	0.333	0	0	0	0.3
Co(1)	3*a*	0.333	0	0	0	0.3
Mn(1)	3*a*	0.333	0	0	0	0.3
O(1)	6*c*	1	0	0	0.25966(7)	0.5
LiC_6						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	6*k*	1	0	0.333	1/2	0.3
LiC_{12}						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	12*n*	1	0	0.333	0.25	0.3

For $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Space group $R\bar{3}m$ (166), a = 2.81520(6) Å, c = 14.5048(10) Å, Phase fraction = 17.59%, R_B = 11.78%, R_F = 15.75%. For LiC_6: Space group *P6/mmm* (191), a = 4.31108(9) Å, c = 3.6964(2) Å, Phase fraction = 7.57%, R_B = 6.11%, R_F = 9.61%. For LiC_{12}: Space group *P6/mmm* (191), a = 4.28801(5) Å, c = 7.0384(5) Å, Phase fraction = 6.50%, R_B = 6.42%, R_F = 11.65%. R_{wp} = 1.67%, R_p = 1.26%, R_e = 0.37%, S = 4.50.

f

Atom	Site	*g*	*x*	*y*	*z*	*B*/Å^2
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$						
Li(1)	3*b*	0.481(8)	0	0	1/2	0.9
Ni(1)	3*a*	0.333	0	0	0	0.3
Co(1)	3*a*	0.333	0	0	0	0.3
Mn(1)	3*a*	0.333	0	0	0	0.3
O(1)	6*c*	1	0	0	0.25894(7)	0.5
LiC_6						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	6*k*	1	0	0.333	1/2	0.3
LiC_{12}						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	12*n*	1	0	0.333	0.25	0.3

For $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Space group $R\bar{3}m$ (166), a = 2.81481(6) Å, c = 14.5136(10) Å, Phase fraction = 17.59%, R_B = 11.62%, R_F = 16.09%. For LiC_6: Space group: *P6/mmm* (191), a = 4.31053(11) Å, c = 3.6979(2) Å, Phase fraction = 6.78%, R_B = 6.47%, R_F = 9.12%. For LiC_{12}: Space group *P6/mmm* (191), a = 4.28874(4) Å, c = 7.0268(3) Å, Phase fraction = 7.29%, R_B = 6.55%, R_F = 11.24%. R_{wp} = 1.67%, R_p = 1.26%, R_e = 0.36%, S = 4.64.

g

Atom	Site	*g*	*x*	*y*	*z*	*B*/Å^2
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$						
Li(1)	3*b*	0.503(8)	0	0	1/2	0.9
Ni(1)	3*a*	0.333	0	0	0	0.3
Co(1)	3*a*	0.333	0	0	0	0.3
Mn(1)	3*a*	0.333	0	0	0	0.3
O(1)	6*c*	1	0	0	0.25954(7)	0.5
LiC_6						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	6*k*	1	0	0.333	1/2	0.3
LiC_{12}						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	12*n*	1	0	0.333	0.25	0.3

For $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Space group $R\bar{3}m$ (166), a = 2.81597(6) Å, c = 14.5053(10) Å, Phase fraction = 17.59%, R_B = 9.99%, R_F = 15.41%. For LiC_6: Space group *P6/mmm* (191), a = 4.31029(13) Å, c = 3.6988(3) Å, Phase fraction = 5.99%, R_B = 6.53%, R_F = 8.75%. For LiC_{12}: Space group *P6/mmm* (191), a = 4.28796(4) Å, c = 7.0325(4) Å, Phase fraction = 8.08%, R_B = 5.88%, R_F = 10.49%. R_{wp} = 1.67%, R_p = 1.25%, R_e = 0.36%, S = 4.60.

h

Atom	Site	*g*	*x*	*y*	*z*	*B*/Å^2
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$						
Li(1)	3*b*	0.577(8)	0	0	1/2	0.9
Ni(1)	3*a*	0.333	0	0	0	0.3
Co(1)	3*a*	0.333	0	0	0	0.3
Mn(1)	3*a*	0.333	0	0	0	0.3
O(1)	6*c*	1	0	0	0.25905(7)	0.5
LiC_6						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	6*k*	1	0	0.333	1/2	0.3
LiC_{12}						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	12*n*	1	0	0.333	0.25	0.3

For $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Space group $R\bar{3}m$ (166), a = 2.81900(6) Å, c = 14.4838(10) Å, Phase fraction = 17.59%, R_B = 11.57%, R_F = 15.41%. For LiC_6: Space group *P6/mmm* (191), a = 4.3068(2) Å, c = 3.7061(6) Å, Phase fraction = 3.55%, R_B = 10.41%, R_F = 13.08%. For LiC_{12}: Space group *P6/mmm* (191), a = 4.28693(3) Å, c = 7.0309(3) Å, Phase fraction = 10.52%, R_B = 4.43%, R_F = 13.17%. R_{wp} = 1.80%, R_p = 1.29%, R_e = 0.36%, S = 4.98.

i

Atom	Site	*g*	*x*	*y*	*z*	*B*/Å^2
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$						
Li(1)	3*b*	0.549(8)	0	0	1/2	0.9
Ni(1)	3*a*	0.333	0	0	0	0.3
Co(1)	3*a*	0.333	0	0	0	0.3
Mn(1)	3*a*	0.333	0	0	0	0.3
O(1)	6*c*	1	0	0	0.25842(7)	0.5
LiC_6						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	6*k*	1	0	0.333	1/2	0.3
LiC_{12}						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	12*n*	1	0	0.333	0.25	0.3

For $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Space group $R\bar{3}m$ (166), a = 2.82023(5) Å, c = 14.4760(9) Å, Phase fraction = 17.59%, R_B = 15.73%, R_F = 16.61%. For LiC_6: Space group *P6/mmm* (191), a = 4.3070(2) Å, c = 3.7062(6) Å, Phase fraction = 2.77%, R_B = 13.98%, R_F = 13.88%. For LiC_{12}: Space group *P6/mmm* (191), a = 4.28630(2) Å, c = 7.0324(2) Å, Phase fraction = 11.30%, R_B = 3.75%, R_F = 11.19%. R_{wp} = 2.05%, R_p = 1.40%, R_e = 0.36%, S = 5.66.

j

Atom	Site	*g*	*x*	*y*	*z*	*B*/Å^2
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$						
Li(1)	3*b*	0.602(8)	0	0	1/2	0.9
Ni(1)	3*a*	0.333	0	0	0	0.3
Co(1)	3*a*	0.333	0	0	0	0.3
Mn(1)	3*a*	0.333	0	0	0	0.3
O(1)	6*c*	1	0	0	0.25828(7)	0.5
LiC_6						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	6*k*	1	0	0.333	1/2	0.3
LiC_{12}						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	12*n*	1	0	0.333	0.25	0.3

For $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Space group $R\bar{3}m$ (166), a = 2.82210(5) Å, c = 14.4594(9) Å, Phase fraction = 17.59%, R_B = 13.06%, R_F = 15.02%. For LiC_6: Space group *P6/mmm* (191), a = 4.2980(5) Å, c = 3.7101(11) Å, Phase fraction = 2.19%, R_B = 15.79%, R_F = 15.12%. For LiC_{12}: Space group *P6/mmm* (191), a = 4.28589(3) Å, c = 7.0280(3) Å, Phase fraction = 11.88%, R_B = 4.14%, R_F = 13.29%. R_{wp} = 2.00%, R_p = 1.37%, R_e = 0.36%, S = 5.50.

k

Atom	Site	*g*	*x*	*y*	*z*	*B*/Å^2
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$						
Li(1)	3*b*	0.647(9)	0	0	1/2	0.9
Ni(1)	3*a*	0.333	0	0	0	0.3
Co(1)	3*a*	0.333	0	0	0	0.3
Mn(1)	3*a*	0.333	0	0	0	0.3
O(1)	6*c*	1	0	0	0.25849(7)	0.5
LiC_6						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	6*k*	1	0	0.333	1/2	0.3
LiC_{12}						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	12*n*	1	0	0.333	0.25	0.3

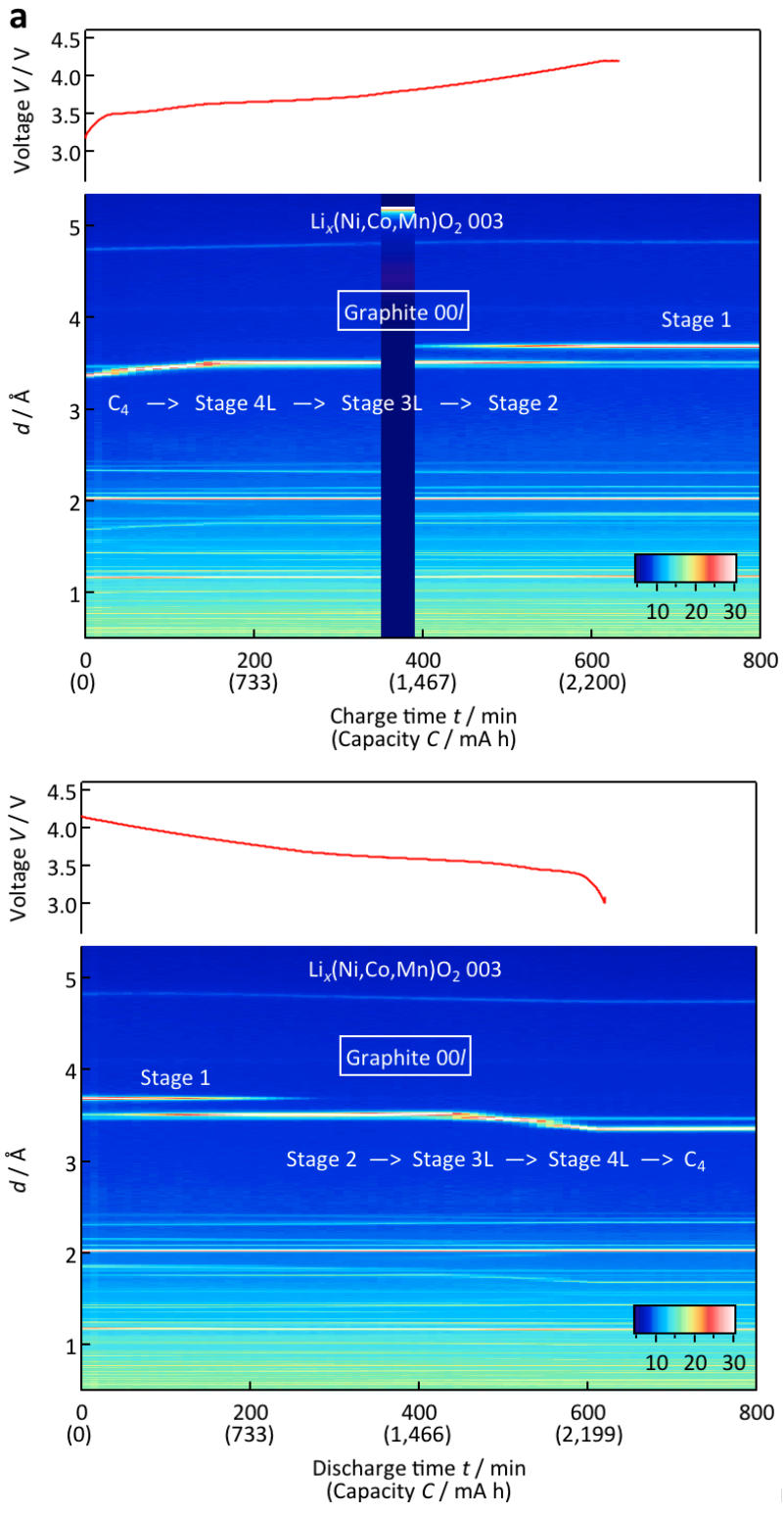
For $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Space group $R\bar{3}m$ (166), a = 2.82306(6) Å, c = 14.4512(11) Å, Phase fraction = 17.59%, R_B = 11.43%, R_F = 17.62%. For LiC_6: Space group *P6/mmm* (191), a = 4.2799(4) Å, c = 3.7127(6) Å, Phase fraction = 1.44%, R_B = 11.92%, R_F = 20.06%. For LiC_{12}: Space group *P6/mmm* (191), a = 4.28612(5) Å, c = 7.0281(3) Å, Phase fraction = 12.63%, R_B = 4.88%, R_F = 14.34%. R_{wp} = 2.22%, R_p = 1.48%, R_e = 0.38%, S = 5.89.

l

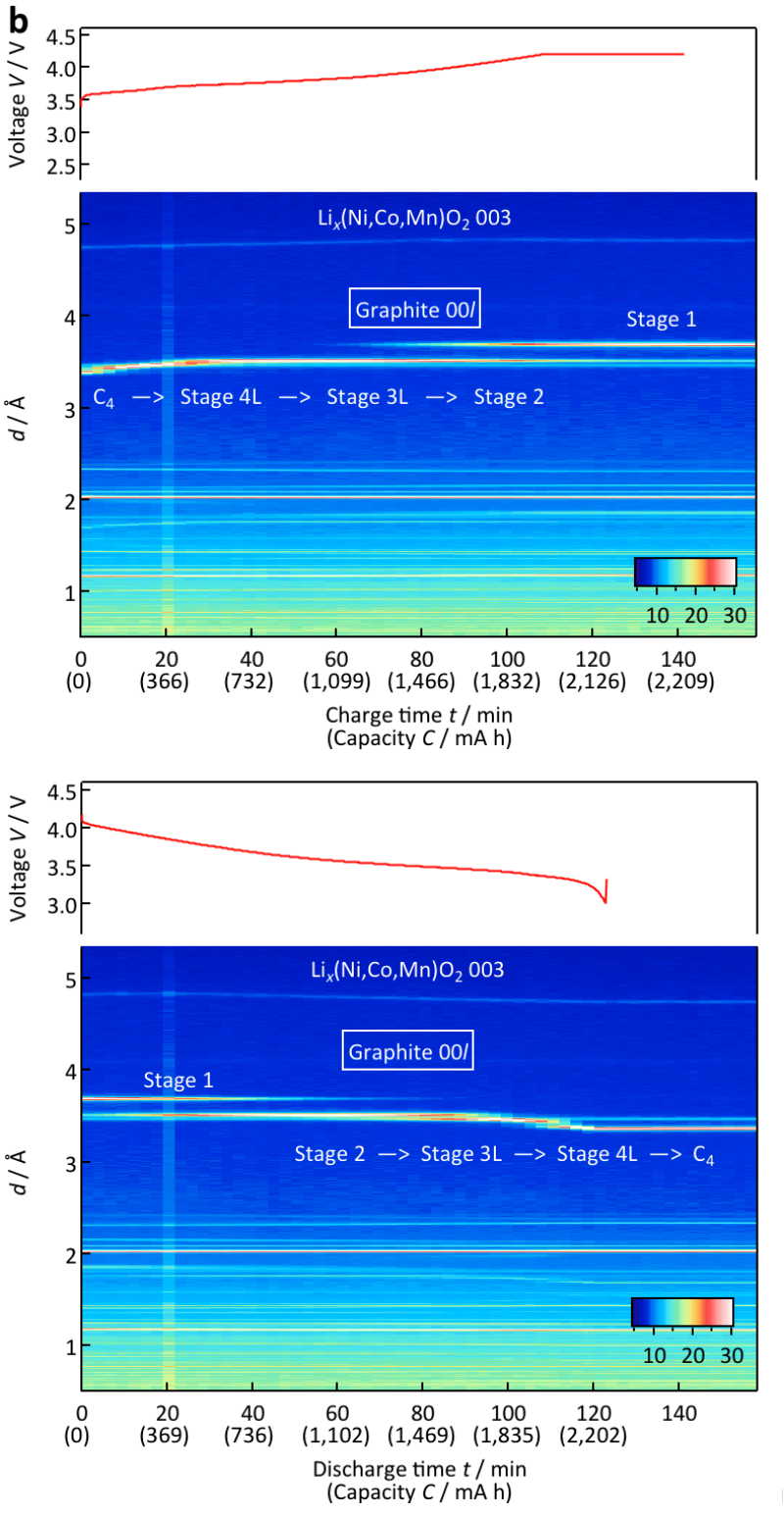
Atom	Site	*g*	*x*	*y*	*z*	*B*/Å^2
$Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$						
Li(1)	3*b*	0.643(8)	0	0	1/2	0.9
Ni(1)	3*a*	0.333	0	0	0	0.3
Co(1)	3*a*	0.333	0	0	0	0.3
Mn(1)	3*a*	0.333	0	0	0	0.3
O(1)	6*c*	1	0	0	0.26072(8)	0.5
LiC_6						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	6*k*	1	0	0.333	1/2	0.3
LiC_{12}						
Li(1)	1*a*	1	0	0	0	0.9
C(1)	12*n*	1	0	0.333	0.25	0.3

For $Li_xNi_{1/3}Co_{1/3}Mn_{1/3}O_2$: Space group $R\bar{3}m$ (166), a = 2.82494(6) Å, c = 14.4344(8) Å, Phase fraction = 17.59%, R_B = 11.78%, R_F = 17.27%. For LiC_6: Space group *P6/mmm* (191), a = 4.2771(5) Å, c = 3.7124(8) Å, Phase fraction = 0.96%, R_B = 28.45%, R_F = 23.24%. For LiC_{12}: Space group *P6/mmm* (191), a = 4.28562(4) Å, c = 7.0266(3) Å, Phase fraction = 13.11%, R_B = 3.72%, R_F = 17.41%. R_{wp} = 2.26%, R_p = 1.46%, R_e = 0.36%, S = 6.23.

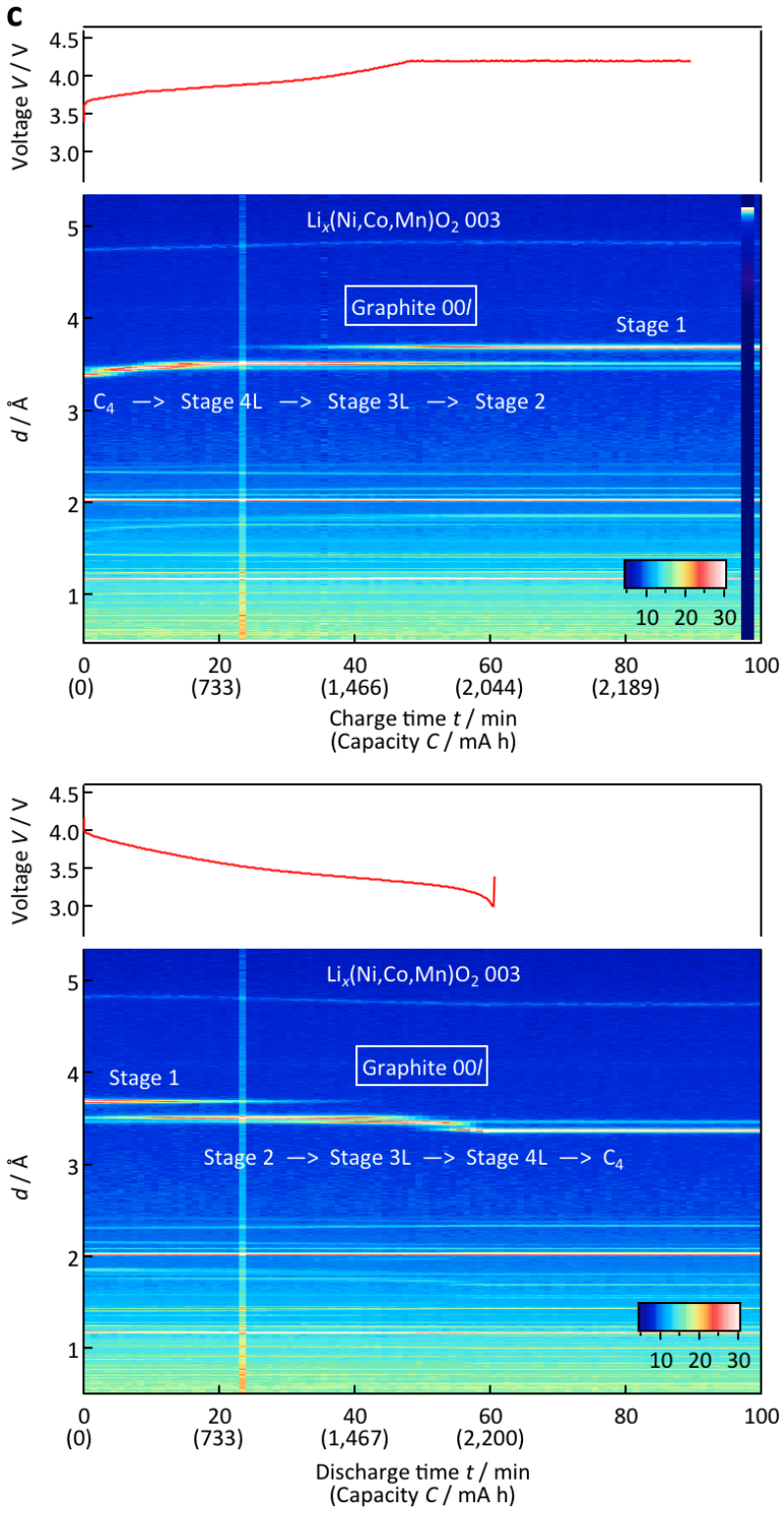
Supplementary Figures



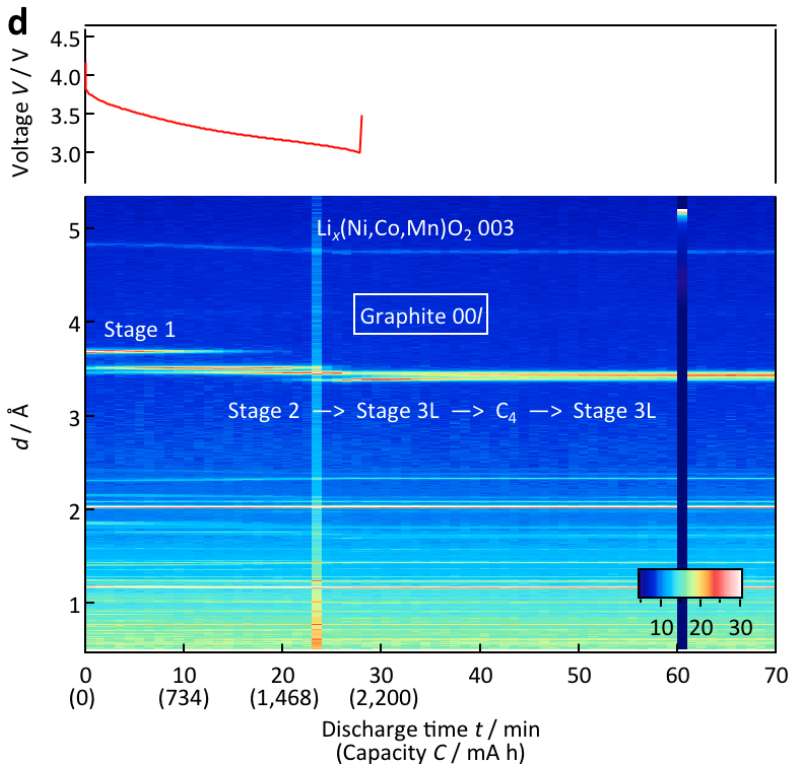
Supplementary Figure S1a



Supplementary Figure S1b

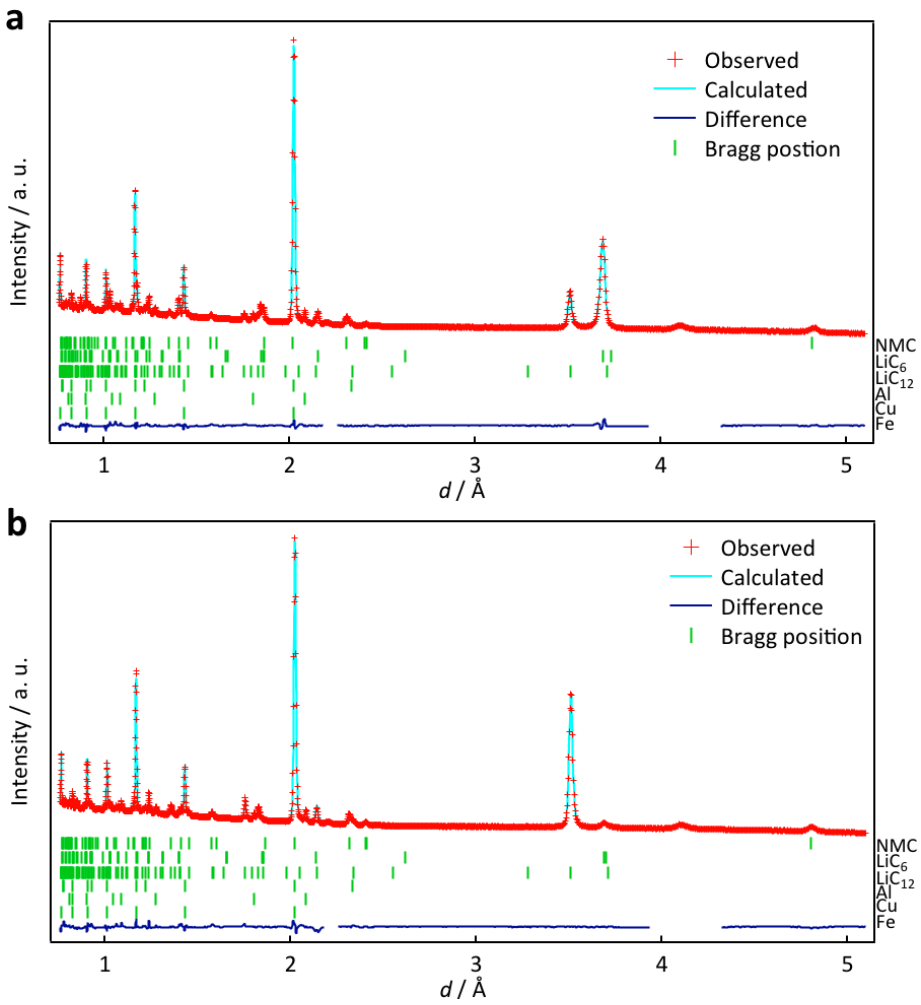


Supplementary Figure S1c

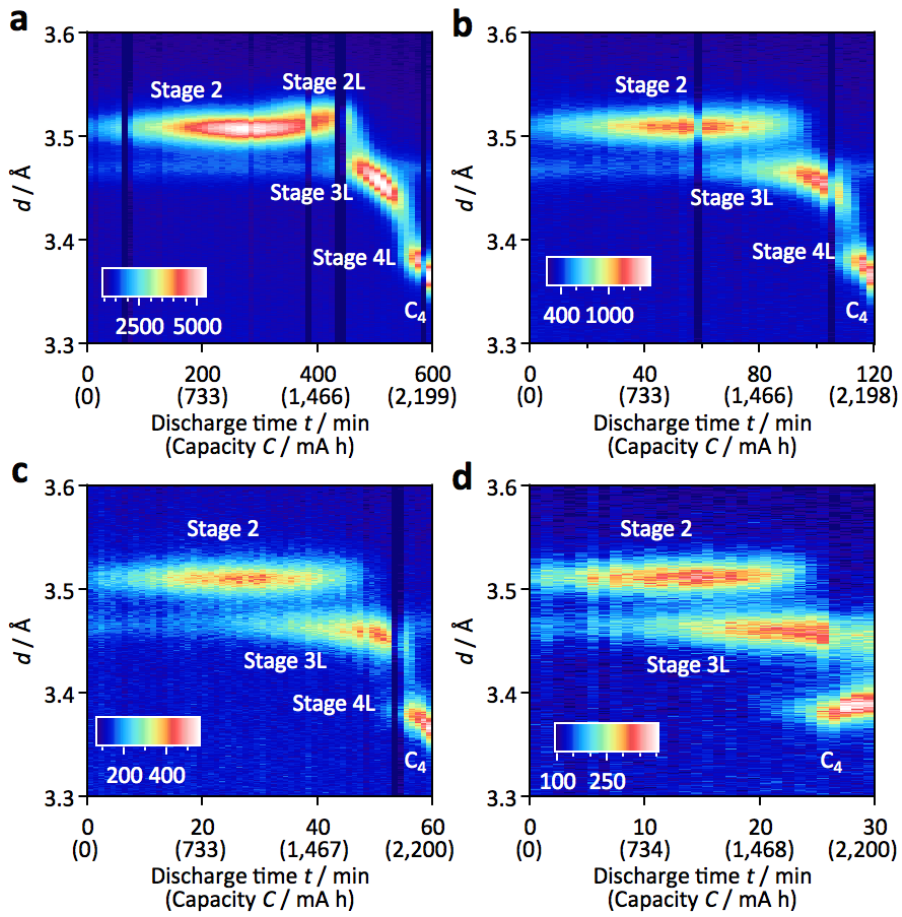


Supplementary Figure S1d

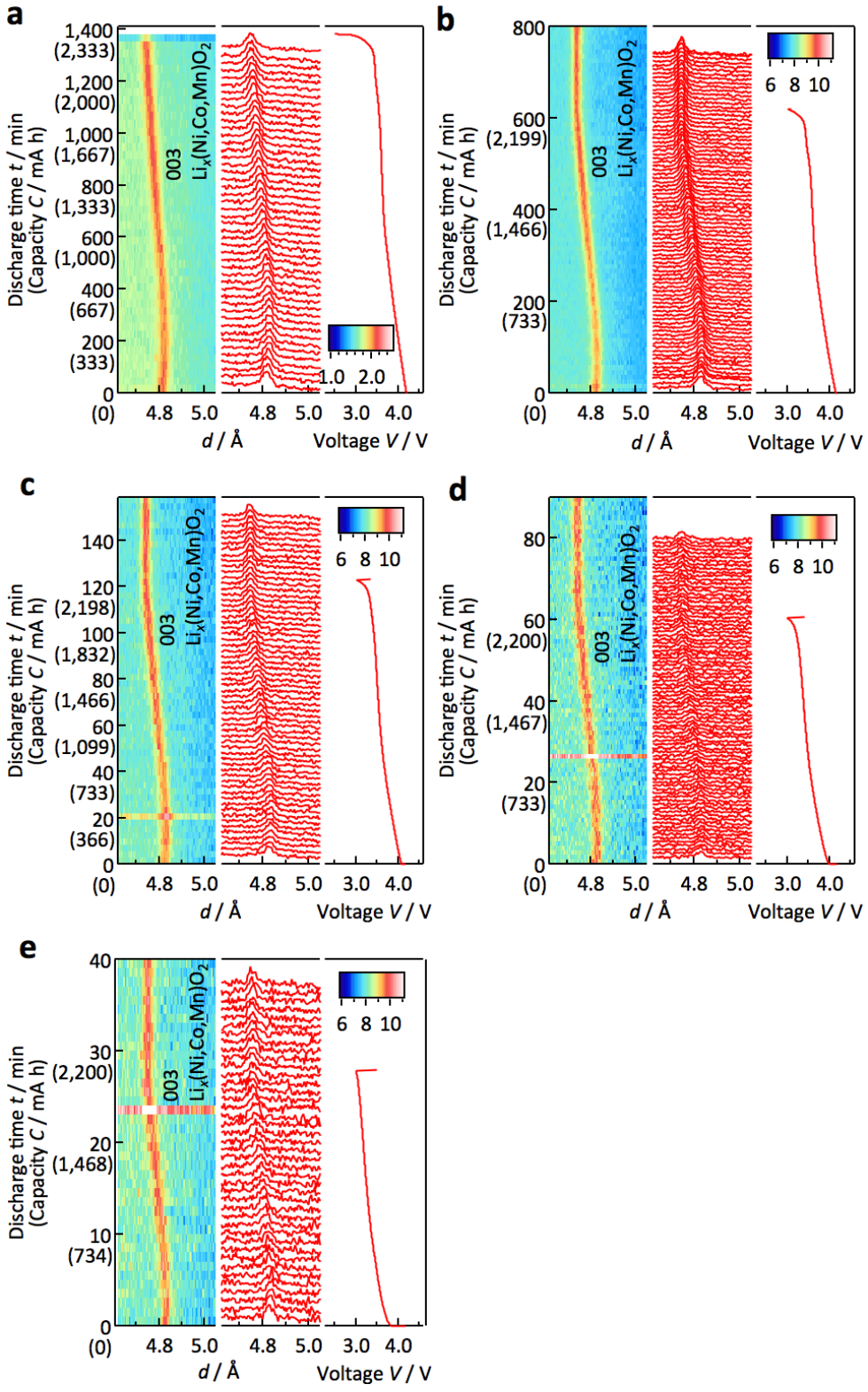
Supplementary Figure S1 | Neutron diffraction profiles during the battery reaction. Total diffraction profiles of the batteries during charge and discharge experiments. The charge and discharge rates were 0.1 (a), 0.5 (b), 1 (c), and 2 C (d). The profile changes at the 2 C rate are only indicated for the discharge process because the charge reaction was conducted at the 1 C rate. The voltage profiles of the charge and discharge reactions are indicated for each diffraction profile.



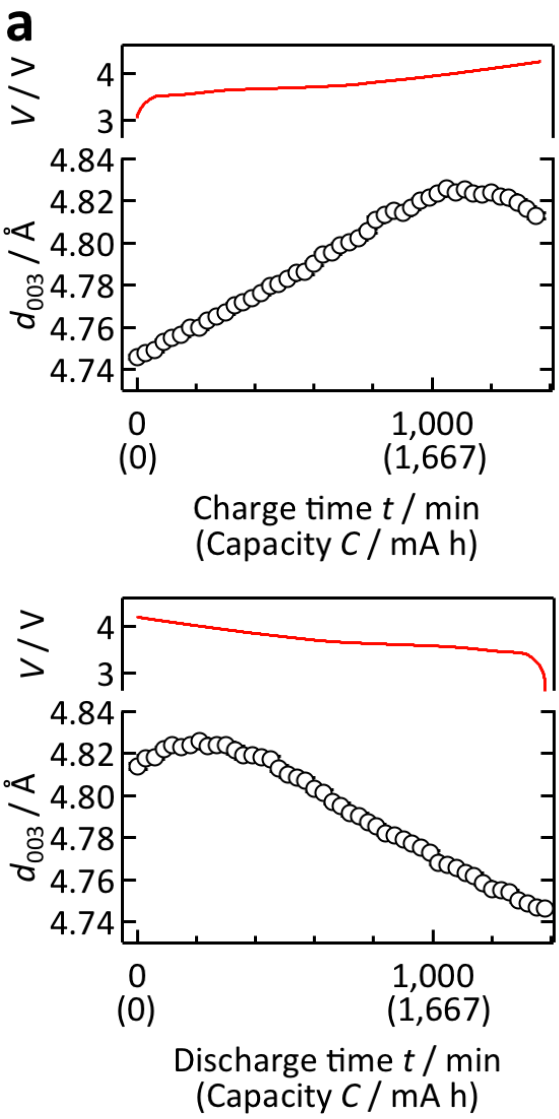
Supplementary Figure S2 | Rietveld-refined neutron diffraction patterns. Rietveld refinement patterns for the NMC cathode during the charge and discharge experiments. The refinement patterns are shown for the initial (a) and post-discharge (b) states. Green dashes indicate the positions of Bragg reflections for the battery components.



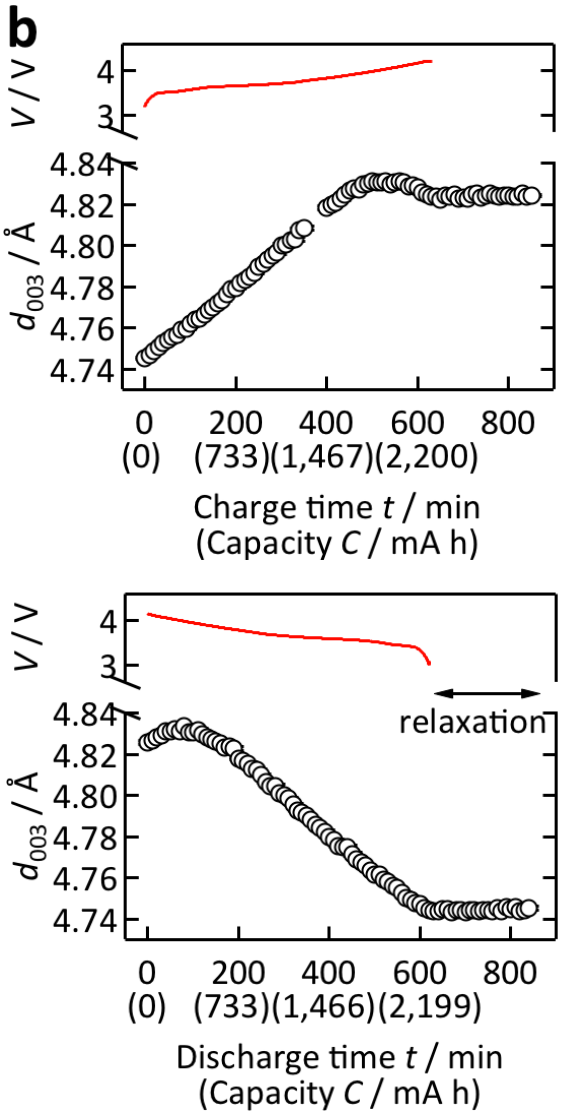
Supplementary Figure S3 | Rate dependence of the phase change mechanism for the carbon material during the discharge reaction. Two-dimensional diffraction profiles near the stage 2, stage 2L, and stage 3L mixture regions at discharge rates of 0.1 (a), 0.5 (b), 1 (c), and 2 C (d). The 2L phase was not observed over the discharge rate of 0.5 C.



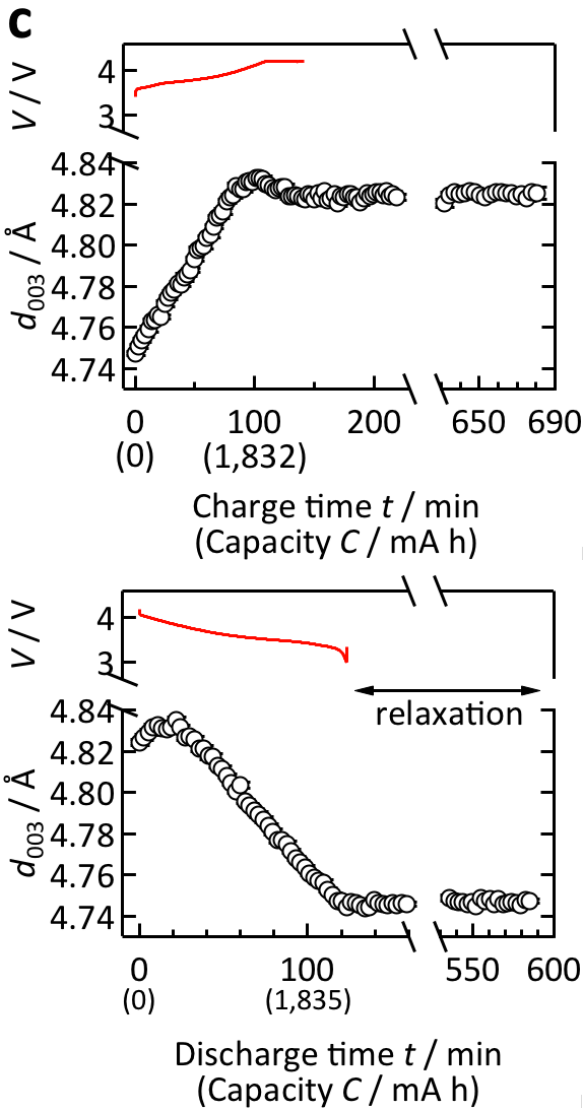
Supplementary Figure S4 | Neutron diffraction profiles of 003 reflections for the cathode material. Graphical and one-dimensional profiles of the diffraction patterns for the cathode during the discharge reactions. The 003 diffraction peaks are indicated in the figure. The discharge rates were 0.05 (a), 0.1 (b), 0.5 (c), 1 (d), and 2 C (e). The voltage profiles of the discharge reactions are indicated for each diffraction profile.



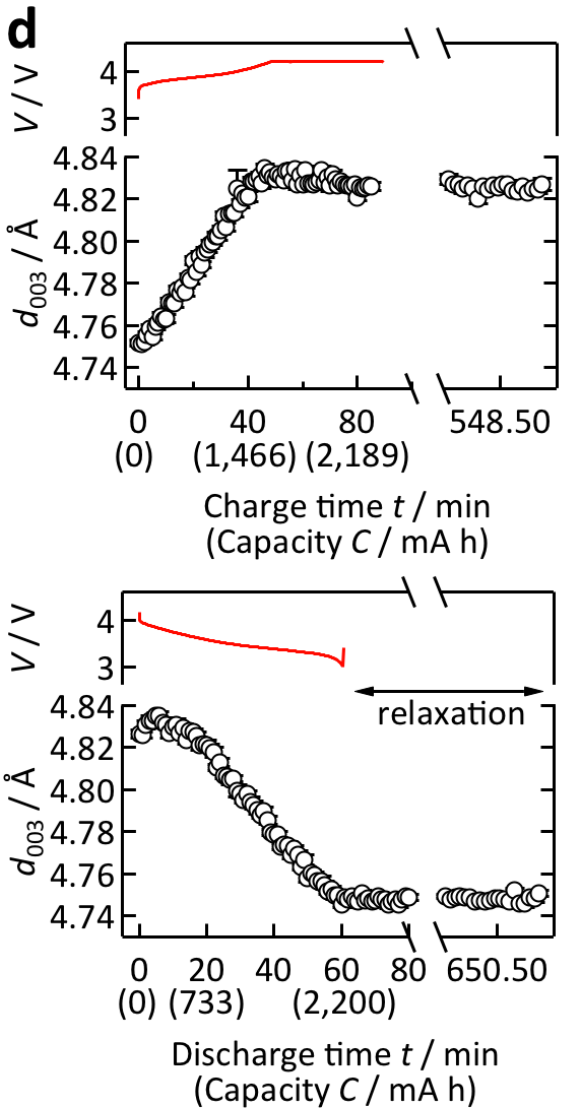
Supplementary Figure S5a



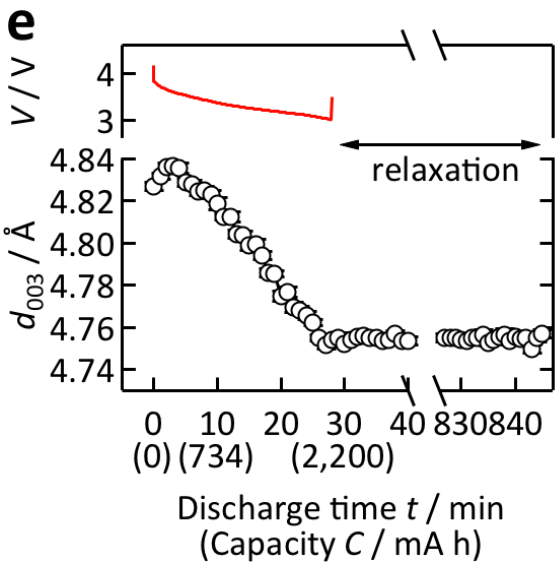
Supplementary Figure S5b



Supplementary Figure S5c



Supplementary Figure S5d



Supplementary Figure S5e

Supplementary Figure S5 | Structural changes during battery reactions. *d*-value changes of the 003 reflection for the cathode Li(Ni,Mn,Co)O_2 during the charge and discharge reactions. The charge and discharge rates were 0.05 (a), 0.1 (b), 0.5 (c), 1 (d), and 2 C (e). The profile changes at the 2 C rate are only indicated for the discharge process because the charge reaction was conducted at the 1 C rate. The voltage profiles of the charge and discharge reactions are indicated in each diffraction profile.

Supplementary References

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