Supplementary Material:
Revealing In-operando Nanoparticle Transformation Dynamics in Lithium-ion Battery Cathodes using X-Ray Microbeam Diffraction

1 SUPPLEMENTARY DATA

Supplementary Material should be uploaded separately on submission. Please include any supplementary data, figures and/or tables.

Supplementary material is not typeset so please ensure that all information is clearly presented, the appropriate caption is included in the file and not in the manuscript, and that the style conforms to the rest of the article.

2 SUPPLEMENTARY TABLES AND FIGURES

For more information on Supplementary Material and for details on the different file types accepted, please see the Supplementary Material section of the Author Guidelines.

2.1 Figures

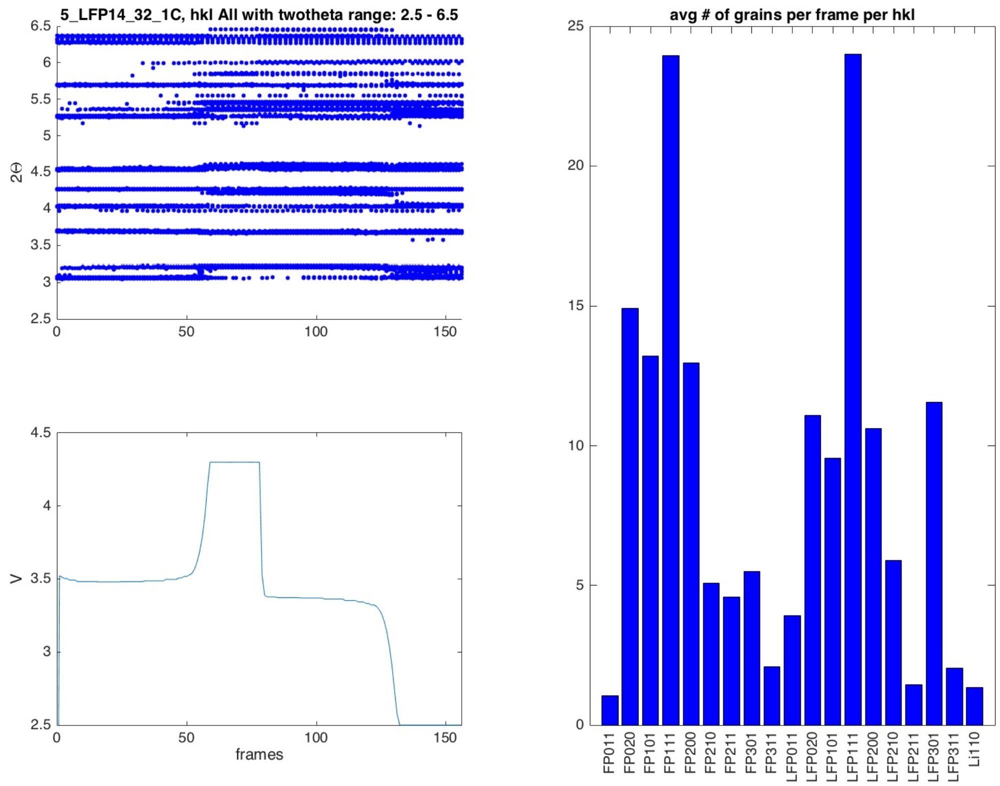

Figure S1. The average number of hkl reflections found per frame in an LFP 1C charge/discharge experiment.

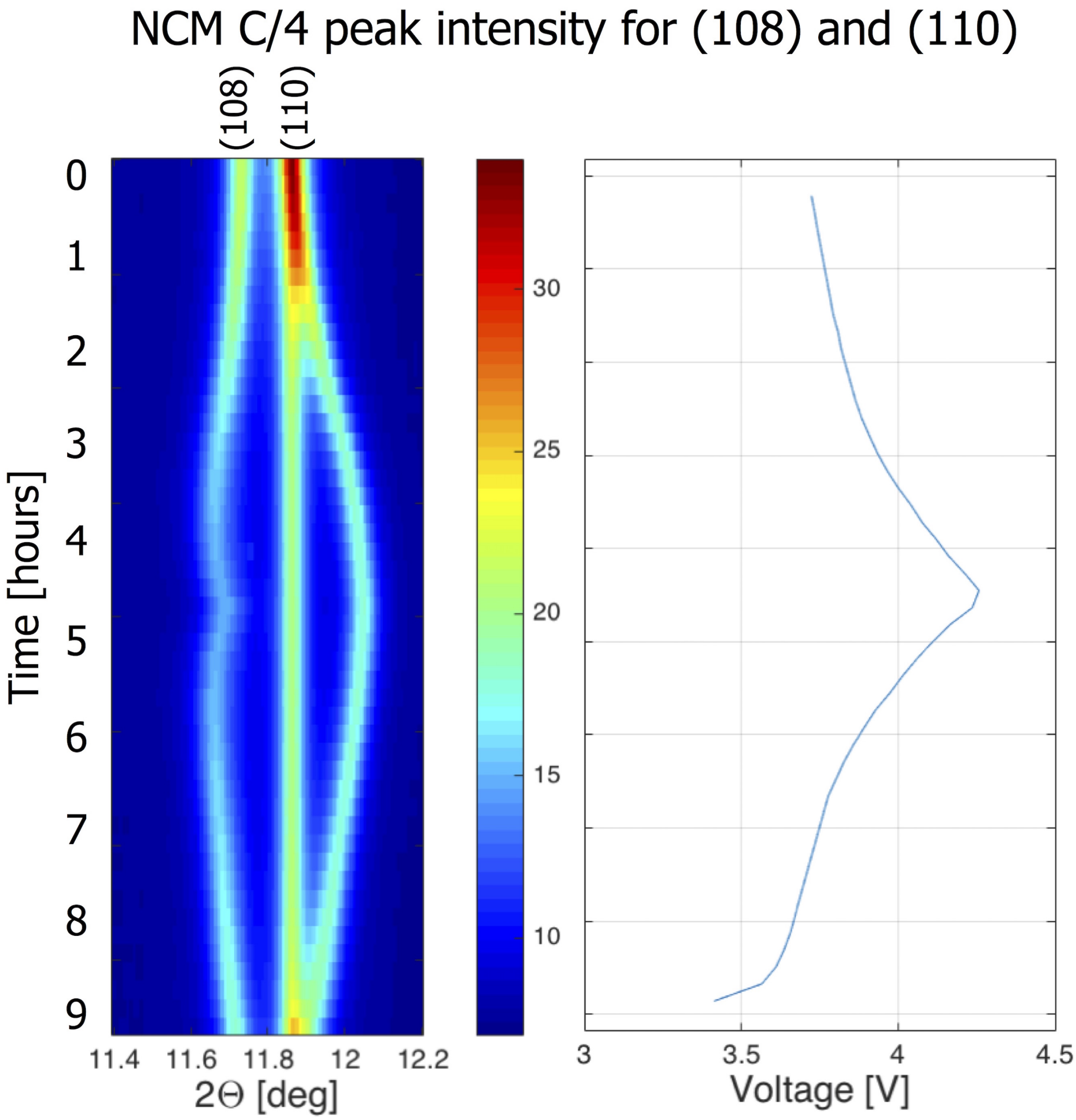

Figure S2. Time runs from top to bottom showing the reflection intensity in the left graph, and the electrochemistry in the right graph. Specifically the 2Θ angles for reflections (108) and (110) are shown for cathode material NCM. The (108) reflection is a clear line, moving from 2Θ = 11.75 – 11.6 deg and back, with no intensity on either side. This shows that practically all diffracted grains are active. For the (110) reflection we see the same single line of intensity moving from 2Θ = 11.85 – 12.1 deg and back. The straight vertical line at 2Θ = 11.85 deg is an Al reflection.

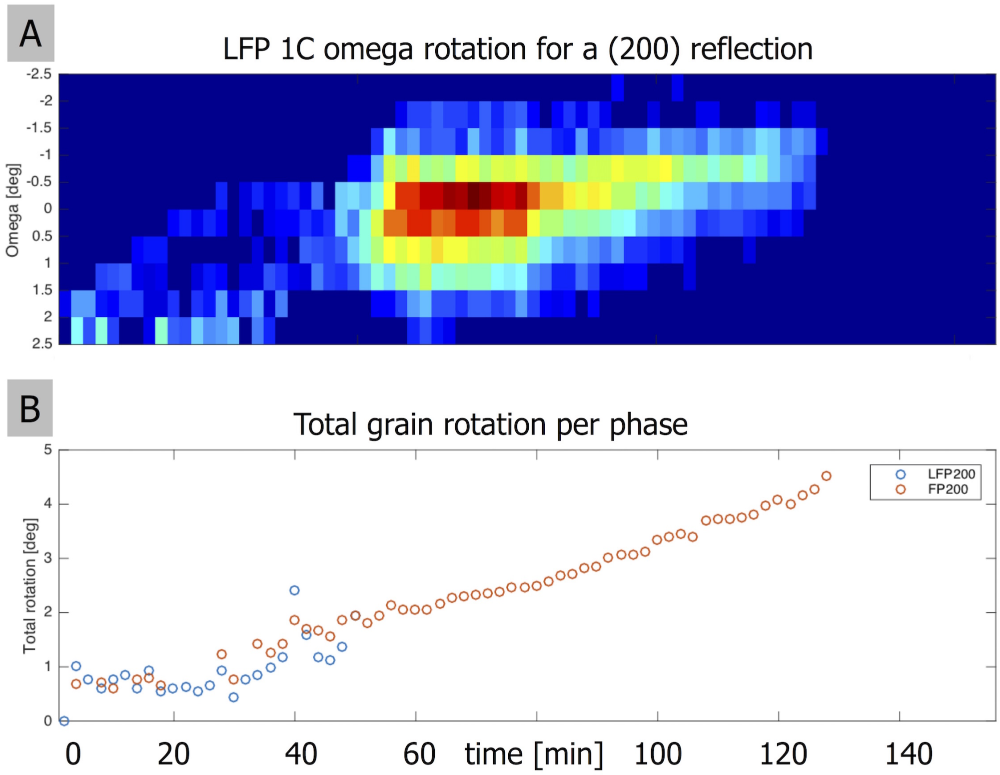

Figure S3. Showing the grain rotation of the reflection depicted in Figure 5A from the LFP 1C experiment. A. The intensity plot shows the grain rotation with regards to omega as a function of time during a 1C charge/discharge experiment. During charge (from t = 0 – 80 min) this grain reflection rotates $\sim$ 2.5 deg from omega = -2.5 – 0 deg. After about t = 30 min this reflection stays within the scanned omega range. B This graph shows the total grain rotation by combining the observed omega rotation and eta shift.

2.2 Tables

Grain reflection	LFP 1C (200)	LFP 5C (210)	LFP 10C (020)	NCM C/4 (108)
expname	ma3372	ma3372	ma3372	ma2905
expnr	5	6	7	32
snapshot	2	2	2	1
labelnr	343	163	322	2
framenr	7	2	112	328
point	A	A	A	B
eta [deg]	305.4812	54.40147	285.08124	177.05272
omega [deg]	1.25	0	0	-2.75
twotheta [deg]	3.05076	4.03857	5.44234	11.70879
deviation [%]	0.20516	0.16235	0.24358	0.00434
dspace [Å]	5.17511	3.90965	2.90171	1.44498
hkl	LFP(200)	LFP(210)	FP(020)	L1.0(108)
xmin	1183	1241	1145	144
xmax	1190	1247	1157	148
ymin	777	1324	525	1076
ymax	783	1328	531	1081
intensity	11668	4261	5373	1280

Table S1. For each experiment grain reflections were identified and stored. Typically up to a few hundred grain reflections per frame were identified. Here the reflection properties determined for each reflection are shown as an example. For each experiment, see Table 1, one of the identified reflections is shown. See 2.2.1 for the legenda, explaining the labels used in the first column.

Labelname	LFP 1C (200)	LFP 5C (101)	LFP 10C (301)	NCM C/4 (110)
expname	ma3372	ma3372	ma3372	ma2905
expnr	5	6	7	32
snapshot	2	2	2	1
labelnr	1	180	58	159
nr-of-refs	153	146	399	48
min-framenr	0	7	0	7
max-framenr	1224	206	416	383
nr-of-hkl	2	2	2	1
eta-initial	151.48807	23.83702	329.85486	166.15564
eta-min	149.62868	20.71399	328.0957	166.15564
eta-max	153.13777	24.11357	330.90073	166.56956
eta-diff	3.5091	3.39958	2.80503	0.41391
twotheta-initial	3.06483	3.69421	5.69022	11.87241
twotheta-min	3.06148	3.67387	5.69022	11.87241
twotheta-max	3.22178	3.69421	5.85003	12.05916
twotheta-diff	0.1603	0.02034	0.15982	0.18675
omega-min	-2.25	0	0	-2.75
omega-max	0.75	0	0	-2.75
xmin	761	1334	1471	142
xmax	792	1355	1505	162
ymin	1128	1130	726	1237
ymax	1156	1170	766	1248

Table S2. Reflections found in different frames over time were labeled. See 2.2.1 for the legenda, explaining the labels used in the first column. For the (101) reflection set for the 5C experiment shown in the second column, the first (101) reflection for this grain was found in frame 7 and the last in frame 206. The η for the first reflection is 151.49 deg. This was used to scan for reflection with the same hkl and an η value close to the initial η value. A total of 146 reflections were found that way. The min/max of the 2Θ and the difference is stored, a measure for how active this grain was. The nr-of-hkl indicates whether different phases were found. Here both LFP and FP phases were found with hkl (101) meaning a phase transition took place. The collected meta data gives the possibility to search for reflections sets with for instance phase transitions or with a large η shift. Typically for each experiment a few hundred reflection sets were found with more than twenty reflections.

Charge/discharge experiment	LFP 1C	LFP 5C	LFP 10C	NCM C/4
Constant-current charge cap. [mAh]	0.516	0.487	0.450	0.177
Constant-current discharge cap. [mAh]	0.463	0.370	0.325	0.173
Coulombic efficiency	90%	76%	72%	98%
Active material [mg]	4.02	4.02	4.02	11.16
Weight capacity charge [mAh/g]	128	121	112	159
Weight capacity discharge [mAh/g]	115	92	81	155
Cathode surface [cm^2]	1.29	1.29	1.29	1.29
Active material loading [mg/cm^2]	3.12	3.12	3.12	8.67
Surface capacity charge [mAh/cm^2]	0.40	0.38	0.35	1.38
Surface capacity discharge [mAh/cm^2]	0.36	0.29	0.25	1.35

Table S3. Overview of electrochemical details of the four different cycling experiments. For all three LFP experiments, 1C, 5C and 10C, one charge/discharge cycle was executed. The same cell for all three rates was used which was pre-cycled with a constant-current C/4 rate before the 1C experiment. For all three LFP experiments the following charge/discharge regime was used. Constant-current charge until voltage > 4.2 V, followed by constant-voltage = 4.2 V until $I < 0.025$ mA. Constant-current discharge until voltage < 2.5 V, followed by constant-voltage = 2.5 V until $I < 0.025$ mA. The Coulombic efficiency was calculated using only the capacities realized during the constant-current regime. For the NCM experiment one constant-current charge/discharge C/4 cycle was executed. This was the second cycle as this cell had also been pre-cycled with a constant-current C/4 rate.

2.2.1 Legenda for Tables S1 and S2

expname:	reference to the ESRF name of the beam line reservation
expnr:	experiment number for internal use
snapshot:	experiment sub-reference for internal use
labelnr:	unique number that links grain reflections found in different frames
framenr:	frame number in which the reflection was found
point:	y-z position of the sample that was probed with the X-ray beam
eta:	the angle η (along the diffraction ring) of the reflection
omega:	the ω angle (z-rotation) of the sample
twotheta:	the 2Θ angle of the grain reflection
deviation:	the deviation in pct from the equilibrium 2Θ angle
dspace:	the dspace in Å of this reflection
hkl:	the miller index belonging to the reflection
xmin:	the upper left corner (pixel number) of the rectangle drawn around the reflection
xmax:	the lower left corner (pixel number) of the rectangle drawn around the reflection
ymin:	the upper right corner (pixel number) of the rectangle drawn around the reflection
ymax:	the lower right corner (pixel number) of the rectangle drawn around the reflection
intensity:	cumulative intensity [a.u.] of all pixels belonging the the grain reflection
nr-of-refs:	the number of reflections for this particular label (series of reflections belonging to the same grain)
eta-initial:	the η angle of the first reflection in the series
eta-min:	the minimum η angle of all reflection in the series
eta-max:	the minimum η angle of all reflection in the series
eta-diff:	the difference between the minimum and maximum η angle of all reflection in the series
twotheta-min:	the minimum 2Θ angle of all reflection in the series
twotheta-max:	the minimum 2Θ angle of all reflection in the series
twotheta-diff:	the difference between the minimum and maximum 2Θ angle of all reflection in the series
omega-min:	the minimum ω angle (z-rotation) this reflection was visible for
omega-max:	the maximum ω angle (z-rotation) this reflection was visible for

2.3 Total grain rotation

The total grain rotation is estimated using the change in ω (rotation along the z-axis) and the shift in η (movement along the diffraction ring, i.e. rotation along the beam line or x-axis) with the following formula:

$$\text{total grain rotation} = \sqrt{(\Delta\omega)^2 + (\Delta\eta)^2} \tag{S1}$$

where $\Delta\omega = \omega_{initial} - \omega_{current}$
and $\Delta\eta = \eta_{initial} - \eta_{current}$
using $\sin(\alpha) \approx \alpha$ for small α.