

Identifying the chemical and structural irreversibility in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ - A model compound for classical layered intercalation

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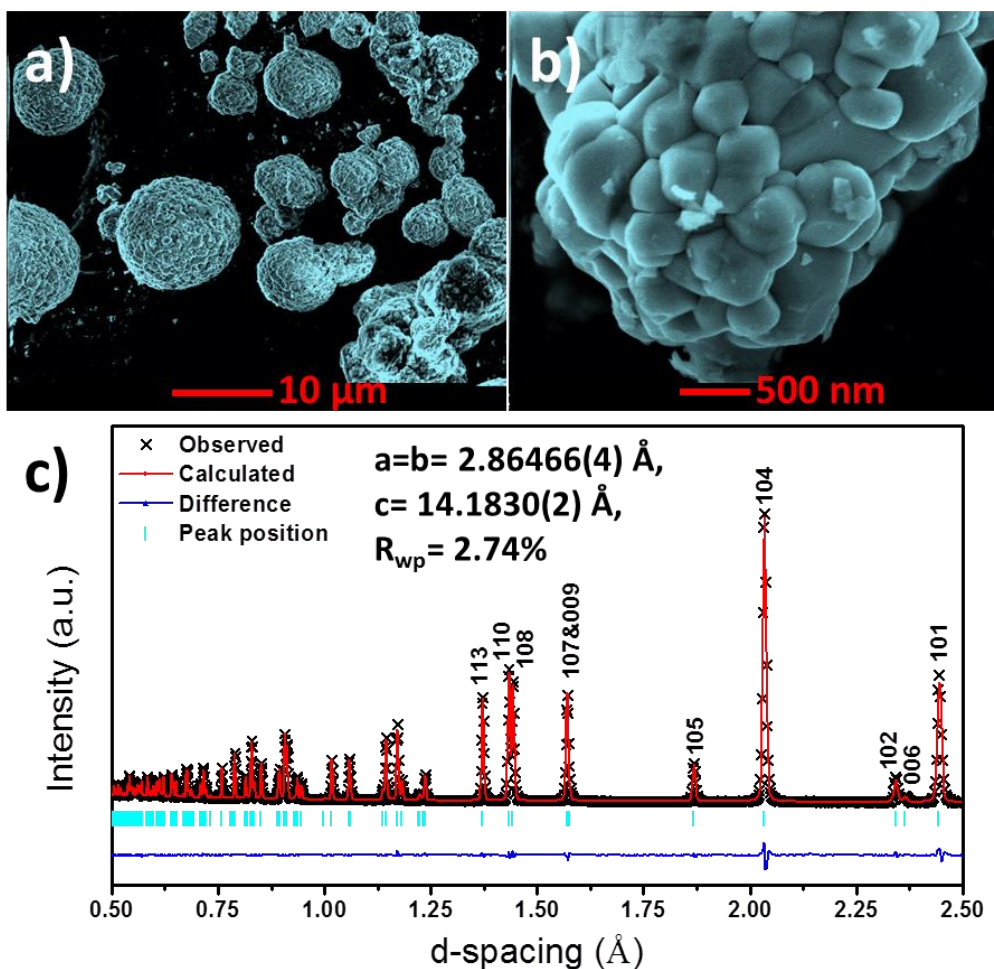


Figure S1. a) and b) SEM of NCA. c) Neutron powder diffraction of NCA.

Table S1. Neutron diffraction data refinement results of NCA pristine powders.

| Pristine, Space Group: $R\bar{3}m$ $a=b=2.86466(4) \text{ \AA}$, $c=14.1830(2) \text{ \AA}$, Neutron: $R_{wp}=2.74\%$ | | | | | | |
|---|---|---|------------|-----------|--------------------------|--------------|
| Atom type | x | y | z | Occupancy | 100*U (\AA^2) | |
| Li | 0 | 0 | 0 | 0.010(2) | U11=U22= 0.41(2) | U33= 0.27(3) |
| Ni | 0 | 0 | 0 | 0.790(2) | U11=U22= 0.41(2) | U33= 0.27(3) |
| Co | 0 | 0 | 0 | 0.150 | U11=U22= 0.41(2) | U33= 0.27(3) |
| Al | 0 | 0 | 0 | 0.050 | U11=U22= 0.41(2) | U33= 0.27(3) |
| Li | 0 | 0 | 0.5 | 0.990(2) | Uiso= 1.40(6) | |
| Ni | 0 | 0 | 0.5 | 0.010(2) | Uiso= 1.40(6) | |
| O | 0 | 0 | 0.25936(4) | 1.000 | Uiso= 0.95(2) | |

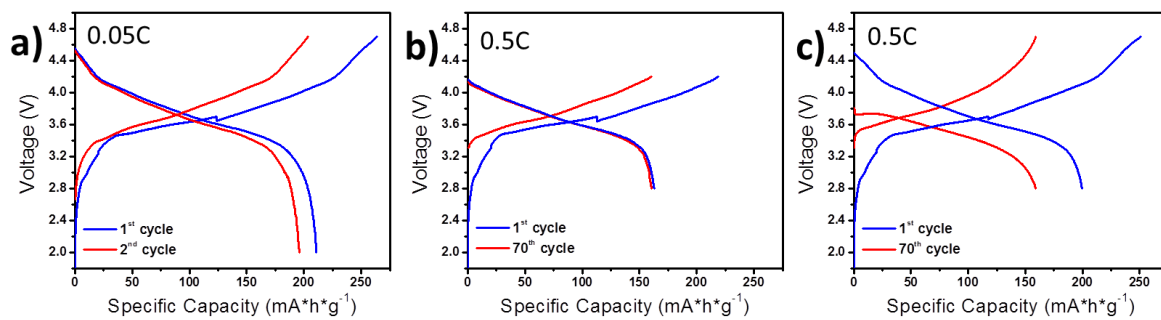


Figure S2. Voltage profiles of NCA pouch cell (vs. graphite). a) 2.0 -4.7 V, C/20. b) 2.8 -4.2 V, C/2. c) 2.8-4.7V, C/2.

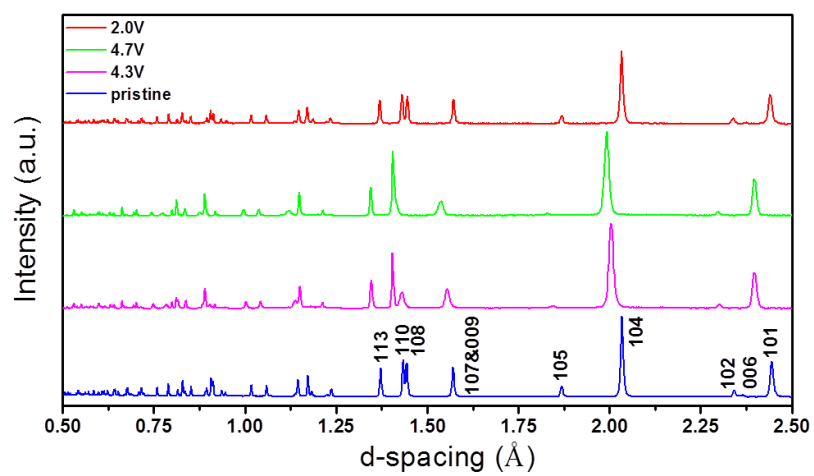


Figure S3. Neutron diffraction patterns of NCA at different states of (dis)charge during the 1st cycle.

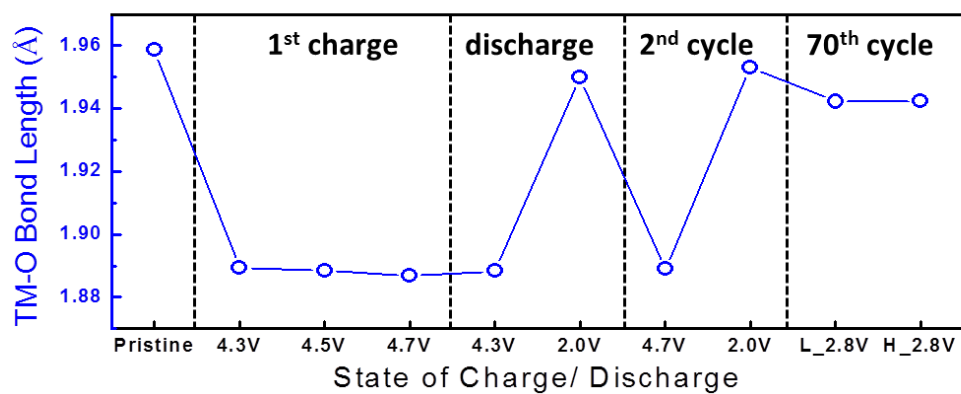


Figure S4. The TM-O bond length obtained from X-ray and Neutron diffraction joint refinement.

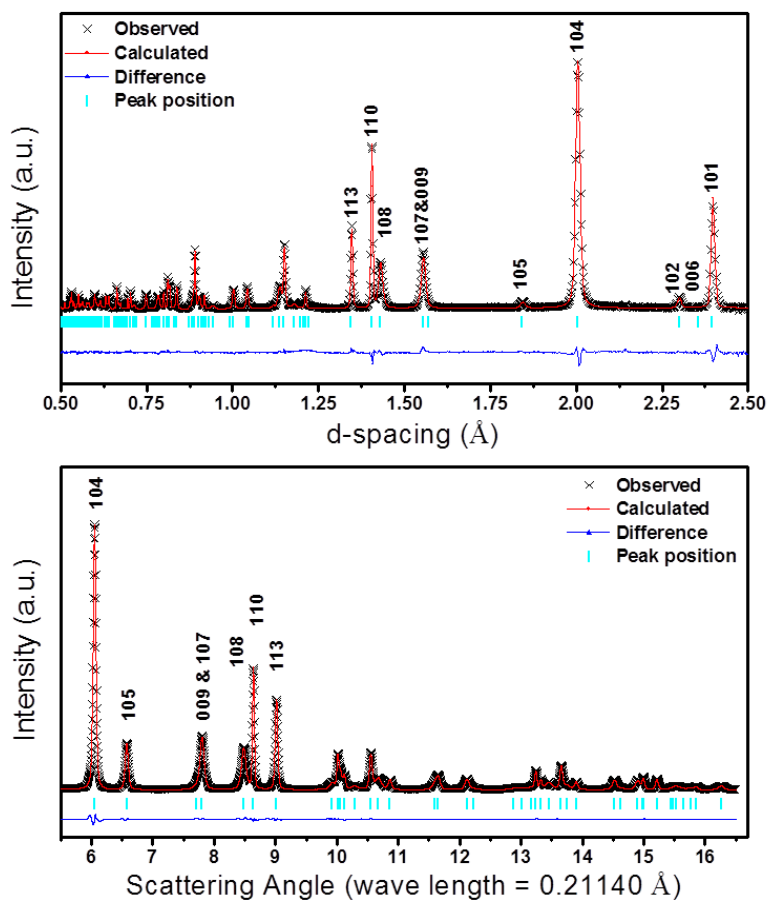


Figure S5. X-ray and Neutron diffraction data joint refinement of NCA at 1st cycle 4.3V charged state. Neutron (upper) and X-ray (lower).

Table S2. X-ray and Neutron diffraction data joint refinement results of NCA at 1st cycle 4.3V charged state.

| 1 st cycle 4.3V, Space Group: $R\bar{3}m$ $a=b= 2.80623(4)$ Å, $c= 14.1331(4)$ Å, X-ray: $R_{wp}= 3.80\%$, Neutron: $R_{wp}= 3.66\%$ | | | | | | |
|--|---|---|------------|-----------|-------------------------|--------------|
| Atom type | x | y | z | Occupancy | 100*U (Å ²) | |
| Li | 0 | 0 | 0 | 0.000 | U11=U22= 0.26(1) | U33= 1.23(3) |
| Ni | 0 | 0 | 0 | 0.784(1) | U11=U22= 0.26(1) | U33= 1.23(3) |
| Co | 0 | 0 | 0 | 0.150 | U11=U22= 0.26(1) | U33= 1.23(3) |
| Al | 0 | 0 | 0 | 0.050 | U11=U22= 0.26(1) | U33= 1.23(3) |
| Li | 0 | 0 | 0.5 | 0.166(14) | Uiso= 1.58(35) | |
| Ni | 0 | 0 | 0.5 | 0.016(1) | Uiso= 1.58(35) | |
| O | 0 | 0 | 0.26455(5) | 1.000 | Uiso= 0.86(2) | |

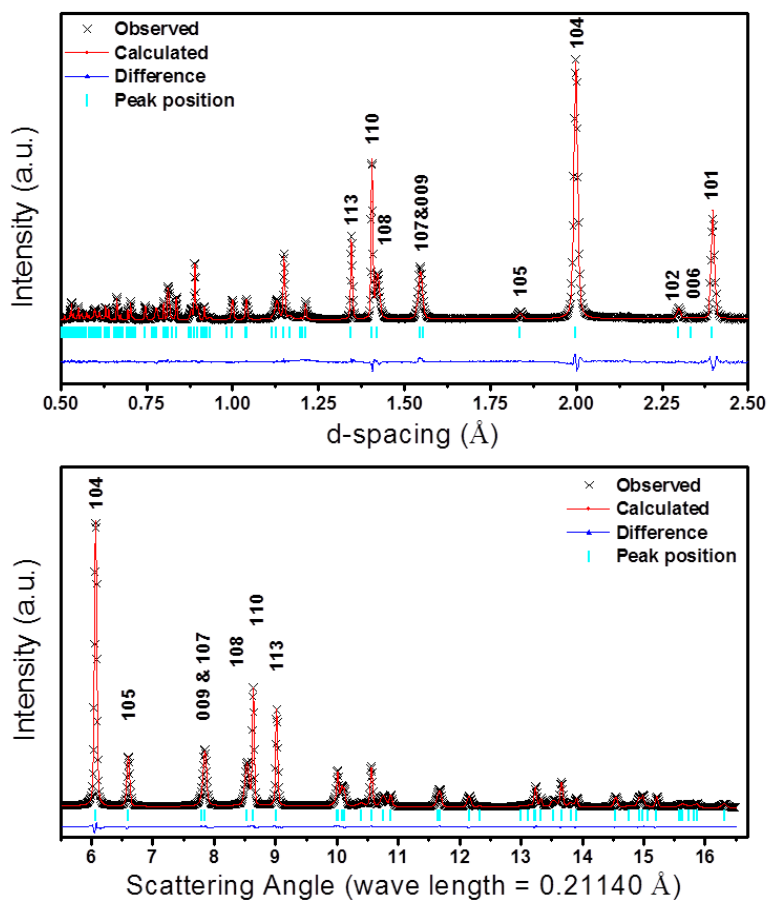


Figure S6. X-ray and Neutron diffraction data joint refinement of NCA at 1st cycle 4.5V charged state. Neutron (upper) and X-ray (lower).

Table S3. X-ray and Neutron diffraction data joint refinement results of NCA at 1st cycle 4.5V charged state.

| 1 st cycle 4.5V, Space Group: $R\bar{3}m$ $a=b= 2.80717(3) \text{ \AA}$, $c= 13.9972(3) \text{ \AA}$, X-ray: $R_{wp}= 2.72\%$, Neutron: $R_{wp}= 3.59\%$ | | | | | | |
|--|---|---|------------|-----------|--------------------------|--------------|
| Atom type | x | y | z | Occupancy | 100*U (\AA^2) | |
| Li | 0 | 0 | 0 | 0.000 | U11=U22= 0.26(1) | U33= 1.76(3) |
| Ni | 0 | 0 | 0 | 0.784(1) | U11=U22= 0.26(1) | U33= 1.76(3) |
| Co | 0 | 0 | 0 | 0.150 | U11=U22= 0.26(1) | U33= 1.76(3) |
| Al | 0 | 0 | 0 | 0.050 | U11=U22= 0.26(1) | U33= 1.76(3) |
| Li | 0 | 0 | 0.5 | 0.147(17) | Uiso= 2.43(46) | |
| Ni | 0 | 0 | 0.5 | 0.016(1) | Uiso= 2.48(46) | |
| O | 0 | 0 | 0.26406(6) | 1.000 | Uiso= 0.89(2) | |

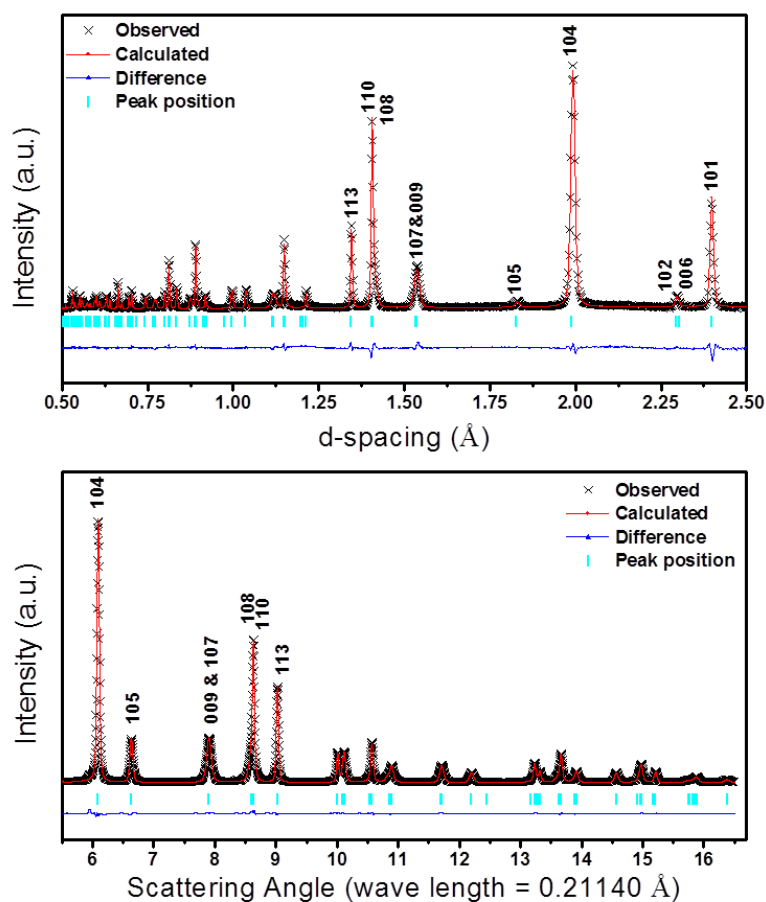


Figure S7. X-ray and Neutron diffraction data joint refinement of NCA at 1st cycle 4.7V charged state. The ADP parameters of transition metals are set as isotropic. Neutron (upper) and X-ray (lower).

Table S4. X-ray and Neutron diffraction data joint refinement results of NCA at 1st cycle 4.7V charged state.

| 1 st cycle 4.7V, Space Group: $R\bar{3}m$ $a=b= 2.80885(4) \text{ \AA}$, $c= 13.8216(4) \text{ \AA}$, X-ray: $R_{wp}= 3.97\%$, Neutron: $R_{wp}= 3.57\%$ | | | | | | |
|--|---|---|------------|-----------|--------------------------|--------------|
| Atom type | x | y | z | Occupancy | 100*U (\AA^2) | |
| Li | 0 | 0 | 0 | 0.000 | U11=U22= 0.18(1) | U33= 1.90(4) |
| Ni | 0 | 0 | 0 | 0.786(1) | U11=U22= 0.18(1) | U33= 1.90(4) |
| Co | 0 | 0 | 0 | 0.150 | U11=U22= 0.18(1) | U33= 1.90(4) |
| Al | 0 | 0 | 0 | 0.050 | U11=U22= 0.18(1) | U33= 1.90(4) |
| Li | 0 | 0 | 0.5 | 0.097(12) | Uiso= 1.79(23) | |
| Ni | 0 | 0 | 0.5 | 0.014(1) | Uiso= 1.79(23) | |
| O | 0 | 0 | 0.26355(6) | 1.000 | Uiso= 0.81 (2) | |

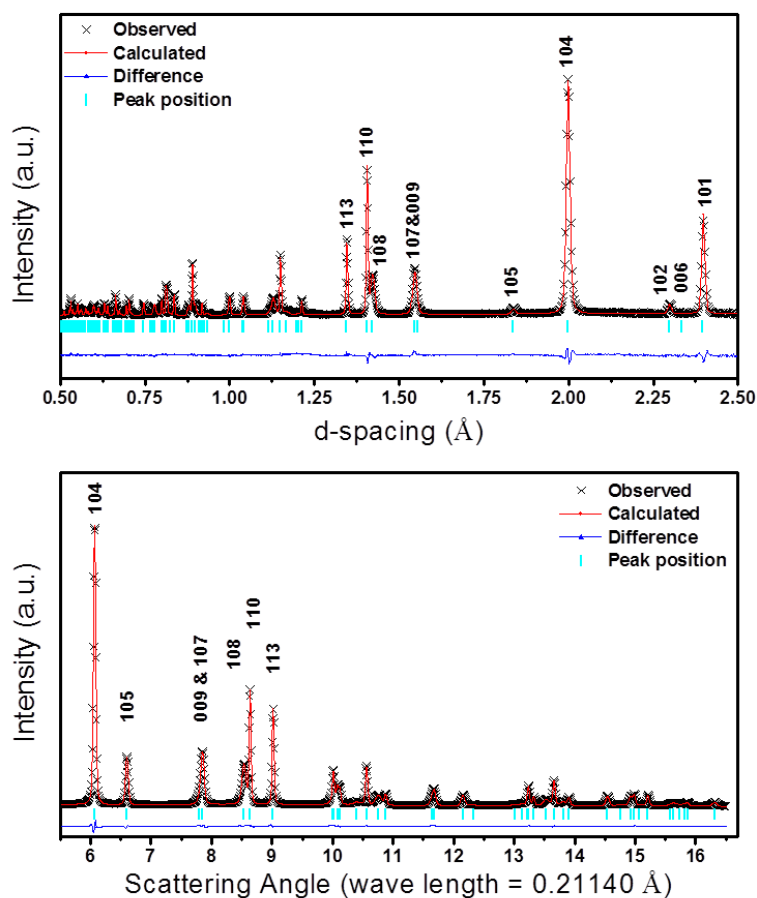


Figure S8. X-ray and Neutron diffraction data joint refinement of NCA at 1st cycle 4.3V discharged state. Neutron (upper) and X-ray (lower).

Table S5. X-ray and Neutron diffraction data joint refinement results of NCA at 1st cycle 4.3V discharged state.

| 1 st cycle 4.3V (discharge), Space Group: $R\bar{3}m$ $a=b= 2.80728(4) \text{ \AA}$, $c= 13.9942(4) \text{ \AA}$, X-ray: $R_{wp}= 2.70\%$, Neutron: $R_{wp}= 3.62\%$ | | | | | | |
|--|---|---|------------|-----------|--------------------------|---------------|
| Atom type | x | y | z | Occupancy | 100*U (\AA^2) | |
| Li | 0 | 0 | 0 | 0.000 | U11=U22= 0.26(1) | U33= 1.76 (3) |
| Ni | 0 | 0 | 0 | 0.784(1) | U11=U22= 0.26(1) | U33= 1.76 (3) |
| Co | 0 | 0 | 0 | 0.150 | U11=U22= 0.26(1) | U33= 1.76 (3) |
| Al | 0 | 0 | 0 | 0.050 | U11=U22= 0.26(1) | U33= 1.76 (3) |
| Li | 0 | 0 | 0.5 | 0.143(17) | Uiso= 2.47(46) | |
| Ni | 0 | 0 | 0.5 | 0.016(1) | Uiso= 2.47(46) | |
| O | 0 | 0 | 0.26408(6) | 1.000 | Uiso= 0.88 (2) | |

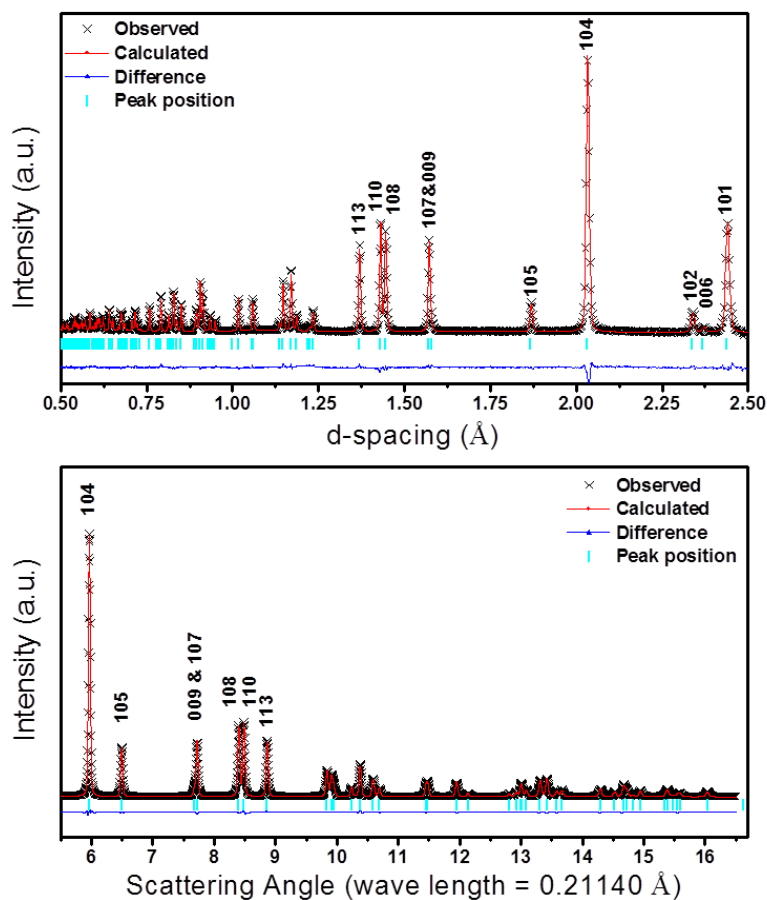


Figure S9. X-ray and Neutron diffraction data joint refinement of NCA at 1st cycle 2.0V discharged state. Neutron (upper) and X-ray (lower).

Table S6. X-ray and Neutron diffraction data joint refinement results of NCA at 1st cycle 2.0V discharged state.

| 1 st cycle 2.0V, Space Group: $R\bar{3}m$ $a=b=2.85742(2)$ Å, $c=14.2106(1)$ Å, X-ray: Rwp= 2.51%, Neutron: Rwp= 3.18% | | | | | | |
|---|---|---|------------|-----------|-------------------------|--------------|
| Atom type | x | y | z | Occupancy | 100*U (Å ²) | |
| Li | 0 | 0 | 0 | 0.000 | U11=U22= 0.30(1) | U33= 0.45(1) |
| Ni | 0 | 0 | 0 | 0.784(1) | U11=U22= 0.30(1) | U33= 0.45(1) |
| Co | 0 | 0 | 0 | 0.150 | U11=U22= 0.30(1) | U33= 0.45(1) |
| Al | 0 | 0 | 0 | 0.050 | U11=U22= 0.30(1) | U33= 0.45(1) |
| Li | 0 | 0 | 0.5 | 0.883(8) | Uiso= 1.27(3) | |
| Ni | 0 | 0 | 0.5 | 0.016(1) | Uiso= 1.27(3) | |
| O | 0 | 0 | 0.26019(3) | 1.000 | Uiso= 1.02(1) | |

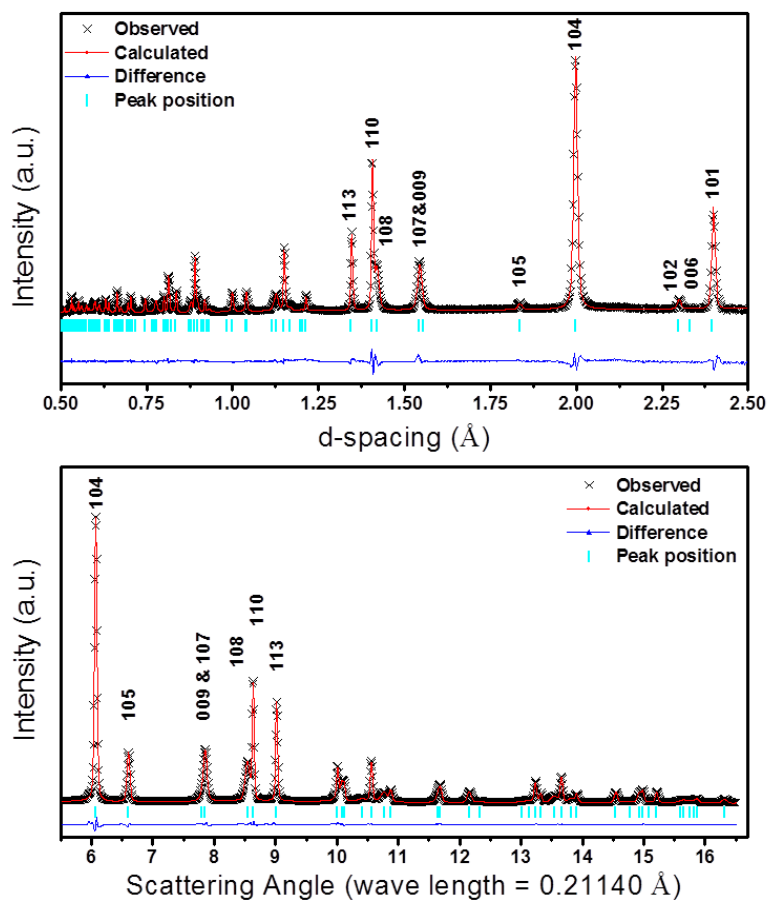


Figure S10. X-ray and Neutron diffraction data joint refinement of NCA at 2nd cycle 4.7V charged state. Neutron (upper) and X-ray (lower).

Table S7. X-ray and Neutron diffraction data joint refinement results of NCA at 2nd cycle 4.7V charged state.

| 2 nd cycle 4.7V, Space Group: $R\bar{3}m$ $a=b= 2.80756(4)$ Å, $c= 13.9783(5)$ Å, X-ray: $R_{wp}= 3.37\%$, Neutron: $R_{wp}= 3.77\%$ | | | | | | |
|--|---|---|------------|-----------|-------------------------|--------------|
| Atom type | x | y | z | Occupancy | 100*U (Å ²) | |
| Li | 0 | 0 | 0 | 0.000 | U11=U22= 0.29(2) | U33= 1.78(4) |
| Ni | 0 | 0 | 0 | 0.784(1) | U11=U22= 0.29(2) | U33= 1.78(4) |
| Co | 0 | 0 | 0 | 0.150 | U11=U22= 0.29(2) | U33= 1.78(4) |
| Al | 0 | 0 | 0 | 0.050 | U11=U22= 0.29(2) | U33= 1.78(4) |
| Li | 0 | 0 | 0.5 | 0.138(20) | Uiso= 2.25(55) | |
| Ni | 0 | 0 | 0.5 | 0.016(1) | Uiso= 2.25(55) | |
| O | 0 | 0 | 0.26394(7) | 1.000 | Uiso= 0.93(3) | |

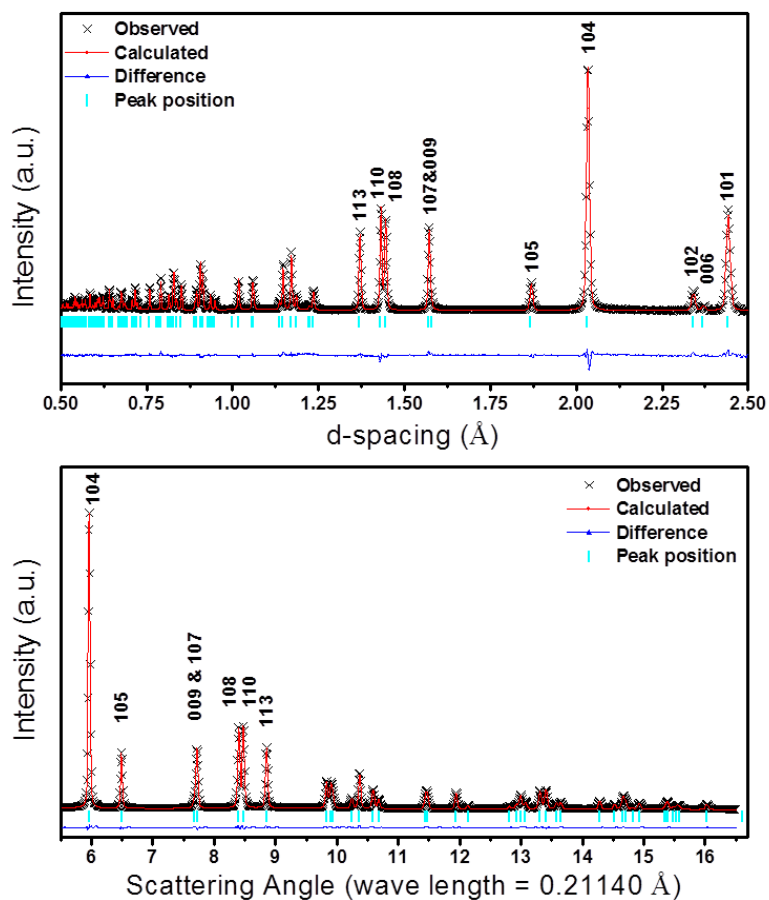


Figure S11. X-ray and Neutron diffraction data joint refinement of NCA at 2nd cycle 2.0V discharged state. Neutron (upper) and X-ray (lower).

Table S8. X-ray and Neutron diffraction data joint refinement results of NCA at 2nd cycle 2.0V discharged state.

| 2 nd cycle 2.0V, Space Group: $R\bar{3}m$ $a=b= 2.86075(3) \text{ \AA}$, $c= 14.2067(2) \text{ \AA}$, X-ray: $R_{wp}= 2.53\%$, Neutron: $R_{wp}= 3.19\%$ | | | | | | |
|--|---|---|------------|-----------|--------------------------|--------------|
| Atom type | x | y | z | Occupancy | 100*U (\AA^2) | |
| Li | 0 | 0 | 0 | 0.000 | U11=U22= 0.34(2) | U33= 0.48(1) |
| Ni | 0 | 0 | 0 | 0.782(2) | U11=U22= 0.34(2) | U33= 0.48(1) |
| Co | 0 | 0 | 0 | 0.150 | U11=U22= 0.34(2) | U33= 0.48(1) |
| Al | 0 | 0 | 0 | 0.050 | U11=U22= 0.34(2) | U33= 0.48(1) |
| Li | 0 | 0 | 0.5 | 0.906(10) | Uiso= 1.24(4) | |
| Ni | 0 | 0 | 0.5 | 0.018(2) | Uiso= 1.24(4) | |
| O | 0 | 0 | 0.25994(4) | 1.000 | Uiso= 1.05(2) | |

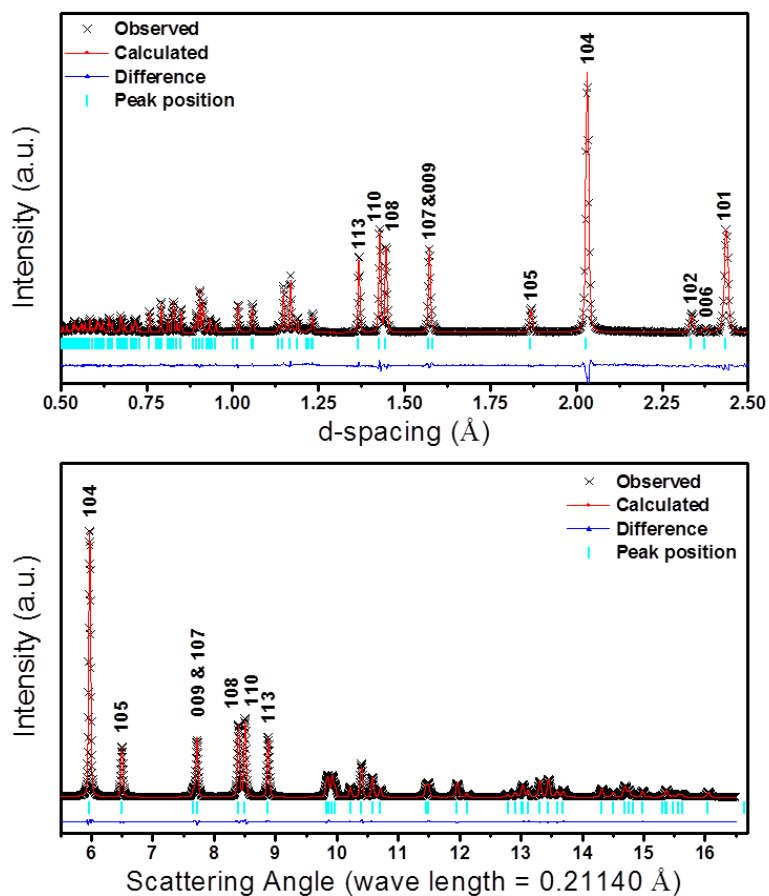


Figure S12. X-ray and Neutron diffraction data joint refinement of NCA at 70th cycle 2.8V discharged state. Neutron (upper) and X-ray (lower).

Table S9. X-ray and Neutron diffraction data joint refinement results of NCA at 70th cycle 2.8V discharged state.

| 70 th cycle 2.8-4.2V discharged, Space Group: $R\bar{3}m$ $a=b= 2.85095(2)$ Å, $c= 14.2402(1)$ Å, X-ray: Rwp= 3.12%, Neutron: Rwp= 3.30% | | | | | | |
|---|---|---|------------|-----------|-------------------------|--------------|
| Atom type | x | y | z | Occupancy | 100*U (Å ²) | |
| Li | 0 | 0 | 0 | 0.000 | U11=U22= 0.28(1) | U33= 0.47(1) |
| Ni | 0 | 0 | 0 | 0.785(1) | U11=U22= 0.28(1) | U33= 0.47(1) |
| Co | 0 | 0 | 0 | 0.150 | U11=U22= 0.28(1) | U33= 0.47(1) |
| Al | 0 | 0 | 0 | 0.050 | U11=U22= 0.28(1) | U33= 0.47(1) |
| Li | 0 | 0 | 0.5 | 0.814 (9) | Uiso= 1.34(4) | |
| Ni | 0 | 0 | 0.5 | 0.015(1) | Uiso= 1.34(4) | |
| O | 0 | 0 | 0.26092(4) | 1.000 | Uiso= 0.98(2) | |

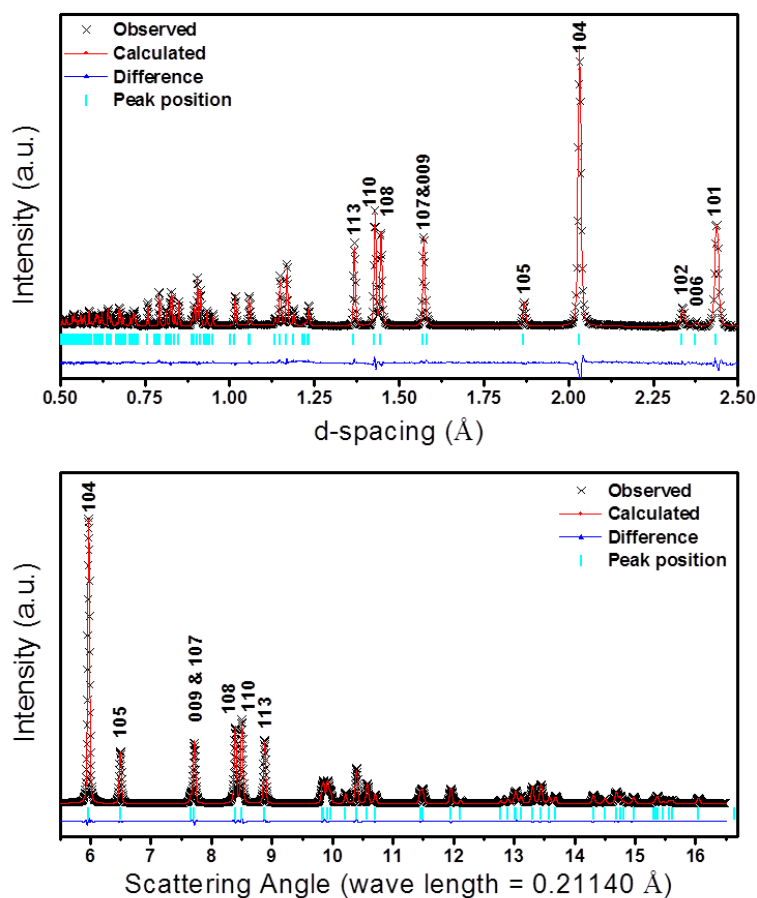


Figure S13. X-ray and Neutron diffraction data joint refinement of NCA at 70th cycle 2.8V discharged state. Neutron (upper) and X-ray (lower).

Table S10. X-ray and Neutron diffraction data joint refinement results of NCA at 70th cycle 2.8V discharged state.

| 70 th cycle 2.8-4.7V discharged, Space Group: $R\bar{3}m$ $a=b= 2.85174(2) \text{ \AA}$, $c= 14.2461(1) \text{ \AA}$, X-ray: Rwp= 3.28%, Neutron: Rwp= 3.25% | | | | | | |
|---|---|---|------------|-----------|--------------------------|--------------|
| Atom type | x | y | z | Occupancy | 100*U (\AA^2) | |
| Li | 0 | 0 | 0 | 0.000 | U11=U22= 0.28(1) | U33= 0.52(1) |
| Ni | 0 | 0 | 0 | 0.779(1) | U11=U22= 0.28(1) | U33= 0.52(1) |
| Co | 0 | 0 | 0 | 0.150 | U11=U22= 0.28(1) | U33= 0.52(1) |
| Al | 0 | 0 | 0 | 0.050 | U11=U22= 0.28(1) | U33= 0.52(1) |
| Li | 0 | 0 | 0.5 | 0.787(10) | Uiso= 1.49(4) | |
| Ni | 0 | 0 | 0.5 | 0.021(1) | Uiso= 1.49(4) | |
| O | 0 | 0 | 0.26099(4) | 1.000 | Uiso= 1.03(2) | |

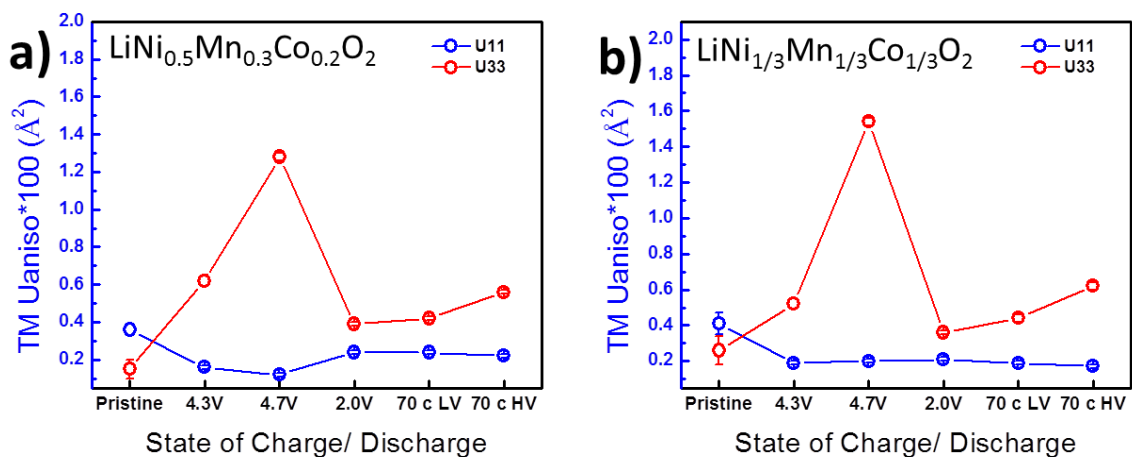


Figure S14. Atomic displacement parameters from X-ray and Neutron diffraction data joint refinement. a) $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$; b) $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$.

Modeling the ^7Li NMR spectra of cycled NCA

The ^7Li NMR spectra of $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ at different states of discharge were modeled with a simple random solution model similar to the one used in ref.¹ The ^7Li spectrum of delithiated NCA depends on the number of paramagnetic Ni^{3+} ions in the nearest neighbor (nn) and next nearest neighbor (nnn) environments that form 90° and 180° Li-O- Ni^{3+} bond pathways, respectively. For a dynamic Jahn-Teller distortion, the rapid averaging of the Jahn-Teller lengthened and Jahn-Teller shortened Ni-O bonds means that only a single contribution to the ^7Li shift is expected for each Li-O- Ni^{3+} bond pathway as discussed in ref.²

In total there are $6 \times 90^\circ$ Li-O- M (nn) and $6 \times 180^\circ$ Li-O- M bond pathway configurations, where $M = \text{Ni}^{3+}$, Ni^{4+} , Al^{3+} and Co^{3+} . To simplify the model, it was assumed that only $\text{Ni}^{3+} \rightarrow \text{Ni}^{4+}$ oxidation was occurring and so the probability of a metal species P_M being in a nn or nnn environment around Li is given by the Li composition (x) as $P_{\text{Ni}^{3+}} = (x - 0.2)$, $P_{\text{Ni}^{4+}} = (1 - x)$, $P_{\text{Co}^{3+}} = 0.15$ and $P_{\text{Al}^{3+}} = 0.05$.

The total probability f_{Li} of a Li site having k Ni^{3+} neighbors in the 6 nn and 6 nnn sites is given by;

$$f_{\text{Li},\text{Ni}^{3+}} = \binom{6}{k_{\text{nn}}} \binom{6}{k_{\text{nnn}}} (P_{\text{Ni}^{3+}})^{k_{\text{nn}} + k_{\text{nnn}}} (1 - P_{\text{Ni}^{3+}})^{12 - k_{\text{nn}} - k_{\text{nnn}}}$$

where:

$$\binom{6}{k} = \frac{6!}{k! (6 - k)!}$$

For each possible Li configuration the Fermi contact shift, δ , is calculated by summing up the individual ^7Li Li-O- M bond pathway contributions. Dynamically Jahn-Teller averaged ^7Li NMR bond pathway contributions of -15 and 110 ppm obtained from a previous experimental study were used for the 90° and 180° Li-O- Ni^{3+} bond pathways, respectively, and all other Li-O- M pathway contributions were assumed to be 0 ppm.³ The overall ^7Li spectrum was calculated by modeling each Li environment with shift, δ , and intensity, $f_{\text{Li},\text{Ni}^{3+}}$, with a Gaussian peak of width 60 ppm. The model spectra at different states of discharge corresponding to experimentally observed compositions, i.e. $x = 1$ (pristine), $x = 0.85$ (1st discharge to 2 V), $x = 0.8$ (70 cycles low voltage window) and $x = 0.71$ (70 cycles high voltage window) are shown in Figure S15.

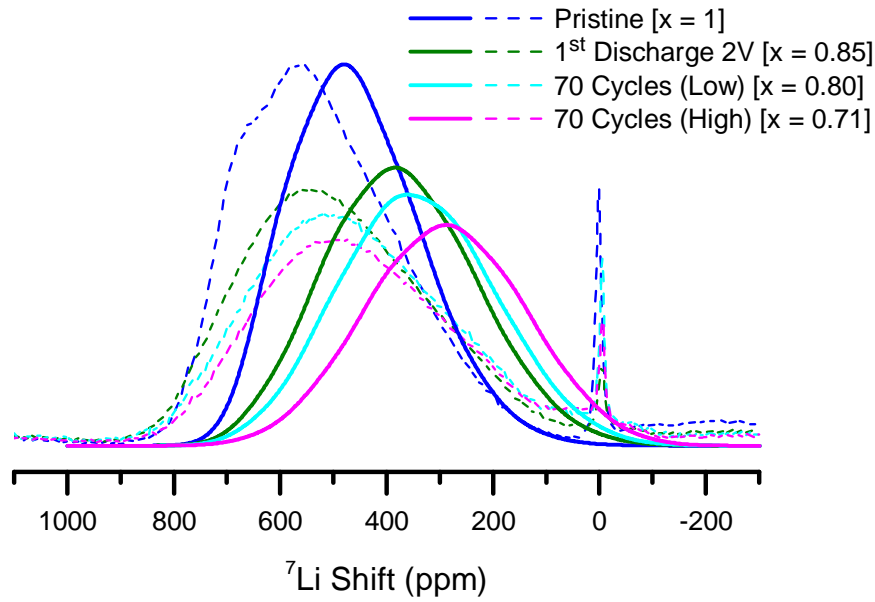


Figure S15 Comparison of experimental ${}^7\text{Li}$ NMR spectra (dashed lines) and model spectra (solid lines) of $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cycled to different discharged states (x). The model spectra were produced with a random solution model in which $M = (x-0.2)\text{Ni}^{3+}$, $(1-x)\text{Ni}^{4+}$, 0.05Al^{3+} and 0.15Co^{3+} ions were randomly distributed in the $6 \times 90^\circ$ Li-O- M (nearest neighbor) and $6 \times 180^\circ$ Li-O- M (next nearest neighbor) environments around Li. Dynamic Jahn-Teller averaged ${}^7\text{Li}$ NMR bond pathway contributions of -15 and 110 ppm were used for the 90° and 180° Li-O- Ni^{3+} bond pathways, respectively. Each Li resonance in the random solution model was modeled with a Gaussian peak with a width of 60 ppm.

It can be seen from Figure S15 that although the absolute value of the ${}^7\text{Li}$ shift is underestimated in the model spectra, the systematic decrease in the ${}^7\text{Li}$ NMR shift with Li content (x), as result of $\text{Ni}^{3+} \rightarrow \text{Ni}^{4+}$ oxidation is well represented. The difference in the experimentally observed and modeled ${}^7\text{Li}$ NMR shifts may in part be related to the magnitude of the bond pathway contributions used which were taken from the Co-rich phase of $\text{LiNi}_{0.3}\text{Co}_{0.7}\text{O}_2$.³ The simple random solution model in this work also does not include any effects of Li and $\text{Ni}^{3+}/\text{Ni}^{4+}$ ordering or $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$ oxidation, which may lead to slight deviations in the distribution. However, even without these additional effects, the simple model used in this work does suggest that the variation in the ${}^7\text{Li}$ spectrum after extended cycling is predominantly due to the differences in Li content/ Ni-oxidation state instead of from extensive structural rearrangement of Co, Al and Ni.

Table S11. Magnetic parameters of NCA samples at different cycling stages.

| Sample | C_M , emu K/ mol TM | Θ , K | χ_0 , 10^{-4} emu/mol TM | M_R , emu/ mol TM | T_f , K | μ_{exp} , μ_B | μ_{theor} , μ_B |
|------------|-----------------------------|-----------------|---------------------------------------|------------------------------|--------------|-----------------------|----------------------------|
| pristine | 0.489(1) | 17.1(1) | 2.0 | 9.2 | 6.5 | 1.98 | 1.60 |
| 4.3 V ch1 | 0.016(1) | -4.3(6) | 1.9 | 0.20 | - | 0.36 | 0.33 |
| 4.5 V ch1 | 0.021(1) | -12.6(4) | 2.8 | 0.16 | - | 0.41 | 0.41 |
| 4.7 V ch1 | 0.027(3) | -5.3(3) | 2.8 | 0.15 | - | 0.47 | 0.57 |
| 4.7 V ch2 | 0.021(1) | 2.8(1) | 2.1 | 0.27 | - | 0.41 | 0.44 |
| 4.3 V dis1 | 0.021(1) | -7.0(2) | 2.6 | 0.22 | - | 0.41 | 0.42 |
| 2.0 V dis1 | 0.354(1) | 27.1(1) | 1.0 | 16.5 | 6.5 and 100 | 1.68 | 1.47 |
| 2.0 V dis2 | 0.363(1) | 27.4(1) | 3.0 | 20.6 | 6.5 and 100 | 1.70 | 1.49 |
| 2.8 V 70L | 0.344(1) | 21.8(2) | 3.0 | 19.6 | 6.5 and 100 | 1.66 | 1.39 |
| 2.8 V 70H | 0.324(1) | 24.1(1) | 3.8 | 17.1 | 6.5 and 100 | 1.61 | 1.36 |

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