Supporting Information

Probing Sources of Capacity Fade in LiNi$_{0.6}$Mn$_{0.2}$Co$_{0.2}$O$_2$ (NMC622): An *Operando* XRD Study of Li/NMC622 Batteries During Extended Cycling

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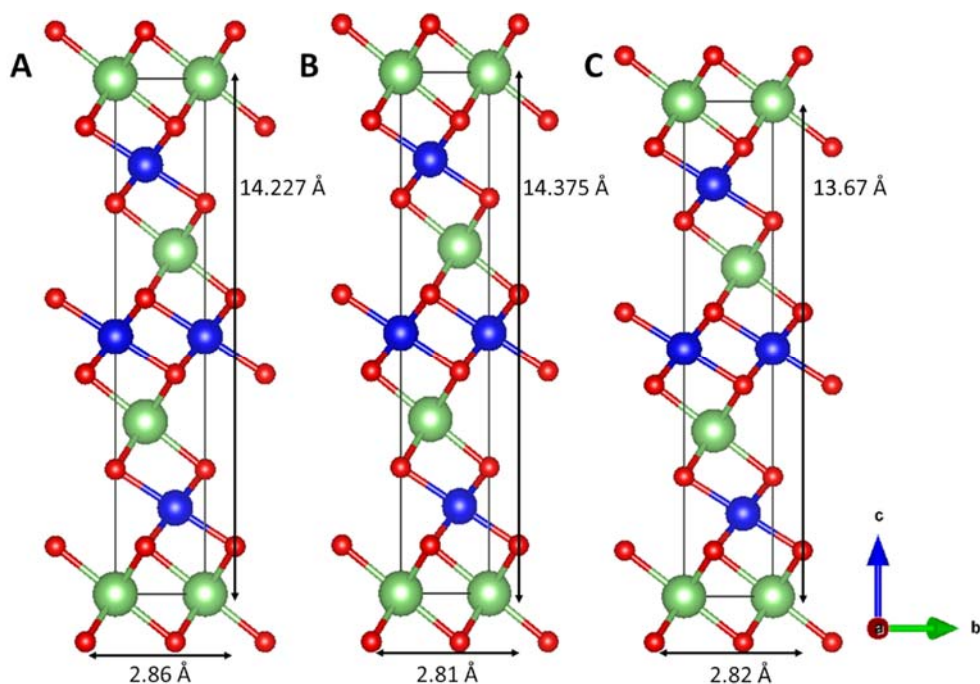*Corresponding author: amy.marschilok@stonybrook.edu (ACM)

Figure S1. Crystal structures of the *(A)* H1, *(B)* H2, and *(C)* H3 phases of LiNi$_{ix}$Mn$_y$Co$_z$O$_2$, lithium is green, oxygen is red, and the Ni/Mn/Co is blue.
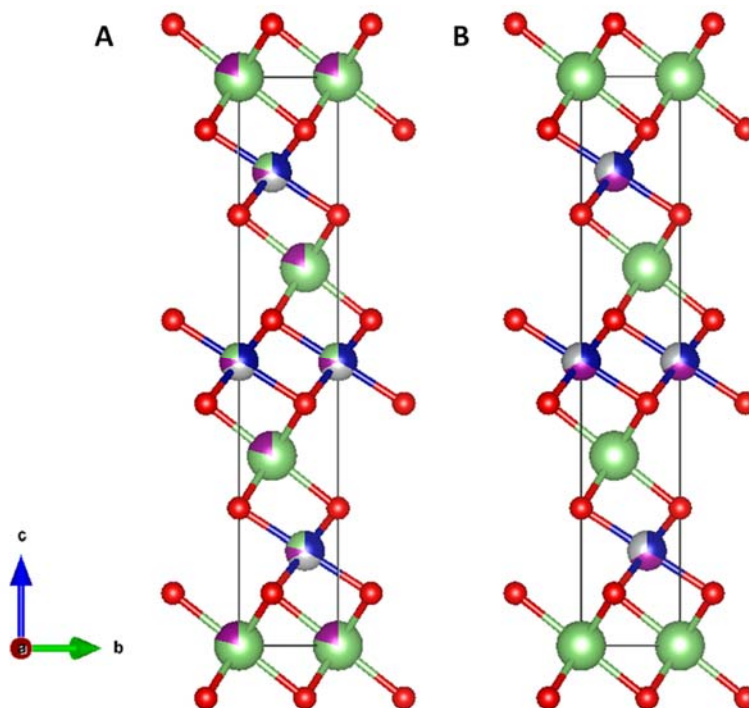

Figure S2. Crystal structure of NMC111 with Li-Ni site disorder *(A)* and without disorder *(B)*. Lithium is green, oxygen is red, nickel is purple, manganese is grey, and cobalt is blue.
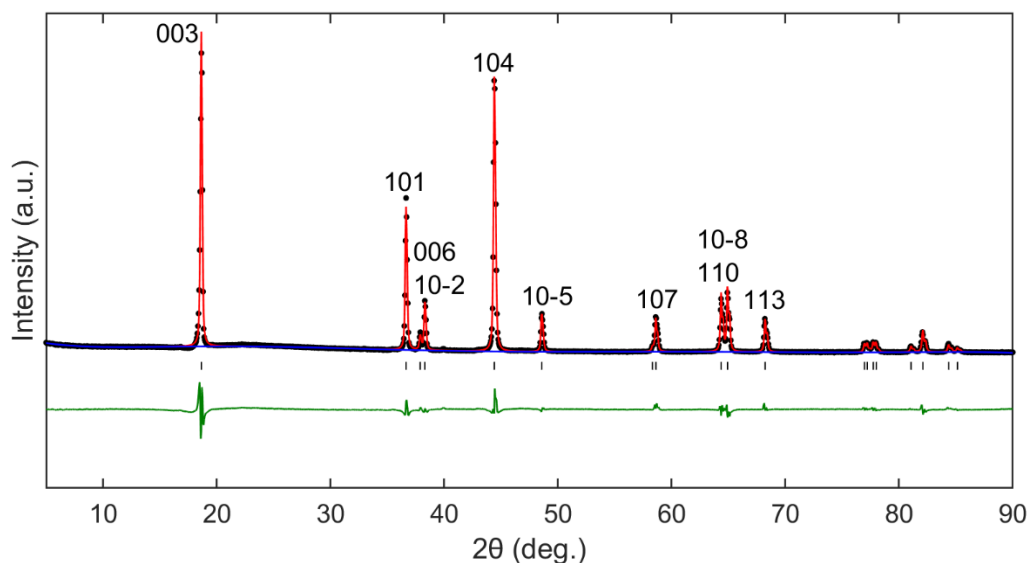
Figure S3. Rietveld refinement of NMC622. The data is in black, the calculated fit is in red, the background is in blue, and the difference is in green. The black lines correspond to the expected peak positions for NMC. The NMC peaks are indexed according to a prior structural report.[1]
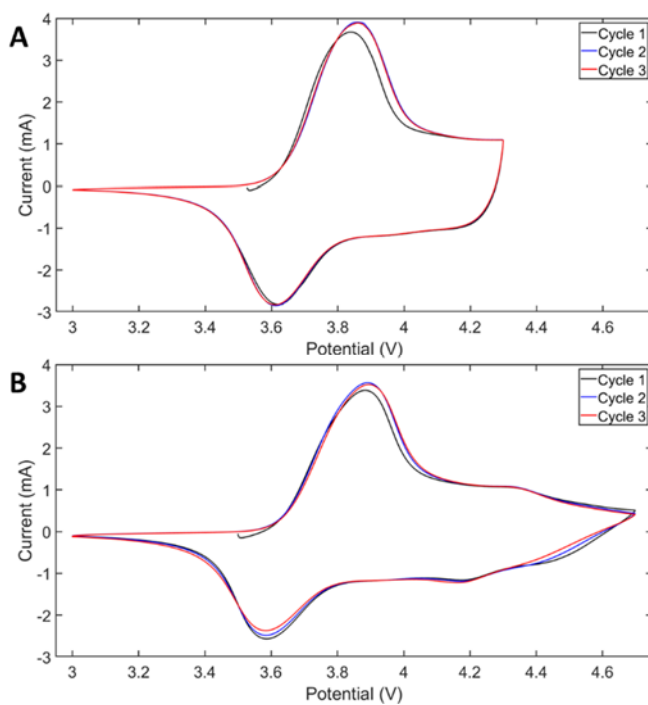

Figure S4. Cyclic voltammetry data of Li/NMC coin cells cycled from *(A)* 3-4.3 V and *(B)* 3-4.7 V.
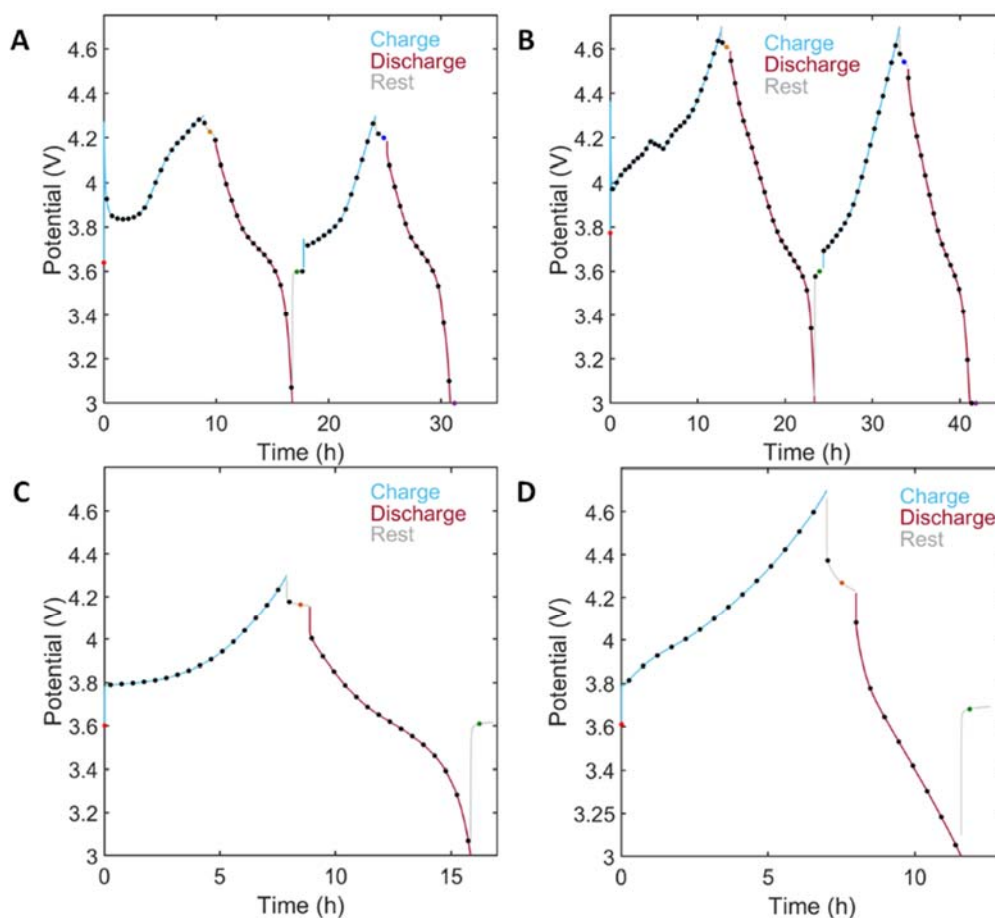
Figure S5. Galvanostatic cycling data of pouch cells used for operando measurements. The black points indicate when XRD scans were collected. The colored points indicate the key states of charge. *(A)* Cycles 1&2 for the 4.3 V cell, *(B)* cycles 1&2 for the 4.7 V cell, *(C)* cycle 101 for the 4.3 V cell, and *(D)* cycle 101 for the 4.7 V cell.
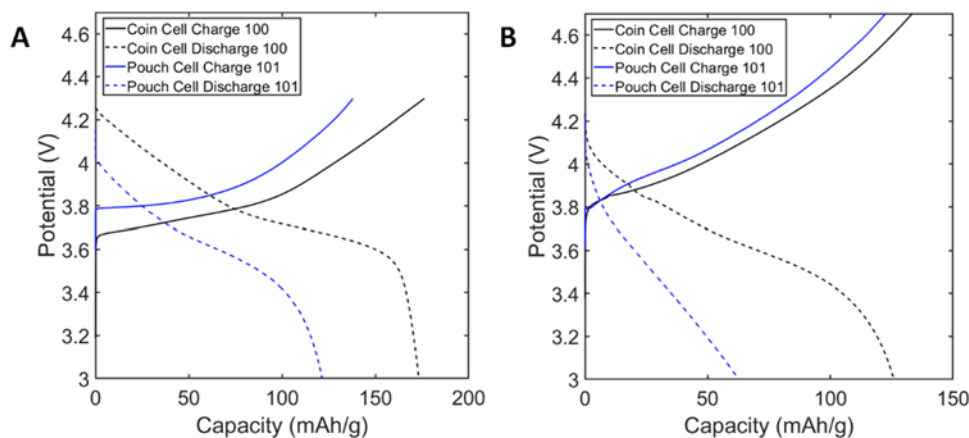

Figure S6. Galvanostatic cycling for coin cells at cycle 100 and pouch cells at cycle 101. *(A)* Cells cycled from 3-4.3 V, and *(B)* cells cycled from 3-4.7 V.
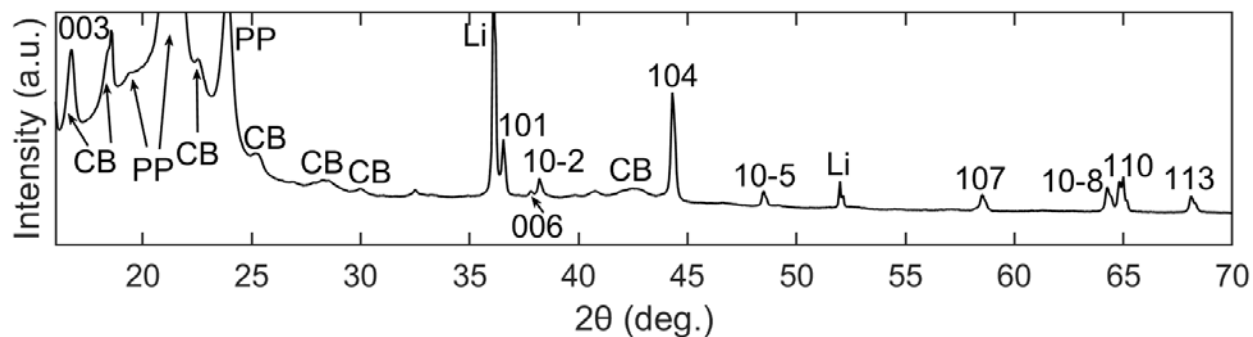
Figure S7. XRD pattern of the 3-4.3 V pouch cell prior to cycling. Peaks labelled as Li, CB, and PP correspond to lithium, the cell block, and polypropylene respectively.
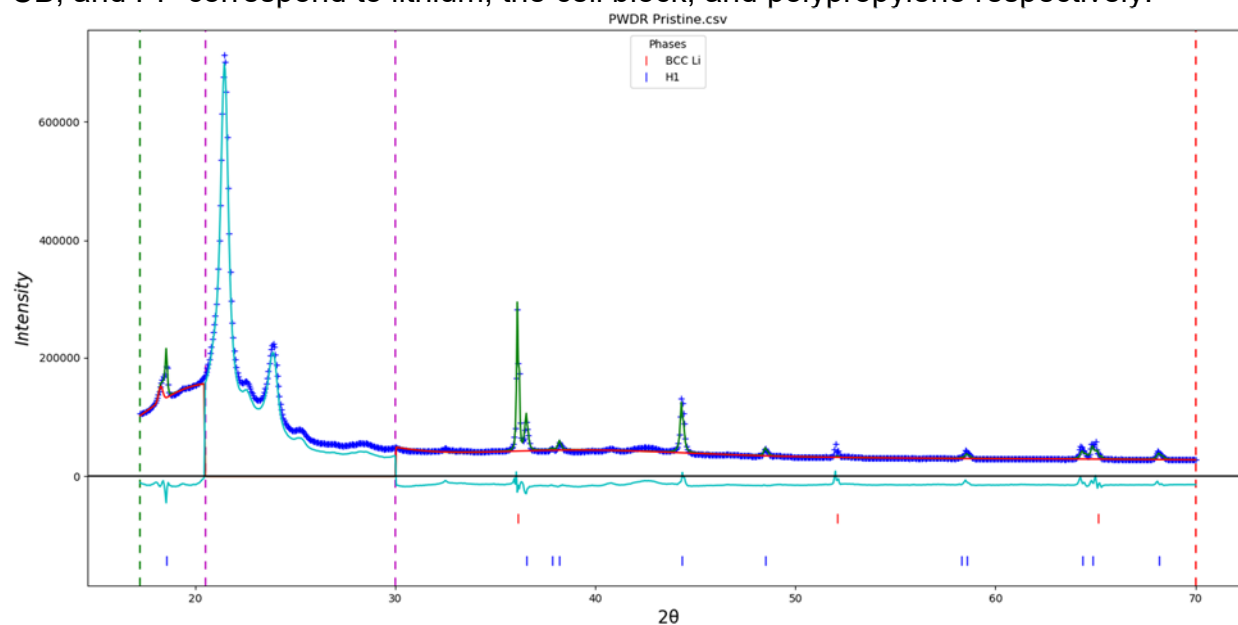

Figure S8. Rietveld refinement of the XRD pattern collected on the 3-4.3 V NMC622 pouch cell prior to cycling. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. The background peak at 18.3° was consistent with a peak associated with the cell block and was used for all cycle 1 and 2 refinements. %R_{wp}=4.30.
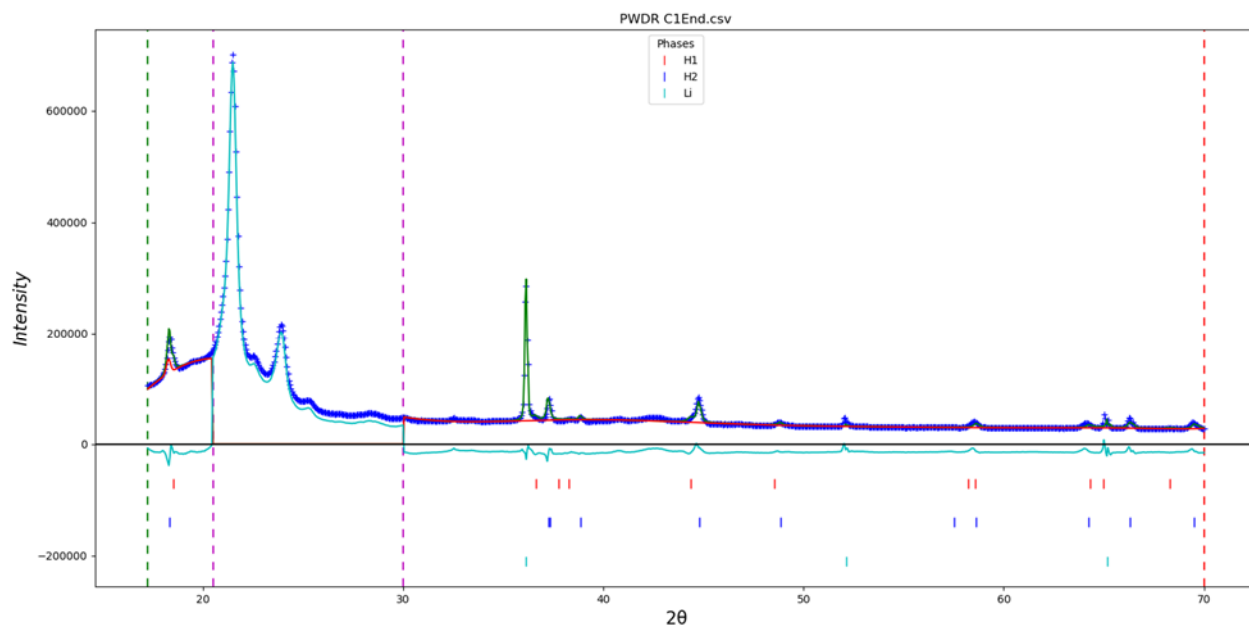
Figure S9. Rietveld refinement of the XRD pattern collected on the 3-4.3 V NMC622 pouch cell at the end of the 1st charge. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. %R_{wp}=4.49.
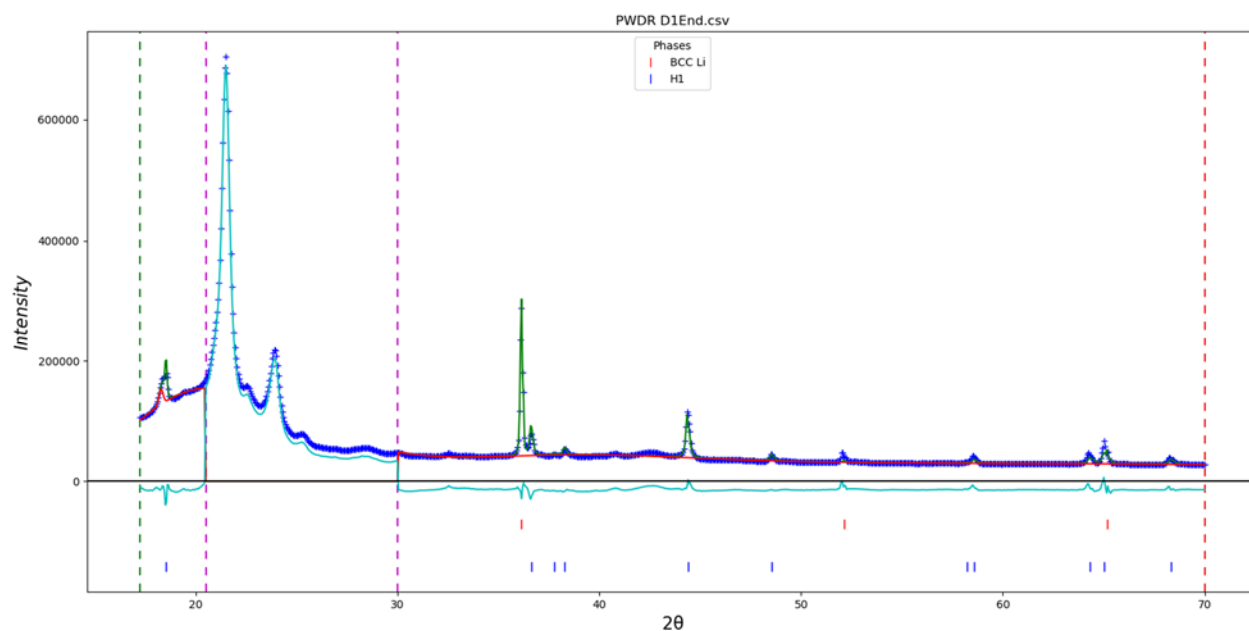

Figure S10. Rietveld refinement of the XRD pattern collected on the 3-4.3 V NMC622 pouch cell at the end of the 1st discharge. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. %R_{wp}=4.20.

Figure S11. Rietveld refinement of the XRD pattern collected on the 3-4.3 V NMC622 pouch cell at the end of the 2nd charge. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. %R$_{wp}$=4.45.
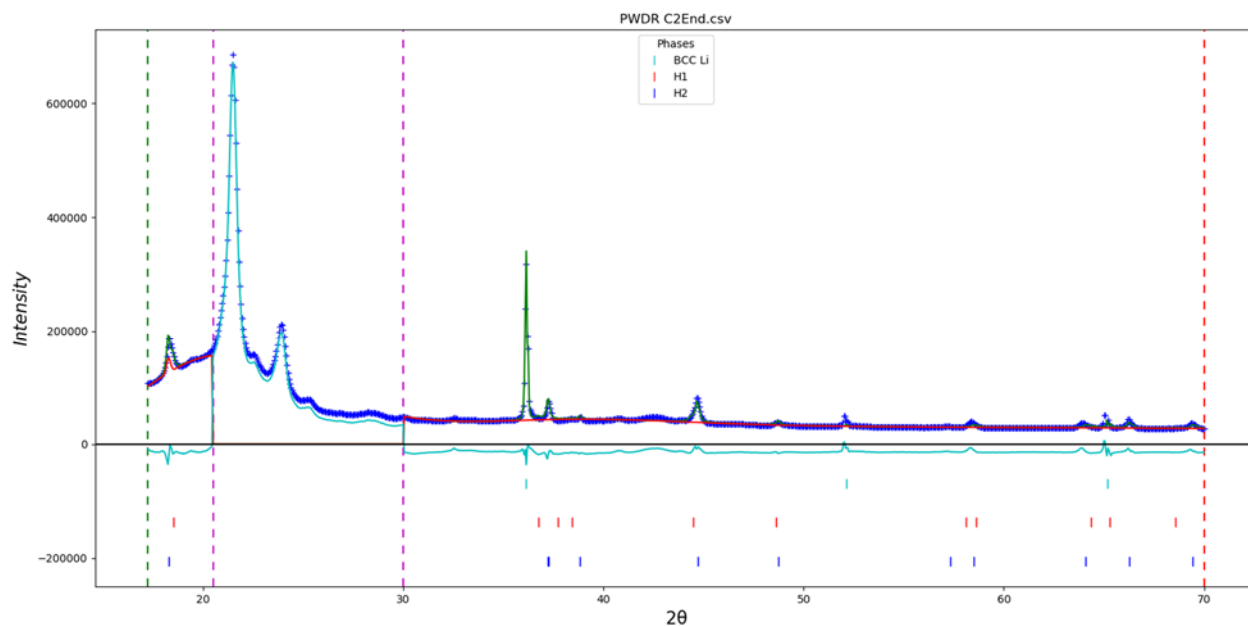

Figure S12. Rietveld refinement of the XRD pattern collected on the 3-4.3 V NMC622 pouch cell at the end of the 2nd discharge. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. %R$_{wp}$=4.27.
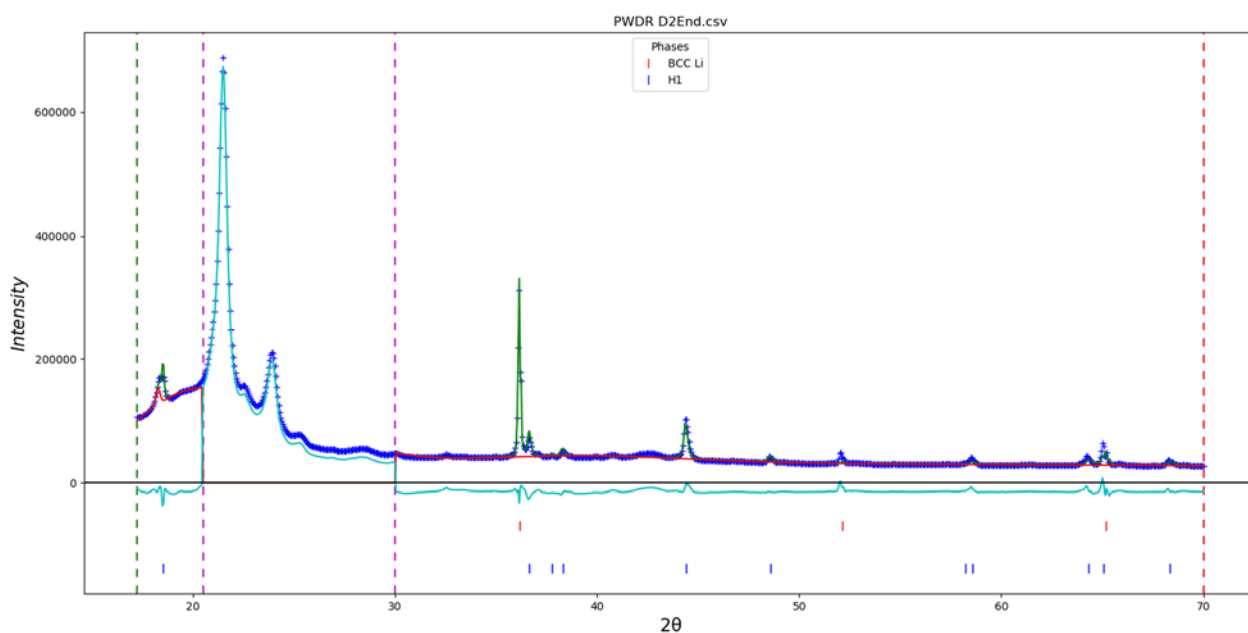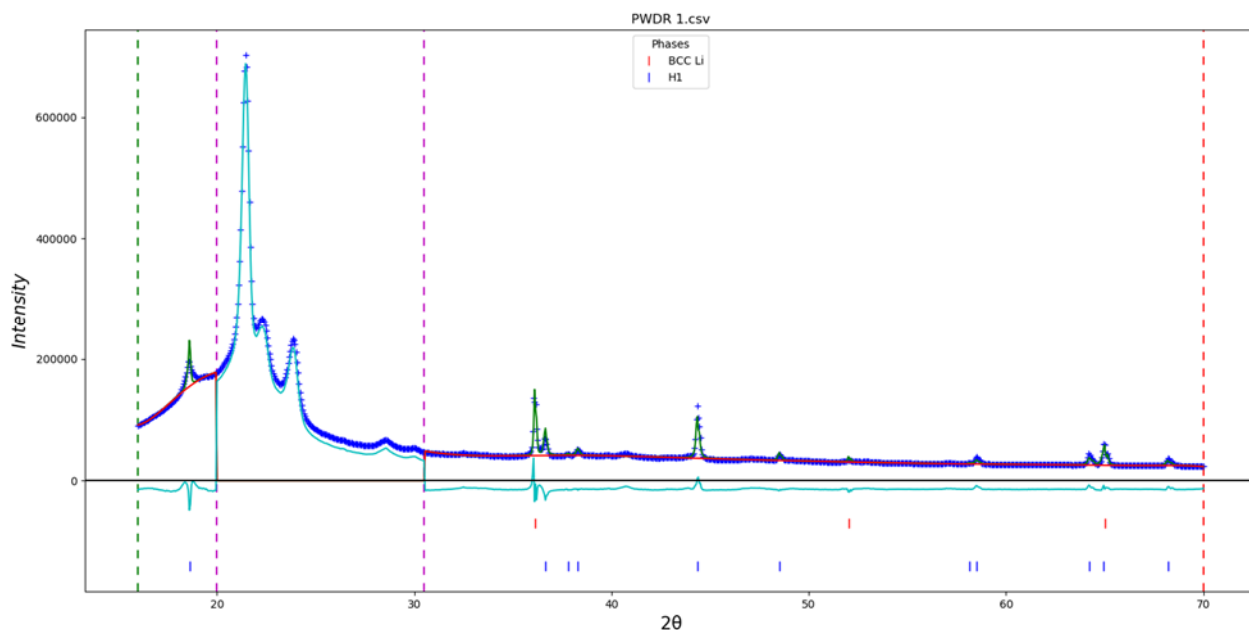
Figure S13. Rietveld refinement of the XRD pattern collected on the 3-4.3 V NMC622 pouch cell prior to the 101st cycle. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. A background peak was not used for the cycle 101 refinements as a less diffracting cell block was used. %R_{wp}=3.90.
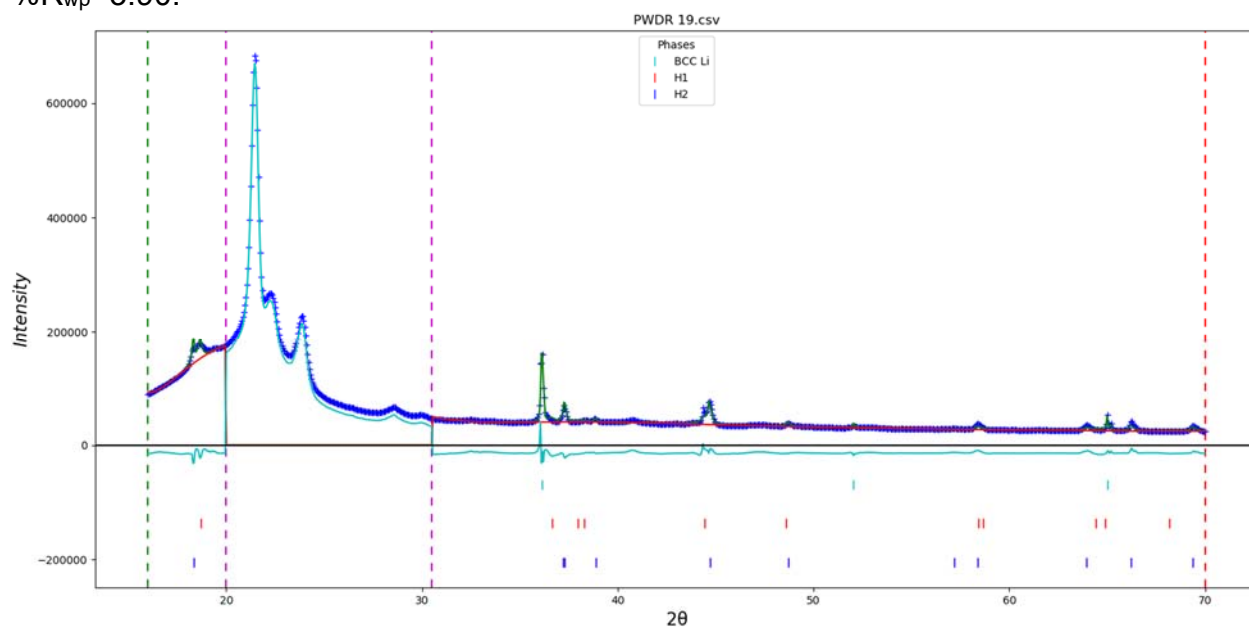

Figure S14. Rietveld refinement of the XRD pattern collected on the 3-4.3 V NMC622 pouch cell at the end of the 101st charge. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. %R_{wp}=3.61.
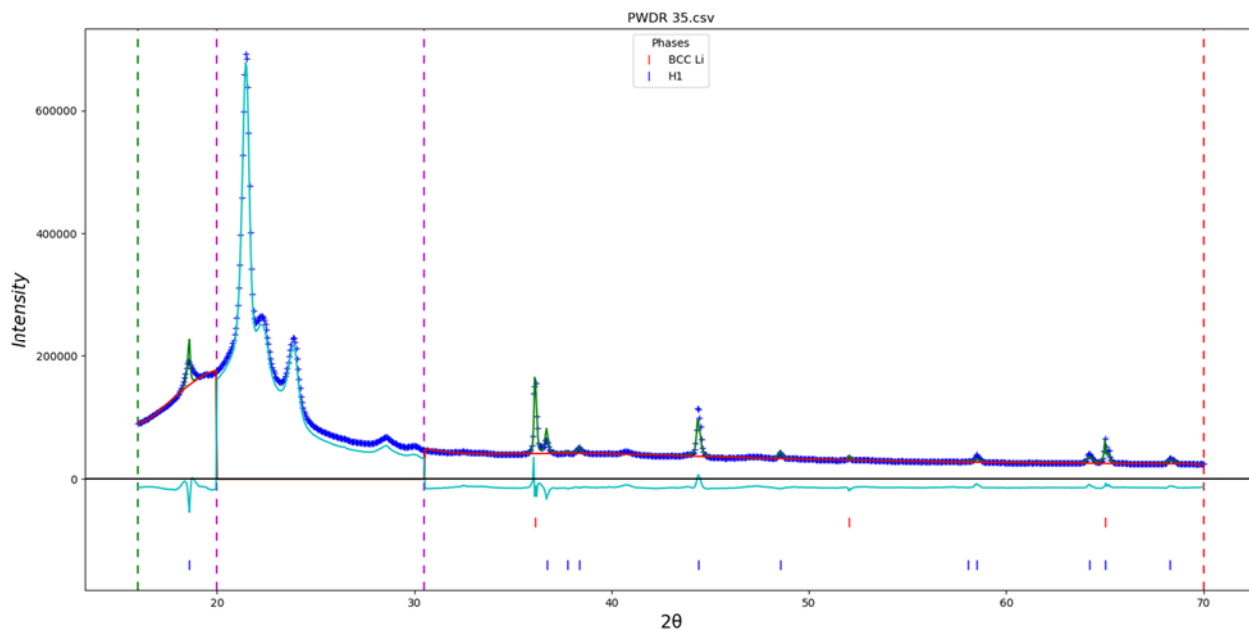
Figure S15. Rietveld refinement of the XRD pattern collected on the 3-4.3 V NMC622 pouch cell at the end of the 101st discharge. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. $\%R_{wp}=3.80$.

Figure S16. Rietveld refinement of the XRD pattern collected on the 3-4.7 V NMC622 pouch cell prior to cycling. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. $\%R_{wp}=3.78$.
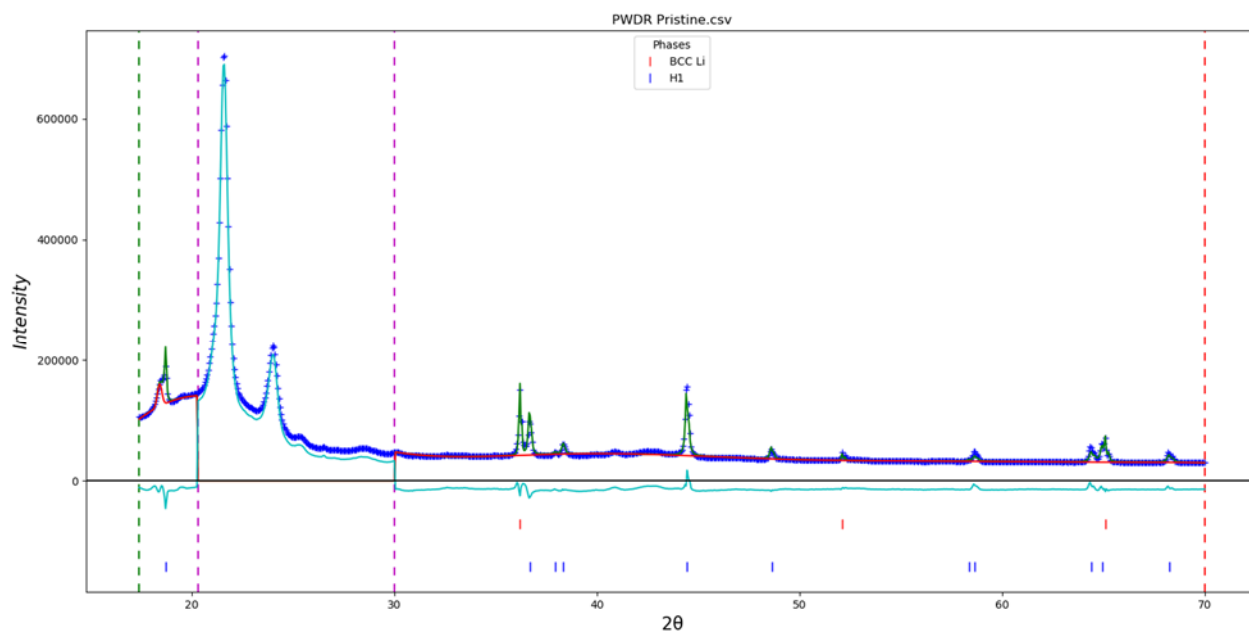
Figure S17. Rietveld refinement of the XRD pattern collected on the 3-4.7 V NMC622 pouch cell at the end of the 1st charge. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. %R_{wp}=5.31.
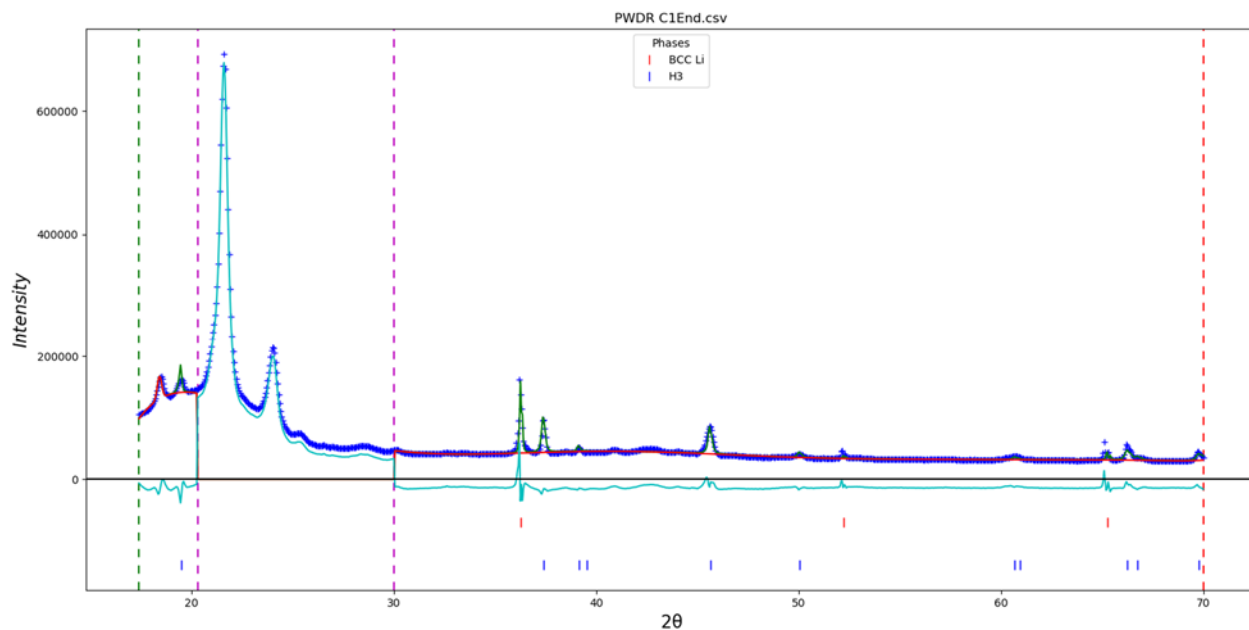

Figure S18. Rietveld refinement of the XRD pattern collected on the 3-4.7 V NMC622 pouch cell at the end of the 1st discharge. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. %R_{wp}=3.90.
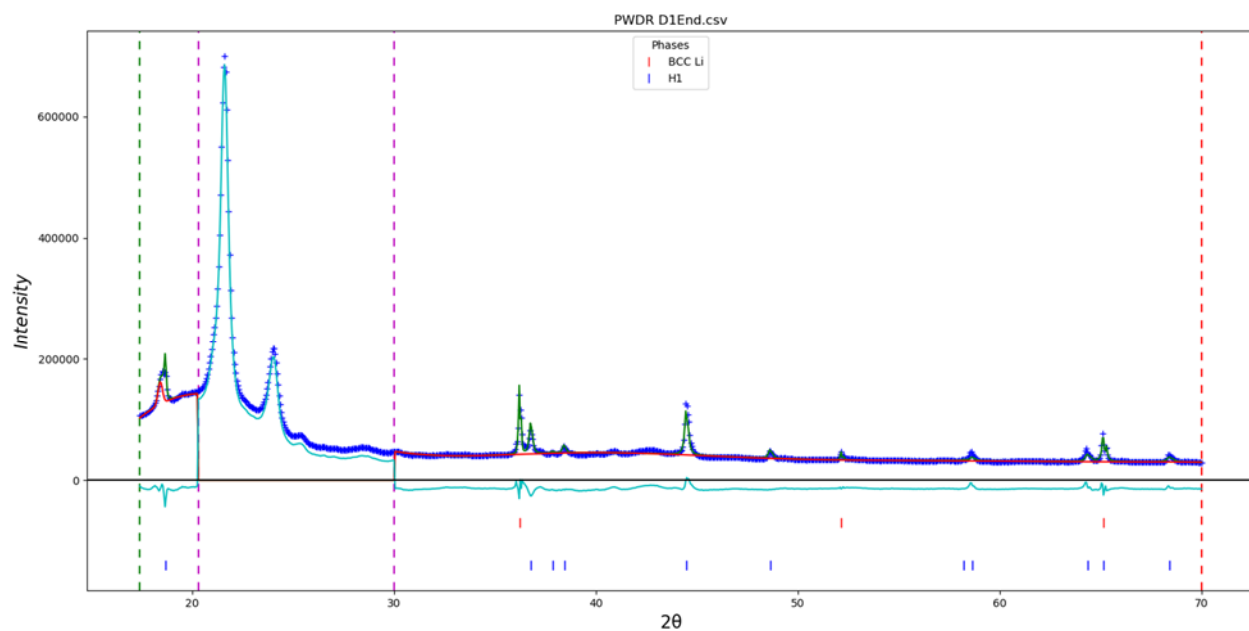
Figure S19. Rietveld refinement of the XRD pattern collected on the 3-4.7 V NMC622 pouch cell at the end of the 2nd charge. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. %R_{wp}=4.30.
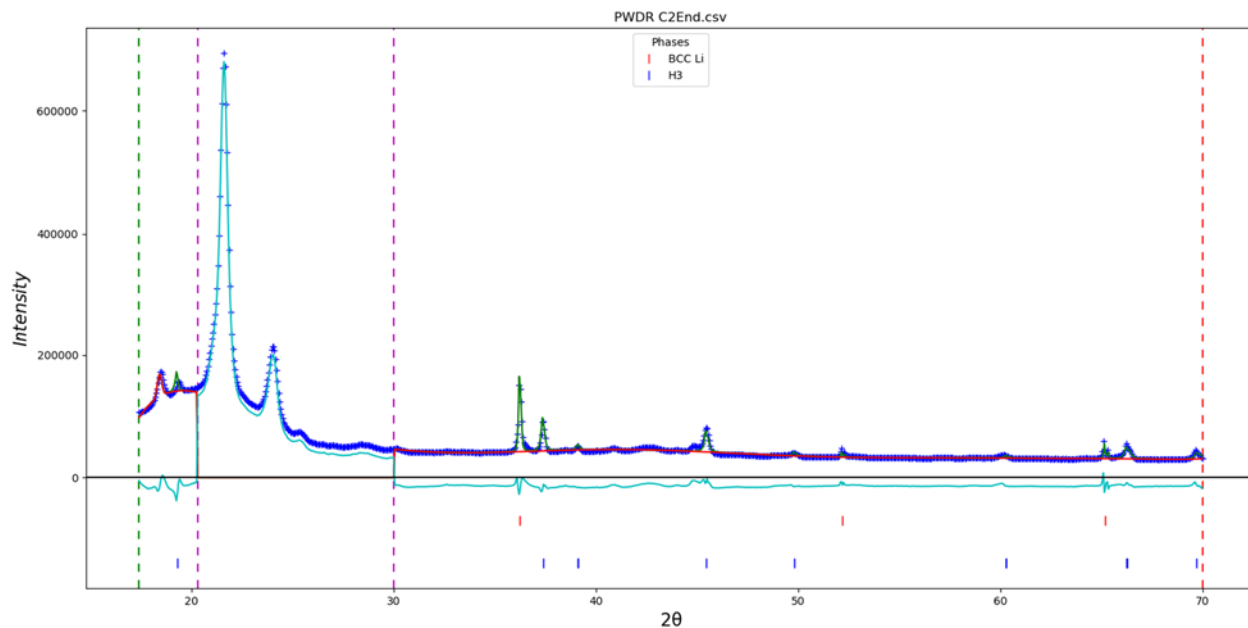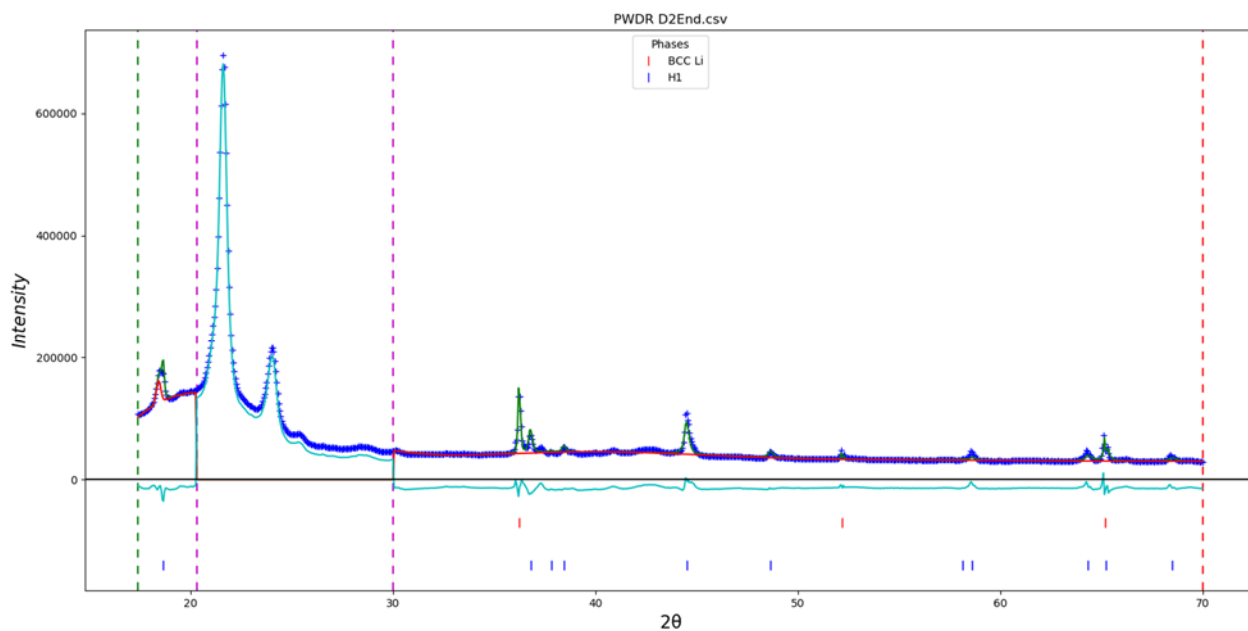

Figure S20. Rietveld refinement of the XRD pattern collected on the 3-4.7 V NMC622 pouch cell at the end of the 2nd discharge. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. %R_{wp}=4.20.
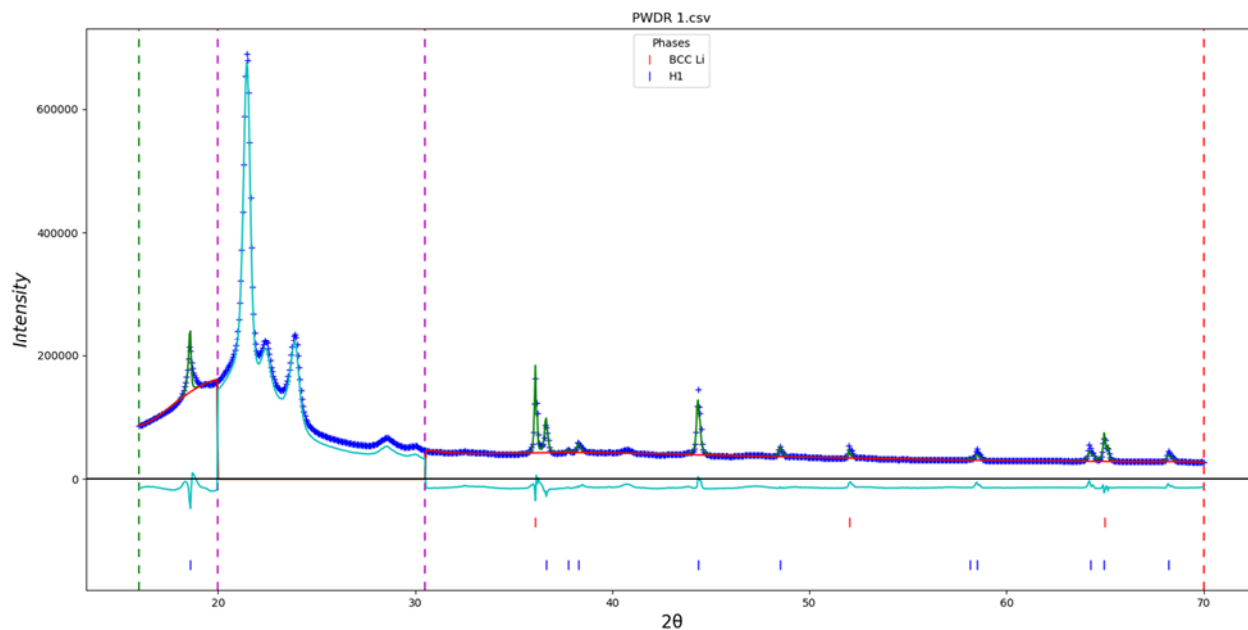
Figure S21. Rietveld refinement of the XRD pattern collected on the 3-4.7 V NMC622 pouch cell prior to the 101st cycle. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. %R_{wp}=3.64
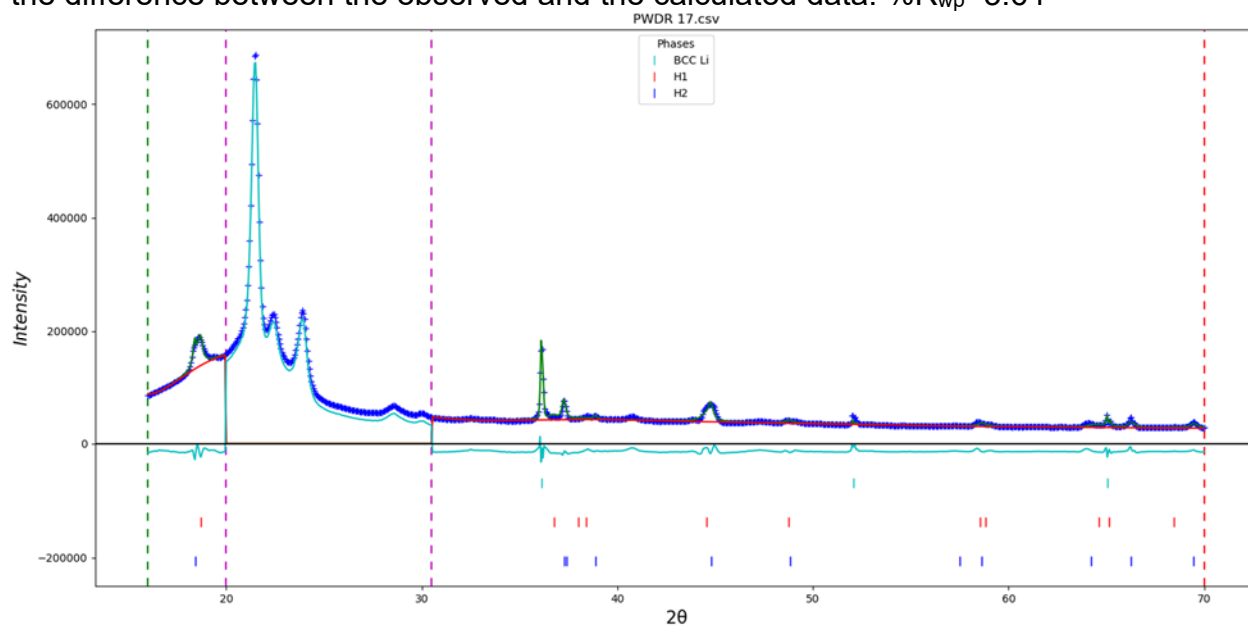

Figure S22. Rietveld refinement of the XRD pattern collected on the 3-4.7 V NMC622 pouch cell at the end of the 101st charge. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. %R_{wp}=3.50.

PWDR 26.csv

Figure S23. Rietveld refinement of the XRD pattern collected on the 3-4.7 V NMC622 pouch cell at the end of the 101st discharge. The blue points mark the experimental data, the green line is the calculated fit, the red line is the background, and the light blue line is the difference between the observed and the calculated data. %R$_{wp}$=3.92.
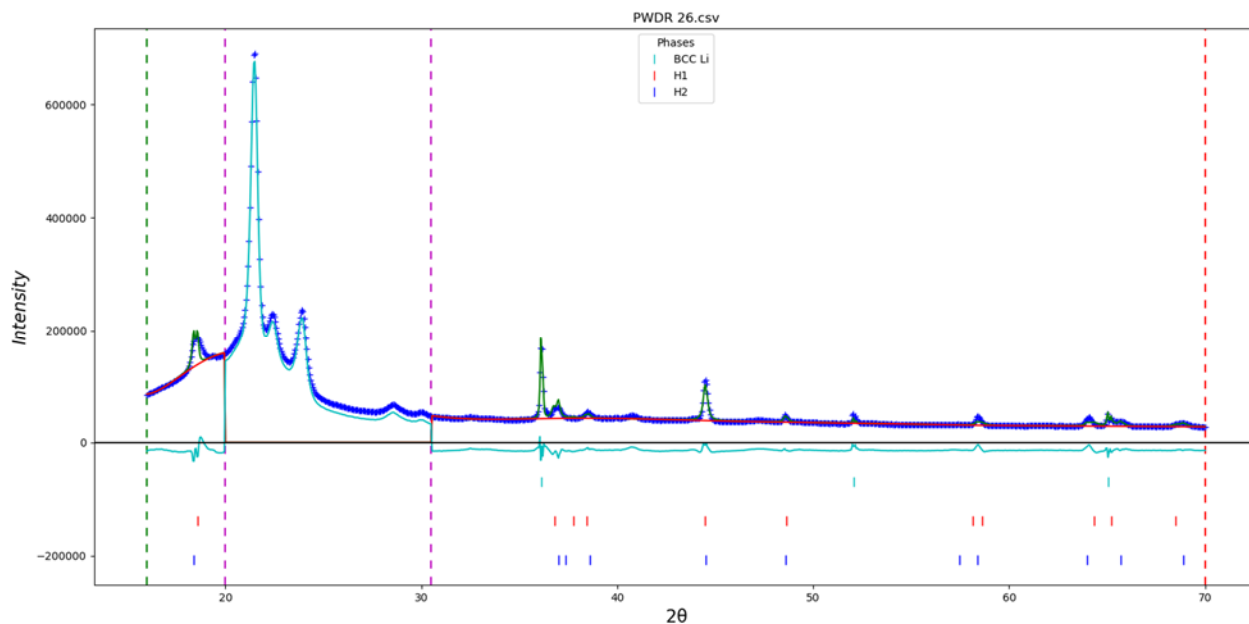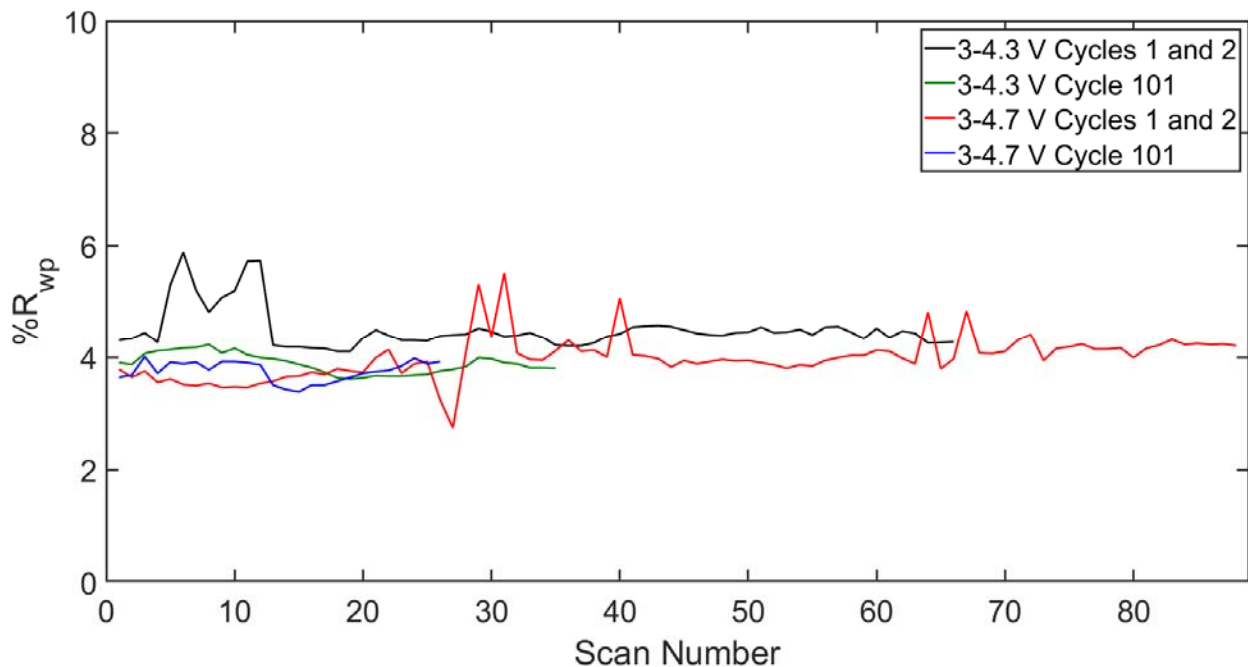

Figure S24 %R$_{wp}$ values for the Rietveld refinements. *(A)* Values for cycles 1 and 2 of the 3-4.3 V cell, *(B)* Values for cycle 101 of the 3-4.3 V cell, *(C)* Values for cycles 1 and 2 of the 3-4.7 V cell, and *(D)* Values for cycle 101 of the 3-4.7 V cell.
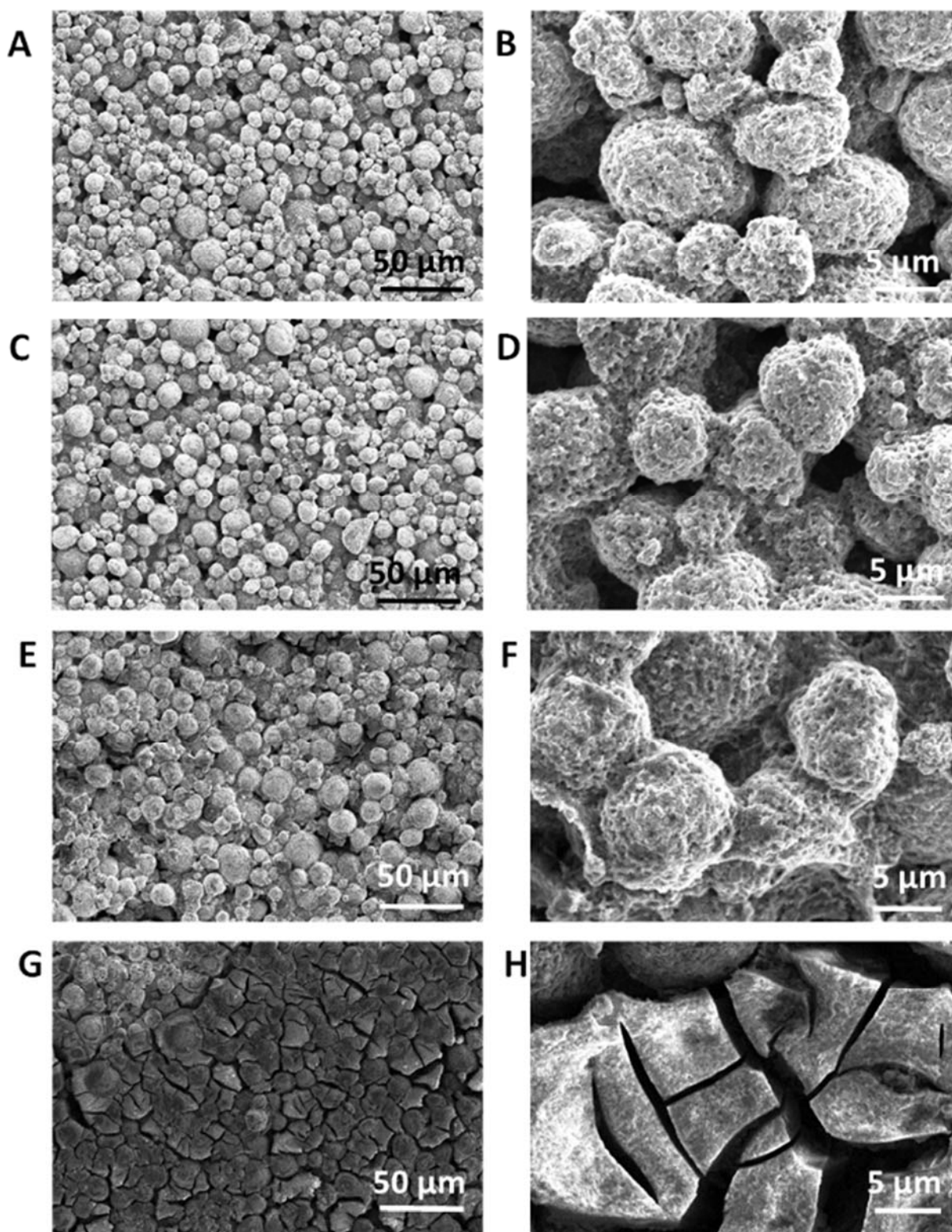
Figure S25. SEM images of an electrode cycled 100 times at 3-4.3 V at *(A,C)* 500X and *(B,D)* 4000X magnification. Images of an electrode cycled 100 times at 3-4.7 V at *(E,G)* 500X and *(F,H)* 4000X magnification.
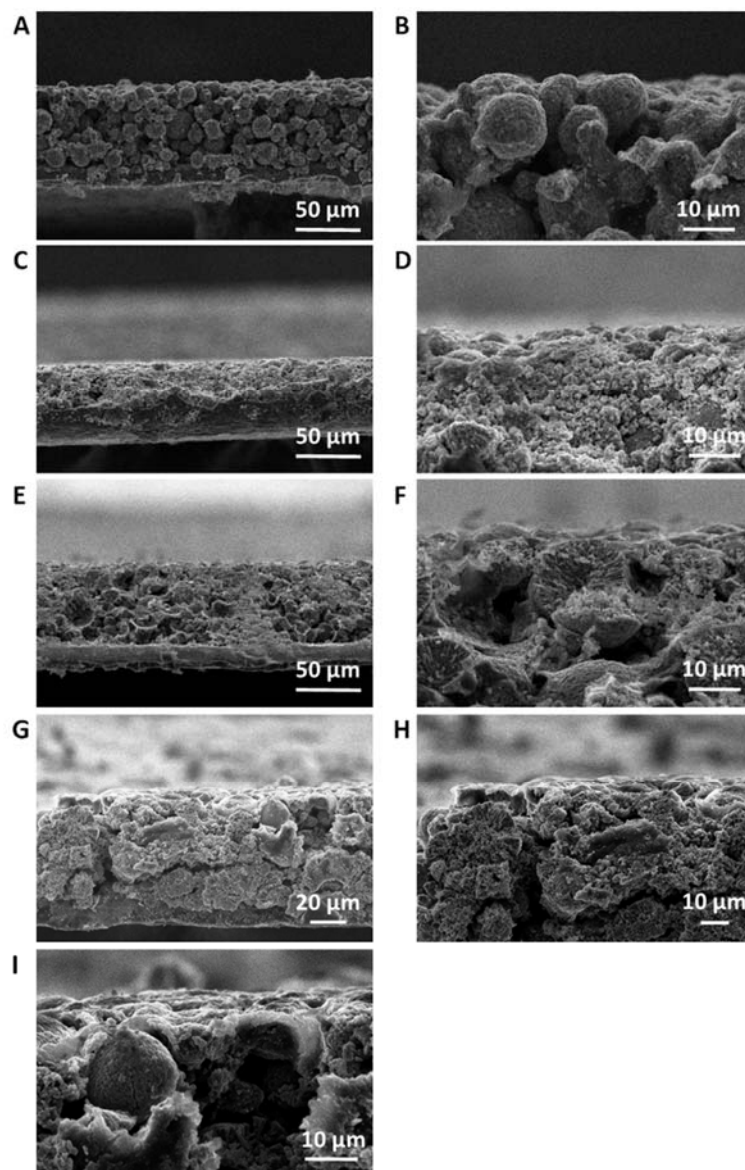
Figure S26. Cross sectional SEM images of a pristine NMC622 electrode at *(A)* 500X and *(B)* 2000X magnification. Images of an electrode cycled 100 times at 3-4.3 V at *(C)* 500X and *(D)* 2000X magnification. Images of an electrode cycled 100 times at 3-4.7 V at *(E)* 500X, *(F)* 2000X, *(G)* 650X, *(H)* 1000X, and *(I)* 2000X magnification

Table S1. Coin cell electrochemistry for cells cycled one hundred times at either 3-4.7 V or 3-4.3 V. Values are reported as Mean(SD). Capacities (cap.) are in mAh/g, charge is abbreviated C, discharge is abbreviated D, and CE is Coulombic efficiency.

Window	C1 cap.	D1 cap.	Cycle 1 CE	C2 cap.	D2 cap.
3-4.3 V	208(2)	186(2)	89.30(8)%	187(1)	186(1)
3-4.7 V	249(7)	224(7)	90.1(4)%	224(7)	221(7)
Window	Cycle 2 CE	C100 cap.	D100 cap.	Cycle 100 CE	Cap. fade (cycle 2→100)
3-4.3 V	99.60(8)%	175(2)	170(2)	97(1)%	6(1)%
3-4.7 V	98.5(8)%	100(20)	100(20)	93(1)%	50(10)%

References

1.   Yin, S. C.; Rho, Y. H.; Swainson, I.; Nazar, L. F., X-Ray/Neutron Diffraction and Electrochemical Studies of Lithium De/Re-Intercalation in Li1-Xco1/3ni1/3mn1/3o2 (X = 0 → 1). *Chem. Mater.* **2006**, *18*, 1901-1910.