Supporting Information

Kinetic Limitations in Cycled Ni-Rich NCM Cathodes and Their Effect on the Phase Transformation Behavior

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Figure S1. (a) Contour plot of *operando* XRD patterns obtained on a cycle-aged NCM851005/graphite pouch cell at C/10 and 25 °C in the voltage range between 2.8 and 4.2 V (including 1 h CV step at the cutoff voltages). The different single-phase regions and the less and more active phase transformation region are highlighted for clarity.¹ (b) Rietveld refinement analysis of the initial XRD pattern of the contour plot. The measured pattern is in blue, the calculated pattern in red, and the difference profile is shown in gray.



Figure S2. Changes in lattice parameter *a* of the cycle-aged NCM851005 during equilibration under CV conditions. The NCM851005/graphite pouch cell was charged to 4.2 V at C/10 and 25 °C with ~60 h CV step at the cutoff voltage. The single-phase region is in gray, the less and more active NCM phases in the two-phase region are shown in red and blue, respectively. The two-phase region is highlighted for clarity.



Figure S3. Example of two-phase matching. The cycle-aged NCM851005/graphite pouch cell was charged from initially ~2.9 to 4.2 V at C/10 and 25 °C. (a) Beginning of CC charging, (b) reaching the maximum in lattice parameter c, (c) beginning of two-phase region, with the less and more active NCM phases denoted by blue and black ticks, respectively, (d) end of CC charging including 1 h CV period, and (e) after ~60 h CV step, with <10 wt% of the less active phase remaining.



Figure S4. (a) Single-phase, (b, c, f-o) two-phase, and (d, e) multiple-phase detection for the cycle-aged NCM851005 during charging to 4.2 V at C/10 and 25 °C: (a) 2.9 V (beginning of CC charging), (b) 4.13 V (beginning of two-phase region), (c) 4.2 V (end of CC charging), (d-o) 4.2 V with increasing time interval of 1 h during the CV step. The XRD patterns were analyzed using the software XPSPEAK 4.1.



Figure S5. *c*-axis evolution versus lithium content for the (pristine) NCM851005. After formation, the half-cell was cycled at C/10 and 25 °C in the voltage range between 3.0 and 4.3 V versus Li⁺/Li. The collapse region for the C/5-CV and C/10-CV cycles is denoted by the solid gray circle. The triangles and diamonds with different outline (pale blue = beginning of two-phase region, green = end of CC charging, and yellow = end of CV step) and interior colors (the less and more active NCM phases are shown in red and blue, respectively) represent the different SOC [*x*(Li)] achieved in the C/5-CV and C/10-CV cycles, respectively.



Figure S6. Changes in lattice parameters *a* and *c* of the cycle-aged NCM851005 during equilibration under OCV conditions. The NCM851005/graphite pouch cell was charged to 4.2 V at C/10 and 25 °C followed by a >30 h OCV period. The single-phase region is in gray, the less and more active NCM phases in the two-phase region are shown in red and blue, respectively. The two-phase region is highlighted for clarity.

 Schweidler, S.; de Biasi, L.; Garcia, G.; Mazilkin, A.; Hartmann, P.; Brezesinski, T.; Janek, J. Investigation into Mechanical Degradation and Fatigue of High-Ni NCM Cathode Material: A Long-Term Cycling Study of Full Cells. *ACS Appl. Energy Mater*. 2019, *2*, 7375–7384.