

Resolving complex intralayer transition motifs in high-Ni-content layered cathode materials for lithium-ion batteries

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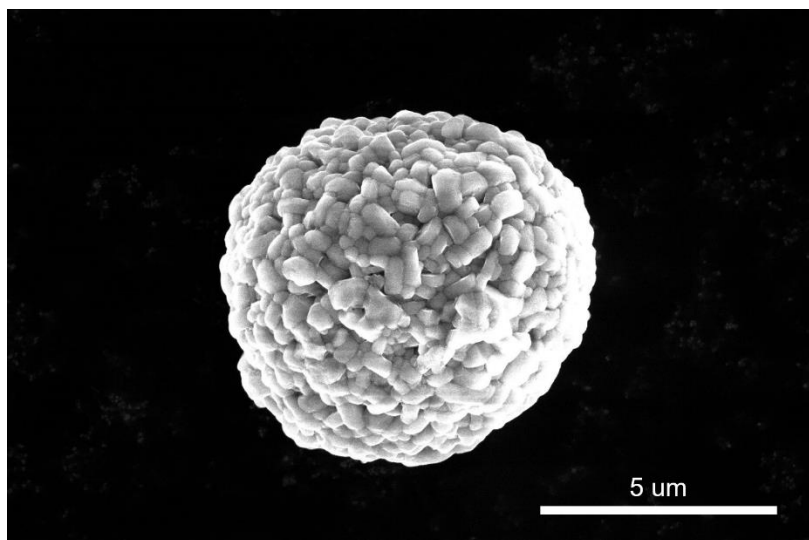


Figure S1. Scanning electron microscopy (SEM) image showing the microstructure of the NMC-811 secondary particle.

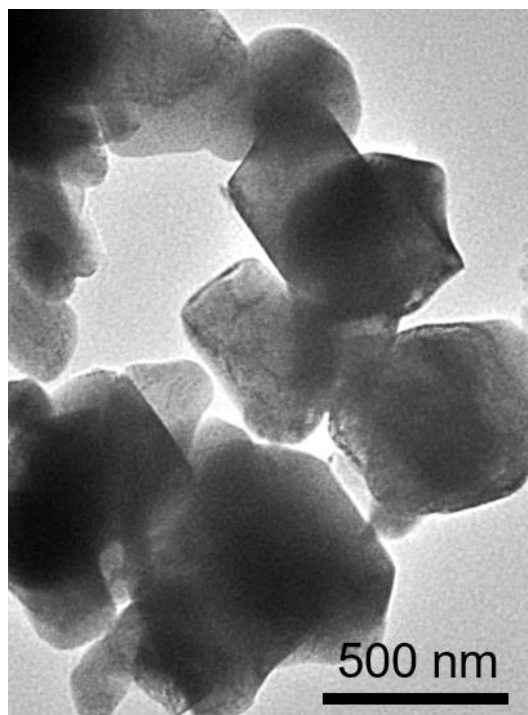


Figure S2. Bright-field transmission electron microscopy (BF-TEM) images showing the morphology of the NMC-811 primary particles. The particles have an average size of ~400nm.

Statistical orientation analysis was performed to check the proportion of the twinned particles from a statistically significant amount of primary particles. To do that, orientation mapping and analysis were performed by using precession electron diffraction (PED) in TEM. PED is a technique similar to EBSD. The difference is that PED uses electron diffraction patterns rather than Kikuchi patterns for the orientation map. Figure S3 shows orientation maps obtained from a few randomly chosen secondary particles prepared by the focused ion beam (FIB) technique. Indeed, we found twins inside some primary particles (black circled). In addition, interestingly, we found that some primary particles, although contain no twins, they share a twin relationship with other primary particles (white circled). Furthermore, statistics (Fig. S4) show that only 22 out of 585 primary particles contain twins, accounting for $\sim 4.4\%$ of all particles. Particles without twins but sharing a twin relationship with others account for $\sim 3.2\%$ of all particles (strictly speaking, these boundaries are not twin boundaries because the two primary particles are supposed to be not covalently bonded but most likely bonded by van der Waals force¹). Regardless of the above strict considerations, by adding them up, the proportion of twinned particles is still as low as $\sim 7\%$. Similar statistical orientation mapping (Fig. S5) and analysis (Fig. S6) were also performed on charged NMC-811 primary particles. The results show that 13 out of 324 primary particles contain twins, accounting for $\sim 4.0\%$ of all particles. Particles without twins but sharing a twin relationship with others account for $\sim 3.1\%$ of all particles. These values are quite similar to that of the pristine sample, indicating the twins observed in charged states most likely already exist in the pristine state. From the above, it can be concluded that growth twins exist yet are not dominant in either pristine or charged primary particles.

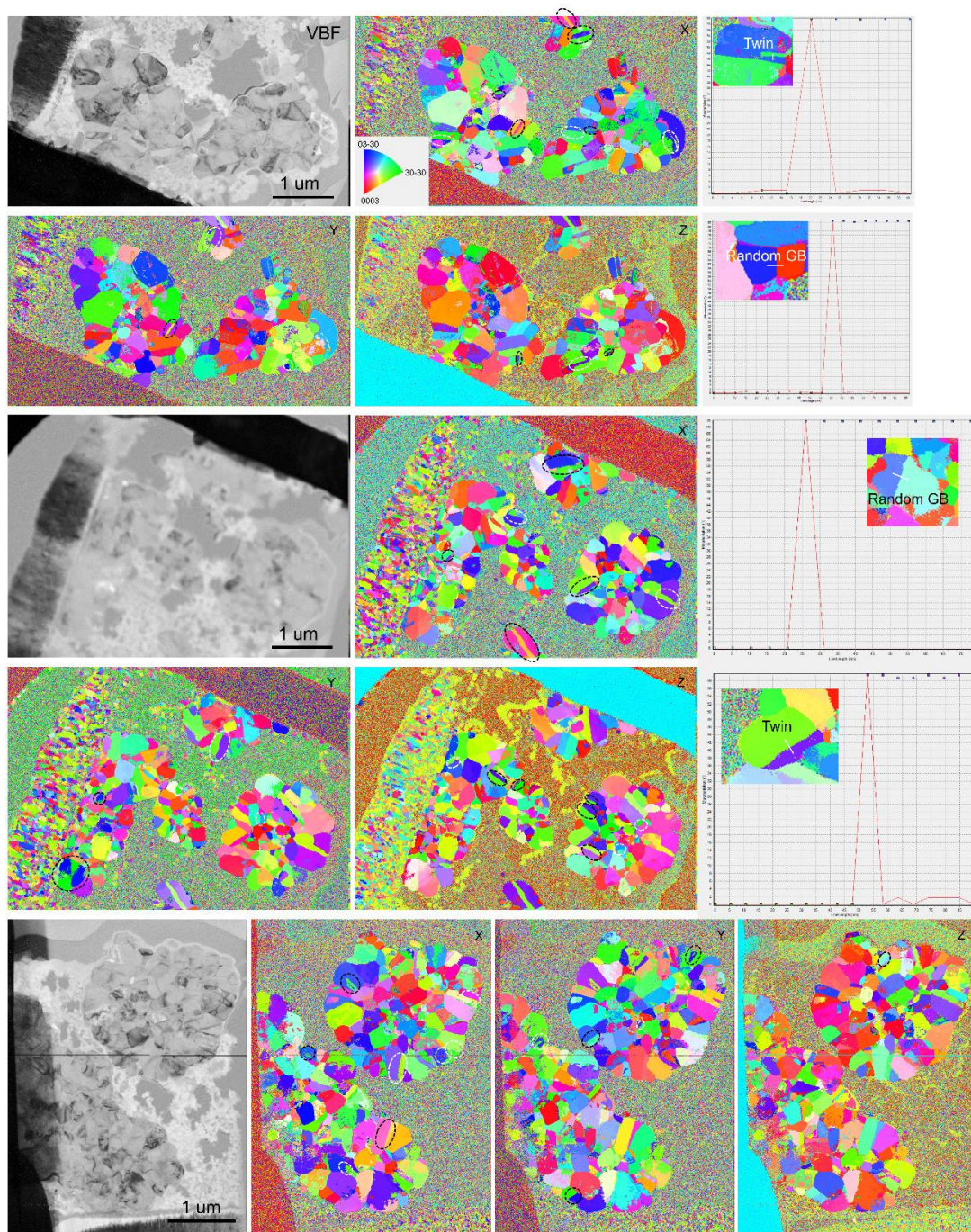


Figure S3. Crystallographic orientation analysis of pristine NMC-811 primary particles. The results are acquired by nanobeam diffractions using an ASTAR system (NanoMEGAS). The samples are prepared by focused ion beam (FIB). The scanning step for the data collection is 5 nm.

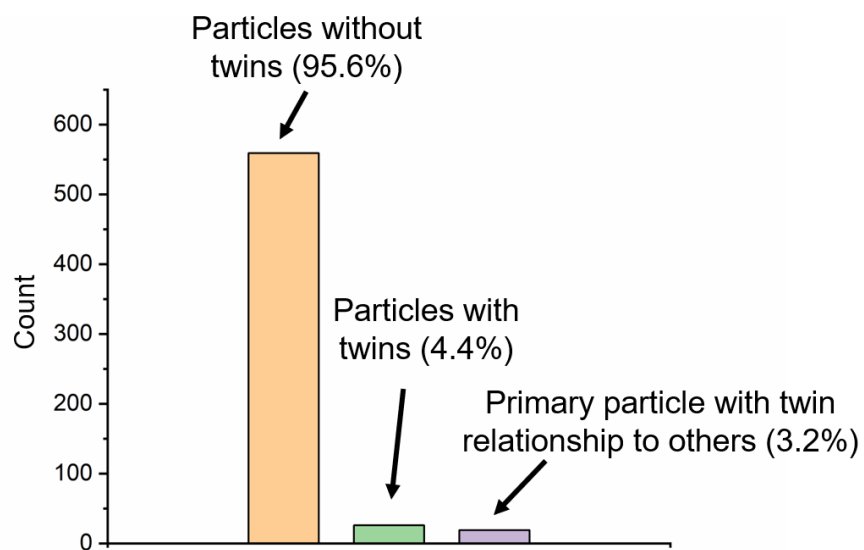


Figure S4. Histogram of the number of pristine NMC-811 primary particles with and without twins as well as the number of particles which has twin relationship with others. The sampling number is 585 from eight randomly chosen secondary particles.

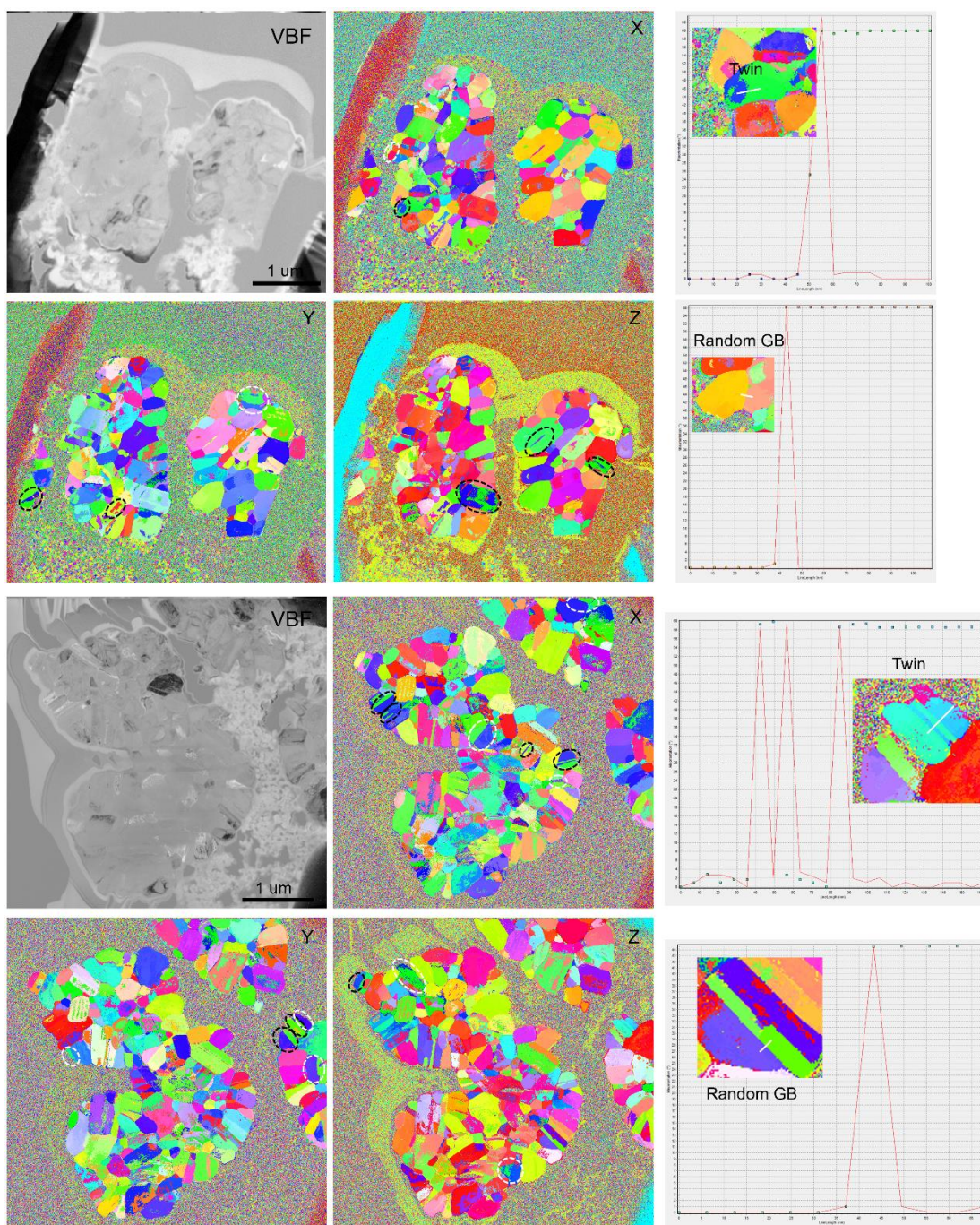


Figure S5. Crystallographic orientation analysis of charged NMC-811 primary particles based on nanobeam diffractions using an ASTAR system (NanoMEGAS). The samples are prepared by focused ion beam (FIB). The scanning step for the data collection is 5 nm.

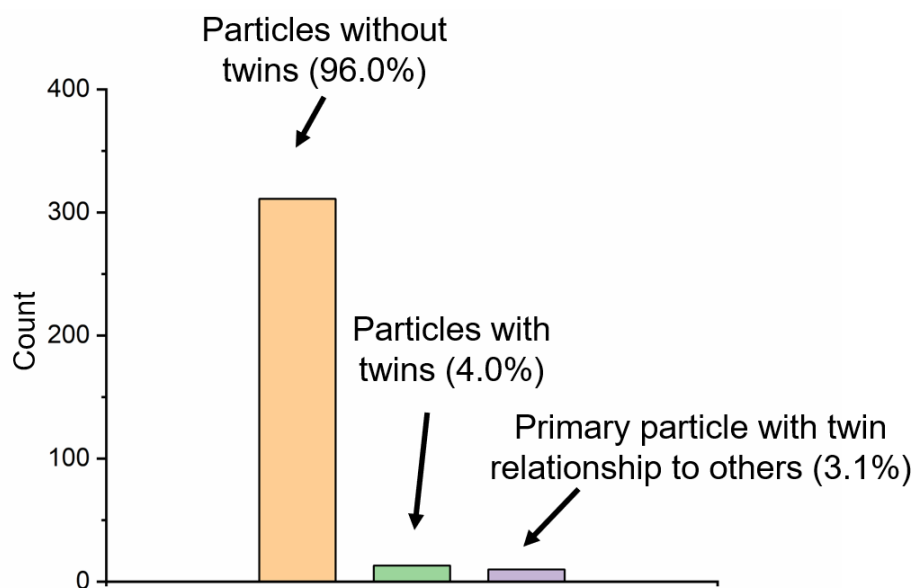


Figure S6. Histogram of the number of charged NMC-811 primary particles with and without twins as well as the number of particles which has twin relationship with others. The sampling number is 324 from six randomly chosen secondary particles.

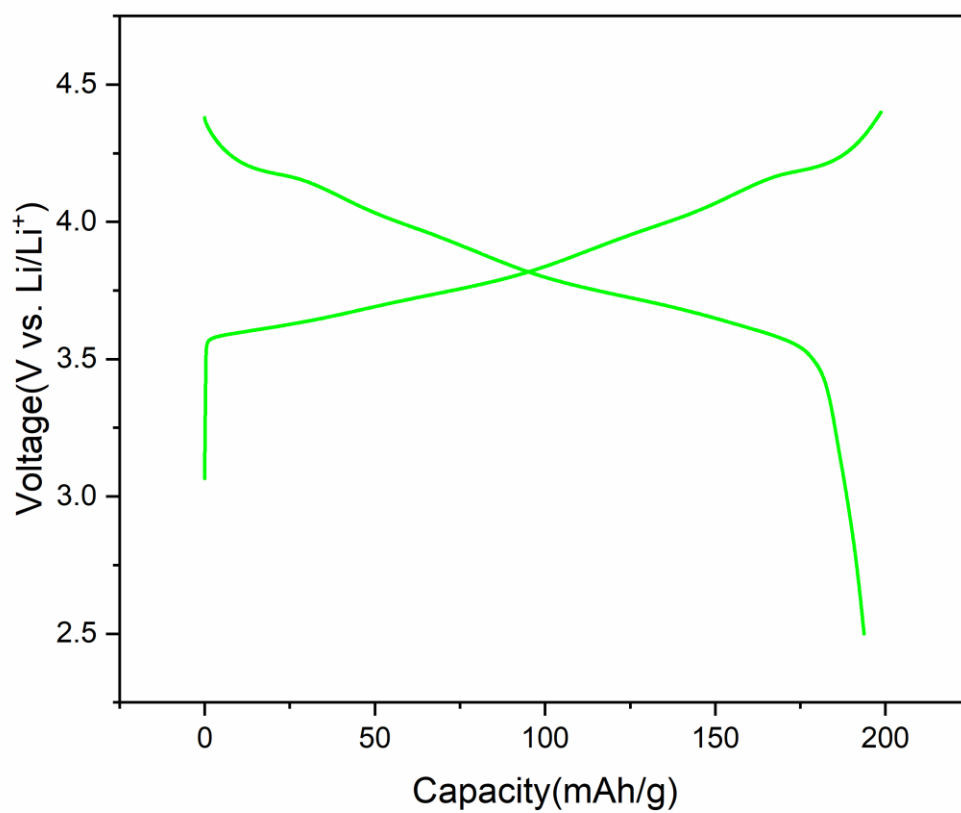


Figure S7. Charge–discharge profiles of the NMC-811 coin cell at 0.1C between 2.5 and 4.4 V vs Li⁺/Li.



Figure S8. Demonstration of atom segmentation and localization by *AtomSegNet*. The left panel shows an atomic resolution high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of a delithiated NMC-811 particle. The right panel shows the *AtomSegNet*-processed super-resolution image corresponding the image in the left panel.

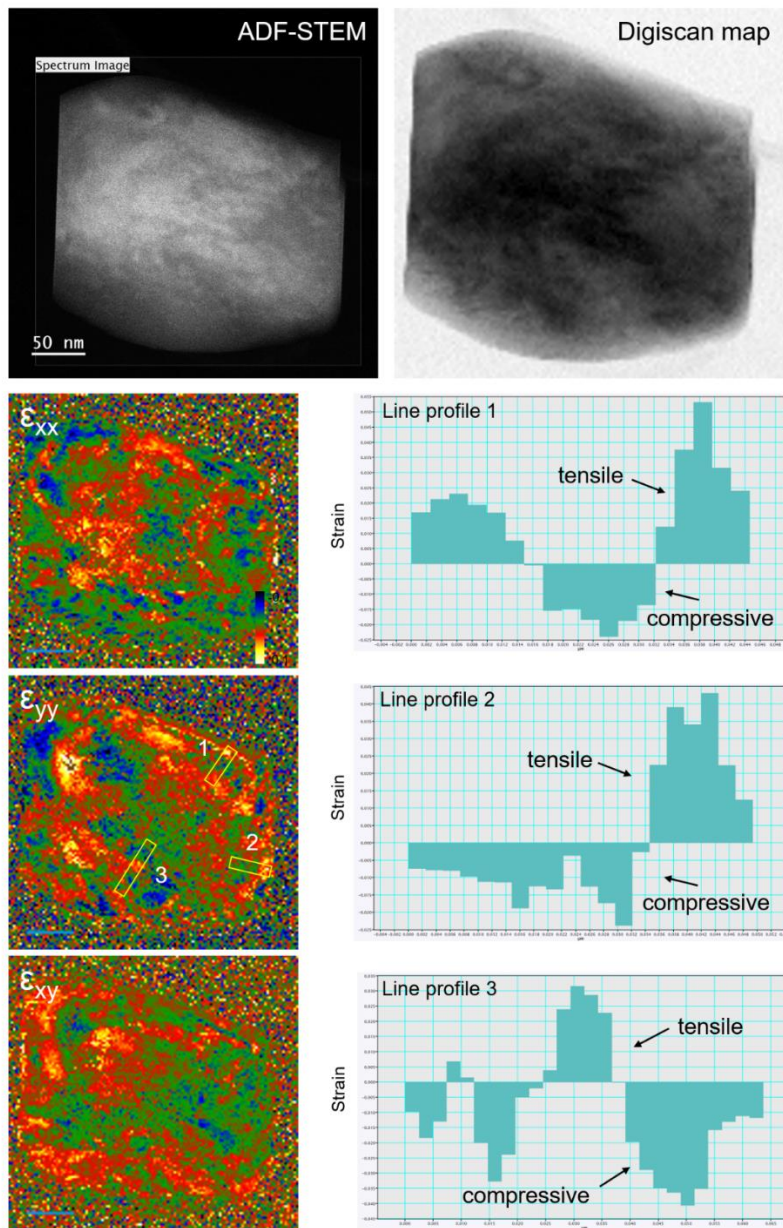


Figure S9. Strain mapping and analysis of a charged NMC-811 primary particle by 4D-STEM experiment.

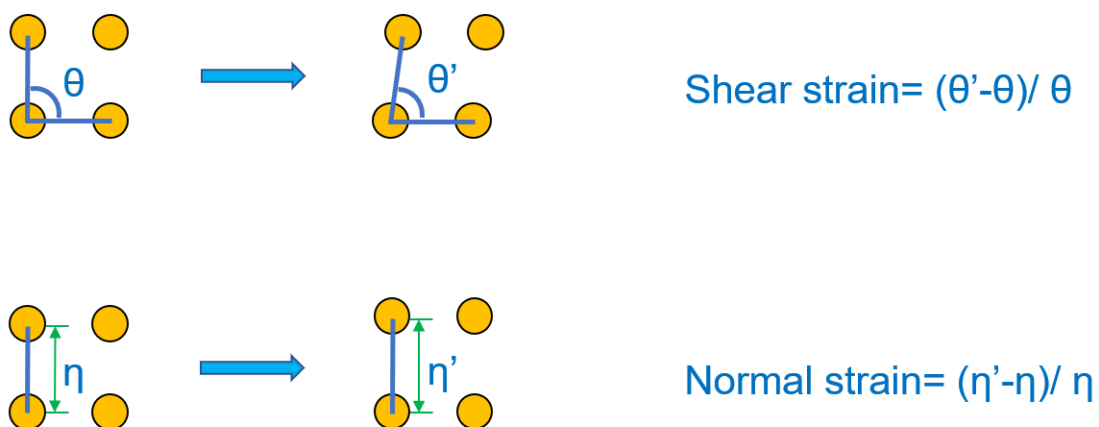


Figure S10. Schematic illustration showing the lattice strain analysis. The shear strain is determined by the change of the characteristic angle θ and the normal strain is determined by the change of the characteristic lattice spacing.

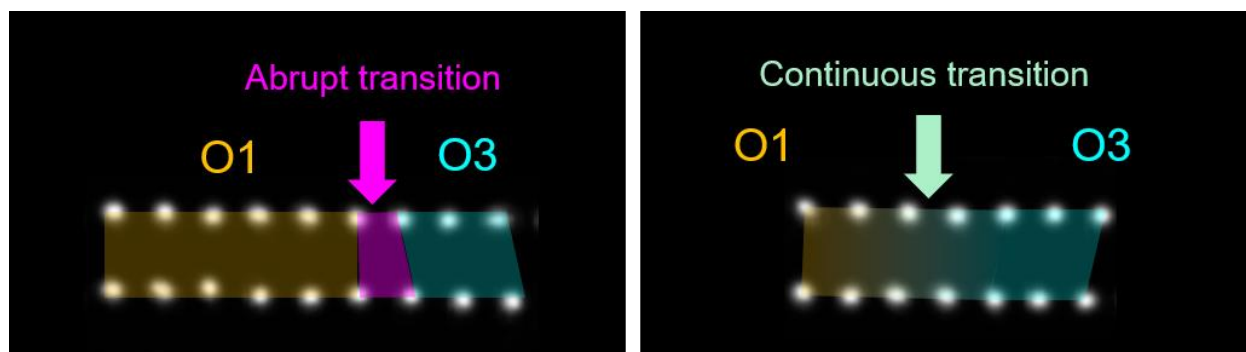


Figure S11. Identification of two types of O1-O3 interfaces in pure LiNiO_2 cathode. The left panel shows a representative abrupt transition O1-O3 interface composed of a trapezoidal structural unit (highlighted in magenta). The right panel shows a continuous transition O1-O3 interface enabled by a continuous shear transition zone.

Five different slab models were constructed to investigate the O3-O1 transitions. O3-Li_{0.25}NiO₂ slab model in Fig. S12a is used as the starting point structure for the O3-O1 phase transition process since the Li_{0.25}NiO₂ has been demonstrated in previous works² as the last ordered O3 phase before O1 phase transformation. A Li-vacancy ordering reported in previous studies³ was employed in our slab model. The slab model in Fig. S12b represents the partially delithiated O3-Li_{0.25-x}NiO₂ phase where some Li atoms were intentionally taken out from the O3-Li_{0.25}NiO₂ slab. Fig. S12c shows the slab model of O1-NiO₂ phase which is the ending point structure for the O3-O1 phase transition. Also, partially lithiated phase O1-NiO₂, i.e., O1-Li_xNiO₂ with some lithium ions at the empty octahedral sites is also constructed (Fig. S12d). Besides, a O3-NiO₂ slab model is also built to simulate the situation where O3-O1 phase transition occurs after all lithium ions are fully extracted. Previous computational studies have reported that NiO₂ phase in O3 stacking is merely 7 meV/f.u. higher in energy than the O1 stacking³. Therefore, fully delithiated NiO₂ region in O3 stacking could be accessible in highly state. In contrast, fully lithiated LiNiO₂ in O1 form is highly unstable and not accessible according to our calculation.

For layered cathode material in O3 stacking, Ni atoms are stacked following the ABCABC... sequence. For O1 stacking, in-plane Ni atoms are still close packed while adjacent layers of Ni atoms are stacked exactly on top of each other occupying the same sites (AAA/BBB/CCC). The transformation between O3 and O1 stacking can be simply achieved by gliding one layer of Ni atoms from one lattice site (A/B/C) to either one of the other two (Fig. S13). Based on symmetry analysis, there are four inequivalent types of translations as indicated by arrows in Fig. S13. Type I and type II translations result in O3→O1 transformation, and Type III and type IV result in O3→twin-like structure formation. For delithiated O3- Li_{0.25-x}NiO₂ slab and lithiated O1-Li_xNiO₂ slab, the gliding part of the Ni-O layer is chosen to be the section without and with Li atoms. We constructed both “continuous” and “abrupt”

transition configuration for each slab model and used them as input structures for structural optimization.

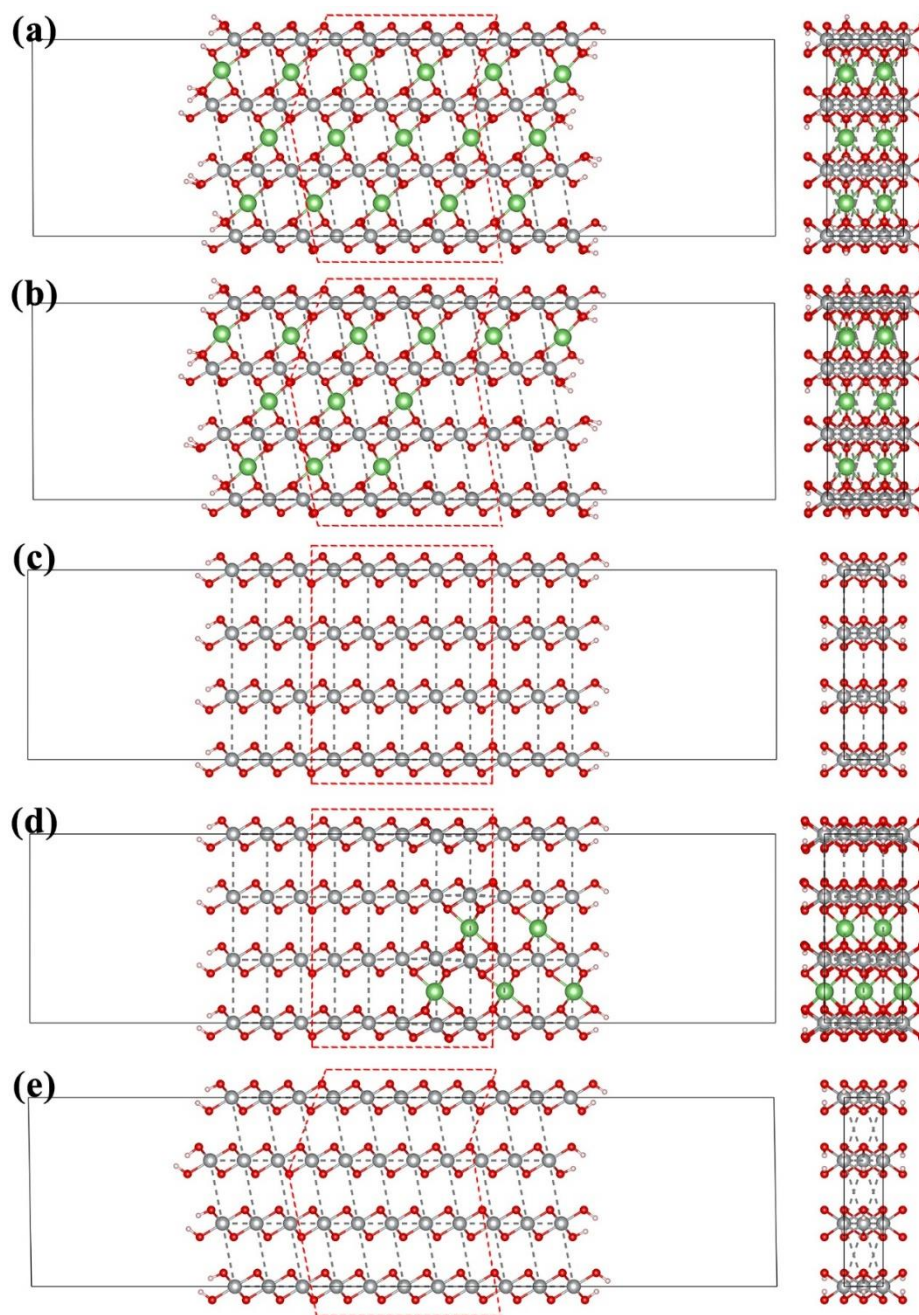


Figure S12. Slab models constructed to simulate in-plane O3-O1 phase transition: (a) O3- $\text{Li}_{0.25}\text{NiO}_2$, (b) partially delithiated O3- $\text{Li}_{0.25-x}\text{NiO}_2$, (c) O1- NiO_2 , (d) partially lithiated O1- NiO_2 , (e) O3- NiO_2 . O3-O1 phase transition configurations are built by gliding part of middle Ni-O layer. (Ni: silver; O: red; Li: green; H: white)

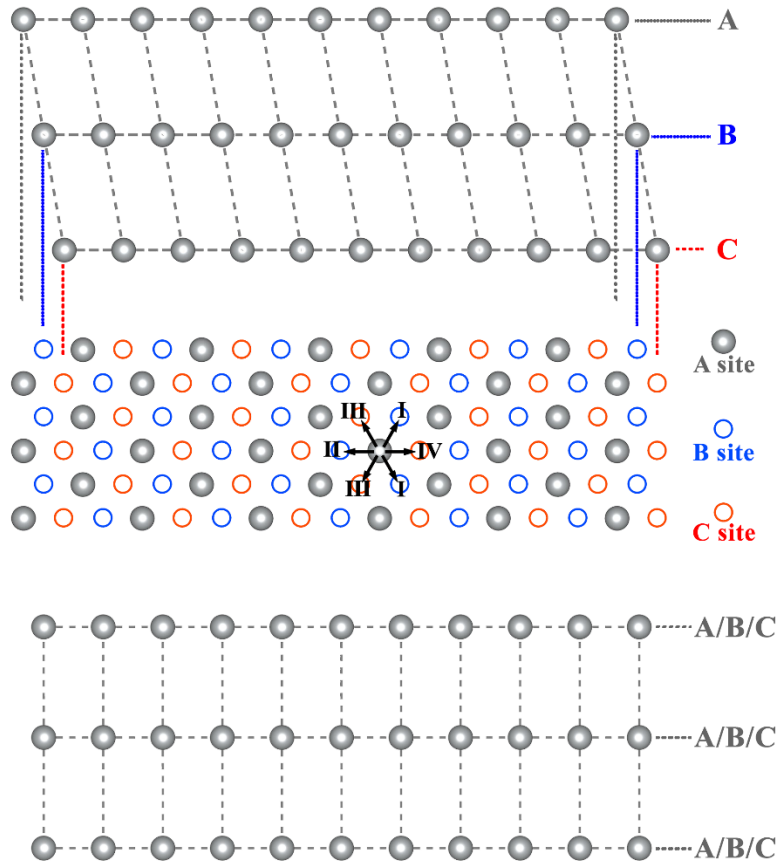


Figure S13. Different translation pathways in O3 lattice. Schematics of O3 (upper panel) and O1 (lower panel) stacking of Ni atom layers. Different translation pathways are marked out on the top view of the close-packed lattice. Type I and type II translations result in O3→O1 transformation, and Type III and type IV result in O3→twin-like structure formation. (A site: silver; B site: Blue circle; C site: red).

To further clarify the influence of the charging rate and voltage on the O3-O1 interface structures, we performed new experiments with different electrochemical parameters. The new results validate that O3-O1 phase transition widely exists in NMC-811 under different operation conditions. For example, Fig. S14 shows the super-resolution images of the NMC-811 sample charged to 4.4V at 0.3C rate and 4.3V at 0.1C rate, respectively. Similar intralayer O3-O1 transitions are observed in both cathodes, indicating that with either faster charging rate or lower cut-off voltage, local O1 transformation still occurs.

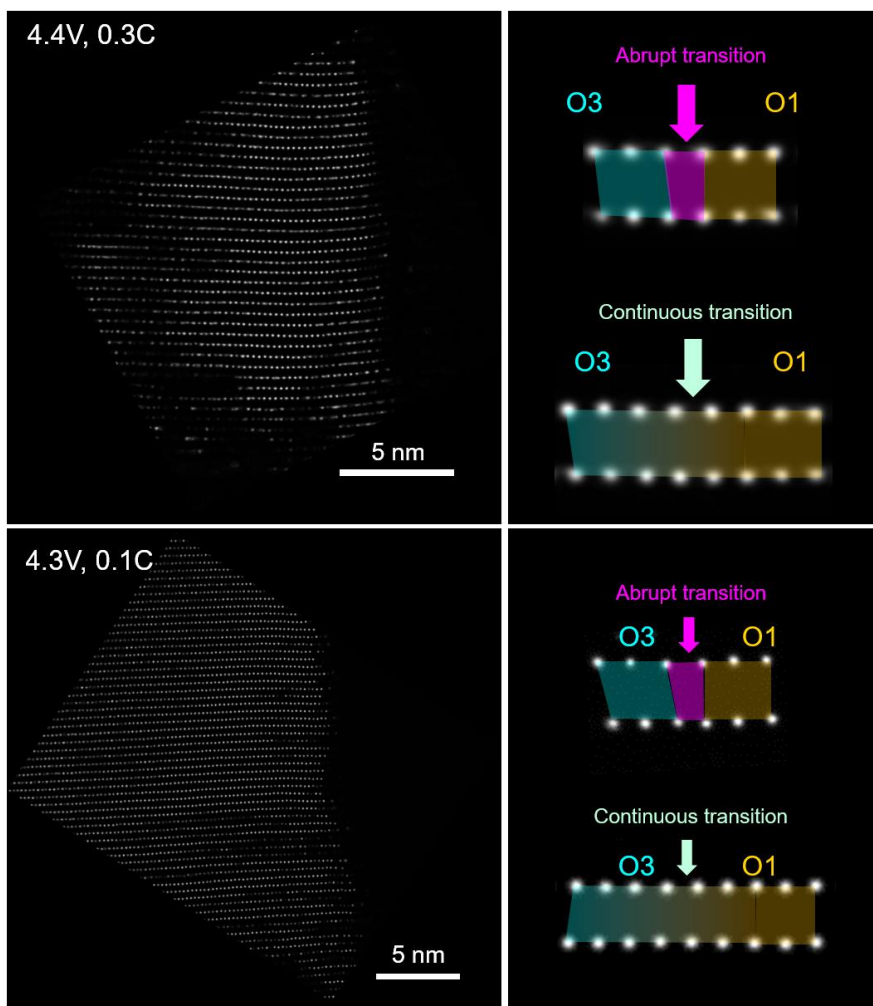


Figure S14. Super-resolution images of NMC-811 cathode charged to 4.4V at 0.3C rate and 4.3V at 0.1C rate, respectively. O3-O1 transitions similar to that shown in the main text are also observed.

References

- 1 Xu, R., de Vasconcelos, L. S., Shi, J., Li, J. & Zhao, K. Disintegration of Meatball Electrodes for $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ Cathode Materials. *Experimental Mechanics* **58**, 549-559, doi:10.1007/s11340-017-0292-0 (2017).
- 2 Arroyo y de Dompablo, M. E. & Ceder, G. First-principles calculations on Li_xNiO_2 : phase stability and monoclinic distortion. *Journal of Power Sources* **119-121**, 654-657, doi:10.1016/s0378-7753(03)00199-x (2003).
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