

Supporting Information

Investigating Cathode Electrolyte Interphase Formation in NMC 811 Primary Particles through Advanced 4D-STEM ACOM Analysis

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4D-STEM analysis

General parameters

Library for bank generation in ASTAR was obtained using CIF file from ICSD website, the files used for all the searched programs were:

-NMC 811 collection code 143110

-LiOH collection code 27543

-Li₂CO₃ collection code 66942

-LiF collection code 41409

Sample (4.3 cut off voltage)

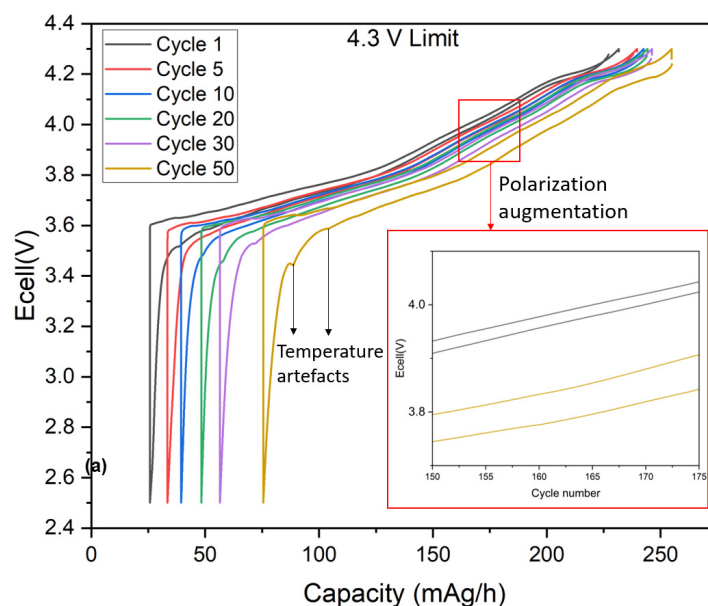


Figure S1: a) Potential vs. capacity electrochemical curve of cycled NMC 811 at an upper high voltage of 4.3 V. Evidence of polarization change by zoom in at BoL (Beginning of Life) and EoL (End of Life) curves

For sample 4.3V-limit (figure 3b-e in the article) the following analysis condition were used:

Lacey carbon films 200 MESH grind was used for particle analysis. The scanning conditions for particle of zone 1 where 110 pixels X, 270 pixels Y, step width of 15 giving as a result a scanning area of 0.41 by 1.01 μm and a step size of 3.75 by 3.75 nm. The exposition time for each individual scan (diffraction pattern) was 20 ms

For zone 2, the scanning conditions were 190 pixels X, 140 pixels Y, step width of 15, giving as result a scanning area of 0.71 by 0.53 μm and a step size of 3.75 by 3.75 nm. The exposition time for each individual scan (diffraction pattern) was 20 ms

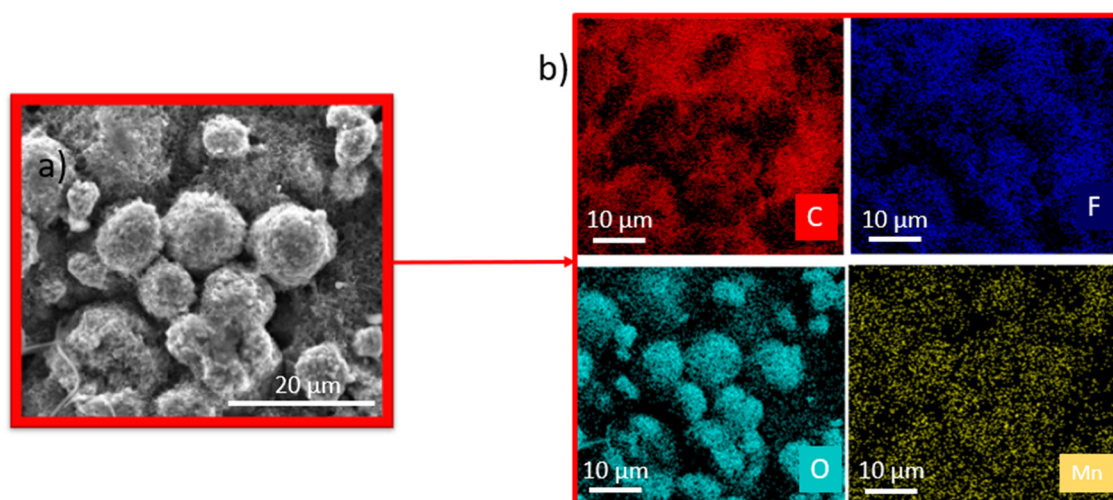


Figure S2: a) secondary electron (SE) image of NMC secondary particles in cathode sheet after cleaning from 4.3V-limit cell, b)EDX analysis for elemental identification c) secondary electron (SE) image of NMC single secondary particle in cathode sheet after cleaning from 4.3V-limit cell, d)EDX analysis for elemental identification.

Sample (4.5 cut off voltage)

For sample 4.5V-limit (figure 6a-e in the article) the following analysis condition were used:

Lacey carbon films 400 MESH grind was used for particle analysis. The scanning conditions for particles where 150 pixels X, 150 pixels Y, step width of 15 giving as a result a scanning area of 1.13 by 1.13 μm and a step size of 7.5 by 7.5 nm. The exposition time for each individual scan (diffraction pattern) was 20 ms

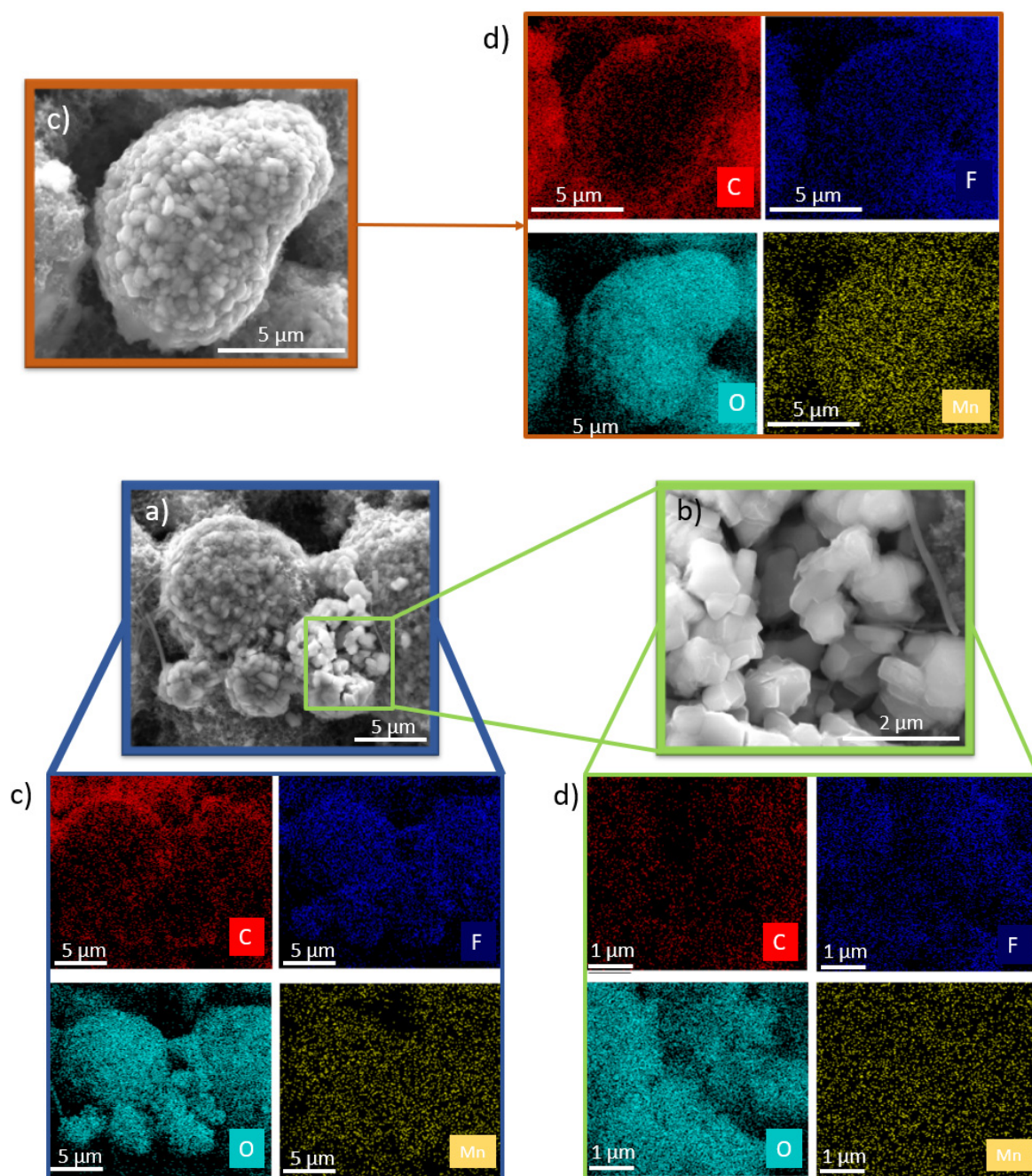


Figure S3: a) secondary electron (SE) image of NMC secondary particles in cathode sheet after cleaning from 4.5V-limit cell, b) zoom in over cracked particle in a), c) EDX analysis for elemental identification of different particles d) EDX analysis for elemental identification in cracked particle

The edge energy for Mn and F are similar, this could give as result the misinterpretation of F as Mn in the analysis software, for this reason both, Mn and F cartography, are presented for the sample 4.3V-limit (figure S2) and 4.5V-limit (figure S3). In both cases for the secondary particle agglomerate (figure S2a-b and figure S3a-c) and single secondary particle (figure S2c-d and figure S3b-d) the distribution of Mn in regards of F is not equal, allowing us to affirm the presence of both elements.