Supplementary Information (SI) for EES Batteries.

- *Supplementary Information* -

Non-Linear Damage Response to Voltage Revealed by Operando X-ray Tomography in Polycrystalline NMC811

Huw C. W. Parks *et al.*

To whom correspondence should be addressed; Email: Rhodri.Jervis@ucl.ac.uk

Glossary

Absolute Damage Factor was calculated as the sum of the positive values of $B - A$. Where A is an array of mean normalised grey levels in different radial layers for a particle at a particular SoC, and B is a similar array where each radial layer is the mean normalised grey level for that layer averaged across all particles in the pristine state.

$$DF = \sum_{i=1}^{n} max(0, \begin{bmatrix} b_1 \\ \vdots \\ b_n \end{bmatrix} - \begin{bmatrix} a_1 \\ \vdots \\ a_n \end{bmatrix})$$

Relative Mean Grey Level was calculated as the difference in mean grey level for a particle at different SoC. Calculated as $i - j$, where i was the mean grey level at a particular SoC and j was the mean grey level in the pristine state. Often the phase contrast enhancement volume around the edge of the particle was removed from both volumes using image masks calculated from the particle distance transform.

Total Grey Level Change was calculated as the sum of values in the resulting array from $M - N$. Where M and N were arrays calculated from images of a particle at a given state of charge and in the pristine state respectively. These particle images were first registered onto each over, a logical elementwise AND() was then calculated from binary masks of the two registered images, and the resulting array was then used to mask both registered images, resulting in the arrays M and N.

$$\Delta GL_{tot} = \sum M - N$$

Euclidean Distance Transform was calculated using the Scikit Image library on a particle-by-particle basis for the whole dataset. Below we show a typical example of the distance transform. Values were rounded to the nearest integer. The distance transform was calculated from the particle edge.

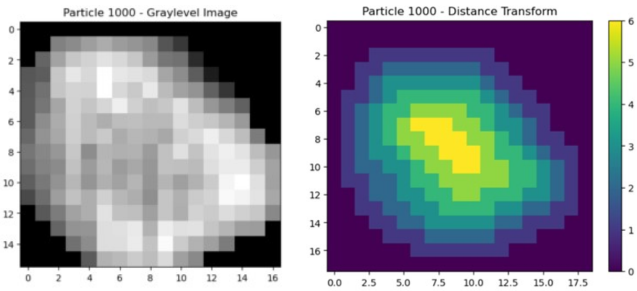

Figure S1.Left) Greyscale image of particle 1000. Right) Euclidean distance transform of particle 1000, colour scale shows distance from edge.

Radial Layer Grey Levels were calculated using the distance transform map of the particle. We created a mask of each radial layer of the particle from each integer value in the distance transform and calculate the mean grey level in that radial layer.

Radial Layer Normalised Grey Levels were calculated using the distance transform map of the particle. We created a mask of each radial layer of the particle from each integer value in the distance transform and calculate the mean grey level in that radial layer. Each mean grey level is then normalised by the maximum radial layer mean grey level in that particle.

Full and Phase Removed Analysis was performed at a number of points throughout the article. Full particle contains all voxels and radial layers within the segmented particle region defined at the radial grey level intensity maximum. Phase removed analysis removed the first 5 radial layers from the particle segmentation, and thus only assessed the grey level from radial layers above 5, meaning particles with fewer than 5 radial layers were omitted from the analysis all together. Centre 50% represents the centre 50% of radial layers in the partials segmented region. See figure S1 for a schematic representation of the analysis performed.

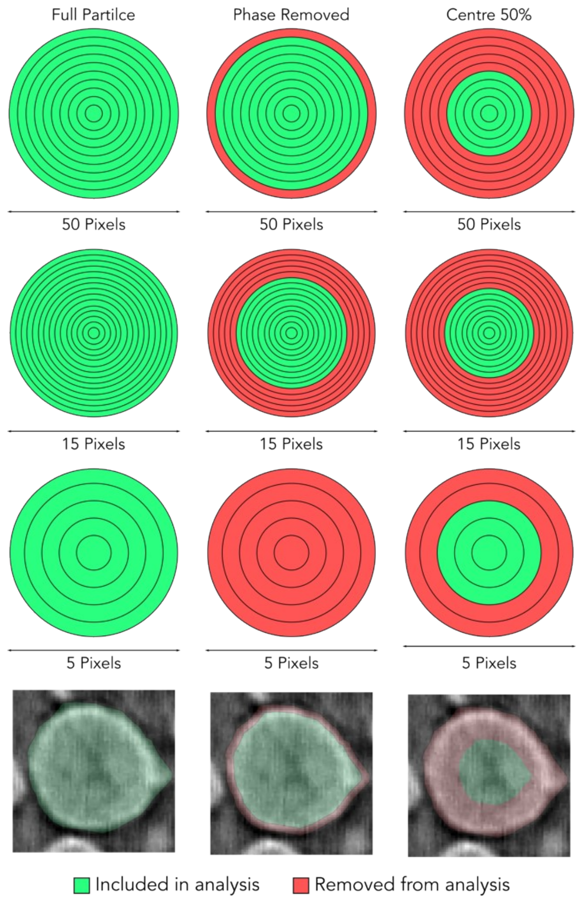

Figure S2. Schematic representation of nomenclature used within this article, for a particle of 50 pixels in diameter (Top), and particle of 15 pixels in diameter (Middle), and a particle of 5 pixels in.

Supplementary Information

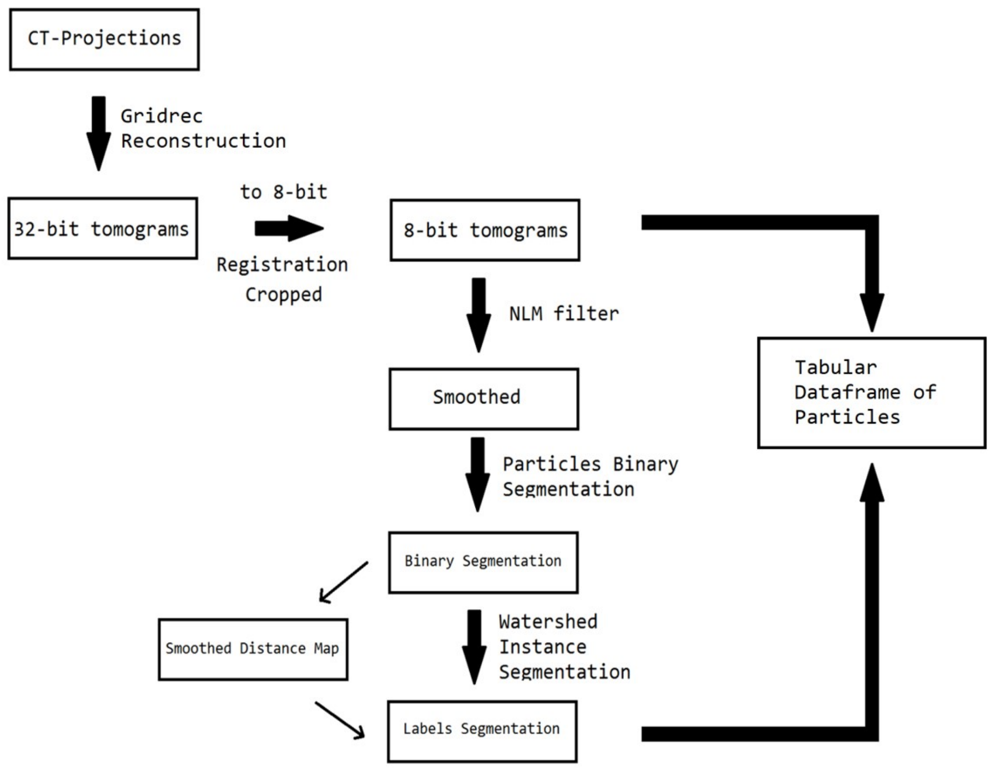

Figure S3. Schematic of image processing pipeline.

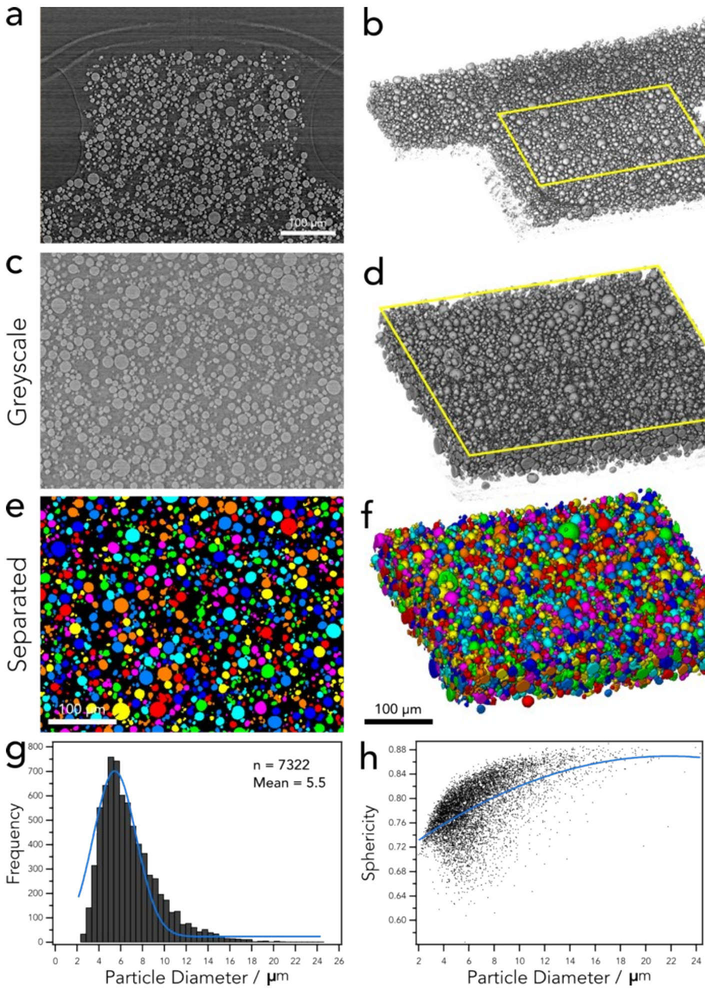

Figure S4: a) Ortho slice of full tab area and electrode geometry in pristine state. b) 3-D rendering of tab electrode, yellow box shows the analysed area for greyscale analysis. c&d) Ortho slice and 3D rendering of analysed area. e&f) Separated object view of analysed area where the colour applied is arbitrary and only helps to observe the randomly assigned unique label given to each particle. g) Particle size distribution of pristine electrode from analysed area, fitted with normal distribution in blue. h) Particle sphericity with fit in blue.

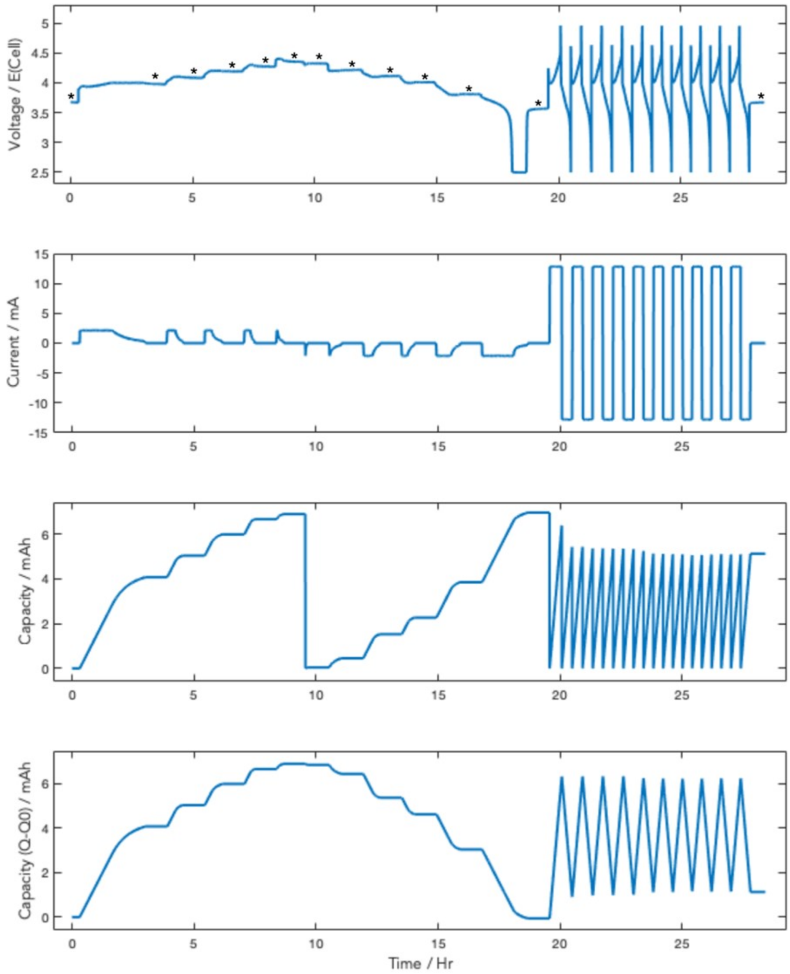

*Figure S5. Electrochemical profiles for imaged pouch cell. * Represents positions where X-ray CT was performed*

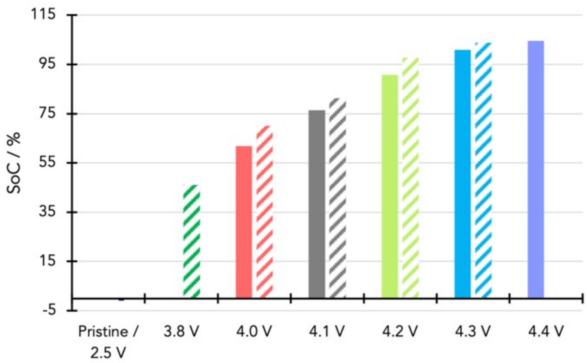

Figure S6. State of Charge (SoC) estimation of voltage cut-offs.

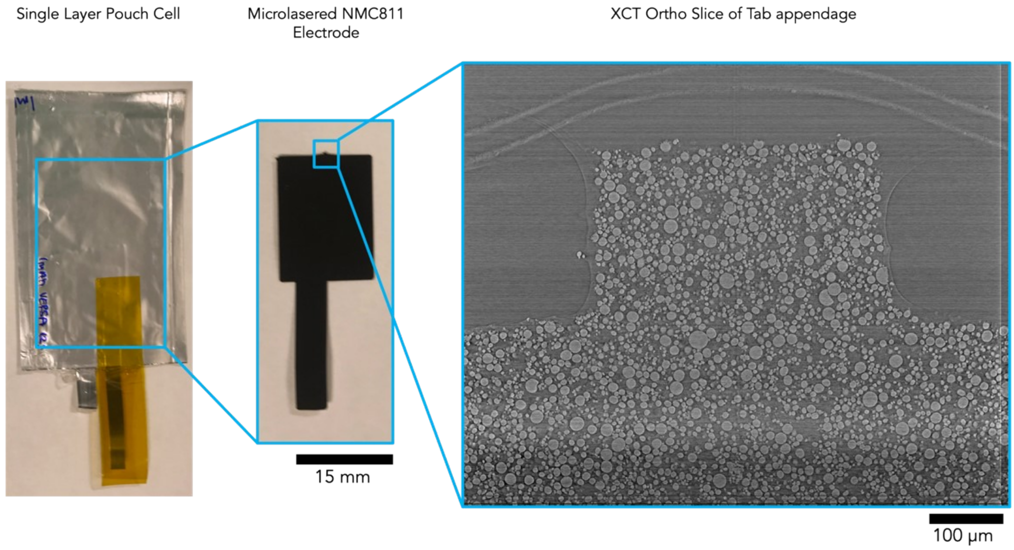

Figure S7. Image of single layered pouch cell used in XCT experiment, the NMC811 micro-lasered electrode, and ortho slice of tab appendage.

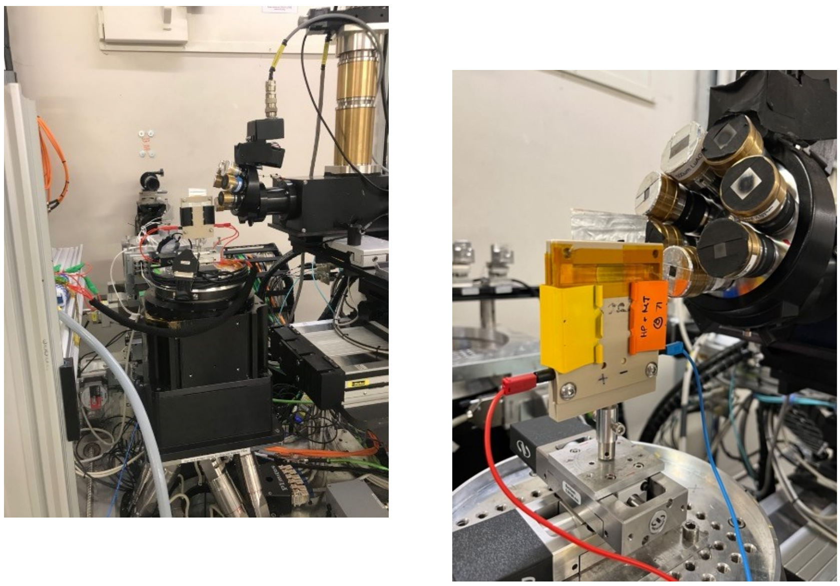

Figure S8. On beam operando set up for XCT in custom built pouch cell holder.

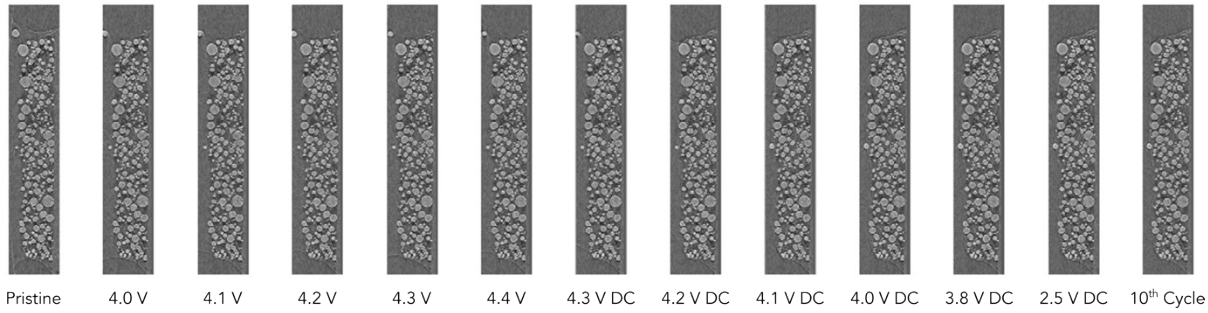

Figure S9. Centre slice of registered 8-bit volume from all tomograms collected.

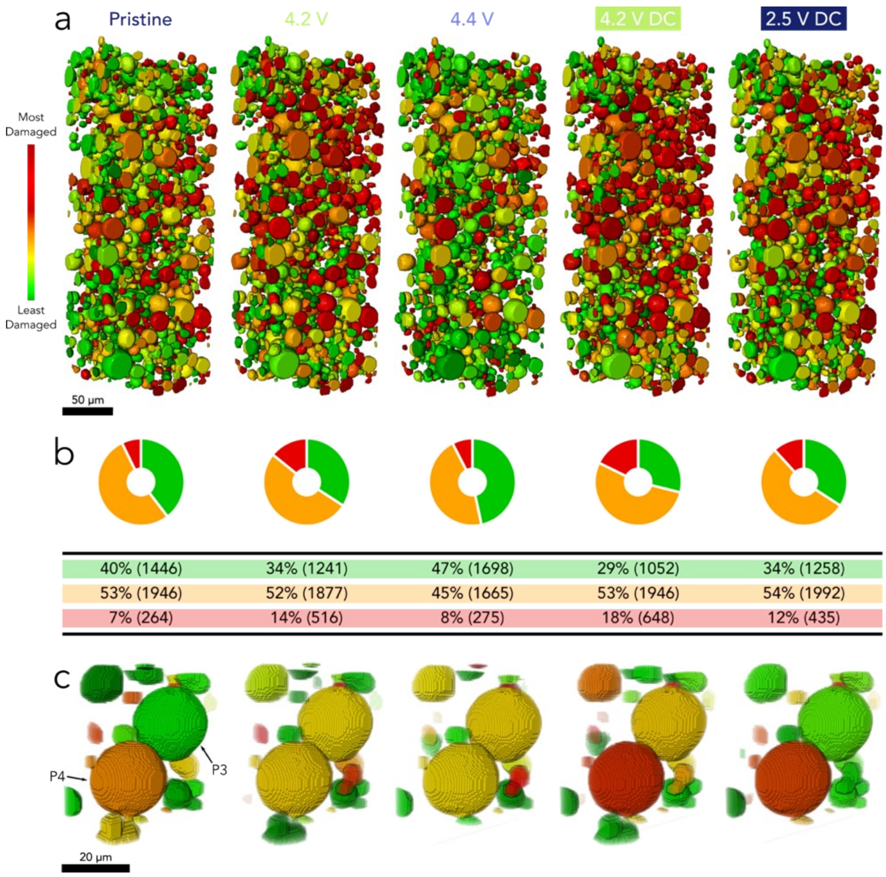

Figure S10: a) Damage maps of the electrode tab (cropped region displayed here for ease of visualisation, statistics are applied to the full tab volume highlighted in Figure 1d, showing the most damaged particles in red and least damaged particles in green. b) Pie charts of % of particles in each damage classification. c) Exemplar particles extracted to show the progression of the damage variable assigned to these particles at the voltages stated.

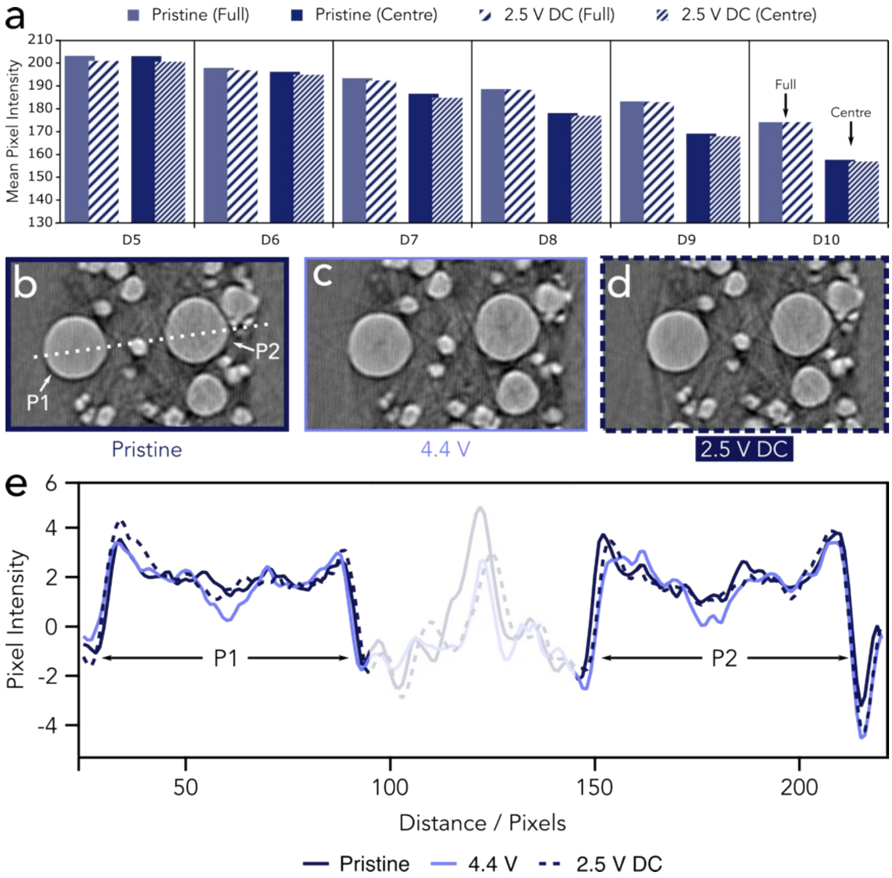

Figure S11: a) Mean pixel intensity for particles at Pristine (block) and discharged (stripes) states, split into the largest deciles D10-D5, for the full particle (left bars) as well as the centre (right bars) is presented. b – d) Ortho slice of two particles that show a reduction in pixel intensity at high voltages and particle reformation after discharge. e) Line scans through the particle in part b, along the dotted white lines as shown, for the pristine state (Blue), charged state (4.4 V, Purple) and discharged state (2.5 V DC, dashed Blue). Pixel size is 325 nm, thus P1 is approximately 17.55 µm diameter, and P2 is approximately 17.88 µm diameter.

SoC	Minimum Damage (%)	Maximum Damage (%)	Minimum Damage (No. Particles)	Maximum Damage (No. Particles)
Pristine	34	4.6	1575	202
4.0 V	17.3	3.4	802	150
4.1 V	9.1	3.6	420	158
4.2 V	2.3	11.7	108	512
4.3 V	1.3	9.3	62	407
4.4 V	1.1	6.5	51	282
4.3 V DC	3.6	8.8	165	385
4.2 V DC	14.8	34.6	684	1510
4.1 V DC	2.6	4.2	122	185
4.0 V DC	2.1	3.3	99	145
3.8 V DC	1.1	6.2	51	271
2.5 V DC	10.7	3.7	498	162

Table S1. State-of-Charge at which minimum and maximum damage is observed. Data displayed in Figure.7a and b.

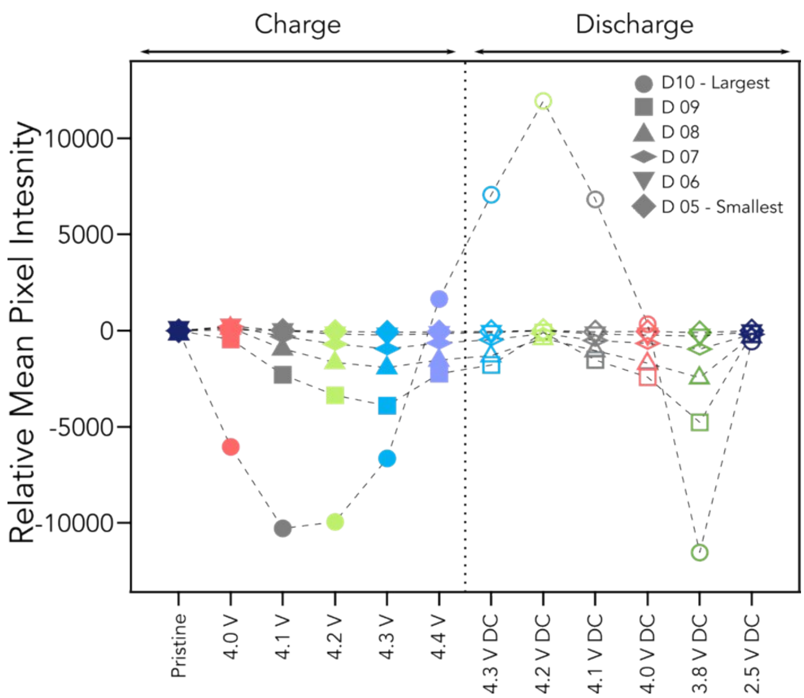

Figure S12. Relative mean pixel intensity for 6 largest deciles. This figure is alternative to Figure. 3c, here shown as a full voxel count as opposed to per unit volume.

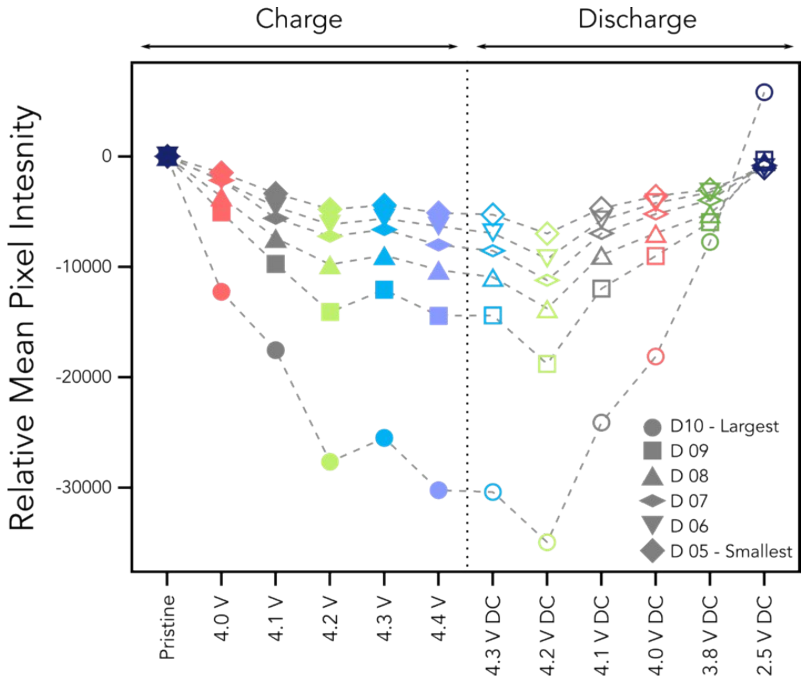

Figure S13. Relative mean pixel intensity changes for only the 5 outer radial layers of each particle in deciles 10-5.

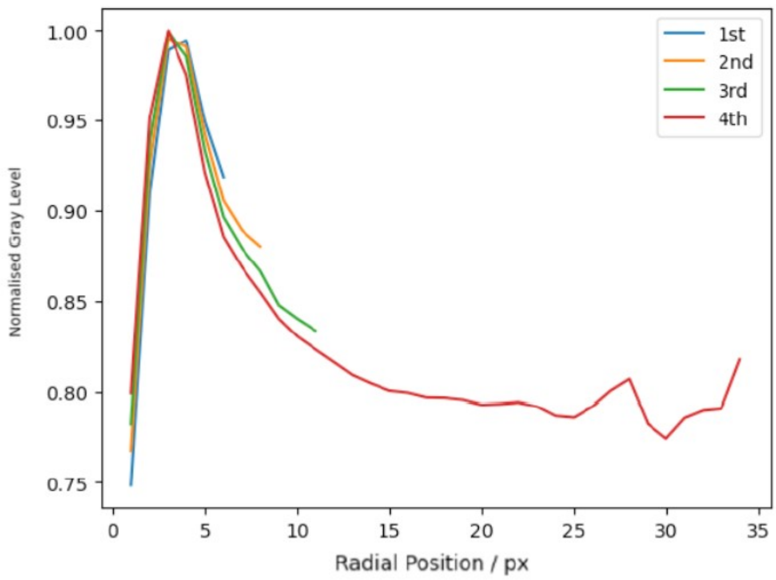

Figure S14. Average radial grey level curves for each quartile of pristine scan.

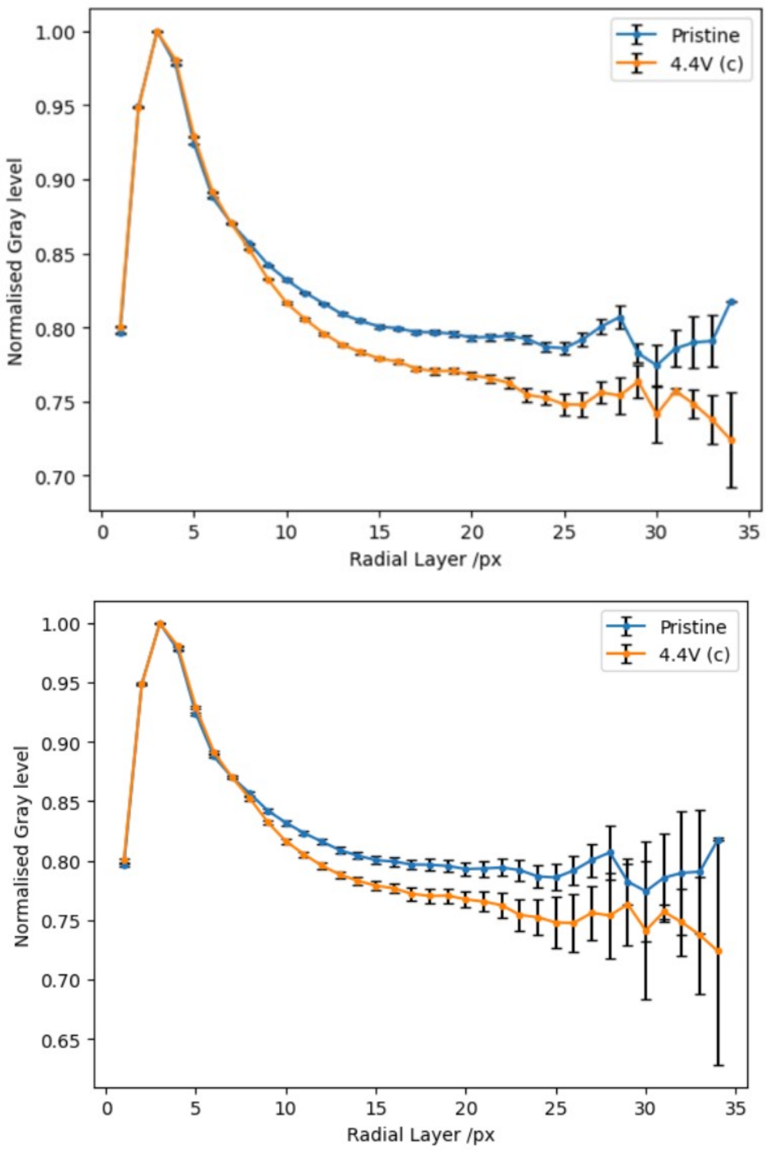

Figure S15. Average radial grey level for particles in Q4 at Pristine (Blue) and 4.4 V (Orange). Error bars are: Top: 2 S.E for each radial layer and Bottom: 3 S.E for each radial layer, at higher values of radial layer the data is under sampled due to fewer large particles.

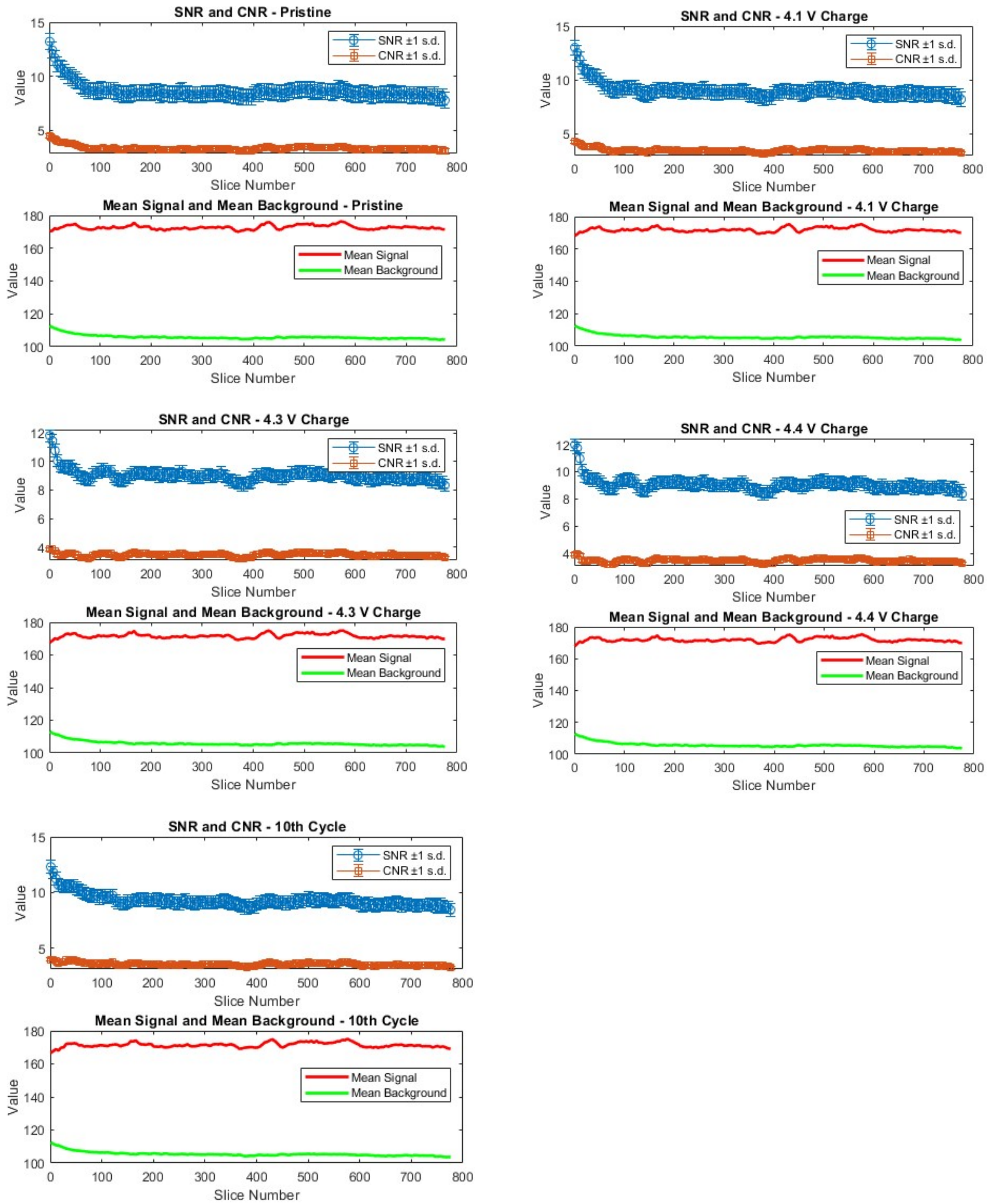

Figure S16. Signal to Noise (SNR) and Contrast to Noise (CNR) of each slice for 5 selected electrochemical samples, with +- 1 SD error bars. Mean signal grey level value and mean background grey level value for through each slice in the same 5 selected samples.

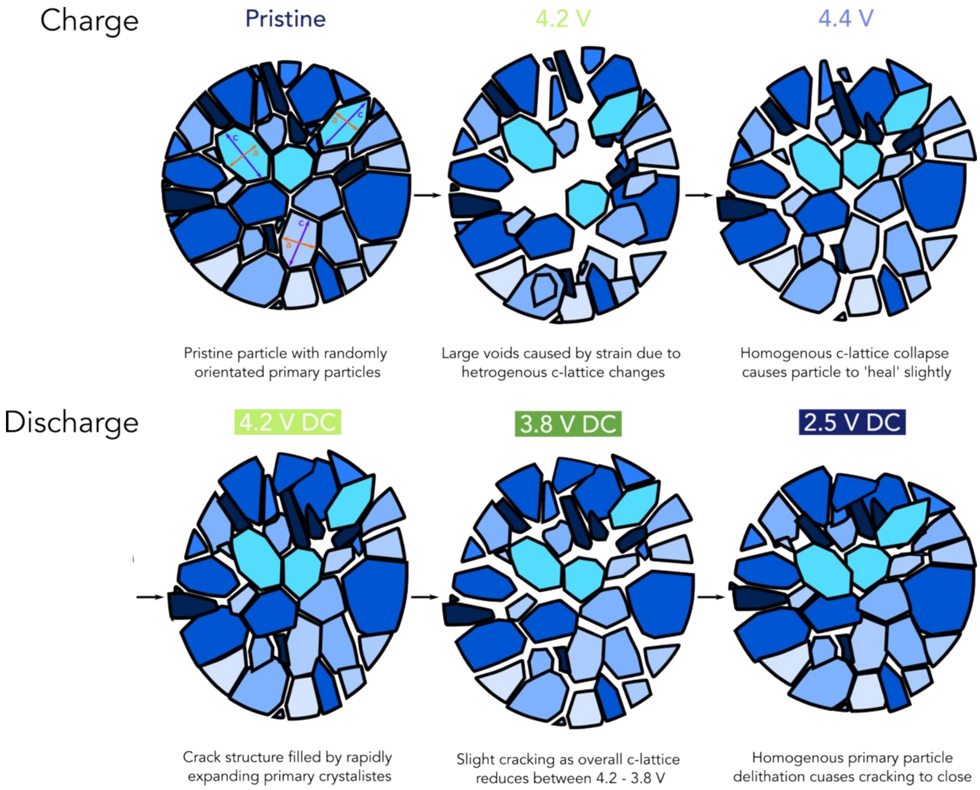

Figure S17. Potential explanation for the increase and reduction in grey level intensities through the first cycle.

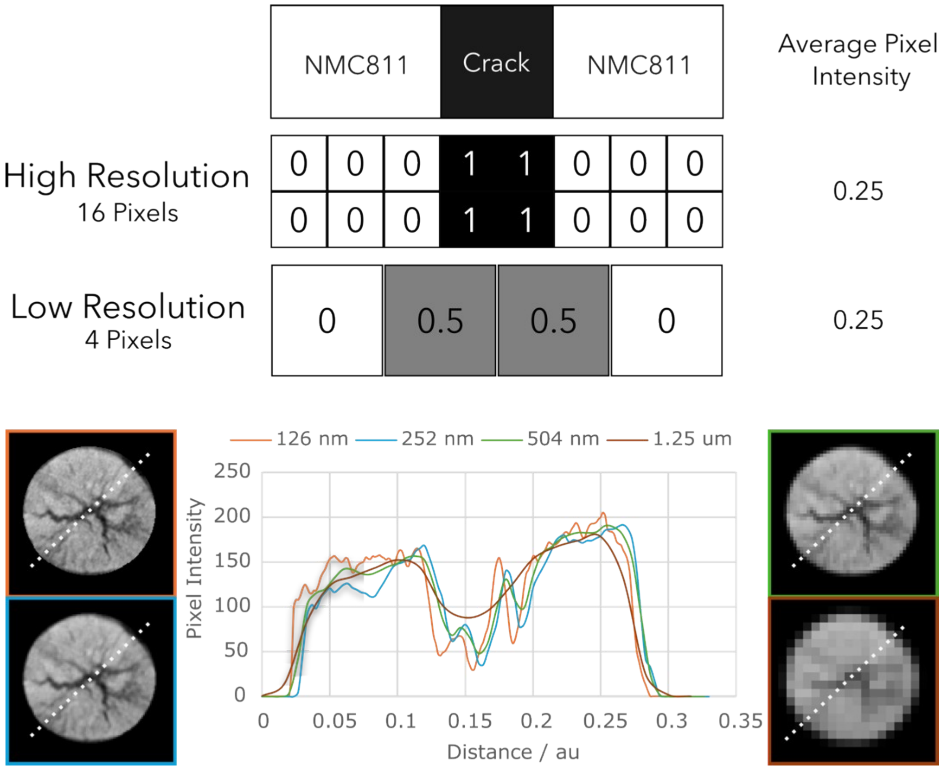

Figure S18. Top: Schematic representation of why low-resolution imaging still contains all the information required for grey level analysis, as the average pixel intensity calculated to be equal even though resolution is reduced by 4x. Bottom: Line graph from nano-CT of NMC811 particle at 4.5 V vs. Li+. Each image is artificially reduced in resolution, however, only when the resolution falls above 1250 nm does the image quality suffer to an extent that may not be suitable for grey level analysis.