Supplementary material

X-ray Imaging Conditions

Zeiss Xradia Versa 520

Full cell tomography: the sample was placed 25 mm from the source and 83 mm from the detector. The accelerating voltage and current were 80 kV and 88 µA respectively. An objective lens giving an optical magnification of 0.4 was used with binning 1 to give an effective pixel size of 7.92 µm. The exposure time was 5 s and the reconstruction consisted of 1601 projections across a 360 ° rotation. Three images taken at different locations along the vertical axis of the battery with a 15% overlap were stitched together to give the full cell reconstruction shown in the main manuscript.

Fresh $LiCoO_2$ and Al current collector: the sample was placed 16 mm from the source and 9 mm from the detector. The accelerating voltage and current were 60 kV and 84 µA respectively. An objective lens giving an optical magnification of 20 was used with binning 1 to give an effective pixel size of 0.424 µm. The exposure time was 50 s and the reconstruction consisted of 2401 projections across a 360 ° rotation.

***Post-mortem* $LiCoO_2$ and Al current collector:** the sample was placed 14 mm from the source and 12 mm from the detector. The accelerating voltage and current were 30 kV and 66 µA respectively. An objective lens giving an optical magnification of 20 was used with binning 1 to give an effective pixel size of 0.36 µm. The exposure time was 40 s and the reconstruction consisted of 1241 projections across a 360 ° rotation.

Zeiss Xradia Ultra 810

P*ost-mortem* scan of $LiCoO_2$ particles showing cracks: Sample was imaged in large field of view (LFoV) in absorption mode. An objective lens giving an optical magnification of 20 was used with 10.3 X-ray magnification with binning 2 × 2 with effective pixel size of 0.1262 µm. The reconstructions consisted of 901 projections with 15 s exposure each.

P*ost-mortem* scan of $LiCoO_2$ particles showing presence of Co: Sample was imaged in large field of view (LFoV) in absorption mode. An objective lens giving an optical magnification of 20 was used with 10.3 X-ray magnification with binning 2 × 2 with effective pixel size of 0.1262 µm. The reconstructions consisted of 1601 projections with 7 s exposure each.

Attenuation coefficients

The $LiCoO_2$ particles were imaged using the Zeiss Xradia Ultra 810 which uses a 5.4 keV quasi-monochromatic beam. Attenuation coefficients of relevant materials were calculated by using elemental mass attenuation coefficients from the NIST website[1]. Greyscale values in the reconstructed tomograms scale linearly with attenuation coefficients for a monochromatic X-ray beam (5.4 keV). The attenuation coefficient of compounds such as $LiCoO_2$ and CoO can be estimated using eqn. S1.

$$\frac{\mu}{\rho} = \sum w_i \left(\frac{\mu}{\rho}\right)_i \quad \text{(S1)}$$

Where μ is the attenuation coefficient, ρ is the mass density, and w is the fraction of element i in the compound by mass.

Table S1. Attenuation coefficients of $LiCoO_2$ and post-thermal runaway compounds.

Material	Mass attenuation coefficient μ/ρ (cm^2/g) (@5.4 keV)	Density ρ (g/cm^3)	Molar mass m_{mol} (g/mol)	Molar volume V_{mol} (cm^3/mol)	Molar attenuation coefficient μ_{mol} (cm^2/mol)	Attenuation coefficient μ (cm^{-1})
Li	1.37	0.53	6.94	13.09	9.48	0.72
Co	130.06	8.90	28.00	3.15	3641.68	1157.53
C	15.85	1.70	12.00	7.06	190.22	26.95
$CoCO_3$	51.16	4.13	88.00	21.31	4501.70	211.27
$LiCoO_2$	61.21	4.90	66.94	13.66	4097.69	299.95
CoO	87.84	6.44	44.00	6.83	3864.94	565.69
Li_2CO_3	11.90	2.11	73.88	35.01	878.98	25.10

As shown in Figure S1 the greyscale value in the Co phase is approximately 1.56 times greater than that in the CoO phase in the core of the particle. From the SEM and EDS images included in the main manuscript, it is seen that there is a surface layer of Co on the particles. The compound that most closely matches the difference in the perceived greyscale in Figure 1 (and hence attenuation coefficient) is CoO, which is also the most likely material to be present in the core of the particle following thermal runaway. However, the attenuation coefficient differs from that of CoO by a factor of 2.05 (Table S1) which is greater than the measured difference in greyscale of 1.56. SEM micrographs appear to show the Co phase to be porous, which would decrease its perceived attenuation coefficient. If the remaining central material were $LiCoO_2$, the greyscale value would differ by a factor of up to 3.9 from Co. Therefore, based on the greyscale values, the most likely material occupying the centre of the particles is CoO.

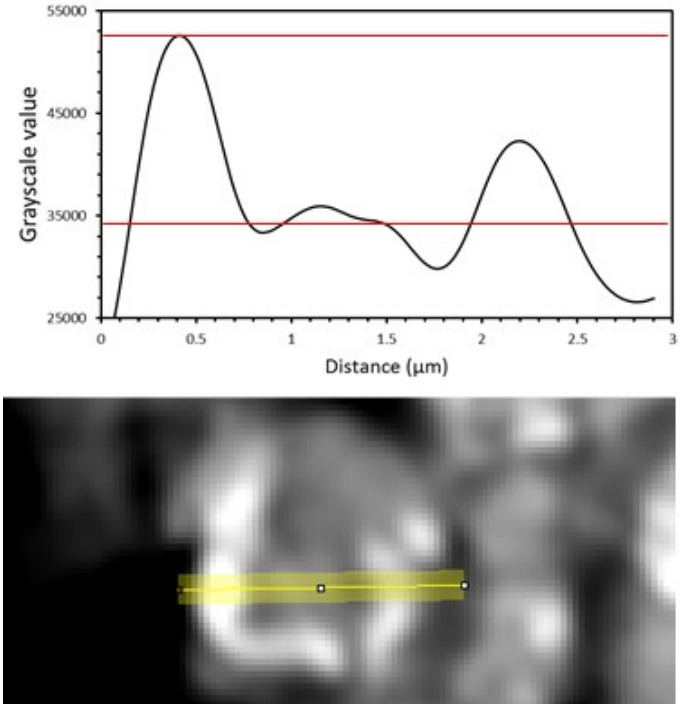

Figure S1. (Top) Plot of greyscale values averaged in the vertical direction across the yellow line shown in the tomogram slice of a $LiCoO_2$ particle following thermal runaway (bottom). The maximum greyscale value is found to be 53,000 which corresponds to the Co surface layer, and average greyscale value of the phase in the centre of the particle is 34,000. Hence, the greyscale value of the Co layer is 1.56 times that of the central material.

References

1. Hubbell, J. H.; Seltzer, S. M., Tables of X-Ray Mass Attenuation Coefficients and Mass Energy-Absorption Coefficients from 1 keV to 20 MeV for Elements Z = 1 to 92 and 48 Additional Substances of Dosimetric Interest. In *NIST Physical Reference Data, NIST Standard Reference Database 126*, NIST, Ed. http://www.nist.gov/pml/data/xraycoef/, 2004.