Mapping internal temperatures during high-rate battery applications

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Electric vehicles (EV) demand high charge/discharge rates creating potentially dangerous temperature rises. Lithium-ion cells are sealed during their manufacture, making internal temperatures challenging to probe[1]. Tracking current collector expansion using X-ray diffraction (XRD) permits non-destructive internal temperature measurements[2]; however, cylindrical cells are known to experience complex internal strain[3,4]. Here, we characterise the state-of-charge (SoC), mechanical strain, and temperature within Lithium-ion 18650 cells operated at high rates (>3C) via two advanced synchrotron XRD methods: firstly, as entire cross-sectional temperature maps during open-circuit cooling and secondly, single-point temperatures during charge/discharge cycling. We observed that a 20-minute discharge on an energy-optimised cell (3.5Ah) resulted in internal temperatures >70°C, whereas, a faster 12-minute discharge on a power-optimised cell (1.5Ah) resulted in substantially lower temperatures (< 50°C). However, when comparing the two cells under the same electrical current, the peak temperatures were similar, e.g., a 6A discharge resulted in 40°C peak temperatures for both cell types. We observe that the *operando* temperature rise is due to heat accumulation, strongly influenced by the charging protocol e.g., constant-current (CC) and/or constant-voltage (CV); mechanisms that worsen with cycling, as degradation increases the cell resistance. Design mitigations for temperature-related battery issues should now be explored using this novel methodology to provide opportunities for improved thermal management during high-rate EV applications.

Introduction

The electrification of transport will depend heavily on the improvement of lithium-ion (Li-ion) battery technologies. For example, aviation demands very high discharge rates during flight take-off[5], and similarly, extreme fast charging of automotive vehicles will be required to mitigate charging-point congestion and downtime for goods transport[6]. To meet these demands many high-rate solutions are emerging[7-9], however, thermally induced degradation remains problematic[10,11]. To advance cell designs such that these degradation issues can be mitigated, we must be able to accurately quantify internal temperatures during operation. This is challenging because cells are sealed during their manufacture for protection from contamination[12] and short-circuit[13]. To non-destructively measure temperature, the thermal expansion of metals[14] such as the current collector[2] have been measured via X-ray diffraction (XRD), but to resolve internal temperatures directly has required modification of the cell to incorporate thermocouples[1].

Computed tomography (CT) methods allow non-destructive measurements to be resolved spatially[15] and has uncovered many complex distributions of strain[3] and SoC[4]. Recently XRD-CT has revealed unprecedented insights into the internal SoC distributions within Li-ion cells[16]. Alas, lattice changes due to thermal expansion are orders of magnitude lower than those associated with lithiation. For instance, a 10 °C temperature change in copper would result in a $6x10^{-4}$ Å lattice parameter expansion, whereas the lattice changes during lithium intercalation (or de-intercalation) of the cathode active material are two to three orders of magnitude greater[2]. Therefore, SoC can be extracted without characterising the thermal and mechanical strain due to their negligible contributions, but resolving temperature requires mechanical and thermal strain deconvolution, and the greater the number of spatial dimensions that are resolved (e.g., 1, 2, 3D) the more complex this becomes.

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Materials demand is set to expand rapidly with the electrification of transport[17] and two contrasting cathode chemistries are lithium iron phosphate (i.e., LFP or $Li_{1-x}FePO_4$) and the layered nickel-rich transition metal oxides (e.g., NMC811 or $Li_{1-x-y}Ni_{0.8}Mn_{0.1}Co_{0.1}O_2$). LFP boasts longer lifetimes and enhanced safety, ideal for power-optimised cells; whereas NMC offers higher volumetric and gravimetric energy densities, more suitable for energy-optimised cell designs[18]. Similarly, many commercial anodes are fabricated from either graphite (e.g., Gr or Li_xC_6, Li_xC_{12}, Li_xC_{18}), silicon (e.g., Si or Li_xSi_y), silicon-oxide (e.g., SiO or $Li_xSi_yO_z$), or a composite of the two (e.g., Gr-Si, Gr-SiO_z). Note that the oxygen content in Si electrodes is often not known, hence it is commonplace to denote the material SiO_z, where z may be zero or negligible[19]. Si offers very high theoretical specific capacities however Gr undergoes significantly less expansion during cycling, accompanied by reduced stress[20]. Therefore, a plethora of materials combinations will compose the global Li-ion battery market, but a comparison of these key materials, which represent examples of power- and energy-optimised cells, can produce a suitable overview.

Here, we explain two methods of non-destructive temperature measurements for commercial cylindrical cells (e.g., 18650 format) via monitoring of the expansion/contraction of the Cu current collector crystal structures from XRD. Firstly, full cross-sectional temperature maps can be generated from conducting XRD-CT, ideal for exploring spatial distributions at the end of charge or discharge (e.g., 2D maps). And secondly, a multi-channel-collimator (MCC) can be used to resolve the temperature within arbitrarily selected internal locations (e.g., 1D lines) for real-time quantifications during operation. This article focuses on two contrasting commercially available 18650 cells, one with a Ni-rich NMC811 cathode vs. Gr-SiO_i anode, and a second with an LFP cathode vs. a Gr anode. The subsequent sections will discuss validation of temperature quantifications without electrochemical operation (*ex situ*), then acquisition via XRD-CT (*in situ*), and MCC-XRD (*operando*).

Ex situ temperatures

Cylindrical 18650 cells are assembled as jellyrolls as seen in the laboratory X-ray attenuation CT cross-sectional image in **Fig. 1a,b**. A similar cross section can be produced (at a lower spatial resolution) by monitoring the metallic current collector lattice spacing[2] to calculate the temperature (**Fig. 1c**) and reconstructing a spatially resolved image using XRD-CT **(Fig. 1d,e)**. XRD-CT can accurately reconstruct only quantities which are invariant for rotation around the tomographic rotation axis, temperature maps can be obtained since the thermal induced strain is in most materials a scalar quantity. The result is a spatiotemporal map of the internal cell temperature. As a simple proof-of-concept experiment the authors first mapped the internal temperatures within two 18650 cells after heating within a furnace (without electrochemical operation). The internal temperatures are displayed within **Fig. 1** as cross-sectional slices taken from the same region-of-interest (RoI) within the cell as the cells cooled over the course of ca. 30 minutes.

The temperature quantifications calculated by fitting the data of the Cu d-spacing closely followed fittings based on Newton's law of cooling (**Fig. 1c,** and see methods), indicating a high level of confidence in the quantifications. To the authors' knowledge, this is the first report of a spatially resolved temperature map within a commercial 18650 Li-ion cell without disassembly or modification. We will now consider the far more complex determination of temperatures driven by electrochemical operation. Note that all error bars throughout this article indicate statistical errors (standard deviation), the precision error is ca. ± 3 °C throughout.

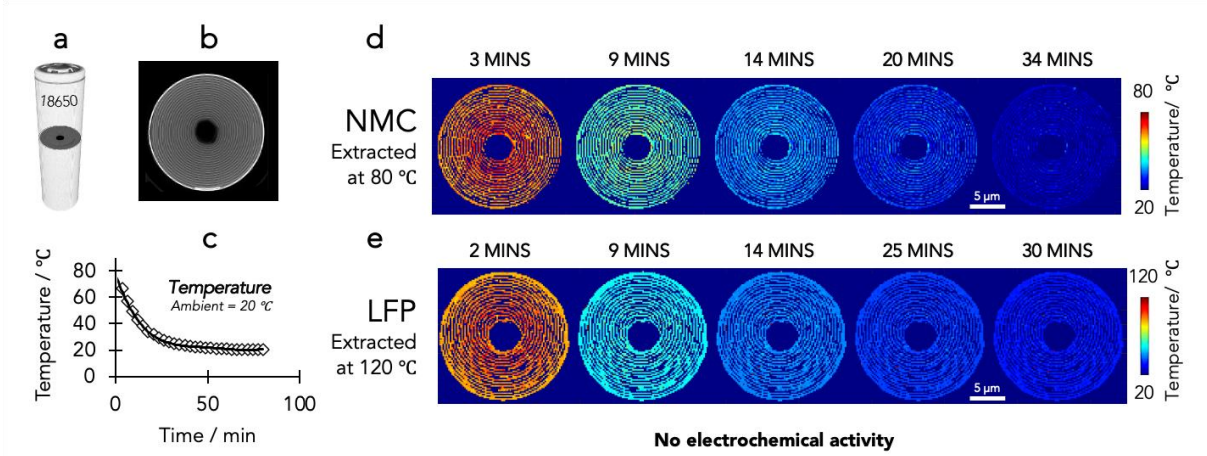

Fig 1. Spatiotemporal temperature mapping within 18650s without electrochemical operation. **a,b,** Laboratory X-ray CT (a) volume render and (b) ortho-slice of the NMC cell displaying the steel casing and internal jellyroll assembly. **c,** Internal temperatures within the NMC cell during cooling immediately after removal from the oven at 80 °C. **d,e,** A similar ortho-slice as shown in the laboratory CT (a) but instead representing the internal cell temperature obtained from synchrotron XRD-CT for (d) the NMC cell removed at 80 °C and (e) the LFP cell removed at 120 °C. Note that ambient temperature was assumed to be a consistent 20 °C.

In situ temperatures

To conduct electrochemical operation while also obtaining temperature measurements via XRD methods, a bespoke 18650 cell holder was designed and optimised to deliver sufficient XRD signal-to-noise (SNR) while also permitting high electrical currents with low circuit losses (**Extended Data Fig. 1**). Examples of the integrated XRD patterns and refinement can be found within the supplementary material (**Extended Data Fig. 2**). Employing this set-up allowed both Coulomb counting of the electrochemical data and XRD analysis of the active electrode materials[2] to give indications of the SoC, and further, reconstruction via XRD-CT generated spatial maps of the SoC for each material[16]. In addition to SoC, mechanical strain information has proven highly important within 18650 cells[3,4,] and similar to SoC, XRD methods can also be used to extract this mechanical strain. Temperature measurements are the focus of this article but *operando* SoC and mechanical strain calculations can be found within the supplementary material (**Extended Data Fig. 3-7**).

As demonstrated for the oven-heating experiment (**Fig. 1**), internal temperatures could be mapped as 2D cross-sections as the cell cooled. **Fig. 2** displays the temperature values recorded during the transition to open circuit voltage (OCV) after discharge at various rates (approx. temperature peak values shown in **Fig. 2a**). To inspect peak internal thermal gradients the cell was divided into 8 radial zones (rings in **Fig. 2b**) but also compared to 8 azimuthal zones (segments in **Fig. 2c**). Increasing the C-rate from 1C to 3C increased the cell temperature by an additional ~ 40 ℃, which overshadowed the influence of any thermal gradients across the 8 radial (and azimuthal) zones, which were on the order of ±5 ℃; this was also true for the LFP cell (**Extended Data Fig. 8**).

Although internal spatial variations are not significant relative to a change in C-rate, these heterogeneities should not be overlooked. For instance, a small up-tick in temperature was observed towards the cell core i.e., furthest from the cell walls. This may prove important when optimising active thermal management techniques or when incorporating/informing high-precision multi-scale modelling, and therefore the authors wish to emphasise that, although spatial variations are small (relative to the influence of C-rate) they should still be considered for accurate prediction and characterisation in future studies.

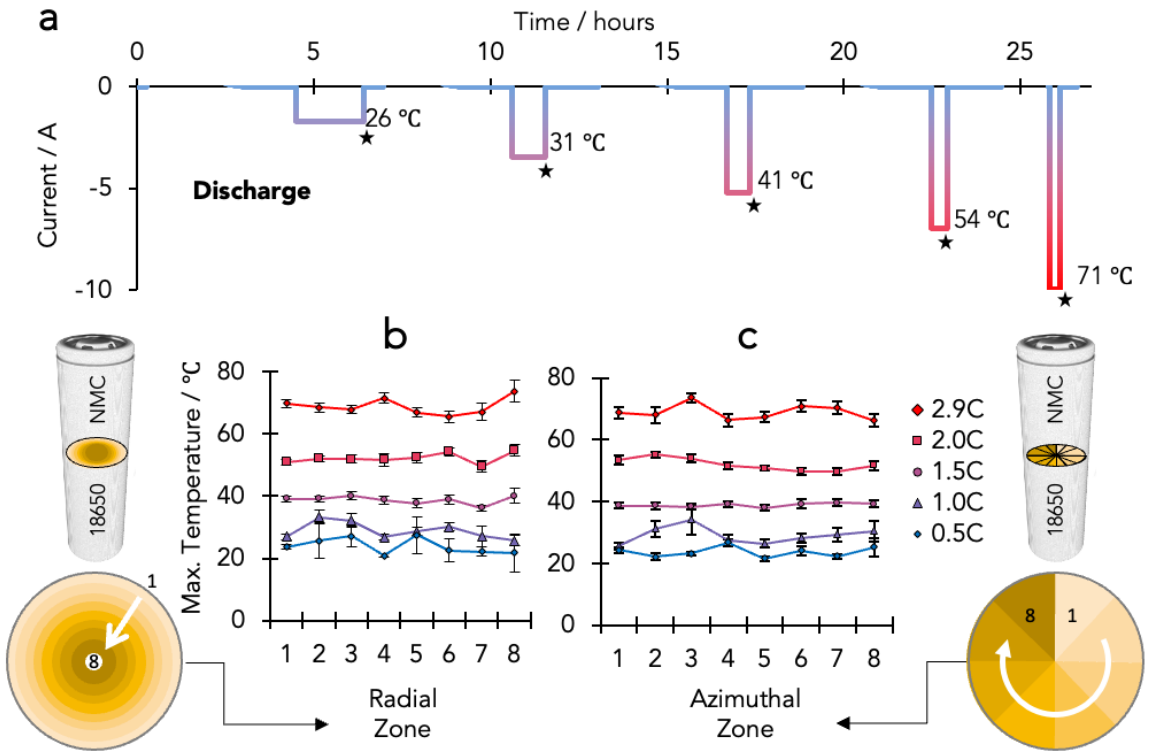

Fig. 2 ***In situ*** **internal temperature maps via XRD-CT. a,** The high-rate discharge currents for a commercial 18650 with measurement of the peak temperature during the open circuit transition (stars). **b,c,** Internal temperatures for 8 zones divided as (b) radial and (c) azimuthal zones. All error bars are statistical, precision error is ca. ± 3 °C throughout. Note that ambient temperature was assumed to be a consistent 20 °C.

Since the cell capacity dictates the electrical current for a particular C-rate, the contrasting power-optimised 18650 cell (LFP vs. Gr) was also assessed and compared to the energy-optimised counterpart (**Fig. 3a,b**), with the maximum temperature plotted with respect to the discharge current within **Fig. 3c** (circles) alongside two NMC cells (diamonds and triangles). The maximum temperature recorded grew similarly with discharge current irrespective of the cell type, e.g., at a discharge current of 6 A the maximum temperature was approximately 40 °C for all cells regardless of chemistry and this correlation held well throughout all discharge currents explored (i.e., up to approx. 10 A).

The thermal conductivities of the current collectors (assumed to be 398 and 235 W/m/K for copper and aluminium, respectively) are three orders of magnitude higher than the electrodes, and four orders higher than the separator. Therefore, it is unlikely that large amounts of heat are transferred rather through the electrodes or directly through the separator material. Instead, it is more probably that heat is preferentially and efficiently transferred around the jelly-roll winding through the metallic current collectors. Additionally, heat transfer from the interior to the exterior of the cell is very inefficient due to the much lower thermal conductivity of the steel case (~45 W/m/K). These factors explain the degree of homogeneity observed throughout the cell in **Fig. 2**, the current collector promotes temperature uniformity via high thermal conduction. Similarly, the strong dependence of the electrical current upon the peak temperature (**Fig. 3**) can be explained by the inefficient thermal properties of the casing design, which promotes heat accumulation, and the subsequent temperature rises. See further discussions within the Supplementary Material. This also indicates that Joule heating (at least for high currents) dominates heat generation, rather than reaction heating. Power-optimised LFP chemistries, with lower capacities, therefore present a favourable heat (and temperature) management option for high-rate applications since a lower relative electrical current can achieve a higher C-rate, thus faster charge/discharge and SoC change, although at the cost of lower energy densities. Therefore, if onboard energy density can be compromised, i.e., if shorter driving or flight ranges are acceptable in certain applications e.g., agricultural drones or warehouse robots, power-optimised cells such as these can offer improved thermal management.

The similarities of peak temperatures within the two cells at various discharge currents suggests that fundamental cell design alterations would be required to mitigate high temperatures (via improved heat dissipation) during high electrical currents, i.e., to enter the green 'target zone' visualised in **Fig 3c.** Consequently, the authors concluded that a method for understanding *operando* temperature changes (i.e., measurements during charge transfer) would be essential to explore how the heat is accumulated during operation.

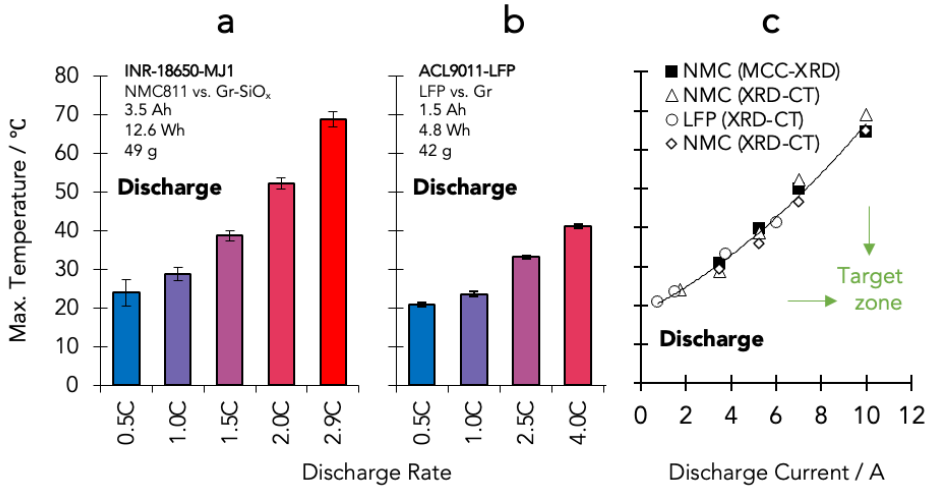

Fig. 3 ***In situ*** **internal temperature maxima via XRD-CT. a,b,** The internal temperature maxima within the commercial (a) energy- and (b) power-optimised cells immediately after discharge at various C-rates. **c,** The maximum internal temperature correlated with discharge current for two energy cells and one power cell, obtained at the end of discharge/start of OCV, via XRD-CT or MMC-XRD. Note that ambient temperature was assumed to be a consistent 20 °C.

Operando temperatures

During cell charge and discharge, in addition to thermal strain due to the Joule heating effect, the Cu current collector develops mechanical elastic strain caused by stress build up inside the cell, originated by different volumetric expansion/contraction of anode and cathode. To separate the mechanical from thermal strain and explore the temperature during stages that precede the peak temperatures reported in **Fig 3**, the methodology for a second XRD measurement was developed by employing a Multi-Channel Collimator (MCC) **(Extended Data Fig. 9**) which allows high speed (sub-second), high angular resolution and high SNR XRD measurements from a given spatial location (gauge volume). MCC-XRD measurements were performed along the same radial line, at two orthogonal orientations of the cell.

The *operando* MCC current collector tangential and radial strain measurements, combined with *operando* XRD-CT axial strain measurements permitted the analysis of temperature dynamics during the whole charge/discharge process, not only during open circuit. **Fig. 4** displays the temperature values recorded for zone 4 within an NMC cell during four charge-discharge cycles, whereby all four charges were conducted at 1C but each discharge was increased until the manufacturer's specified maximum electrical current of c. 10 A was reached. For completeness, **Fig. 3c** also reports the MCC data, showing close agreement with the XRD-CT values. The temperature and radial stress during the four charge profiles (at 1C, 3.5 A) were highly repeatable with minimal variation (**Fig. 4a,b**). Furthermore, the transition (dashed vertical line, ca. 45 mins) between the constant current (CC) and constant voltage (CV) stages was clearly distinguishable.

During CC the temperature rises due to the heat accumulation but once the current is allowed to decay under CV (or OCV) the temperature reduces, as heat loss to the surroundings exceeds that generated due to Joule heating. Consequently, there is a clear correlation between the electrical current employed and the temperature rise observed (as shown in **Fig. 4a**) but subsequently, the internal temperature at the end of charge will be dictated by the profile of the electrical current over the entire duration of the charge profile. For instance, other charging protocols such as current pulse or constant

power may produce different temperature profiles to that seen here (under CC-CV) because the trade-off between heat generation and loss (to the surroundings) is different.

Discharge was conducted without a CV hold, i.e., only under CC. The temperature rise during the CC discharge followed a similar (but inverted) profile to the cooling after removal from the oven in the first experiment (compare heating in **Fig. 4b** to cooling in **Fig. 1d**); whereby initially the temperature changes rapidly but then slowing with time.

Naturally, unlike the thermal dynamics, the mechanical stress does not reduce during the CV stage due to the intercalation (and de- intercalation) mechanisms occurring during charge (**Fig. 4c**). This stress is only relieved once the discharge process is completed (**Fig. 4d**). Marginal stress hysteresis, observed as non-zero stress values at the end of discharge, may be attributed to the inaccessible discharge capacities at higher rates (**Extended Data Fig. 7**). It should also be noted that stress was most dependent upon the SoC (see stress-capacity in **Fig. 4e,f**) and showed no correlation with C-rate (**Fig. 4f**).

It should also be noted that it is possible (through the collection of temporally resolved temperature data) to calculate effective heat transfer coefficients. By exploring the temperature decay time (τ), assuming the cell mass to be 49 g, and the cell to be sufficiently represented by a perfect cylinder i.e., flat caps, using a reference for the cell heat capacity e.g., 960 J / kg / K from Maleki *et al.*[21], the heat transfer coefficient for the energy cell is calculated to be ca. 17.6 W / m^2 / K. Full workings can be found within the Methods. Such calculations may inform cell and pack computational modelling in predictive studies, that in turn, may inform future experiments.

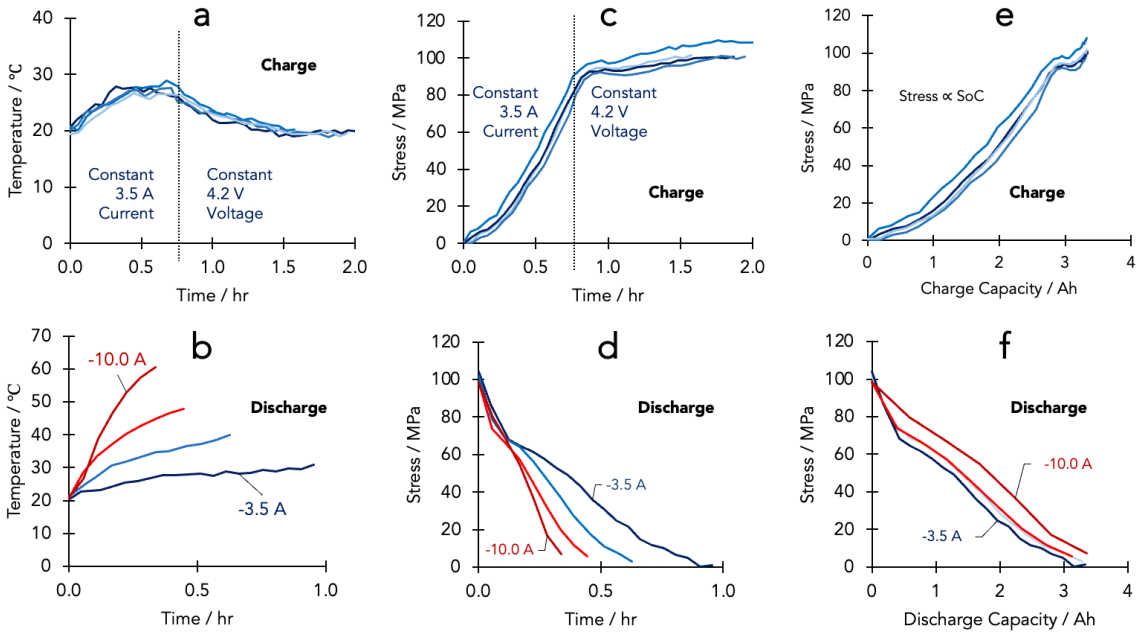

Fig. 4 ***Operando*** **internal temperatures via MCC-XRD. a,b,** The temperature during (a) charge and (b) discharge for the four cycles. **c,d,** The stress during (c) charge and (d) discharge for the four cycles. **e,f,** Assessing the relationship between the SoC (capacity) and the stress for the four (e) charge cycles all at 1C and (f) discharge cycles at various C-rates. Note that ambient temperature was assumed to be a consistent 20 °C.

Temperatures after degradation

The characterisation of cell temperatures is important not only at the beginning of use but throughout the cell's lifetime. So, in addition to exploring temperatures extracted from pristine cells i.e. as supplied from the manufacturer; **Fig. 5** presents insight into the implications for thermal management after significant operation (e.g. beyond 1,000 operational cycles).

Firstly, prolonged cycling is known to lead to increased resistance as a result of cell degradation that restricts the accessible cell capacity[18] (see the discharge capacity loss with each operational cycle, **Fig. 5a**). To translate this to real-world applications, this means that the total driving range for an EV will decrease with each recharge (assuming controlled conditions e.g., no substantial temperature changes, etc.). Many degradation mechanisms can be observed in the form of microstructural changes as seen in the magnified cell contents in **Fig. 5a**, and the full cross-section in **Fig. 5b**.

Fig. 4b provides an indication of the possible implications of degradation on cell temperatures. The longer the cell is held at constant current, the higher the internal temperature rise, i.e. the internal cell temperature correlates with the magnitude of the current and the time spent at CC (units ampere-hour, Ah). This gives rise to two key probabilities for degraded cells based upon their discharge capacity. Scenario 1: capacity remains high (e.g. >80%), thus can still withstand a significant time at CC but under a higher internal resistance, producing more heat and higher temperatures than pristine. Scenario 2: capacity has declined significantly (e.g. <80%), thus cannot withstand significant time at CC, thus even with substantial internal resistance, produces lower temperatures than pristine. The real-world consequence of scenario 2 is possibly a warranty failure of the EV, the battery would require replacement; whereas the significantly more serious consequence of scenario 1 is the potential compromise of the safety measures designed for pristine cells, endangering the user.

Fig. 5c provides an example of scenario 1. The visibly degraded cell (**Fig. 5a,b**) exhibits signs of delamination and cracking at the cell-level which gives rise to a higher internal temperature after discharge that is most notable at higher C-rates (**Fig. 5c**) and electrical currents (**Fig. 5d**). Under a 7 A discharge the aged sample was ca. 4 °C higher than the pristine, a consistent but small increase relative to the influence of C-rate e.g. doubling the C-rate from 1 to 2C resulted in an additional temperature rise of approx. 30 °C. Nonetheless, a plethora of degradation mechanisms are known to elevate cell internal resistances, and this is only one example. Future studies may explore other chemistries, geometries, microstructures and charging protocols.

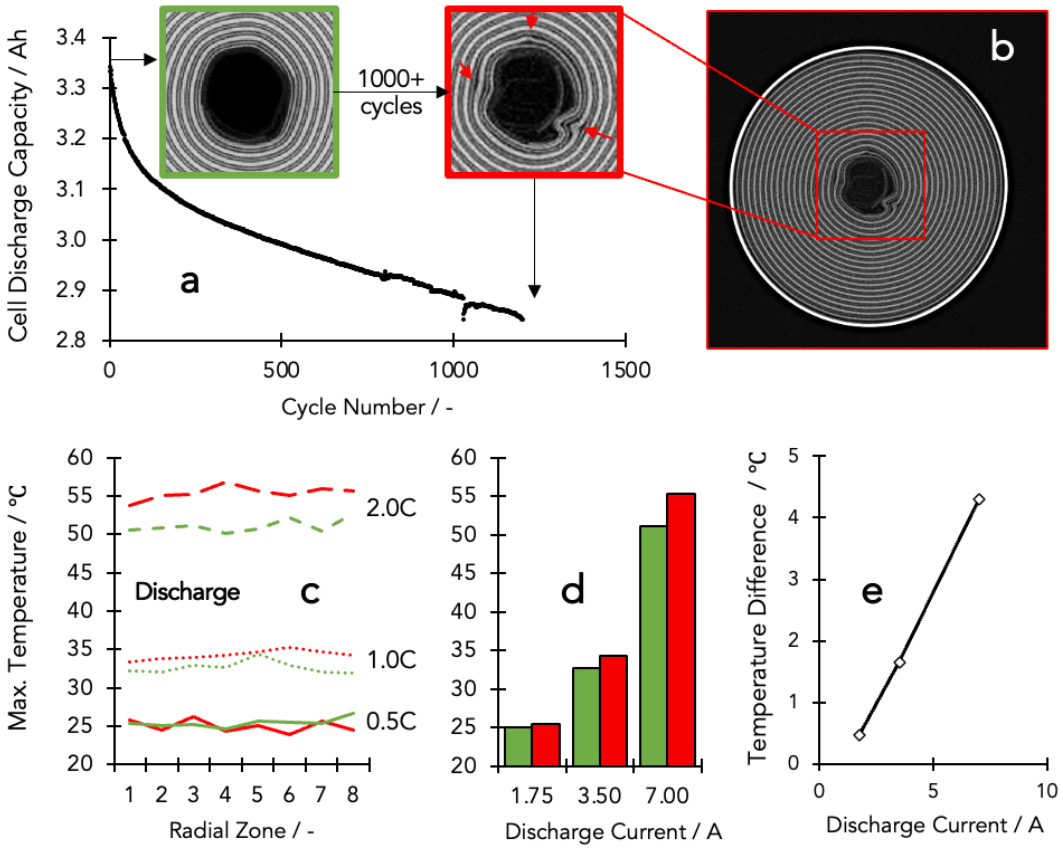

Fig. 5 ***Internal temperatures after cycling.*** **a,b,** The (a) electrochemical and (b) structural data from an energy-optimised 18650 3.5 Ah nominal capacity cell before (green) and after (red) long-duration cycling. **c,** The maximum temperature recorded for the eight radial zones. **d,** The average temperature immediately after each

discharge current. **e,** The difference between the cycled and pristine cell temperatures after three discharge currents. Note that ambient temperature was assumed to be a consistent 20 °C.

Future thermal management

In conclusion, 1D point and 2D mapping measurements[2] have provided substantial insight into the possibilities of thermo-mechanical characterisations of operational cells, however, are inherently restricted in the information that can be extracted. The ability to resolve additional spatial dimensions (3D), permitting internal measurements and the decoupling of thermal from mechanical contributions to electrochemical changes, as presented here, offers a step-change advancement in the possible insight available. For instance, internal distributions (see Fig.1,2) are only possible with spatially resolved methods (i.e., 3D). Moreover, incorporating bespoke set-ups (e.g., MCC) allow suitable measurement precision whilst under fast operation dynamics (i.e., internal *operando* studies).

We present here two methodologies to accurately (± 3 °C) quantify internal temperatures during high-rate (up to 10.0 A) operation of commercial Li-ion 18650s without cell modification or disassembly. These methods should be applicable to the vast majority of, if not all, commercial 18650s, and may be conducted by any specialist XRD synchrotron beamline with the cell holder (described within the methodology and supplementary) and using the correct imaging setup. Moreover, minor alterations would permit the study of other cell geometries, e.g., 2170 and 4680, and non-standard microstructures e.g., ultra-thin current collectors.

Temperature mapping using XRD-CT revealed that the peak temperatures reached within the cell are relatively homogeneous (spatially) at the end of discharge and the magnitude of this temperature peak is largely dictated by the electrical current employed. The MCC-XRD temperature mapping method then revealed that this temperature peak is reached due to an accumulation of heat and is strongly influenced by the charging protocol (e.g., the use of CC or CC-CV, etc.). Finally, we discuss the implications for used cells (e.g. 1,000+ cycles), proposing two key undesired scenarios. The first where cells can no longer withstand high currents, thus are unable to generate large amounts of Joule heating, and are therefore likely to fail warranty and require replacement. The second scenario has potential safety implications, where cells that are still able to receive high electrical currents but also experience significantly higher internal resistance than in their pristine state, produce increased heat and higher internal temperatures potentially endangering the user. Future studies may expand upon these scenarios with real-time quantifications that can inform computational modelling[22,23], potentially with the inclusion of statistical analysis indicating the probability of each scenario.

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Figure legends

Fig 1. Spatiotemporal temperature mapping within 18650s without electrochemical operation. a,b, Laboratory X-ray CT (a) volume render and (b) ortho-slice of the NMC cell displaying the steel casing and internal jellyroll assembly. **c,** Internal temperatures within the NMC cell during cooling immediately after removal from the oven at 80 °C. **d,e,** A similar ortho-slice as shown in the laboratory CT (a) but instead representing the internal cell temperature obtained from synchrotron XRD-CT for (d) the NMC cell removed at 80 °C and (e) the LFP cell removed at 120 °C. Note that ambient temperature was assumed to be a consistent 20 °C.

Fig. 2 *In situ* internal temperature maps via XRD-CT. a, The high rate discharge currents for a commercial 18650 with measurement of the peak temperature at the point of open circuit (stars). **b,c,** Internal temperatures for 8 zones divided as (b) radial and (c) azimuthal zones. All error bars are statistical, precision error is ca. ± 3 °C throughout. Note that ambient temperature was assumed to be a consistent 20 °C.

Fig. 3 *In situ* internal temperature maxima via XRD-CT. a,b The internal temperature maxima within the commercial (a) NMC and (b) LFP cells immediately after discharge at various C-rates. **c,** The max internal temperature correlated with discharge current for two NMC cells and the LFP cell, obtained at the start of open-circuit/end of discharge, obtained either via XRD-CT or MMC-XRD. Note that ambient temperature was assumed to be a consistent 20 °C.

Fig. 4 *Operando* internal temperatures via MCC-XRD. a,b, The temperature during (a) charge and (b) discharge for the four cycles. **c,d,** The stress during (c) charge and (d) discharge for the four cycles. **e,f,** Assessing the relationship between the SoC (capacity) and the stress for the four (e) charge cycles all at 1C and (f) discharge cycles at various C-rates. Note that ambient temperature was assumed to be a consistent 20 °C.

Methods

18650 Li-ion cells. The commercial cell testing was performed on 3.5 Ah nominal capacity LG Chem INR-18650-MJ1 cells (Nkon, Netherlands). These cells are assembled using nickel-rich ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$) cathodes and composite graphite-silicon anodes. Where stated, a comparison cell was also analysed: the 1.5 Ah nominal capacity ACL9011, composed of a lithium iron phosphate (LFP) cathode and graphite anode.

Laboratory X-ray CT. The lab X-ray CT data was collected using a Nikon XT H225 (Nikon Metrology, Inc. U.S.A.) by rotating the sample through 2,278 angular projections and exposing the sample at each increment to a polychromatic X-ray beam of characteristic peak energy of 58 keV (W-Kα), each with an exposure time of 1 s; with an isotropic 36 μm reconstructed voxel length. This data has been published openly elsewhere and is free to download[23]. All data was reconstructed using commercial software employing cone-beam filtered-back-projection (FBP) algorithms ("CT Pro 3D," Nikon Metrology, Inc. U.S.A.).

Laboratory data visualisation. All lab data was visualised using Avizo Fire software (Avizo, Thermo Fisher Scientific, Waltham, Massachusetts, U.S.A.). Volume renders and ortho-slice cross-sections were generated based upon the raw, unprocessed greyscale data within the tomogram.

Synchrotron. All synchrotron experiments were performed at the ID15A beamline[24] at the ESRF – The European Synchrotron, Grenoble, France. During the XRD-CT measurements the sample was continuously rotated while being translated horizontally across the X-ray beam path in steps defined by the horizontal beam size (**Extended Data Fig. 1**). The MCC-XRD data was collected during translation of the sample along either the direction parallel to the beam (x) or perpendicular (y). In both setups the scattered signal was collected at rates of 200-250 Hz using a Pilatus 3X CdTe 2M detector (Dectris, Baden-Dättwil, Switzerland).

Multi-Channel Collimator (MCC). The MCC used in this work consists of two concentric sets of slits radially aligned around the centre of rotation of the diffractometer. The two sets of slits consist of tungsten carbide blades supported by a stainless-steel frame. They contain 75 slits, separated by 0.8°, with a distance of 50 and 200 mm respectively from the sample.[28] Thanks to this geometry it is possible to select the scattering signal from an internal volume in the sample (**Extended Data Fig. 9**). The gauge volume from which the diffraction signal is measured is given by the intersection of the primary X-ray beam with the volume seen by the detector through the MCC slits (**Extended Data Fig. 9**). The dimension of the gauge volume full-width-half-maximum (FWHM) along x axis (δx) is approximated by the formula as:

Equation 1
$$\delta x = \frac{a}{\left(1-\frac{r_1}{r_2}\right)\sin 2\theta} + \frac{\delta y}{\tan 2\theta},$$

Where, a = 50 μm is the width of the inner slits; r_1 and r_2 are the inner and outer slit radii, respectively; and δy is the horizontal beam size. As shown by equation 1, the gauge volume varies with the diffraction angle, 2θ. The gauge volume dimensions along *y* and *z* directions correspond to the X-ray beam cross section. Sample diffraction patterns without and with multichannel collimator are compared in **Extended Data Fig. 10**.[28,29]

Commercial 18650 cell holder. All *in situ* and *operando* measurements were conducted using the same cell set-up during operational charge-discharge cycling (**Extended Data Fig. 1**), allowing crystallographic information to be resolved internally through various stages of operation. This holder was capable of handling up to 20 A of continuous electrical current, which should encompass the majority of commercial 18650 cell C-rate capabilities. Note that these experiments were limited to 10 A due to the potentiostat limit. No thermal management method was applied to the cells during these

experiments. The cells were allowed to cool via natural convection cooling to the surroundings. There would be however, scope to integrate both external heating and/or cooling systems for future studies. For example, a heating furnace could be employed to emulate pre-heating conditions and fan cooling could emulate 'active' thermal management methods, both of which may provide closer simulations to cells within a battery module.

Electrochemistry. The cells were cycled using a Biologic SP300 cycler with 10 A booster (Biologic, France). The first XRD-CT experiments were conducted on an NMC cell discharged at: 0.5C (1.75 A), 1.0C (3.50 A), 1.5C (5.25 A), 2.0C (7.00 A), and 2.9C (9.96 A). The first charge was conducted at 0.5C (1.75 A) in order to begin the discharge experiments, all subsequent charges were conducted at 1.0C (3.5 A). After each charge or discharge step, the cell was held at OCV for 30 mins. This was repeated with a second NMC cell. The second XRD-CT experiment was conducted on an LFP cell discharged at: 0.5C (0.75 A), 1.0C (1.50 A), 2.5C (3.75 A), 4.0C (6.00 A), and 5.0C (7.50 A). The first charge was conducted at 0.5C (0.75 A) in order to begin the discharge experiences, all subsequent charges were conducted at 1.0C (1.5 A). After each charge or discharge step, the cell was held at OCV for 30 mins. The MCC-XRD experiment was conducted on an NMC cell discharged at: 1.0C (3.50 A), 1.5C (5.25 A), 2.0C (7.00 A), and 2.9C (10.0 A). The first charge was conducted at 0.5C (1.75 A) in order to begin the discharge experiences, all subsequent charges were conducted at 1.0C (3.5 A). After each charge or discharge step, the cell was held at OCV for 30 mins.

***Ex situ* temperatures.** The *ex situ* oven-heating experiments were performed using ultra-fast XRD-CT with an incident beam energy of 95 keV and a 200 x 200 μm^2 beam size. The detector-sample distance was set to 1000 mm. XRD-CT scans were performed every ~170 seconds. After keeping the LFP cell at 120 °C for three hours, XRD-CT data was collected over the course of 1.25 hours while the cell was cooling to room temperature with no electrochemistry applied. The same measurements were performed every ~255 seconds on an NMC811 cell, during cooling in air, after holding at 80 °C for three hours.

***In situ* temperature measurements.** The *in situ* OCV cooling experiments were performed using ultra-fast XRD-CT while charging and discharging the cell at different rates. The experiments were conducted using an X-ray beam of 100 keV and a 200 x 200 μm^2 size, XRD-CT scans were performed every 3 minutes. The detector-sample distance was set to 1275 mm for NMC cells, and 1770 mm for LFP cells. XRD-CT datasets were collected continuously during charge/discharge for the entire electrochemical cycle on each cell. The cell mounted in the battery holder was connected to the Biologic SP300 potentiostat.

***Operando* temperature measurement.** The *operando* experiments were performed using MCC-XRD. These experiments employed an incident beam energy of 95 keV and a 200 × 25 (VxH) μm^2 beam size to attain a narrow gauge-volume. The cell, mounted in the battery holder, was connected to the Biologic SP300 potentiostat. The detector-sample distance was set to 1000 mm. The sample was translated alternately perpendicular and parallel to the incident beam, collecting multiple diffraction points to select different Cu current collector spirals in each scan.

XRD-CT reconstruction.

It should be noted that, data was acquired over 360° rotations in order to obtain the correct centre of mass for the Cu diffraction peaks (i.e. without the artefacts that would be introduce via traditional 180° rotation acquisition on a large sample). To accurately determine the Cu lattice parameter changes and the temperature only Cu peaks not overlapping with peaks from other cell components (NMC811, Al, Steel, etc) were considered. For each measured XRD-CT slice, the 2D diffraction patterns $I(2\theta,\eta)$ from all rotation and translation positions were integrated over the azimuthal angle (η) using pyFAI software[25]. The azimuthal range was ±15° around the vertical scattering plane, corresponding to a condition where the momentum transfer vector ($\boldsymbol{q}$) is virtually parallel to the sample rotation axis (z, see **Extended Data Fig. 1**). The resulting azimuthally integrated data was corrected for incident flux and sample absorption effects and finally reconstructed through a FBP algorithm implemented in Matlab (Mathworks, Cambridge, U.K.). The Cu 111 and 200 diffraction intensities were consistent

along the (-π, π) range of azimuthal angle, without indications of peaking at certain azimuthal angles, consequently it was considered that diffraction texture did not detrimentally impact the tomographic reconstructions.

Temperature calculations. To calculate internal cell temperatures, position of Cu Bragg peaks were calculated for each voxel in the tomograms and for each of the MCC scans. Peak centre of mass calculations gave accurate *d*-spacings for the available Cu reflections in the different sample/setup combinations used. To inspect internal thermal gradients, spatially resolved data were binned into eight circular regions inside the battery based on their radial position between the internal and the external border of the active area (**Fig. 2b**). Eight azimuthal regions were also defined as shown in **Fig. 2c**. To reduce the statistical error, the mean values were calculated for each region as function of time. The temperature generated from the C-rate discharge applied to the cell in the 8 zones (radial and azimuthal) was calculated by fitting the data of Cu d-spacing from the end of the discharge until the end of the following rest based on Newton's law of cooling. Since the XRD-CT data were taken during OCV in the discharge state, it was assumed that no strains were contributing to the contraction of the Cu crystal lattice during cooling. The function used for the fitting was an exponential decay:

Equation 2 $$\mathrm{d}(t) = \mathrm{d}_0 - \Delta\mathrm{d} \cdot \mathrm{e}^{-\frac{t-t_0}{\tau}}$$

Where t is the time, t_0 the time at which the discharge finished, τ the decay time, Δd the total d-spacing variation of a given Bragg reflection of the Cu current collector, d_0 is the d-spacing at time t_0. Temperature variation ΔT inside the battery at the end of each discharge for the eight zones was calculated from the relative change in d-spacing using Equation 3. The thermal expansion coefficient of Cu was experimentally determined through temperature-dependent XRD on a fragment of the current collector extracted from a 18650 cell.

Equation 3 $$\Delta T = \frac{1}{\alpha}\frac{\Delta\mathrm{d}}{d_o}$$

Strain calculations. The positions of Cu Bragg peaks used for internal temperature calculations were also used to calculate strain values. Likewise, the battery section was split into eight radial zones and values from the voxels in each zone averaged for better statistics. Strain on Cu current collector caused by the volume change due to lithiation of graphite was calculated by measuring the Cu d-spacing before the charge (d_0) and the Cu d-spacing after the charge (d). The final strain after charge was calculated for the eight circular zones inside the battery with the following equation:

Equation 4 $$\varepsilon = \frac{d-d_0}{d_0}$$

Rietveld refinements. Rietveld analysis was performed on the $I(2\theta)$ patterns in the reconstructed tomograms of the cells to calculate the SoC from the varying distribution of lithiated anode phases. Batch fit routines were set up in Topas v7[26] to handle the analysis of the several thousands of diffractograms in each dataset. While the refinement strategy was unconstrained (i.e., letting structural parameters vary within a suitable range), care must be applied when setting parameter limits and initial values in order to ensure that the fit converges and avoids local minima. The fitted model comprised a 2-parameter Chebyshev polynomial background and four rhombohedral graphite-like phases (delithiated graphite and lithiation stages I, II, III). Each phase had refinable lattice parameters, scale factor and one peak-width parameter, whose $Tan(2\theta)$-dependent broadening was convoluted with a fixed Pseudo-Voigt contribution previously refined on the calibrant powder (NIST SRM 674b Cr_2O_3) to yield the final peak shape.

SoC calculations. The number of moles of Li per mole of C_6 was calculated from the mass fractions of the lithiation stages determined by Rietveld analysis.[27] The diffraction patterns were consistent with a choice of four stages: graphite, Stage III, Stage II, and Stage I. Stage III was considered as a solid

solution whose Li content varied linearly with the lattice parameter *c* between LiC_{19} and LiC_{30}. The stoichiometries of Stage II and Stage I were LiC_{12} and LiC_6, respectively. The lithiation state *x* in Li_xC_6 was calculated as:

Equation 5
$$x = 6 \times \frac{\frac{\sum_{S=1}^{3} m_S f_S}{w_{Li}}}{\frac{m_g + \sum_{S=1}^{3} m_S (1 - f_S)}{w_C}}$$

Here w_{Li} and w_C are the atomic weights of Li and C; m_g the mass fraction of graphite; m_s the mass fraction of phase *s* (lithiation stages I-III); f_s the mass fraction of Li in the same phases.

The calculation of the effective heat transfer coefficient was as follows:

Equation 6
$$T(t) = T_{ambient} + (T_{max} - T_{ambient}) * exp\left(\frac{-t \times h \times A}{m \times C_p}\right)$$

T	temperature
t	time
h	heat transfer coefficient
A	cell surface area
m	cell mass
C_p	cell heat capacity

Fits were performed on the experimental data using this formula:

Equation 7
$$T(t) = T_{ambient} + (T_{max} - T_{ambient}) * exp\left(\frac{-t}{\tau}\right)$$

τ	temperature decay time

Solving Equations 6 and 7:

Equation 8
$$\frac{1}{\tau} = \frac{h \times A}{m \times C_p}$$

Solving for h:

Equation 9
$$h = \frac{m \times C_p}{A \times \tau}$$

Using:

m	=	0.049 kg	(The mass of an MJ1)
τ	~	638 s	(As obtained from fits)
C_p	=	960 J / kg / K	(From Maleki et al. *https://doi.org/10.1149/1.1391704)*
A	=	0.004 m^2	(Assuming perfect cylinder with flat caps)

Into (4), yields an effective heat transfer coefficient:

h	=	17.6 W / m^2 / K	(Calculated from this work)

Which is comparable to the reference above:

h	=	13.4 W / m^2 / K	(Reported by Maleki et al.[21]).

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Extended Data Figure legends

Extended Data Fig. 1: Experimental set-up and electrochemical cycling data collected using the operando cell holder.

a, A photograph of the cell holder with electrical connections as mounted on the diffractometer at the ESRF ID15A and an example of the X-ray diffraction rings collected from the cells. b, Example diagram of the sample-detector geometry used for all experiments: the x-ray beam is directed along x and normal to the detector plane; sample translation perpendicular to the beam goes along y; ω is the angle about the rotation axis. c, A schematic image of the cell holder with electrical terminals (red/black) and 18650 cell. d, Electrochemical data obtained using the cell holder during characterisation at various C-rates.

Extended Data Fig 2: X-ray diffraction data collected on MJ1 cell using the operando cell holder for SoC calculations.

Diffraction patterns for the 8 zones in which the battery volume was divided at initial discharged state, final charged state. For each current applied during discharge (3.5A, 5.25A, 7.0A, 10.0A) the patterns are shown at Li x= 0.5. It is possible to distinguish the four graphite stages and their distribution depending on the discharge current applied.

Extended Data Fig 3. Strain components.

a, Ewald's sphere construction and its relation to the scattering vector. b, Strain ellipsoid. c, Intersection of the Ewald's sphere and the strain ellipsoid before (black) and after (blue) rotation of the sample around the z axis.

Extended Data Fig. 4: Resolving mechanical strain using XRD-CT.

a, Semi-transparent volume render of the 18650 cell indicating the spatial location of the cross-section. **b,c,** A sub-sectioned volume render of the cell indicating (b) the location and (c) the magnitude of the inflection point feature. **d,e,f,g,** A horizontal greyscale ortho-slice cross-section taken near the cell base as indicated in (a), with reference to three magnified regions (e) before, (f) during and (g) after the inflection. **h,** Another greyscale ortho-slice taken but in the orthogonal (vertical) plane. The vertical strain component calculated on the two 18650 cells (NMC and LFP) from the Cu d-spacing difference before and at the end of repeated charges at 1C rate after 1h relaxation. Multiple 1C charges were compared to understand the influence of successive cycles. The cell volume was again divided in 8 circular zones to understand the strain variation distribution inside the battery. **i,j, s**how strain on Cu current collector d-spacing at the end of 1C charges as a function of 8 circular zones inside the **i,** NMC and **j,** LFP cells. Notice the strain caused by volume change during graphite-silicon composite anode lithiation is some orders higher than LFP cell graphite lithiation.

Extended Data Fig. 5: Resolving SoC using XRD-CT.

a,b,c, Cross-sections of the cell as schematics of the (a) the outer and (b) the inner zones, and (c) an XRD-CT heatmap of the local SoC at 2.5 V, where blue = low SoC and red = high SoC, for qualitative purposes. **d-k,** The extent of lithiation by quantifying the x in Li_xC_6 for the inner (light gold) and outer (dark gold) regions at the (d,g,h,j) top and (e,g,i,k) bottom of charge for C-rates of (d,e) 0.5C, (f,g) 1.0C, (h,i) 1.5C and (j,k) 2.0C.

Extended Data Fig. 6: Degree of lithiation within the MJ1 18650 anode at the bottom of 1C discharge.

Note: only a section of data is reported here displaying the lithiation states within the eight zones immediately after the 1C discharge.

Extended Data Fig.7: SoC quantifications within the MJ1 18650 at high rates.

The electrical current (top), anode lithiation (middle) and cathode unit cell expansion (bottom) for the first charge (a) and four subsequent discharges (d-e) at increasing C-rates.

Extended Data Fig.8: Comparing internal temperatures within the two 18650 cells.
A repeat of the data presented in Fig. 2b obtained from the NMC cell, with comparison to the LFP cell. Radial zones are shown. All temperature values are reported as the temperature difference between a point in the cell and the ambient temperature.

Extended Data Fig. 9: The multi-channel collimator.

Top, schematic and working principle of the multi-channel collimator (MCC) used for *operando* experiments adapted from [28,29]. The expression for the length of the gauge volume, δx, is given for a pencil beam as a function of front slit opening (a) inner, outer slit radii (r_1, r_2) and scattering angle (2θ).

Bottom, detail of the gauge volume indicated in the top panel, along with the expressions for gauge volume dimensions in the case of a primary beam of width δy; a, r_1, r_2, and 2θ have the same meaning as in the panel above.

Extended Data Fig. 10: Examining the influence of the MCC acquisition.

Comparison of MJ1 diffraction patterns obtained without the MCC (black), and with the MCC (red). Inset: full range of the MJ1 diffraction patterns with and without MCC, along with the calculated intensity from the gauge volume selected with the MCC.

Data and code availability

Correspondence and requests for materials should be addressed to the corresponding author: Professor Paul R Shearing.

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Author contributions

TH led the investigation. TH, MDM, PS conceived the experiments. TH, IM, AL, CT, SC, MDM, M.J., A.J, GG performed the experiments, TH, IM, AL, CT, SC, MDM, M.J., A.J. performed the data analysis. MDM leads work at ESRF as the Scientist in Charge of ID15A. RJ leads work as the Degradation Project Manager for the Faraday Institution. PS and DB lead all work from the Electrochemical Innovation Lab (UCL) and sourced all funding to support this work.

Competing interest declaration

There are no competing interests known to the authors to declare.

Additional information

Supplementary information is available for this paper.

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