Operando optical tracking of single-particle ion dynamics in batteries

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The key to advancing lithium-ion battery technology—in particular, fast charging—is the ability to follow and understand the dynamic processes occurring in functioning materials under realistic conditions, in real time and on the nano- to mesoscale. Imaging of lithium-ion dynamics during battery operation (operando imaging) at present requires sophisticated synchrotron X-ray1–7 or electron microscopy8,9 techniques, which do not lend themselves to high-throughput material screening. This limits rapid and rational materials improvements. Here we introduce a simple laboratory-based, optical interferometric scattering microscope10–13 to resolve nanoscopic lithium-ion dynamics in battery materials, and apply it to follow cycling of individual particles of the archetypal cathode material14,15, Li$_x$CoO$_2$, within an electrode matrix. We visualize the insulator-to-metal, solid solution and lithium ordering phase transitions directly and determine rates of lithium diffusion at the single-particle level, identifying different mechanisms on charge and discharge. Finally, we capture the dynamic formation of domain boundaries between different crystal orientations associated with the monoclinic lattice distortion at the Li$_{0.5}$CoO$_2$ composition16. The high-throughput nature of our methodology allows many particles to be sampled across the entire electrode and in future will enable exploration of the role of dislocations, morphologies and cycling rate on battery degradation. The generality of our imaging concept means that it can be applied to study any battery electrode, and more broadly, systems where the transport of ions is associated with electronic or structural changes. Such systems include nanoionic films, ionic conducting polymers, photocatalytic materials and memristors.

Lithium-ion batteries have emerged as the frontrunner technology for high-power, intermediate-scale energy storage in a broad range of applications, including electric vehicles and portable devices. A major challenge associated with the development of improved batteries is to understand and optimize the processes by which lithium ions intercalate into the active host materials. Operando characterization techniques are needed to examine the fundamental limits to rate performance in working batteries17. However, tracking driven ionic motion in electrodes using established electrochemical methods is highly challenging, because the active particles are often intrinsically disordered at the particle and electrode level, and can behave heterogeneously18. Advanced operando synchrotron-based1–7 and electron microscopy measurements8,9 can probe the length and timescales required to examine individual particles, providing chemical and structural information. For example, operando transmission X-ray microscopy has revealed that non-uniform intercalation in Li$_x$FePO$_4$ causes compositional heterogeneity within particles to be enhanced during delithiation and suppressed during lithiation1. However, such techniques are costly, time-intensive, can suffer from beam-induced sample degradation, and often require highly specialized cell geometries10.

Although underused in battery research, optical microscopy techniques can overcome many of these disadvantages11–13. Here we establish optical interferometric scattering microscopy (iSCAT)10–13,24–26 as a rapid, low-cost imaging platform to visualize and quantify ion dynamics at the single-particle level. iSCAT, which uses elastic scattering of visible light to achieve fast acquisition times and high sensitivity, has not been applied to battery research until now. (We compare iSCAT with other operando imaging methods employed in battery research in Supplementary Information section 8). We study Li$_x$CoO$_2$ (LCO, 0 < x < 1), the archetypal layered cathode material which adopts the rhombohedral α-NaFeO$_2$ structure (Extended Data Fig. 1a)14,15. Despite being almost ubiquitous in portable electronics, the dynamics of phase transitions in LCO are not well understood: for instance, the reported lithium-ion diffusion coefficients vary over six orders of magnitude27–33, and the degree of compositional heterogeneity within single particles is little explored33.

Imaging lithium-ion transport in LCO

Operando iSCAT studies were carried out using an optically accessible commercially available half-cell (Fig. 1a). The working electrode

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comprised single-crystal LCO particles (about 10 μm average size, lengths comparable in all three dimensions, Extended Data Fig. 1c, d), sparsely dispersed in a nanoparticulate carbon and polymer binder matrix, pressed onto an aluminium mesh current collector.

The galvanostatic performance of the electrode in the optical cell, at a rate of 2C (Fig. 1b, c), is in good agreement with previous reports and with performance in a coin cell (Extended Data Fig. 2). In this nC (C-rate) notation, n is the applied current divided by the theoretical current needed to (dis)charge the electrode material to its nominal theoretical (or more generally a specified) capacity in 1 h. Prominent peaks in the differential capacity plots are resolved at about 4.0 V during delithiation and at about 3.8 V during lithiation (I and IV, Fig. 1c), associated with a biphasic transition from the semiconducting lithium-rich phase, of approximate composition L10.86CoO2, to the metallic lithium-poor phase, of approximate composition L10.77CoO2 (Supplementary Information section 5). Smaller peaks in the differential capacity plots (II and III, Fig. 1c) are associated with the lithium ordering transition at L10.5CoO2 and the formation of a monoclinic phase. The sloping regions between peaks I and II, and between peaks III and IV, correspond to a solid solution regime, during which the lithium content and cell parameters change continuously.

Full details of the iSCAT methodology can be found in Methods and Supplementary Information section 1. Briefly, as illustrated in Fig. 1d, e, following widefield illumination at a wavelength of 780 nm, the objective collects back-scattered light from the particle (Ei) as well as reflected light from the glass window/electrolyte interface (Ew). Both components are imaged onto a camera, where they interfere to produce the observed iSCAT image. The resulting iSCAT intensity is determined by the local dielectric properties of the sample material. The method exploits the fundamental correlation between the local lithium content in LCO and the local electronic structure (and thus the local dielectric properties), which controls the scattering intensity. This allows the intercalation dynamics to be probed at the single-particle level, in real time with sub-5 nm precision (Supplementary Information section 3). Critically, our approach works in the absence of optical absorption and can be readily applied to examine multiple particles within the same electrode.

iSCAT images of several individual LCO particles were obtained during delithiation/insertion under galvanostatic conditions. Raw iSCAT images (Fig. If, Extended Data Fig. 1e) show brightly scattering particles on top of a characteristic speckle pattern originating from scattering contributions from the surrounding carbon matrix. The relatively spatially uniform intensity across each particle indicates a mostly-flat scattering surface, implying that the direction of observation is along the c axis of the crystal structure, normal to the layers of CoO6 octahedra (Extended Data Fig. 1), and ideally suited to investigate the in-plane ion transport within the layered host lattice. For comparisons of iSCAT and scanning electron microscope (SEM) images, see Fig. If and Extended Data Fig. If–i. The imaging depth and the effect of particle orientation are discussed further in Supplementary Information section 2.

iSCAT images were obtained during five electrochemical cycles at 2C for a representative LCO particle (approximately 9.6 μm × 6.8 μm, Extended Data Fig. 1e). As Fig. 2a shows for one cycle (other cycles...
in more detail (red shaded region, Fig. 2a). Normalized sequential Li$_{0.95}$CoO$_2$ phase to the metallic Li$_{0.77}$CoO$_2$ phase was then examined. The biphasic insulator–metal transition from the semiconducting Li$_{0.8}$CoO$_2$ phase to the metallic Li$_{0.77}$CoO$_2$ phase was then examined. The biphasic insulator–metal transition later and included in Supplementary Videos 6–10.

Detailed results for a second particle are presented and homogeneous at the beginning of the delithiation and during the cycling (Fig. 2b). The particle intensity remained relatively constant and homogeneous at the beginning of the delithiation and during the sharp increase in cell potential to about 4.0 V (Fig. 2b, A). However, from 3 min to 12 min (exemplified by Fig. 2b, B, 10.2 min), the iSCAT images showed a substantial degree of spatial inhomogeneity in the form of bright and dark features. Similar inhomogeneous features were seen from 39 min to 48 min (exemplified by Fig. 2b, G, 43.8 min), corresponding to an equivalent state of charge upon lithiation.

This confirms that the changes in dielectric properties caused by the underlying electronic structural changes (Supplementary Information section 1) are sufficient to allow the (de)lithiation processes to be monitored.

Next, we investigated the spatially resolved ion dynamics during cycling (Fig. 2b). The particle intensity remained relatively constant and homogeneous at the beginning of the delithiation and during the sharp increase in cell potential to about 4.0 V (Fig. 2b, A). However, from 3 min to 12 min (exemplified by Fig. 2b, B, 10.2 min), the iSCAT images showed a substantial degree of spatial inhomogeneity in the form of bright and dark features. Similar inhomogeneous features were seen from 39 min to 48 min (exemplified by Fig. 2b, G, 43.8 min), corresponding to an equivalent state of charge upon lithiation. Examination of the full iSCAT video (Supplementary Video I) revealed that these bright and dark features propagated across the visible surface of the particle. The durations of these moving features are aligned with the biphasic transitions identified in the overall electrochemistry (red shaded, Fig. 2a), the moving features being assigned to propagating phase boundaries (discussed below). Short-lived propagating features were also observed at about 23 min and equivalently at approximately 27 min (blue shaded, Fig. 2a), at times corresponding to the lithium ordering transitions (see below). Nearly spatially homogeneous intensity changes occurred outside these transitions, that is, during the solid solution regimes (Fig. 2b, C–F).

A further 15 particles across multiple electrodes were examined, yielding similar results, with an increase (decrease) in intensity upon delithiation (lithiation) and the observation of propagating phase boundaries, indicating that the described behaviour is general across the electrode(s). Detailed results for a second particle are presented later and included in Supplementary Videos 6–10.

The biphasic insulator–metal transition

The biphasic insulator–metal transition from the semiconducting Li$_{0.8}$CoO$_2$ phase to the metallic Li$_{0.77}$CoO$_2$ phase was then examined in more detail (red shaded region, Fig. 2a). Normalized sequential differential images, representing the fractional intensity change over 20 s, were extracted to visualize the phase boundaries (see Methods). During delithiation (Fig. 3a), intensity changes initially occurred at the particle edges (4.3 min). After a lag time of about 3 min, new features emerged and spread across the bulk of the particle, originating predominantly from the bottom edge of this particular particle, and developing into a ring-like structure (10.0 min). This ring feature progressively reduced in size and vanished at the end of the biphasic transition (11.0–11.7 min). The ring is assigned to the phase boundary between the lithium-rich phase in the middle and the newly formed lithium-poor phase growing inwards from the edges. This phase boundary movement is consistent with a so-called ‘shrinking core’ mechanism, where the new phase grows inwards from all active surfaces of the particle (Extended Data Fig. 4a)$. This behaviour was found in all cycles (Extended Data Fig. 5). The velocity of the propagating phase boundaries was then extracted, yielding an average of about 20 nm s$^{-1}$ (at 2C), reaching 37 nm s$^{-1}$ at the end of the biphasic transition (Supplementary Information section 4).

Intriguingly, during lithiation (Fig. 3b) a different behaviour was observed, whereby a region of higher intensity first appeared in the top-right corner of the particle (39.3 min) and then spread across the whole particle (40.0–44.0 min). This process is best described as an ‘intercalation wave’ mechanism, where a single phase front (or small number of fronts) originating from one (or a small number of) nucleation point(s) moves across the particle (Extended Data Fig. 4b). Although this mechanism occurred in all cycles, substantial variations were found between cycles, both in the location of the first nucleation point and in the path taken by the new phase (Extended Data Fig. 5).

Dynamic inhomogeneity between electrode particles can occur if the instantaneous current densities experienced by individual particles do not match the overall applied C-rate. For example, during the biphasic process found in LiFePO$_4$, only a small fraction of particles may be active at any given time, leading to temporarily higher C-rates at the single-particle level. Thus, to investigate the LCO biphasic reaction further, the phase fractions in the particle were calculated and used to derive the effective C-rate for the particle under observation (see Methods). This single-particle ‘biphasic C-rate’ corresponds to the current required to achieve the observed pace of conversion between the two coexisting phases. Upon delithiation
(Fig. 3c), the biphasic reaction commenced at similar rate to that of the overall electrode (2C), with the new phase growing in from the particle edges and corners, to transform about 10% of the particle to the Li_{0.8}CoO_2 phase (4.3 min, Fig. 3a). The single-particle C-rate then dropped, remaining low for approximately 3 min, before accelerating rapidly as the phase boundaries moved to form a shrinking ring, finally reaching about 9C at the end of the biphasic transition. This delithiation behaviour was consistent across all cycles. Upon lithiation (Fig. 3d), the new phase filled the particle at a C-rate oscillating around 2C–5C for the selected cycle, but with substantial variations between cycles, which are associated with the different paths travelled by the phase boundaries through the particle. (See Extended Data Fig. 5 and Supplementary Videos 2, 3 for sequential contrast images of the phase boundaries for all cycles.)

A similar LCO particle from another electrode was monitored at applied C-rates from C/2 to 6C to explore the rate-dependant mechanisms. During delithiation at C/2, the integrated single-particle scattering intensity (Fig. 4a) showed a peak during the biphasic transition (0–75 mA h g⁻¹) and a linear increase during the solid solution transition (75–155 mA h g⁻¹), with similar behaviour during the following lithiation. At all applied C-rates, the intensity changes during the solid solution reaction remained linear (with time) and reversible. However, as the current density was increased, the intensity peak at the biphasic transition shifted towards higher capacity during delithiation and lower capacity during lithiation, suggesting that the biphasic reaction in the observed particle lagged behind the ensemble electrochemistry. The single-particle C-rate (Fig. 4b, c) increased sharply with increasing electrode current during the biphasic reaction, reaching 23C and 13C during delithiation and lithiation, respectively, at the highest cell current density (6C). The phase boundary progressed via an intercalation wave mechanism during lithiation at all applied C-rates (Fig. 4d), whereas a shrinking core mechanism occurred during delithiation at 2C–6C, consistent with the particle described above (Fig. 3). At C/2 and 1C, however, delithiation appeared to follow a hybrid of the two mechanisms, with the new phase nucleating at two corners of the particle and propagating to finish at an edge—as opposed to the centre—of the particle (Supplementary Videos 6–10).

The shrinking core mechanism—seen here on delithiation—is a consequence of the higher lithium flux across the active electrochemical surface (for lithium-ion insertion/extraction, quantified via the charge transfer reaction rate), as compared to the lithium flux inside the particle (quantified via the lithium-ion diffusion rate) and is therefore the result of a 'diffusion-limited' process. In contrast, the intercalation wave mechanism is 'charge-transfer-limited' and results in the formation of a phase front, which can have different morphologies depending on the material/particle properties but features a reduced interfacial area that propagates across the particle as the reaction proceeds.

That the shrinking core mechanism seen during high-rate delithiation appears to switch towards an intercalation wave mechanism at lower rates is in line with the decrease of the charge transfer rate at lower currents. This is consistent with recent simulations on LCO, and experimental work on large graphite particles (>100 μm). However, the previous work makes no distinction between the mechanisms on delithiation and lithiation.

Phase field modelling was performed to explore the origins of the observed differences between lithiation and delithiation and identify the parameters that control the phase boundary movement (Supplementary Information section 9). Although highly simplified, our model explains the difference between the delithiation and lithiation mechanisms by considering two things: first, the phase in which the charge transfer reaction occurs, and second, the effect of the much lower lithium-ion diffusion coefficient in the lithium-rich phase than in the lithium-poor phase. During rapid delithiation, once the lithium-poor phase has nucleated, the charge transfer reaction...
proceeds at both the lithium-rich and the lithium-poor surfaces of the particle. Owing to the sluggish lithium-ion transport in the lithium-rich phase, delithiation in this phase becomes diffusion-limited, and the lithium-poor phase builds up around all the active surfaces of the particle, resulting in a shrinking core mechanism (Supplementary Fig. 8). On lithiation, although charge transfer (and thus lithiation) occurs in both phases initially, lithium builds up to saturation in the lithium-rich phase, shutting down this reaction pathway. Most of the charge transfer during lithiation proceeds instead via the high ionic mobility lithium-poor phase, leading to the intercalation wave mechanism for a large range of C-rates, as confirmed experimentally (Supplementary Fig. 9).

The high single-particle C-rates of up to 23C observed at a 6C cell-level rate (Fig. 4b, c) require very high lithium diffusion coefficients. To calculate a lower bound for the diffusion coefficient, delithiation of both particles during the biphasic process was simulated using various concentration-independent diffusion coefficients (Supplementary Figs. 10–12). The extracted velocities of the phase boundaries were compared to the experimentally observed phase boundary velocities (Supplementary Information section 4). Good agreement was achieved using a chemical diffusion coefficient of about 10⁻⁹ cm² s⁻¹ or higher, in line with the higher values estimated previously via theoretical²⁷ and muon spectroscopy²⁸ investigations (Supplementary Fig. 13).

**Lithium ordering in Li₀.₅CoO₂**

We now consider the lithium ordering transition (blue shaded, Fig. 2a). Upon delithiation, the lithium ordering at a composition of Li₀.₅CoO₂ removes the three-fold symmetry axis in the rhombohedral cell, leading to monoclinic symmetry. Early operando X-ray diffraction studies reported a second-order transition¹⁶, but more recent synchrotron reports showed coexistence of the rhombohedral and monoclinic phases, suggesting a biphasic transition⁴⁸. To explore this transition, we computed the total normalized differential iSCAT images (that is, the fractional intensity change for each pixel over the transition) for cycles 1 and 4 at 2C (all five cycles are shown in Extended Data Fig. 6). In cycle 1 (Fig. 5a), the particle intensity increased (decreased) relatively homogeneously upon ordering (disordering). By contrast, in cycle 4 (Fig. 5b), the ordering transition produced bright sharp lines with three-fold symmetry in the particle, which disappeared again upon disordering. The absence of pronounced scattering lines in the bulk of the material in cycle 1 suggests that the monoclinic phase orientation was consistent across the whole particle (Fig. 5c), that is, only one monoclinic domain is present. By contrast, the appearance of bright lines with a three-fold symmetry in cycle 4 suggests the presence of three micrometre-sized ordered monoclinic domains, oriented at 120° with respect to each other, which can be distinguished by brightly scattering domain boundaries (Fig. 5d).
Delithiation Lithiation

(Fig. 5f), the disordered phases grow in from three different locations with and without domain formation. This change caused by the transition. Scale bar, 5 μm. For cycle 4 (before the transition, then subtracting 1, to represent the total intensity values immediately after the transition by those from immediately before the transition, then subtracting 1, to represent the intensity changes over this timescale. The black dashed lines are a guide for the eye, representing the progression of the disordered phase.

To follow the dynamic evolution of these structures, normalized sequential differential images (5 s frame interval) for the transition were then analysed (Supplementary Videos 4, 5). During lithiation in cycle 1 (Fig. 5e), two phase fronts are identified which emerge from opposite sides of the particle and approach each other head-on, travelling at a velocity of about 70 nm s⁻¹. By comparison, during lithiation in cycle 4 (Fig. 5f), the disordered phases grow in from three different locations separated by the visible domain boundaries. It should be noted that the phase boundaries move substantially faster than for the insulator–metal biphasic transition, largely because they involve long-range ordering of lithium ions, rather than a (more substantial) change in lithium-ion concentration. The rapid image acquisition capabilities of optical microscopy are advantageous in studying such fast phase transitions.

Our work builds on the previous ex situ electron diffraction observation of several ordered domains (each with one of three distinct orientations of the monoclinic phase) within a single particle of LCO, by observing the dynamics of the domain formation in real time. Furthermore, we show—for this lithiation ordering transition involving symmetry breaking in LCO—that when new phases originate from multiple nucleation points they cannot readily fuse together if their orientations differ. Instead, the particle retains some memory of the nucleation conditions in the form of domains (Fig. 5b, d). This is opposed to the case of the insulator–metal biphasic transition discussed above, for which symmetry is conserved across the phase transition, so that separate regions of the new phase can join together seamlessly (Fig. 3a, b). Considering the excellent cycling stability of LCO between 3.0 V and 4.2 V, the presence of the monoclinic domains at Li₀.₅CoO₂ does not appear to be detrimental, probably because the monoclinic distortion leads to only a small deformation of the unit cell.

Conclusions and outlook

We have established iSCAT microscopy as a powerful tool to track and quantify phase transitions in LCO on the nanoscale, in real time and under realistic operating conditions. The solid solution, biphasic and lithium ordering transitions were clearly resolved and correlated to the ensemble electrochemistry. Mechanistically, we identified a preference for a shrinking core mechanism for delithiation and an intercalation wave mechanism for lithiation during the biphasic transition. These observations were rationalized in terms of the differences in lithium diffusivity in the two phases, with support from phase field modelling. Single-particle C-rates and phase boundary velocities were extracted to show that individual particles are capable of sustaining much higher C-rates than the overall C-rate of the electrode, highlighting the inherent high-rate capabilities of LCO. Additionally, we observed the real-time formation and destruction of domains in monoclinic Li₀.₅CoO₂.

The results presented here highlight the ability of this scattering microscopy methodology to provide real-time insights into nanoscale electronic or structural phase transitions. We hope that—owing to its straightforward laboratory-based implementation—iSCAT will become an indispensable tool for high-throughput material discovery and mechanistic studies (Supplementary Information section 7), complementing existing synchrotron-based methodologies. For example, future work could examine the effects of grain boundaries and crystal defects on phase transitions and ion intercalation mechanisms. Critically, the principle of using light-scattering to probe charge transport and electronic structure changes is broadly applicable to a wide range of materials (Supplementary Information section 6) and promises to be generally valuable for the study of ferroelectrics, nanoionics, bioelectronics, photocatalytic materials and memristors, in addition to batteries.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions
Methods

Sample preparation
Self-standing electrode films were prepared from LCO powder (Sigma-Aldrich). Super P carbon and a polytetrafluoroethylene suspension (PTFE, 60% in water), combined by grinding together with ethanol in a pestle and mortar. The dry mass ratios of LCO, carbon and PTFE were 20%, 46% and 34%, respectively. Upon drying to a workable consistency, the mixture was rolled flat into a porous self-standing film with a thickness of about 150 μm. The film was fully dried (vacuum oven, 100 °C, overnight) before cutting electrode disks of 5 mm diameter. The electrodes were stored in a dry argon atmosphere before use.

The optical cell (Fig. 1a) is based on a commercially available model (EL-CELL, ECC-Opto-Std test cell), with a homemade lid that was designed to be compatible with our microscope objective and glass observation windows. The cell was assembled in a dry argon atmosphere. The working electrode consisted of the self-standing film, pressed on top of an aluminum mesh current collector. The counter electrode was lithium metal, the separator was glass fibre (Whatman, GF/B glass micro fibre filter), and the cell stack was wetted with LP30 carbonate and dimethyl carbonate). Following assembly, the cell was galvanostatically cycled about 20 times at 2C before obtaining iSCAT measurements. Throughout this work, the quoted C-rates are based on a practical specific capacity of 140 mA h g⁻¹.

Optical setup
The interferometric scattering microscopy (iSCAT) setup used in this work is adapted from previous work by Ortega Arroyo and Kukura. In our implementation, the light source is a high-stability pulsed laser diode (LDH-P-780, SEPIA II laser driver, PicoQuant), which generates about 60-ps pulses at a central wavelength of 780 nm with a maximum repetition rate of 80 MHz. A near-infrared coated telecentric lens system with a 40-μm pinhole (Thorlabs) at the focus selects a Gaussian spatial mode and magnifies the beam to a diameter of about 1 cm. This beam is directed into a home-built inverted widefield microscope equipped with a 1.4 NA oil immersion objective (100×, OLYMPUS) and a custom-made 3D nano-positioned sample stage (Attocube, ECSx3030/AL/RT/NUM).

The illumination path of the microscope consists of a near-infrared coated widefield lens (f = 500 mm, AC254-500B, Thorlabs) placed one focal length away from the back-focal plane of the objective. This results in a widefield Gaussian illumination profile with a full-width at half-maximum (FWHM) of approximately 20 μm in the objective focus. Before reaching the objective, the beam is transmitted through a linearly polarizing beam splitter cube (PBS252, Thorlabs) and a quarter-wave plate (QWP, AHWP05M-600, Thorlabs) to illuminate the sample with circularly polarized light. In this work, circularly polarized illumination was selected in an effort to avoid dipolar selectivity. We note that linearly polarized light may produce additional insights, as it could probe sample anisotropy that may arise if dipoles become ordered in certain orientations.

After interaction with the sample, the reflected/scattered light contributions are collected by the illumination objective and directed back through the QWP. After passing through the QWP for the second time, the returning light has acquired a 90° polarization shift compared to the illumination beam, which results in the returning light being reflected from the polarizing beam splitter cube. The QWP was rotated to maximize the collection efficiency for the reflected light. A near-infrared coated tube lens (f = 500 mm, AC254-500B, Thorlabs) placed one focal length away from the objective’s back-focal plane finally images the returning light onto a 12-bit CMOS camera (FLIR, Grasshopper3, GS3-U3-23S6M-C). The overall magnification of this imaging system is 278× (21.1 nm per pixel), and was confirmed with a resolution target. The 780-nm illumination wavelength and NA of 1.4 produce a lateral resolution of about 280 nm (FWHM).

For the C-rate-dependence studies carried out in Fig. 4 (and the iSCAT images in Fig. 1f, Extended Data Fig. 1f–i), we instead imaged the returning light onto a 16-bit scientific CMOS camera (Hamamatsu, ORCA Flash 4 V3). Here, light collected by the objective was sent through a conjugated telescope to reduce the beam by a factor of 1.25 (f = 500 mm and f = 400 mm, AC254-B, Thorlabs), before being imaged via a final tube lens (f = 500 mm, AC254-500B, Thorlabs) onto the camera. The overall magnification was 347× (18.7 nm per pixel).

Active stabilization of focus control was implemented to avoid long-term focus drift and electrochemically induced defocusing. To achieve this, we used a reflection-based variation of a previously described line-autofocus procedure that operates based on total internal reflection of a reference beam. An approach based on total internal reflection is not feasible for most battery systems owing to the high refractive index electrolyte. The reference beam was generated by a 980-nm diode laser (CPS980S, Thorlabs) and focused via a dichroic mirror (DMSP900, Thorlabs) onto the back-focal plane of the objective. The reflected beam was picked off after the objective, focused through a non-conjugated cylindrical lens (f = 200 mm, Thorlabs) into a line and detected by a CMOS camera (DCC154SM, Thorlabs). The refresh rate for the focus control was set to 10 Hz and allowed us to achieve a steady focus position with a standard deviation of 13 nm over the full course of the experiment.

Data acquisition
For the experiment presented in Figs. 2, 3 and 5, images were acquired with an exposure time of 250 μs, at a frame rate of 2 Hz. Each image was spatially binned (3×3 pixels, giving an effective pixel size of 63.3 nm per pixel) and sets of 10 recorded images were temporally binned to yield an effective frame rate of 0.2 Hz (one saved image every 5 s). We note that while this acquisition speed is relatively slow compared to what can be achieved using iSCAT, it is sufficient to capture the phase transitions occurring in our experiments. To avoid saturation of the detector, the power of the laser was reduced by lowering the repetition rate to 4 MHz and setting the driver current just above the turn-on threshold, occurring in our experiments. To avoid saturation of the detector, the power of the laser was reduced by lowering the repetition rate to 4 MHz and setting the driver current just above the turn-on threshold, resulting in a measured power of <1 mW before entering the objective. At this power, no sample degradation was observed.

Experiments presented in Fig. 4 (and Fig. 1f, Extended Data Fig. 1f–i) were carried out using similar powers at a repetition rate of 5.3 MHz. The camera exposure time was set to 1 ms and each recorded image was spatially binned (4×4, giving 74.9 nm per pixel). Images were recorded at effective frame rates of 0.5, 0.5, 1 and 2 Hz for experiments with applied C-rates of C/2, 1C, 2C, 4C and 6C, respectively. In all experiments except 6C, sets of 2 images were temporally binned to yield the stated effective frame rate, while no temporal binning was employed at 6C.

Galvanostatic control of the sample was achieved using a portable potentiostat (SP-200, BioLogic). The cell was rested at the open-circuit voltage for at least 20 min before each experiment. For the experiment presented in Figs. 2, 3 and 5, a constant current of 0.1525 mA (2C) was applied during cycling, with a voltage range of 3–4.2 V (versus Li/Li⁺). Upon reaching the upper voltage threshold of 4.2 V during charging, the direction of current was inverted. The cell was then discharged until the lower voltage threshold of 3 V was reached. This was repeated for five consecutive cycles, with no noticeable differences in electrochemical performance between cycles. For the investigation into C-rate dependence presented in Fig. 4, two consecutive galvanostatic cycles were completed for each C-rate (C/2, 1C, 2C, 4C, 6C), with a voltage range of 3–4.3 V (versus Li/Li⁺).

Data analysis
Jitter correction and background subtraction. All recorded image stacks were first corrected for jitter in the x-y plane by isolating a bright sub-diffraction limited spot (unrelated to the active particle) and fitting
its position over time using a two-dimensional Gaussian function. The extracted centre positions in x and y for each image were subsequently used to correct for stage drift.

Background-subtracted images are shown in Fig. 2b and in Supplementary Videos 1 and 6–10. To obtain these, the average image over 100 frames before electrochemical cycling was subtracted from each of the remaining frames, to allow direct comparison of the intensity variations across the particle. Finally, the entire image stack was normalized to a linear intensity scale with a range of 1.

**Differential image analysis.** The normalized sequential differential images shown in Fig. 5e, f were obtained by dividing the \((i+1)\)th frame by the \(i\)th frame, and then subtracting 1. The resulting image contrast displays the fractional intensity change over the duration of 5 s (that is, between subsequent frames), with the contrast scale centred around 0. This removes slowly varying background contributions and inhomogeneities in the sample illumination to isolate more rapid changes between the images. The sequential differential images shown in Fig. 3a, b were calculated using the \((i+4)\)th frame and the \(i\)th frame, to represent intensity changes over a 20 s duration (that is, 4 frames).

Normalized total differential images (Fig. 5a, b) were calculated similarly to the sequential differential images. Here, we took a frame from just after the completion of the transition, divided it by another frame from just before the transition, and then subtracted 1. These images therefore represent the fractional intensity change for each pixel over the entire duration of the transition.

The differential images were additionally masked for clarity to exclude regions that are not part of the active particle. To accomplish this, the unprocessed image from Extended Data Fig. 1e was used to generate a binary mask whereby all pixels with a normalized intensity value below 0.23 were set to 0.

**Phase fraction and single-particle C-rate.** The phase fractions shown in Fig. 3c, d were extracted from masked sequential differential images (obtained from consecutive \(i\)th and \((i+1)\)th frames). A temporal window of 1,000 s, containing the relevant insulator–metal biphasic phase transition, was first selected from the differential image stack. Here, each pixel’s time-domain response exhibits a short oscillatory feature associated with the moving phase boundary. A short-window Fourier transform (SWFT) algorithm was used to identify the time at which the phase boundary passed over each pixel in the image. The SWFT algorithm was applied with a Hanning window (160 s width, selected to give the best time-frequency resolution), and the window time at which the Fourier spectrum showed a global maximum was recorded. This time-point was taken to be the time when the phase boundary traversed the given pixel. Owing to residual noise contributions, some pixels do not have well-defined spectral features in the SWFT, but instead exhibit peaks at DC or Nyquist frequencies. To remove these pixels, a maximum-frequency histogram was constructed for all pixels and only pixels which showed a maximum amplitude between 5 mHz and 83 mHz were included in further analysis (about 90% of all pixels). By counting the pixels that had already experienced the phase boundary at each moment and normalizing for the overall particle area, we were able to derive the phase fractions as a function of time. Finally, we assumed that rejected pixels were filled according to the underlying phase fraction dynamics, allowing us to scale the resulting curves to achieve full coverage by the new phase. This procedure was applied for all cycles.

The corresponding biphasic single-particle C-rates were obtained from the time derivative of the new phase fraction and scaled to the relevant capacity units. The scaling factor is 1.268 s, which is the time taken for the lithium content in Li\(_{0.95}\)CoO\(_2\) to change by \(\Delta x = 0.18\) at 1C. This value of \(\Delta x\) corresponds to the miscibility gap between Li\(_{0.95}\)CoO\(_2\) and Li\(_{0.77}\)CoO\(_2\); see Supplementary Information section 5.

A similar analysis was carried out for the results shown in Fig. 4b, c. Here, sequential differential images were first computed (from consecutive \(i\)th and \((i+1)\)th frames) and image stacks containing the insulator–metal biphasic transitions were generated. Subsequently, we temporally binned sets of 10 differential images. An SWFT algorithm (Hanning window with width equivalent to the time duration of the image stack) was then used to extract the time-dependent phase fraction and single particle C-rates, after rejecting pixels associated with DC and Nyquist frequencies (leaving >80% of all pixels), as explained above.

The time-maps presented in Fig. 4d were generated by plotting the time at which each pixel experienced the phase boundary, as determined by the SWFT algorithm, and normalizing to the overall time range of the biphasic transition. This allows the propagation of the phase boundary over the full duration of the transition to be visualized in a single image. Since it can be assumed that any rejected pixels follow the underlying behaviour of the phase transition, we apply an ‘inpainting’ algorithm to interpolate to their expected transition times, which we include in the time-maps. We also refer the reader to Supplementary Videos 6–10, which contain full videos of the relevant biphasic transitions.

**Data availability**

The data underlying all figures in the main text and the Extended Data are publicly available from the University of Cambridge repository at https://doi.org/10.17863/CAM.70023.

**Code availability**

All code used in this work is available from the corresponding authors upon reasonable request.

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Author contributions A.R. conceived the idea. A.R. and C.P.G. planned and supervised the project. C.S. designed the optical setup. Q.J. and A.J.M. prepared samples. C.S., Q.J. and A.J.M. planned all experiments and A.J.M. carried out the measurements. Q.J. developed the phase field modelling. All authors discussed the results and contributed to writing the manuscript.

Competing interests The authors declare no competing interests.

Additional information

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Extended Data Fig. 1 | See next page for caption.
Extended Data Fig. 1 | Structure and orientation of LCO particles, and comparison of iSCAT and SEM images.  

**a**, Crystal structure of LiCoO$_2$. Top left, view down the c axis, showing edge-sharing CoO$_6$ octahedra. Right, angled view showing alternate layers of cobalt-centred and lithium-centred octahedra. Four unit cells are displayed (two repeats in the a and b directions). Lithium transport occurs in the a–b plane.

**b**, X-ray diffraction patterns of the pristine LCO powder (black trace) and the self-standing electrode film (blue trace). The comparatively high intensities of the (00l) reflections indicate that the LCO particles display a preferred orientation within the electrode film, with the [001] direction (that is, the c direction) normal to the electrode film. The peak marked * originates from the conductive carbon.

**c**, Mass-weighted diameter distribution for LCO particles (based on 681 particles).

**d**, SEM image of a dilute working electrode, showing two particles of LCO dispersed in a conductive matrix. Scale bar, 10 μm.

**e**, iSCAT image of a single active LCO particle in the electrode (250 μs exposure time). Intensity values are normalized to a linear scale between 0 (black) and 1 (white). Scale bar, 5 μm.

**f–i**, Left, iSCAT intensity image of an LCO particle, normalized between 0 (black) and 1 (white). Right, corresponding SEM image of the same LCO particle. The white dashed line represents the outline of the bright region in the iSCAT image. All scale bars, 2 μm. Comparisons of iSCAT and SEM images confirm that the bright regions observed by iSCAT correspond to relatively flat areas on the particle surface. The curved sides of each particle are out of focus, and do not contribute substantially to the iSCAT image (Supplementary Information section 2). The flat surfaces imply that, for these particles, the direction of observation is along the c axis of the crystal. This particle orientation is ideally suited to investigate the in-plane ion transport within the layered host lattice.
Extended Data Fig. 2 | Galvanostatic cycling at 2C of LCO in an optical cell and in a coin cell. a, Specific capacity plots for 5 cycles of LCO electrodes in the optical cell (blue trace, as shown in Fig. 1b, c) and in a coin cell (grey trace), each cycled at a rate of 2C from 3.0 V to 4.2 V. b, Corresponding differential capacity plots. The positive absolute value of $dQ/dV$ is displayed for delithiation, and the negative absolute value is displayed for lithiation. Peaks attributed to the biphasic transitions (I and IV) and lithium ordering (II and III) are indicated. Both cells were cycled about 20 times at 2C before obtaining the displayed data. The sets of results are in good agreement with each other and with previous reports for LCO. The slightly higher overpotentials and lower capacity seen in the optical cell compared to the coin cell were probably caused by a higher internal resistance in the optical cell, perhaps due to the lower stack pressure.
Extended Data Fig. 3 | Optical response of an LCO particle over five galvanostatic cycles at 2C. Top, cell voltage (versus Li/Li⁺) during five galvanostatic cycles at 2C (as plotted in Fig. 1b, c), as a function of time. Bottom, normalized (‘norm.’) iSCAT intensity change averaged over the active particle shown in Extended Data Fig. 1e, during this galvanostatic cycling. White and blue vertical bars indicate delithiation (charging) and lithiation (discharging), respectively.
Extended Data Fig. 4 | Schematic showing biphasic mechanisms upon delithiation and lithiation. 

a. Shrinking core mechanism upon delithiation. 
b. Intercalation wave mechanism upon lithiation. Throughout, the lithium-rich phase (Li$_{0.95}$CoO$_2$) is represented in pink and the lithium-poor phase (Li$_{0.77}$CoO$_2$) in blue. Black arrows indicate the direction of lithium-ion transport at the particle surface (that is, charge transfer), and white arrows indicate lithium-ion diffusion in the bulk particle. Black dotted lines highlight the positions of the phase boundaries.
Extended Data Fig. 5 | Behaviour of biphasic transitions upon (de)lithiation for five cycles at 2C. a–j, Sequential differential images of the active particle upon delithiation (a, c, e, g, i) and lithiation (b, d, f, h, j) during the biphasic transition, for all five galvanostatic cycles at 2C (as plotted in Fig. 1b, c). The black dashed lines are a guide for the eye, representing the phase boundary position. Sequential contrast (colour scale) represents the intensity changes over a 20 s timescale, and the colour scale is consistent throughout all images. Scale bar, 5 μm.
Extended Data Fig. 6 | Intensity changes caused by ordering transitions upon (de)lithiation for five cycles at 2C. a–e, Images showing the total contrast (colour scale) resulting from lithium ordering for delithiation and lithiation, for all five galvanostatic cycles at 2C (as plotted in Fig. 1b, c). These represent the total intensity change caused by the transition, and the colour scale is consistent throughout all images. For cycles 3, 4 and 5, the formation of the ordered state produces bright lines at approximately 120°. Scale bar, 5 μm.