Operando monitoring of single-particle kinetic state-of-charge heterogeneities and cracking in high-rate Li-ion anodes

Alice J. Merryweather¹23, Quentin Jacquet¹, Steffen P. Emge¹, Christoph Schnedermann²3, Akshay Rao²3 and Clare P. Grey¹3

To rationalize and improve the performance of newly developed high-rate battery electrode materials, it is crucial to understand the ion intercalation and degradation mechanisms occurring during realistic battery operation. Here we apply a laboratory-based operando optical scattering microscopy method to study micrometre-sized rod-like particles of the anode material Nb₆W₅O₄₄ during high-rate cycling. We directly visualize elongation of the particles, which, by comparison with ensemble X-ray diffraction, allows us to determine changes in the state of charge of individual particles. A continuous change in scattering intensity with state of charge enables the observation of non-equilibrium kinetic phase separations within individual particles. Phase field modelling (informed by pulsed-field-gradient nuclear magnetic resonance and electrochemical experiments) supports the kinetic origin of this separation, which arises from the state-of-charge dependence of the Li-ion diffusion coefficient. The non-equilibrium phase separations lead to particle cracking at high rates of delithiation, particularly in longer particles, with some of the resulting fragments becoming electrically disconnected on subsequent cycling. These results demonstrate the power of optical scattering microscopy to track rapid non-equilibrium processes that would be inaccessible with established characterization techniques.

Li-ion batteries, which store large amounts of energy in only a few minutes, are critical for smart grid systems and electric vehicles. High-rate charging, however, can lead to particle- and electrode-level issues, including inter- or intra-particle state-of-charge (SOC) heterogeneities¹–⁸, polarization-driven side reactions⁹, electrolyte decomposition¹⁰ and mechanical degradation involving particle cracking¹¹–¹². These complex non-equilibrium processes can have profound effects on the overall battery performance, but unravelling such phenomena in an operating battery is highly challenging. The challenge is exacerbated by a lack of operando characterization techniques that can monitor Li-ion dynamics at the nanoscale and at relevant charging rates. State-of-the-art electron¹³¹⁴ and X-ray microscopy techniques¹⁵–¹⁶ that can access nanometre length scales have led to key insights into the ion transport processes occurring in these systems, for example, by exploring the phase transitions occurring in LiFePO₄ (ref. ¹³). However, these single-particle-level imaging techniques are restricted to comparatively slow C-rates of ≤2C (where in this ‘C-rate’ notation, nC, n is the applied current divided by the theoretical current needed to (dis) charge the electrode to a specified capacity in 1 hour)¹⁷. Conversely, ensemble-level characterization techniques such as electrochemical methods and operando X-ray diffraction (XRD) are able to access the relevant timescales, but do not spatially resolve the dynamics at the single-particle level¹⁸–¹⁹. Consequently, our understanding of the single-particle ion dynamics at charging rates faster than 2C, while highly desirable, remains largely unexplored.

Dynamic non-equilibrium SOC heterogeneities have previously been evidenced by ex situ and ensemble operando methods in layered cathode materials during (de)lithiation, even though these materials operate via solid-solution mechanisms²⁰–²¹. The coexistence of differing SOCs has been attributed to the slow diffusion at high Li concentrations, which leads to a ‘kinetic phase separation’ in LiNi⁰.₈Co⁰.₁₅Al⁰.₀₅O₂ (NCA) and other layered Ni-rich phases²⁰, and more recently to the ‘autocatalytic’ composition-dependant reaction kinetics in LiNi₁/₃Mn₁/₃Co₁/₃O₂ (NMC, ref. ²²). However, without the use of single-particle-resolution operando techniques, it is difficult to assess how and where these SOC heterogeneities arise during cycling.

Here, we utilize a recently developed operando optical scattering microscopy technique²³–²⁵ to explore charging rates of up to 30C (where C-rate henceforth refers to the current applied at the cell level) and visualize heterogeneity directly at the single-particle level. We examine Nb₆W₅O₄₄ (NWO), which belongs to a family of promising fast-charging anode materials²⁶–²⁸ with record volumetric capacity and charging rates of up to 350 Ah l⁻¹ obtained for Nb₆W₅O₄₄ at 20C (ref. ²⁹). These high C-rates are substantially too fast to be readily investigated with other existing operando microscopy methods, precluding further rationally guided high-rate optimizations.

By applying operando scattering microscopy to rod-shaped NWO particles during cycling at rates from 1C to 30C, pronounced volume changes of the single particles were directly resolved, which allowed us to quantify changes in SOC at the single-particle level throughout cycling. While operando XRD performed at a slower rate of C/8 showed only solid-solution behaviour, operando scattering microscopy revealed the emergence of ‘kinetic phase separation’, that is, non-equilibrium spatial variation of the SOC within individual particles, both during the early stages of delithiation from low Li content and during rapid (>5C) delithiation from high Li content. We propose that this kinetic phase separation is caused by variation

¹Yusuf Hamied Department of Chemistry, University of Cambridge, Cambridge, UK. ²Cavendish Laboratory, University of Cambridge, Cambridge, UK. ³The Faraday Institution, Didcot, UK. ⁴E-mail: cs2002@cam.ac.uk; ar525@cam.ac.uk; cpg27@cam.ac.uk
of the Li-ion diffusion coefficient with SOC. Finally, we observe NWO particles cracking in real time during delithiation, correlated with the intra-particle SOC heterogeneity. In situ analysis of a large number of particles reveals that the likelihood of particle cracking is higher for longer particles and for faster delithiation rates.

Material properties and bulk characterization of NWO

The crystal structure of NWO is composed of ReO$_3$-like blocks of 4x4 corner-sharing octahedra (Fig. 1a), which connect along the a and b axes via crystallographic shear planes and align along the c axis to form tunnels that enable rapid quasi-one-dimensional (quasi-1D) Li-ion transport in the c direction$^{1,2-10}$. In this work, two particle morphologies are examined: rod-like particles (typically ~20μm in size along the c direction and a few micrometres wide in the a and b directions; Fig. 1a) and shorter low-aspect-ratio particles (~5μm in size along c; Supplementary Section 1). Porous self-standing electrodes of the rod-shaped particles were prepared, assembled in a standard coin cell (Methods) and cycled galvanostatically at various C-rates. The resulting voltage–capacity profiles (Fig. 1b) are typical of solid-solution (single-phase) intercalation behaviour and agree with previous reports$^{12}$. Specific capacities of 150, 114 and 83 mAh g$^{-1}$ were achieved at 1C, 5C and 20C, respectively.

To quantify Li-ion diffusion rates, pulsed-field-gradient nuclear magnetic resonance (PFG-NMR) experiments were performed on a lithiated powder with composition $x \approx 0.42$ (in Li$_{17}$Nb$_4$W$_4$O$_{34}$) of low-aspect-ratio particles (Methods$^{12}$ and Supplementary Sections 2–4). The resulting Arrhenius-type temperature-dependent diffusion coefficients are plotted in Fig. 1c (upper panel). Extrapolating to room temperature yields a self-diffusion coefficient, $D_{\text{diff}}$ of $(1.8 \pm 0.5) \times 10^{-12}$ m$^2$ s$^{-1}$ with an activation energy of $190 \pm 30$ meV. The inset shows typical $^7$Li NMR signals, with a black arrow indicating a reduction in peak intensity with increasing magnetic field gradient. Black circles (bottom) show the variation of $D_{\text{eff}}$ as a function of Li concentration, obtained from GITT, with the blue line representing a polynomial fit to the data points. The absolute values of these GITT results are scaled to match the room temperature value of $D_{\text{eff}}$ for $x \approx 0.42$, obtained from PFG-NMR, which is indicated by a red diamond.

Figure 2c shows optical images of a 20.4-μm-long NWO particle (the same one from the SEM image in Fig. 2a) throughout one galvanostatic cycle at 5C (Supplementary Video 1). At all SOCs, the NWO particle appears more brightly scattering than the surrounding carbon matrix, and the observed shape of the particle is comparable to that seen in the SEM image. The optical contrast arises primarily from surface reflections, with the ability to detect features within the ~320 nm depth of field of our microscope (Supplementary Section 7). Fringe patterns on top and at the edges of the particle arise from optical interference effects, determined by the three-dimensional shape of the particle.

During lithiation, the particle initially became slightly darker before increasing in scattering intensity to become overall more brightly scattering at the end of lithiation (in this case, increasing...
in intensity ~2.1 times). This intensity trend is reversed upon delithiation. For the majority of the cycle, the intensity changes occurred homogeneously across the whole rod (Supplementary Fig. 14a). The general intensity behaviour (Fig. 2c) is typical of all NWO particles and C-rates examined in this study and indicates that the optical scattering intensity changes non-linearly with the SOC, being primarily sensitive to the electronic structure of the material33, which changes with Li concentration (discussion in Supplementary Section 9).

In addition to scattering intensity changes, lithiation also caused pronounced volume expansions along the c axis (that is, the long direction) of the particle, with the reverse occurring during delithiation (Fig. 2c). Figure 2d compares the cell voltage (top) with the quantitative change in particle length (bottom) for a similar particle, with the length increasing by approximately 6, 5 and 3% during lithiation to cell-level capacities of 180, 106 and 68 mA h g\(^{-1}\) at 1C, 5C and 20C, respectively. Lebail refinement of operando XRD at C/8 (grey lines, Fig. 2e) and ex situ synchrotron XRD (grey diamonds, Fig. 2e), as well as previous diffraction studies27, indicate that the ensemble c parameter expands monotonically upon lithiation up to 7% at \(x \approx 0.9\) (that is, 160 mA h g\(^{-1}\)). This c parameter expansion is the origin of the optically observed particle elongation and allows changes in Li concentration to be quantitatively monitored at the single-particle level by tracking the particle length changes using optical scattering microscopy and comparing to ensemble XRD (Supplementary Section 10). It should be noted that the lattice expansions/contractions along the a and b directions14,27 (Supplementary Section 6) are too small to be optically determined for this size of particle.

The single-particle elongation was optically determined for several other particles from various electrodes and cycling protocols, shown in Fig. 2e (hollow circles) as a function of the maximum cell-level capacity. The scatter of points around the operando XRD curves indicates variation in the capacities achieved by the individual particles, caused by local current variations. Interestingly, particles appear to show greater deviation from the ensemble average expansion when the cell is cycled at 20C (yellow circles) compared to slower average C-rates (for example, 5C; red circles), suggesting that higher cell-level cycling rates exacerbate particle-to-particle capacity variation.

**Kinetic phase separation at low Li-ion concentrations**

As presented in Fig. 2c, the homogeneous intensity changes suggest that the SOC was largely spatially homogeneous within the particle for most of the cycle at 5C. However, closer inspection of the beginning of this cycle (electrochemical data presented in Fig. 3a) revealed subtle spatial heterogeneities in intensity (Supplementary Fig. 14a). Differential image analysis (Fig. 3b) highlights these features, where
Fig. 3 | Rapid phase fronts at the beginning of lithiation from low Li concentration. a, Cell voltage (black line) and current (grey line) during a galvanostatic cycle at 5C (light blue rectangle), following a constant voltage hold at 2.8 V. b, Differential images of the active NWO particle at 3, 6 and 9 s after the start of the lithiation shown in a (Supplementary Video 2). The differential contrast represents the fractional intensity changes per second, at each pixel. Panels b, c, e and f share the same colour scale. c, Cell voltage (top) over the first 50 s of lithiation. Time points corresponding to the images shown in b are indicated with small open circles. Corresponding evolution (bottom) of a differential line-cut along the length of the rod (y axis) with time (x axis). Dotted black lines indicate the positions of the particle edges. Black arrows are a guide to the eye, highlighting the phase front motion. d, Cell voltage (black line) and current (grey line) during a galvanostatic cycle at 5C (light grey rectangle), following immediately from the cycle shown in a. e, Differential images of the active NWO particle at 3, 5 and 7 s after the start of the lithiation shown in d (Supplementary Video 2). f, Cell voltage (top) over the first 50 s of lithiation. Time points corresponding to the images shown in e are indicated with small open circles. Corresponding evolution (bottom) of a differential line-cut along the length of the rod. Dotted black lines indicate the positions of the particle edges. g, h, Simulated rate of change of Li concentration along a 1D NWO rod (y axis) with time (x axis), for a 5C lithiation from initial states of x = 0.08 and 0.14, respectively. i, Box and whisker plots showing the spread of phase front velocities (small grey circles) measured for different rod-shaped NWO particles at applied C-rates of 1C, 5C and 20C, based on 16, 41 and 16 different velocity values, respectively (centre line, median; box limits, upper and lower quartiles; whiskers, x1.5 inter-quartile range). Blue circles represent the simulated front velocities at the same C-rates. All scale bars are 5 μm.

Each differential image shows the fractional intensity change between a pair of recorded frames separated by a fixed time interval (Supplementary Section 8). Once current was applied, the particle brightened relatively homogeneously. At the same time, comparatively dark fronts moved from both ends of the particle, along the c axis, towards the middle (Supplementary Video 2). The full front evolution is best represented by differential line-cuts, parallel to the direction of the rod length (Supplementary Section 8). The resulting differential line-cuts for the first 50 s of this 5C lithiation (Fig. 3c) clearly show the fronts moving steadily towards the centre of the rod with approximately constant velocities of 600 ± 70 nm s⁻¹ (from the top end) and 760 ± 50 nm s⁻¹ (from the bottom end), meeting each other after ~15 s. The centre of the particle then continued darkening, with this dark central feature spreading towards the ends over time. The intensity...
changes became homogeneous along the length of the particle after ~40 s, and remained homogeneous for the rest of the cycle.

Figure 3d–f shows the electrochemical data and the differential images and line-cuts of the same particle during a second galvanostatic cycle at 5C, which directly followed the cycle shown in Fig. 3a, with no voltage hold in between. Here, the approximate initial Li concentration was $x \approx 0.14$ (as opposed to $\approx 0.08$). No clear moving fronts occurred in the particle at the beginning of lithiation, and only an initial, spatially homogeneous brightening was observed, albeit lower in intensity (Supplementary Fig. 14b and Supplementary Video 2). While the difference in Li concentration between $x \approx 0.08$ and $x \approx 0.14$ is relatively small, it should be noted that the diffusion coefficient changes dramatically with Li content at these low values of $x$ (Fig. 1c).

Rapid moving fronts during early lithiation following a 2.8 V hold were consistently observed over 20 different particles from five different electrodes, at C-rates of 1C, 5C, 20C and 30C, but not in similar cycles without the 2.8 V voltage hold. In no cases were corresponding fronts observed during the final part of delithiation or during the 2.8 V voltage hold.

The observed spatial heterogeneity in the scattering intensity is consistent with the presence of SOC heterogeneity within a particle. To explore this possibility, dynamic Li concentration profiles during galvanostatic cycling were simulated in a 20.4-μm-long NWO rod using a phase field model. The model (Supplementary Section 13) was parameterized using the voltage and diffusion coefficient profiles obtained from GITT and PFG-NMR. Figure 3g,h shows the simulated differential Li concentration line-cuts during early lithiation at 5C, representing changes in Li concentration over time for each location along the particle, starting from uniform compositions of $x = 0.08$ and 0.14, respectively. When starting from $x = 0.08$, lithiation fronts moved from the ends towards the centre at a velocity of $1.120 \, \text{nm s}^{-1}$, and the composition became spatially uniform after ~20 s. By contrast, when starting from $x = 0.14$, the SOC heterogeneity was less pronounced and more short-lived, reaching a spatially uniform composition after ~3 s. Equivalent simulations at 1C and 20C, starting from $x = 0.08$, resulted in similar lithiation front behaviours. No thermodynamic phase separation for $0.08 < x < 0.14$ is included in the model, meaning that the SOC heterogeneity is kinetically driven and can be rationalized by the large change in Li-ion diffusion coefficient in NWO from $x = 0.08$ to $x = 0.14$.

As shown in Fig. 3i, the simulated lithiation front velocities at 1C, 5C and 20C were 500, 930 and 1,900 nm s$^{-1}$, respectively, while the mean experimentally observed values were $210 \pm 20$, $580 \pm 30$ and $1,300 \pm 100 \, \text{nm s}^{-1}$, respectively. While the simulated front velocities are approximately two times faster than the mean experimentally observed values (Supplementary Section 13 for further discussion), the trend is well reproduced. The spread in the experimentally observed velocity values at each applied C-rate likely originates from variation in the local currents and Li pathways in the electrolyte (that is, local tortuosities). Normalized standard deviations of the measured velocities (30%, 29% and 33% of the mean value, for 1C, 5C and 20C, respectively) display no clear trend, suggesting that the degree of inter-particle reaction heterogeneity at the beginning of lithiation is not greatly affected by the applied C-rate. The order-of-magnitude agreement between simulated and observed lithiation front velocities supports our use of the composition-dependent self-diffusion coefficients determined experimentally from GITT and PFG-NMR (Fig. 1c) and indicates that they are reasonable estimates of the true diffusion coefficient values at low Li concentrations in this material.

**Kinetic phase separation leading to particle cracking**

Having established that the sharp drop in ion diffusivity towards small $x$ can lead to kinetic phase separation during early lithiation, we now turn our attention to the more gradual decrease in Li-ion diffusivity towards high values of $x$ (Fig. 1c). While imaging a 17.9-μm-long NWO particle (Fig. 4a), the electrode was first lithiated (to $x \approx 0.68$, based on length-change analysis of the observed particle) at 5C with a 15 min voltage hold at 1.2 V, and then delithiated at either C/2, 5C or 20C. Aside from the previously discussed rapidly moving fronts during early lithiation, the scattering intensity changes were homogeneous along the length of the particle during lithiation at 5C and during delithiation at C/2 (Fig. 4b and Supplementary Fig. 15). However, during delithiation at 5C, the differential line-cut analysis displayed in Fig. 4c showed the presence of a bright front moving from the bottom of the particle towards the centre (0–260 s). After ~280 s of delithiation (to an average of approximately $x \approx 0.56$, based on length-change analysis assuming uniform Li content), the particle suddenly cracked. The SOC of this particle at the time of cracking corresponds to the point in delithiation with the most rapid changes in the $a$ and $c$ lattice parameters (Supplementary Section 6). The new crack remained visible as a faint dark line running perpendicularly across the rod (Fig. 4d).

The initial bright front (Fig. 4e) moved at an average speed of $44.2 \pm 0.3 \, \text{nm s}^{-1}$, becoming gradually more diffuse over the first ~260 s of delithiation. Differential images of the cracking process (Fig. 4f and Supplementary Video 3) show that the dark crack started at the left side of the particle, propagating perpendicularly across the rod at a velocity of $187 \pm 4 \, \text{nm s}^{-1}$. During and after the formation of the crack, additional front-like features began to spread out from the crack along the length of the two fragments. This indicates that electrolyte was able to penetrate the crack, and the newly cleaved surfaces were active surfaces for delithiation.

The electrode was then re lithiated to $x \approx 0.68$ and delithiated at 20C. Sharp bright delithiation fronts propagating from the bottom of the rod (at $85 \pm 1 \, \text{nm s}^{-1}$) and from both sides of the crack (at $143 \pm 2$ and $128 \pm 1 \, \text{nm s}^{-1}$) were observed (Fig. 4g,h and Supplementary Video 4), again clearly demonstrating that delithiation occurred via the cleaved surfaces. The delithiation fronts do not propagate from the top of this particle at any of the applied C-rates, suggesting that (unlike the particle presented in Fig. 3) the top end does not act as an active surface. At 75 s, continued volume contraction caused the fractured particle to further separate into two distinct pieces (shown in Fig. 4i, following the delithiation). Further cycling resulted in additional cracking of this particle (Fig. 4j).

The homogeneous scattering intensity during rapid delithiation from $x \approx 0.68$ is again indicative of underlying heterogeneity in Li concentration, with the observed rate dependence confirming a kinetic origin. At 5C, intra-particle heterogeneity caused cracking, likely due to severe strain arising from spatial heterogeneity in the crystal lattice parameters. Similar cracking was observed in real time for six out of eight different NWO particles investigated under comparable operando cycling conditions, with cracking always occurring during delithiation.

In order to determine the likelihood of cracking as a function of particle size and shape, a consistent and representative set of NWO particles was imaged by optical scattering microscopy, in situ and in the delithiated state, between consecutive ‘cracking cycles’ involving rapid delithiation at 5C or 20C. Figure 5a summarizes the resulting optically observed particle cracking. The initial number of particles was 67, of which six had already cracked before the first ‘cracking cycle’. Throughout the first 5C delithiation cycles, 77 new cracks were observed, with 77% occurring within the first four cycles. Throughout the following five 20C delithiation cycles, 78 further cracks appeared, with 74% occurring within the first two cycles (red points, Fig. 5a). As a result of cracking, the total number of particles increased to 208 (orange points, Fig. 5a). The number of ‘intact’ particles (that is, unbroken original particles) decreased from 61 to 35 over the 5C delithiation cycles, and to 26 over the 20C delithiation cycles (purple points, Fig. 5a).

The particle lengths and widths were determined to examine any correlations with cracking. Figure 5b shows the number (top panel)
and length distribution (bottom panel) of particles that cracked (red) or that survived without cracking (blue) between adjacent time points. The particles that cracked were significantly longer than the particles that survived, with the median cracking particle almost always falling outside the inter-quartile range of the surviving particles. Nevertheless, the distributions overlap, indicating that additional factors such as defects or varying current distributions may also affect cracking. No correlation was observed with the particle widths (Supplementary Section 12).

Figure 5c displays the location along each particle at which each crack occurred, as a function of the length of the particle that cracked. A distinction in behaviour is apparent, with particles shorter than ~12 µm (orange) tending to crack close to their middle, while this preference is less pronounced for longer particles (purple).

In general, cracking results in the formation of new active surfaces but can also lead to particle disconnection. Figure 5d shows optical images of selected cracked NWO particles in a different delithiated electrode, following cycling. In each image, certain
particle fragments are distinctly more brightly scattering compared to other fragments and neighbouring particles, suggesting that they had become disconnected from the electrode and contain Li that is trapped (schematic, Fig. 5d). For the dataset in Fig. 5a–c, after the last ‘cracking cycle’, seven out of the 208 total fragments showed such an effect, suggesting that this electrical disconnection is a relatively rare phenomenon in our electrodes.

Taken together, our optical studies revealed two distinct regimes of ‘kinetic phase separation’ in NWO: during initial lithiation starting from low Li concentration (Fig. 3), and during rapid (>5C) delithiation starting from high Li concentration (Fig. 4). In both cases, this phase separation is observed when (dis)charging the material from a state with comparatively slow diffusion towards a state with faster diffusion. In addition, the rate of ion (de)insertion (that is, the applied current) must be faster than the ion diffusion in the initial low-mobility phase. Only when both of these conditions are met does the new higher-mobility phase continue to accumulate near the active surfaces faster than ions in the lower-mobility bulk can diffuse towards a uniform equilibrium composition.

Intra-particle kinetic phase separation is likely relevant to many other nominally ‘single-phase’ materials besides NWO, as suggested by recent ensemble and ex situ studies of NCA and NMC (refs. 16,19,20). However, to the best of our knowledge, our work represents the first time that kinetic phase separation has been directly visualized under operando conditions and at the single-particle level, confirming the existence of SOC heterogeneity within individual particles of nominally ‘single-phase’ materials.

When coexisting phases have substantially different lattice parameters, phase separation within particles leads to internal strain that may in turn cause particle fracture, as observed here.
during delithiation of NWO. We have not observed particle cracking during the kinetic two-phase behaviour at early lithiation, where the coexisting phases have more similar Li concentrations and lattice parameters. Based on in situ imaging of a representative population of particles, the likelihood of cracking increases at higher rates of delithiation (20C versus 5C) and in longer particles; that is, cracking is most likely when intra-particle SOC heterogeneity during delithiation is most pronounced. Particle fracture is widely accepted to be one substantial cause of electrode capacity fade across many electrode chemistries due to electrical disconnection of particles, highlighting the importance of understanding cracking and its effect on electronic conduction pathways. Future work will examine its mechanistic origin in more detail, as well as investigating the effects of defects and grain boundaries—including intergrowths of alternative crystal phases—upon particle cracking and capacity fade.

In conclusion, operando optical scattering microscopy can probe changes in the SOC at the single-particle level. These studies—coupled with PFG-NMR and GITT experiments—have shown that variation in Li diffusivity has profound consequences for the (de)lithiation mechanisms in NWO, leading to kinetic phase fronts within individual particles during early stages of lithiation from low Li content and during rapid delithiation from high Li content. Fickian diffusion modelling reproduces the observed phase front behaviour and velocities at a range of C-rates and confirms the kinetic origin. These SOC heterogeneities lead directly to particle cracking, particularly in longer particles, observed in real time during rapid delithiation from high Li content. Most of the resultant fragments continue to (de)lithiate during subsequent cycles, while others may become electrically disconnected from the electrode. These results highlight the ability of our imaging method to capture rapid dynamic processes (often occurring over <1 min) and to provide real-time insights into nanoscale ion transport and particle cracking behaviour. Such studies are not feasible with conventional ensemble characterization methods but are essential to observe non-equilibrium processes on the relevant length scales and timescales. Due to its broad applicability to a wide range of battery materials, our optical scattering microscopy method promises to be highly valuable in advancing future understanding of fundamental ion transport and electrode degradation mechanisms.

Online content
Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41563-022-01324-z.

Received: 17 November 2021; Accepted: 28 June 2022; Published online: 15 August 2022

References
1. Zhang, Y., Yang, Z. & Tian, C. Probing and quantifying cathode charge heterogeneity in Li ion batteries. J. Mater. Chem. A 7, 23628–23636 (2019).
2. Davis, A. L. et al. Rate limitations in composite solid-state battery electrodes: revealing heterogeneity with operando microscopy. ACS Energy Lett. 6, 2993–3003 (2021).
3. Chen, Y. et al. Operando video microscopy of Li plating and re-intercalation on graphite anodes during fast charging. J. Mater. Chem. A 9, 23522–23536 (2021).
4. Xu, Y. et al. In situ visualization of state-of-charge heterogeneity within a LiCoO2 particle that evolves upon cycling at different rates. ACS Energy Lett. 2, 1240–1245 (2017).
5. Xu, J., Deshpande, R. D., Pan, J., Cheng, Y.-T. & Battaglia, V. S. Electrode side reactions, capacity loss and mechanical degradation in lithium-ion batteries. J. Electrochem. Soc. 162, A2026 (2015).
6. Rinkel, B. L. D., Hall, D. S., Temprano, I. & Grey, C. P. Electrolyte oxidation pathways in lithium-ion batteries. J. Am. Chem. Soc. 142, 15058–15074 (2020).
Electrode preparation for operando optical scattering microscopy and X-ray diffraction. Self-standing electrode films were prepared from NWO, Super P carbon and polytetrafluoroethylene suspension (PTFE, 60% in water), combined by adding together with ethanol in a pestle and mortar. For characterization by optical scattering microscopy, the dry mass ratios of long rod-like NWO particles, carbon and PTFE were 80%, 10% and 10%, respectively. Upon drying to a workable rod-like NWO particles, carbon and PTFE were 30%, 40% and 30%, respectively. For characterization by XRD, the dry mass ratios of low-aspect-ratio NWO, carbon and PTFE were 80%, 10% and 10%, respectively. Upon drying to a workable consistency, the mixtures were rolled flat into porous self-standing films with a thickness of ~170 ± 20 μm. The films were fully dried (vacuum oven, 100 °C overnight) before cutting electrode discs (5 mm diameter for optical scattering microscopy, 20 mm diameter for XRD). The electrodes were stored in a dry argon atmosphere prior to use.

X-ray diffraction. Operando XRD was performed using an electrochemical cell with Be windows. Patterns were obtained at 10 min intervals during galvanostatic (delithiation) at C/8, using a Bragg–Brentano geometry (Empyrec, Panalytical) at ambient temperature with a Cu Kα source. (Throughout this work, for nC, n is the applied current divided by the theoretical current needed to (dis)charge to a specified capacity of 178 mA h g⁻¹ in 1 hour). The ex situ samples were sealed in 0.5 mm glass capillaries to prevent exposure to air, and synchrotron XRD was performed at beamline 11-BM (Advanced Photon Source) in transmission geometry. All Lebail refinements were performed using Fullprof.

PFG-NMR. PFG-NMR experiments were carried out using a Bruker 300 MHz (7.1 T) magnet with an Avance III console and a 2D probe head equipped with an extended variable-temperature 5 mm single-tuned ‘Li saddle coil insert. Spectra were recorded with a stimulated-echo PFG sequence to minimize T₂ losses (where T₂ is the time constant of spin–spin relaxation). In order to avoid rapid T₂ relaxation at room temperature, PFG-NMR was performed at temperatures ranging from 375 K to 463 K, which is within the thermal stability window of lithiated NWO (confirmed by XRD; Supplementary Section 3). The ‘opt’ shaped gradient pulse maximum strength and duration were 2,300 G cm⁻¹ and 2 ms, respectively. Long delays (2 ms) were used between PFG pulses and measurements to minimize eddy currents, and as a result no dephasing is observed in the spectra (Supplementary Fig. 4f) with the increase of the magnetic field gradient. Diffusion time, Δ, was varied between 7 and 100 ms. Ex situ samples of the isotopically shaped NWO particles were prepared as detailed above. The low-aspect-ratio particle morphology was chosen to reduce experimental complications, which could arise from having a strong preferred orientation of high-aspect-ratio (rod-like) particles in the sample. The sample was packed into a 5 mm glass NMR tube, sealed with a needle and evacuated. No changes were observed when comparing the T₁ static spectra before and after the PFG sequences. The recycle delay between pulse sequences was set to 1 s. The gradient strength was tested and calibrated on a saturated LiCl solution.

As indicated by recent density functional theory calculations and the structures of these materials, Li diffusion in NWO was considered to be 1D (along the tunnels in the crystal c direction; Fig. 1a)²⁷. Li⁺-ion self-diffusion coefficients (Dₐₙₓ = (〈z²(Δ)〉)/Δ, where 〈z²(Δ)〉 is the mean square displacement of the diffusing species in the direction of the pulsed field gradient during the observation time) at various temperatures were obtained from the PFG decay over short diffusion times (Δ = 10 ms), by fitting the decay using a 1D diffusion model. The expression for the Fick–NMG NMR spin echo attenuation in the case of 1D diffusion is given by equation (1):

$$\Psi(\Delta, g, \gamma, \theta) = \int_0^\infty \exp \left( -\frac{1}{2} \left( \gamma^2 g^2 \Delta^2 + \frac{3}{4} \left( \gamma^2 \Delta^2 \right) \cos^2 \theta \right) \right) \sin \theta \, d\theta.$$  

where $\Psi$, $\Delta$, $g$, $\gamma$, and $\theta$ are the spin echo attenuation, the pulse duration, the gradient strength, the gyromagnetic ratio, and the angle between the diffusion channel and the magnetic field gradient, respectively. Equation (1) assumes that the directions of the 1D diffusion channel and the magnetic field gradient are orthogonal. In practice, the gradient orientations might be slightly different for each diffusivity measurement, and a powder-average orientation in space, in other words, that there is no preferred orientation of the particles in the sample. For fitting the results, the integral in equation (1) was approximated numerically using a sum of 89 angles selected using the Zaremba–Conroy–Wolfsberg scheme²⁸–³⁰ performed using a MATLAB script.

GITT. Electrochemical experiments using GITT were performed using the low-aspect-ratio NWO in a thin and porous electrode (2.3 mg cm⁻² loading; 80% NWO, 10% Super P carbon, 10% polyvinylidene difluoride) coated on Cu foil. The GITT experiment was performed by applying a series of C/10 constant-current pulses, each lasting 30 minutes, with a 5 hour relaxation period between each pulse. Data points were recorded at 1 mV intervals (Supplementary Fig. 5a). At short times after switching on the current pulse, the Fick equation predicts the cell potential to vary linearly with the square root of time (Supplementary Fig. 5b–e), with the slope giving access to the diffusion coefficient according to equation (2):

$$\frac{D_{\text{diff}}}{L^2} = \frac{4}{\pi} \left( \frac{1}{2}\int_0^\infty \left( \frac{dE}{dx} \right)^2 \frac{dx}{dV} \right)^2,$$

where $D_{\text{diff}}$, $L$, $I$, $Z_a$, $E$, $x$, and $t$ are the chemical diffusion coefficient, the diffusion length, the applied current, the number of the electroactive species ($Z_a$), the Faraday constant, the cell voltage, the amount of lithium in $L_i$, $N_{\text{Li}}$, $W$, $O_{\text{chem}}$, and time, respectively. A good agreement of the variation of the reciprocal time constant $D_{\text{diff}}/L^2$ with the voltage was obtained for two cells during lithiation and delithiation. Note that analysis at long times after switching on the current pulse ($t \rightarrow \infty/L^2D_{\text{diff}}$) was also carried out and was in agreement with the results for short times. See Supplementary Fig. 6 for an explanation of the relationship between $D_{\text{diff}}$, $L$ and $O_{\text{chem}}$.

SEM. SEM experiments were performed using a TESCAN MIRA3 field emission gun scanning electron microscope at 5.0 kV with in-beam secondary electron detection. When the same NWO particles were observed both optically and by SEM, the SEM was performed following the removal of the self-standing electrode from the optical cell after completing the optical measurements.

**Optical scattering microscopy.** Optical cell. The optical cell (Fig. 2b) is based on a commercially available model (EL-CELL, ECC-Opto-Std test cell), with a homemade lid designed to be compatible with our microscope and glass observation windows (thickness, 170 μm). The cell was assembled in a dry argon atmosphere. The working electrode consisted of the self-standing film, pressed atop a copper mesh current collector, contacted by a stainless steel pin. The counter electrode was lithium metal, the separator was glass fibre (Whatman, GF/B glass microfiber filter) and the cell stack was wet with LP30 liquid electrolyte.

Optical set-up. Optical scattering microscopy was carried out by adapting our previously described microscope set-up². Briefly, a home-built inverted interferometric scattering microscope equipped with an oil immersion objective (x100, UPIPLAPO100XO, Olympus) and polarization optics in the detection path imaged the reflected and scattered light from the sample. The optical–oxide semiconductor detector (FLIR, Grashopper3, GS3-U3-236M-C) with an overall magnification of x166.7. In this work, the sample was illuminated at 740 nm by a high power light-emitting diode source (Thorlabs SOLIS-740C), equipped with a ground glass diffuser to minimize speckle contributions and homogenize the illumination³. The field of view was controlled by a field aperture and set to achieve a circular illumination profile with a diameter of 35 μm. The sample cell was mounted on a 3D nano-positioner stack (Attocube, ECSS3030/AL/R1/NUM) with an overall travel range of 25 mm in all dimensions. The sample focus position was maintained to within 4 nm via an active external focus stabilization based on a calibrated line-reflection profile of a 980 nm reference laser, as described previously²⁴.

**Data acquisition.** Operando optical scattering studies were carried out to examine 20 different rod-shaped NWO particles, in five different electrodes, using a range of cycling protocols and data acquisition parameters. For the experiments presented in Figs. 2 and 3b,c,e,i, images were acquired with a camera exposure time of 8 ms at a frame rate of 2 Hz. Each recorded image was spatially binned (2×2 pixels, giving an effective pixel size of 69.4 nm pixel⁻¹), and sets of two recorded images were temporally binned together to yield an effective frame rate of 1 Hz. For the data presented in Fig. 4, the exposure time was 7 ms, the frame rate was 101 Hz and each image was spatially binned (2×2 pixels). For the C/2 delithiation, sets of 15 images were temporally binned (0.67 Hz effective frame rate), while sets of five were used for the 5C and 20C delithiation experiments (2 Hz effective frame rate). For the data presented in Fig. 5a–c, in situ images were obtained between ‘cracking cycles’ using an exposure time of 5 ms, temporally binned sets of five images, with no spatial binning.
Electrochemical control was achieved using a Gamry potentiostat (Interface 1010). Image acquisition and synchronization of instruments was performed using in-house-developed LabVIEW routines.

Image analysis. Supplementary Section 8 provides details of the image analysis procedures.

In situ studies of particle cracking. To obtain the data presented in Fig. 5a–c, optical images of rod-like NWO particles were obtained, in situ, in the delithiated state, between electrochemical cycles designed to promote cracking. Initially, the cell was cycled for one galvanostatic formation cycle (at 2C) and then for 15 consecutive ‘cracking cycles’, each consisting of 5C lithiation, a 20 min hold at 1.2 V, 5C delithiation (for the first ten cycles) or 20C delithiation (for the next five cycles), and a 20 min hold at 2.8 V. A consistent set of 40 representative regions of the electrode were imaged prior to the first ‘cracking cycle’ and again after the 1st, 2nd, 4th, 6th, 8th, 10th, 11th, 12th, 13th, 14th and 15th ‘cracking cycles’. Following this optical characterization, SEM images of the same regions of the electrode were obtained.

Based on the optical and SEM images, particles that were partly obscured by the carbon matrix were excluded from further analysis. In the remaining particles, new cracks were visually identified from the optical images by the emergence of a dark line/gap running across a particle. The time at which each crack appeared (that is, the number of cycles performed) was recorded. Following the appearance of a new crack, the resulting particle fragments were henceforth counted as new independent particles, such that the total number of particles increased with the number of cracks. This method likely underestimates the true number of cracks formed, as the narrower cracks cannot always be optically resolved in static images. We note that phase fronts observed under operando conditions would reveal the presence of such cracks.

The lengths and widths of each particle were obtained using Fiji image analysis software. The particle lengths were determined from the optical images and were taken to be the maximum distance along the particle, parallel to the rod. Due to the limited depth resolution of the optical microscope (Supplementary Section 7) and the rounded cross-sectional shape of the particles, widths could not be reliably determined from the optical images. Instead, widths were determined from the SEM images of the same particles, measured perpendicular to the rod (at the crack location, or the maximum width for particles that did not crack). For each particle that cracked, the position of the crack (that is, the distance along the particle, relative to the closest end) was measured using the optical images.

Phase field modelling. A simplified phase field model was used to simulate the Li concentration profile in typical NWO particles during battery cycling (Supplementary Section 13 for further description). The inputs to the model, that is, the Li-ion self-diffusion coefficient and the chemical potential, were parameterized from GITT and PFG-NMR experiments. For the simulations constructed the optical set-up and carried out the optical measurements. Q.J. performed the XRD and GITT measurements and the modelling. Q.J. and S.P.E. carried out the PFG-NMR experiments. All authors discussed the results and contributed to writing the manuscript.

Data availability
The data underlying the figures in the main text are publicly available from the University of Cambridge repository at https://doi.org/10.17863/CAM.85438.

Code availability
The code used to perform phase field modelling is publicly available from the University of Cambridge repository at https://doi.org/10.17863/CAM.85438.

References
34. Morcrette, M. et al. In situ X-ray diffraction techniques as a powerful tool to study battery electrode materials. Electrochim. Acta 47, 3137–3149 (2002).
35. de Souza, B., Farias, G., Neese, F. & Izsák, R. Predicting phosphorescence rates of light organic molecules using time-dependent density functional theory and the path integral approach to dynamics. J. Chem. Theory Comput. 15, 896–904 (2019).
36. Zaremba, S. K. Good lattice points, discrepancy, and numerical integration. Ann. Mat. Para Appl. 73, 293–317 (1966).
37. Conroy, H. Molecular Schrödinger equation. VIII. A new method for the evaluation of multidimensional integrals. J. Chem. Phys. 47, 5307–5318 (1967).
38. Cheng, V. R., Suzukawa, H. H. & Wolfsberg, M. Investigations of a nonrandom numerical method for multidimensional integration. J. Chem. Phys. 59, 3992–3999 (1973).
39. Deng, Y. & Chu, D. Coherence properties of different light sources and their effect on the image sharpness and speckle of holographic displays. Sci. Rep. 7, 5893 (2017).
40. Schindelin, J. et al. Fiji: an open-source platform for biological-image analysis. Nat. Methods 9, 676–682 (2012).

Acknowledgements
This work was supported by the Faraday Institution, FIRG012 and FIRG024. A.J.M. acknowledges support from the Engineering and Physical Sciences Research Council (EPSRC) Cambridge NanoDTC, EP/L015978/1. C.S. acknowledges financial support by the Royal Commission of the Exhibition of 1851. We acknowledge financial support from the EPSRC and the Winton Program for the Physics of Sustainability. This project has received funding from the European Research Council under the European Union’s Horizon 2020 research and innovation programme (grant agreement no. 758826). C.P.G., S.P.E. and A.J.M. were supported by a European Research Council Advanced Investigator Grant for C.P.G. (ERC H2020 835073). Use of the Advanced Photon Source at Argonne National Laboratory was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract no. DE-AC02-06CH11357. We thank S. Nagendran and J. Thullier for their help with synthesizing the materials and with the PFG-NMR measurements. P. Magusin for advice regarding the PFG-NMR measurements, B. Mockus for help with the code development and F. Alford for useful discussions regarding analysis of optical data.

Author contributions
C.P.G. and A.R. conceived the idea and supervised the project. A.J.M., Q.J. and C.S. planned all experiments. Q.J. and A.J.M. prepared samples. A.J.M. and C.S. constructed the optical set-up and carried out the optical measurements. Q.J. performed the XRD and GITT measurements and the modelling. Q.J. and S.P.E. carried out the PFG-NMR experiments. All authors discussed the results and contributed to writing the manuscript.

Competing interests
C.P.G. is a major shareholder and cofounder of Nyobolt, a start-up company developing fast-charging batteries based on high-rate anode materials. The remaining authors declare no competing interests.

Additional information
Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41563-022-01324-z.
Correspondence and requests for materials should be addressed to Christoph Schniedermann, Akshay Rao or Clare P. Grey.
Peer review information Nature Materials thanks Santhi Faer, Justin Sambruch and Venkatasubramanian Viswanathan for their contribution to the peer review of this work.
Reprints and permissions information is available at www.nature.com/reprints.