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Operando X-Ray and Postmortem Investigations of High-Voltage Electrochemical Degradation in Single-Crystal-LiNiO₂–Graphite Cells

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Single-crystalline LiNiO2 (SC-LNO), a high-energy-density Li-ion cathode material, suffers from poor long-term electrochemical performance when cycled above 4.2 V (vs Li⁺/Li). In this study, this degradation is evaluated using SC-LNO-graphite pouch cells electrochemically aged within a stressful voltage window (2.5-4.4 V) using a constant-current constant-voltage (CC-CV) protocol. Notable capacity fade is observed after one hundred cycles at C/3 rate, in addition to an increase in the overall electrochemical cell impedance. Operando X-ray diffraction data reveal that, despite no significant long-range bulk structural changes, (de-)lithiation of the aged SC-LNO becomes kinetically hindered after 100 cycles. Aging-induced changes in the short-range structure and charge compensation are evaluated through a multi-model quantitative analysis of the operando X-ray absorption spectroscopy data. While the electrochemical aging does not result in particle cracking, soft X-ray absorption spectroscopy data revealed the reconstruction of the cathode surface to a dense rock salt-like layer after long-term cycling, which acts as a kinetic trap for Li⁺ diffusion. Therefore, even under stressful conditions, it is the surface reconstruction that dominates the overall cathode degradation by reducing the Li⁺ mobility and leading to the capacity fade. Cathode surface engineering will therefore be key to improving the long-term electrochemical performance of SC-LNO cathodes.

1. Introduction

LiNiO₂ (LNO) is a high-energy-density Li-ion battery cathode material that can deliver specific capacities over 240 mAh g^{-1} when cycled up to 4.3 V (vs Li⁺/Li at C/20 rate).^[1] With a lower toxicity (via absence of Co) and industrially viable synthesis pathways, it is a promising cathode material that has been studied for over three decades.^[2-4] However, due to its moisture sensitivity, rapid electrochemical degradation above 4.2 V (vs Li⁺/Li) and thermal instability, it has not yet been commercialised.^[4-7] Above 4.2 V, the ability of LNO to reversibly (de-)intercalate Li-ions (Li⁺) deteriorates.^[5,8,9] At its surface, due to the ligand-hole dominated charge compensation, delithiated LNO is prone to O loss, the products of which react with the electrolyte to produce CO₂ and CO.^[10-14] In addition to posing safety concerns, O loss also results in the transformation of the surface from a layered structure

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into a cubic (rock salt and/or spinel) one that exhibits reduced Li+ mobility.^[15] Structurally, bulk delithiation of LNO up to 4.3 V (vs Li⁺/Li) proceeds via multiple crystallographic phase transformations (H1, M, H2, and H3 where H and M stand for hexagonal and monoclinic, respectively). While the initial H1 to M to H2 transition only involves a gradual structural expansion, the subsequent H2 to H3 transition results in a drastic contraction, leading to the rapid shortening of the interlayer distances.^[1,5,7] During cycling, repeated occurrences of this expansion-contraction phenomenon produce substantial mechanical strain, which can lead to intergranular cracking in polycrystalline LNO particles and expose new surface area to parasitic electrolyte-electrode reactions.^[8,9,16] This can be overcome by using single-crystalline morphologies, where their monolithic architecture prevents the accumulation of internal stresses and, by extension, cracking. The improved electrochemical performance of single-crystalline LNO (SC-LNO) cathodes over their polycrystalline counterparts was recently demonstrated by Mesnier et al. and Kaneda et al through extensive full cell testing between 2.5 and 4.2 V.^[17,18]

Without intergranular particle cracking, the high-voltage electrochemical degradation of SC-LNO cathodes fundamentally depends on the evolution of their crystallographic structure and electronic charge compensation during cycling. This is often not straightforward to characterise due to the differences in bulk and surface evolution.^[19,20] Therefore, an accurate multi-modal characterisation of these material properties as a function of cycling is critical to understand their degradation mechanisms. Several studies, including those dating back to 1989,^[21,22] have shown that Ni-rich layered oxides possess strong metal-ligand (Ni 3d -O 2p) hybridisation and thus, undergo charge compensation via the formation of oxygen/ligand-holes (L) rather than a localised transition metal redox reaction where oxidation state changes are solely confined to Ni.^[10-12,14,23-25] In other words, the redoxinduced electronic changes in the Ni 3d - O 2p hybridised orbitals are more accurately described as $3d^8 \leftrightarrow 3d^8L \leftrightarrow 3d^8L^2$ instead of $3d^8 \leftrightarrow 3d^7 \leftrightarrow 3d^6$. Complexity arises throughout these materials, including pristine LNO, which has been reported to exist in a high-entropy, charge- and bond-disproportionated glass-like state with an approximately equal concentration of 3d8, 3d8L, and 3d⁸L² configurations.^[24] Therefore, a simple Ni-centric ionic description does not accurately explain the (de-)lithiation-induced redox mechanism and charge compensation in these materials. Furthermore, a ligand-hole centric description of their electronic charge compensation also explains their tendency to lose O, which is a key degradation pathway.

In this work, we explore long-term high-voltage electrochemical degradation in high-mass-loading SC-LNO–graphite singlelayer pouch cells (≈118 gsm, 2.6 mAh cm⁻²) through *operando* X-ray diffraction (XRD) and Ni K-edge X-ray absorption spectroscopy (XAS) studies. Electrochemical cycling is performed between 2.5 and 4.4 V to promote O loss and exacerbate surface reconstruction.^[5,13] To further understand short-range structural changes and electronic charge compensation mechanisms, a quantitative analysis of the *operando* XAS data is carried out using three NiO₆ models (conventional, Jahn–Teller distorted, and size disproportionated) from the literature.^[14] Postmortem electron microscopy and soft X-ray absorption spectroscopy studies were also performed to complement the *operando* data.

2. Results and Discussion

2.1. Electrochemical Testing in Single-layer Pouch Cells

Powder XRD data of as-synthesised LNO were fit by Rietveld method to a $R\bar{3}m$ unit cell model, as shown in Figure S1a (Supporting Information). The fit resulted in *a* and *c* lattice parameters of 2.87974(3) and 14.2029(3) Å, respectively, with a Li-Ni site mixing of approx. 1% and no evidence for additional phases. The refined parameters are provided in Table S1 (Supporting Information). As seen in Figure S1b (Supporting Information), singlecrystalline particles of LNO, 2-3 µm in size, were obtained. Electrochemical testing of the SC-LNO cathode was performed in a single-layer pouch cell with a balanced graphite electrode. The electrochemical cycling was performed in three stages at different rates: two formation cycles at C/20, 100 aging cycles at C/3, and two diagnostic cycles at C/20 (1C = 220 mA g^{-1}). To expedite degradation, a wide voltage window (2.5-4.4 V) and CCCV (constant-current constant-voltage) aging protocol was deliberately used.

Figure 1a shows the evolution of the specific charge and discharge capacities of the SC-LNO-graphite cell over the course of cycling. The corresponding voltage-capacity profiles from formation, (first and last) aging, and diagnostic cycles are included in Figure 1b. During the first formation cycle, charge and discharge capacities of \approx 237 (\approx 0.86 mol delithiation) and 206 mAh g⁻¹, respectively, were obtained.^[1,5,17,18] As expected, the high charging voltage and state of delithiation in the first formation charge lead to a low Coulombic efficiency upon discharge. It is also likely that the formation of the solid-electrolyte interphase (SEI) layer on the graphite anode leads to some loss of Li inventory.^[26] In the second formation cycle, lower charge and discharge capacities were observed (171 and 169 mAh g^{-1} , respectively) but with 99% Coulombic efficiency. Upon increasing the cycling rate to C/3 for aging cycles, a larger drop in capacity was observed, which continued with further aging. The discharge capacities increased by \approx 16% during the final two C/20 diagnostic cycles (compared to the 100th C/3 aging cycle). Identical trends are also observed in the normalised discharge capacity data (Figure S2, Supporting Information). This indicates a notable and irreversible capacity fade over the course of cycling. However, the diagnostic cycles also reveal that a portion of the overall capacity loss is dependent on the cycling rate. This influence of cycling rate on the capacity is further illustrated by the capacities observed upon moving between the cycling stages, i.e., formation to aging, and then aging to diagnostic. The charge capacities obtained during the first aging and diagnostic cycles are highlighted in Figure 1a using square and circle symbols, respectively. During the first aging cycle, the charge capacity is notably greater than its subsequent discharge capacity. Considering that the next 99 cycles show similar charge and discharge capacities, the higher capacity during the first aging cycle charge is most likely due to high(er) cathode lithiation during the preceding slow (C/20) discharge. Likewise, during the first diagnostic charge (within the circle in Figure 1a), the capacity obtained is comparable to that in the preceding (100th) C/3 aging cycle, whereas, in the next discharge, a sharp increase in the capacity is observed. This implies that a significant amount of Li+ remains in the graphite, which could be extracted during the slow discharge. Consequently, the second diagnostic charge shows sig-

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Figure 1. The (a) specific capacities versus cycle number from the SC-LNO–graphite cell. b) Voltage versus capacity profiles from selected cycles. The charge capacities from the first aging and diagnostic cycles are highlighted using square and circle symbols, respectively. c) Differential capacity plot of the first formation cycle annotated with the points of structural transitions. d) Differential capacity plots of the cycles shown in (b). e) Current versus time profiles during the CV holds from selected aging cycles. f) Top – equivalent circuit model used for the EIS data fitting; bottom – Nyquist plots of EIS data collected at 3.8 V from the after-formation (AF) and aged cells.

nificantly higher capacity than the first. The corresponding differential capacity (dQ/dV) vs voltage plots of those cycles plotted in Figure 1b are shown in Figures 1c,d. Data from the first formation cycle is plotted in Figure 1c with annotations highlighting the points of H1 \leftrightarrow M, M \leftrightarrow H2, and H2 \leftrightarrow H3 structural transitions during electrochemical (de-) lithiation.^[5,17,18] The first C/3 aging cycle (Figure 1d) shows those same features at higher and lower voltages for charge and discharge, respectively. This is indicative of greater cell polarisation owing to the faster cycling rate. Additionally, the feature between 4.1 and 4.2 V, typically ascribed to the H2 \rightarrow H3 transition, appears significantly suppressed. For the 100th C/3 aging cycle, only the first \rightarrow feature (\approx 3.9 V) is visible,

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and it is shifted to a higher voltage by ≈ 0.3 V. In the following diagnostic cycles, the same feature is shifted to a lower voltage, but without any other features that were visible in the formation or the first aging cycles. Thus, the cell shows significant voltage hysteresis over the course of cycling, representing the buildup of significant polarisation and electrode slippage.^[27,28] While the former leads to poorer Li⁺ kinetics in the cell, the latter expedites cathode degradation by forcing it to cycle at higher voltages. Further evidence for this is observed in the current evolution during the aging-cycles' constant-voltage holds and the electrochemical impedance spectroscopy (EIS) data.

The constant-voltage (CV) holds at 4.4 V during the aging cycles provides insight into the delithiation kinetics of the SC-LNO cathode at that stage of aging. As seen in Figure 1e, the time taken to reach the C/30-limit during the CV hold doubles over the course of aging, indicating that it becomes progressively harder to achieve uniform delithiation across the cathode upon aging. Thus, there must be changes at the cathode, either in the bulk or at the surface, that hinder Li⁺ kinetics, making delithiation more difficult. This is also supported by the EIS data, shown as Nyquist plots in Figure 1f, measured at 3.8 V after formation and end of cycling (formation + aging + diagnostic cycles). The validity of the data was checked through linear Kramers-Kronig tests^[29] as implemented in the *impedance.py* package (Figure S3, Supporting Information).^[30] As three distinct semi-circular features were visible in the spectra, the data were fit with an equivalent circuit model consisting of a resistor, three R-CPE (resistorconstant phase element) circuits, and another CPE in series (Figure 1f). These are conventionally attributed to the ohmic, surface/SEI, anode charge transfer, cathode charge transfer, and the solid-state diffusion resistances, respectively.^[31] The fitted values, along with the corresponding Bode plots, are provided in Table S2 and Figure S4 (Supporting Information). In the aged cathode, all resistive components increase in magnitude and contribute to an overall increase in cell impedance. Notably, the resistance of the high frequency component (R_1), conventionally assigned to surface/SEI diffusion processes^[32] grows more rapidly than the other components. This suggests that surface-related Li+ diffusion processes become dominant with cell aging. Previous studies also point toward the cell degradation being dominated by the cathode due to the high upper cutoff voltage.^[28,33-40] Therefore, to examine cathode microstructural changes and surface vs bulk contributions to capacity fade, operando and postmortem investigations were performed.

2.2. Post-Mortem and Operando Investigations

2.2.1. Microstructural and Surface Changes in the SC-LNO Cathode

Figure 2a,b shows the cross-sectional scanning electron microscopy (SEM) images of the pristine (before pouch cell assembly) and cycled SC-LNO (formation + aging + diagnostic + *operando* cycles) cathodes, respectively. The aged cathode was extracted from the pouch cell in the discharged state following the cycling and *operando* studies. No particle cracking, similar to that reported for polycrystalline systems, is observed in the aged cathode.^[41] However, fine microcracks, similar to those reported by Kaneda et al., can be seen (indicated by yellow circles)

in Figure 2b; Figure S5, Supporting Information).^[18] A possible origin for the microcracking behaviour could be the nonuniform stresses generated in the micron-sized single-crystalline particles due to the spatial gradients in Li⁺ concentration. At faster rates, the concentration gradients become more significant, which could result in the formation of microcracks.^[42] Although it is difficult to quantify the exact influence of the microcracks on the electrochemical performance of the SC-LNO cathode, it is reasonable to assume that they do not significantly contribute to the drastic capacity fade seen here.

Figure 2c shows the O K- (left) and Ni L-edge (right) X-ray absorption spectroscopy data from an aged SC-LNO cathode (100 cycles, 2.5-4.4 V vs graphite) charged to 4.4 V, collected in the surface-sensitive total electron yield (TEY) mode with a probe depth <10 nm. Data from pristine and delithiated (charged to 4.4 V vs Li+/Li) SC-LNO electrodes are included for reference. The 534-eV peak in the O K-edge data (red triangle) indicates the presence of Li₂CO₃ on the pristine cathode surface, commonly present in Ni-rich cathodes (Figure S6, Supporting Information).^[43] The O K-edge pre-peak from SC-LNO visible at \approx 528 eV, arising due to the electronic transitions from the O 1s orbital to the Ni 3d - O 2p hybridised states, indicates that the Li₂CO₃ "layer" is thinner than the probe depth ($\approx 10 \text{ nm}$).^[44] Upon delithiation, the weakening of the 534-eV peak indicates decomposition of the surface Li₂CO₃, which leads to exposure of more of the SC-LNO surface.[45,46] Additionally, due to the delithiation-induced charge compensation creating more empty states in the hybridised Ni 3d – O 2p orbitals, the pre-peak feature becomes significantly stronger. The third notable feature in the spectra, centred at \approx 540 eV and arising from the transitions to the Ni 4s/4p – O 2p hybridised states, only shows minor changes between the pristine and delithiated reference samples. The data from the aged cathode is considerably different. An absence of the Li₂CO₃ peak is noted, and the pre-peak and \approx 540-eV features are considerably suppressed, indicating the presence of an additional surface phase on the cathode. Based on the 532 eV feature (green triangle), this is attributed to a reduced rock salt-like layer with a nominal formula, Li, Ni, O $(x + y \le 1)$.^[7,47] Considering that the pre-peak at 528 eV from SC-LNO is still visible, it is unlikely that the thickness of this phase be more than 10 nm. Therefore, in line with previous investigations,^[18,47] extended high-voltage cycling leads to a layered-to-cubic reconstruction at the LNO surface. As per the electron microscopy investigation by Kaneda et al., the thickness of such a cathode surface "layer" after 500 cycles (2.5-4.2 V vs graphite) was 8-10 nm, which, considering the micron-sized SC particles, is relatively small. Similar observations have also been made for LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (2.5-4.3 V vs graphite).^[36] Therefore, it is more likely that the rock salt-like phase does not grow thicker with extended cycling but rather, gets more densified and acts to impede the Li⁺ kinetics. Additionally, due to the O loss induced by the high-voltage CCCV cycling, it is likely that electrolyte oxidation and CEI (cathode-electrolyte interphase) formation also occur at the surface.^[34,35] The Ni L-edge data in Figure 2c (right panel) also corroborate the formation of the reduced NiO-like layer on the SC-LNO surface. Compared to the pristine and delithiated samples, the aged sample is significantly more reduced, even at the charged state. Although a definitive characterisation of the cathode surface is challenging,^[48,49] it is clear that its reconstruction into a rock salt-like layer, although

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Figure 2. Cross-sectional SEM images of the a) pristine and b) cycled SC-LNO cathodes. Microcracks are highlighted in (b) using yellow circles. c) The background-subtracted, normalised O K- (left) and Ni L-edge (right) spectra of aged SC-LNO cathode collected in the total electron yield (TEY) mode. The green and red triangles in (c) indicate the rock salt and Li_2CO_3 phases, respectively. Data from pristine and delithiated (charged to 4.4 V vs Li⁺/Li) SC-LNO cathodes are shown in grey and blue, respectively.

<10 nm in thickness, kinetically hinders the Li⁺ diffusion in and out of the particles.^[50–52] Following this, aging-induced changes in the electrode bulk were investigated using *operando* XRD and Ni K-edge XAS.

2.2.2. Operando XRD of SC-LNO–Graphite Pouch Cells: After-Formation Versus Aged

Figure 3a shows the XRD data of the fully discharged SC-LNO– graphite pouch cell measured after the formation cycles and the end of cycling (formation + aging + diagnostic cycles), respectively. The latter will be henceforth referred to as aged. The data, collected immediately before the *operando* XRD measurements, includes contributions from all cell components, with the major peaks corresponding to SC-LNO, graphite, and the metallic current collectors (Al and Cu). Diffuse scattering from the polymeric cell components (pouch, separator, etc.) is also observed at lower scattering angles. Note that the metallic current collector peaks overlap between the datasets, indicating that there were no cell positioning differences (i.e., sample displacement) between the measurements, and the two patterns are comparable. The aged SC-LNO cathode has retained its long-range structural order, with no visible peak splitting, shifts, and broadening compared to the data from the after-formation cell. Multi-phase Pawley fittings of the XRD data sets are also performed with the results and corresponding figures provided in Tables S3a,b (Supporting Information) and Figure S7 (Supporting Information), respectively. The changes in the lattice parameters of aged SC-LNO-graphite pouch cell are nominal, i.e., a/b (Å) = 2.847 (1) and c (Å) = 14.13 (1) of the aged cathode compared with the a/b (Å) = 2.841 (2) and c (Å) = 14.11 (1) at the after-formation stage. The fitting reliability parameters (R_{wp} and goodness of fit are also comparable for both fittings. However, there is a shift ($\approx 0.13^{\circ}$) in the graphite (002) reflection toward lower scattering angles in the aged cell, implying that it is in a comparatively higher state of lithiation (highlighted plots are shown in Figure S8, Supporting Information). Corresponding data were also collected after the operando experiments (Figure S9, Supporting Information) and show the same trend. Although loss of active Li⁺ to the graphite anode via growth of the surface SEI layer has been reported during the high-voltage cycling of Ni-rich layered oxide cathode full cells,^[28,40] this is



Figure 3. a) XRD data collected from the SC-LNO-graphite pouch cells in the discharged states after formation and aging. b) Scans corresponding to the open-circuit voltage (OCV), charged and discharged states from the *operando* experiments on the (left) after-formation and (right) aged cells. The OCV data is shown in blue and yellow for the after-formation and aged cells, respectively. The charged and discharged data are shown in red and black, respectively.

unlikely to reveal itself in bulk-sensitive XRD data. Hence, the incomplete delithiation of graphite may be due to the fast cycling rate during aging and the absence of a CV hold at the end of the discharge. Significant overlap of peaks from active material and from battery cell components, together with the insensitivity of XRD to Li and Ospecies, prevents a reliable quantitative structural analysis.

Operando XRD measurements were performed to examine phase behaviour after formation and aging. The measurements were directly performed on the pouch cells without any modifications between 2.5 and 4.4 V and a C/3 cycling rate at ambient conditions. The annotated XRD data from the two operando measurements, at the start (OCV, open circuit voltage), charged and discharged states, are shown in Figure 3b. The full operando dataset, including the electrochemical cycling data, is provided in Figure S10 (Supporting Information). During the operando experiments with the after-formation and aged cells, discharge capacities of \approx 135.4 and 75.6 mAh g⁻¹ were obtained, respectively. This corresponds to differences of approx. 6% and 9%, respectively, from the values obtained during the regular galvanostatic cycling (Figure 1). During the operando experiment with the afterformation cell (Figure 3b left panel), the SC-LNO (003) reflection shows the expected shift toward lower scattering angles in the initial stages of delithiation (charge) before rapidly moving toward higher angles as the voltage approaches 4.4 V. At the fully charged state, the coexistence of the H2 and H3 phases is visible from the splitting of the (003) reflection. The (101) reflection shifts toward higher angles before plateauing toward the end of the charge. During the re-lithiation of the cathode upon discharge, both reflections return to their original positions, confirming the reversibility of these structural transitions. The graphite (002) reflection shifts toward lower angles during delithiation, followed by the return to scattering angles close to the start upon discharge. As the cathode approaches the end of charging, the peak corresponding to the LiC₆ phase can also be seen (Figure S11, Supporting Information). After aging (Figure 3b, right panel), the SC-LNO (003) reflection shows minimal shifts on charging, indicating the limited bulk structural (de-)lithiation of the cathode at the C/3 rate. Hence, the SC-LNO cathode is operating in a reduced state-of-charge window where the 003 evolution is minimal, similar to that reported for other Ni-rich cathodes that show aging-induced structural fatigue.^[53,54] On the other hand, the (101) reflection, whose evolution does not linearly depend on the state of lithiation,^[55] displays a peak shift comparable to that in the after-formation cell data. Correspondingly, the graphite peak evolution is also suppressed compared to the first after-formation cell operando experiment, and no LiC₆ phase is observed (Figure S11, Supporting Information). Together with the electrochemistry data, this evidences anode slippage reminiscent of that reported for LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂,^[28] albeit at an earlier stage of electrochemical aging. Therefore, the XRD data show that aging has not induced any notable loss of long-range structural order in the SC-LNO cathode. Nevertheless, the bulk electrochemical (de-)lithiation of the electrodes at a specific rate has significantly

reduced after aging. To further probe this behaviour, *operando* Ni K-edge XAS was performed to investigate local structural and oxidation state changes in the cathode.

2.2.3. Operando XAS of SC-LNO–Graphite Pouch Cells: After-Formation Versus Aged

Figure 4 shows the evolution of energy-calibrated normalised Ni K-edge XANES (X-ray absorption near-edge structure) spectra, along with the pre-edge data in the inset, for the after-formation and aged cell. For comparison, NiO and BaNiO₃ were also measured as formal $3d^8$ and $3d^8L^2$ standards, respectively.

The XANES datasets corresponding to both stages of cycling exhibit the expected edge shift to higher energies during charging and to lower energies during discharging. The extent of edge shift is visibly smaller in the aged cell, signifying that the extent of cathode redox activity has reduced. This is in line with the operando XRD data, which also showed reduced delithiation in the aged cell. The pre-edge peak in LNO, shown in the insets, also exhibits the same trends as the absorption edge. The corresponding magnitude part of the Fourier-transformed EX-AFS (extended X-ray absorption fine structure) data in R-space is shown in Figure 4b. The positions of the Fourier-transformed peaks, particularly the first and second peaks-corresponding to the nearest-neighbour oxygen (Ni-O) and the next-nearestneighbour Ni (Ni-Ni) coordination shells in the LiNiO₂ structure, respectively-reflect their bond lengths. Variations in these peaks indicate changes in the average bond lengths of the corresponding coordination shells. The amplitude of the Ni-O peak increases with delithiation during charge and reduces upon Li⁺ re-insertion during discharge.^[56] This evolution is comparatively suppressed in the aged cell, indicating reduced cathode redox activity. Two additional aspects of note are also seen. First, similar to the absorption edge, the peak amplitude in the discharged state does not reach the same values as those at OCV. This is most likely due to incomplete re-lithiation of SC-LNO during discharge, as deduced from previous operando XRD experiments. Second, the two spots in the aged cell show dissimilar XANES and EXAFS data evolution, implying different electrochemical redox activity. Although the data collection points on the cells were chosen randomly, it is plausible that electrochemical aging has led to spatial heterogeneity in the electrochemical activity of the cathode. But, considering that the operando measurements were conducted without any stack pressure, it is not possible to conclusively attribute the difference to cycling-induced heterogeneity. This spatial difference in redox activity is most evident when comparing the SC-LNO data to that of BaNiO₃. Apart from spot 1 of the aged cell, the cathode reaches very close to the 3d8L2 state at the fully charged state in all other cases. The raw EXAFS spectra in the wavevector (k) space are included in Figure S12 (Supporting Information).

2.2.4. Quantitative Analysis of Operando XAS Data

Figure 5 shows the electrochemical voltage profile from the *operando* XAS measurements, together with the Ni K-edge half-height energy ($E_{0.5}$), which is defined as the energy at which

the normalised absorption reaches 0.5. Ni K-edge half-height changes have historically been attributed to Ni oxidation, but it was recently demonstrated that the changes in ligand/O electronic structure, without any changes to the Ni centre, can produce similar effects.^[10] For the operando experiment with the after-formation cell, the E_{0.5} evolution at both spots is very similar. It increases from ≈8345 eV during charge, before plateauing around 8346 eV at the fully charged states, followed by returning to values close, but not identical, to the OCV state during discharge. This indicates that the re-lithiation of SC-LNO during discharge is not complete (as compared to the charge) even in the early stages of cycling. The starting E_{0.5} values for the aged cell, which are higher than the after-formation cell by ≈ 0.35 eV, indicate that the aged cathode displays a greater degree of oxidation. Furthermore, the $E_{0.5}$ values from the two spots begin to diverge during charging, with a difference of ≈ 0.4 eV at the maximum, before reconverging during discharge. This divergence indicates dissimilar electrochemical redox activity at the two spots. Complementing the XANES data, EXAFS analysis provides quantitative information about the local crystallographic and electronic structure evolution around Ni species in the SC-LNO cathode during cycling. Multiple Ni-O₆ octahedral models have been proposed for LiNiO₂ including conventional, Jahn-Teller (JT) distorted, and size-disproportionated (SD) models.^[2,14,24] The conventional model supposes that all six Ni-O bonds in the Ni-O₆ octahedron are of equal length, with any distortion in the Ni–O₆ octahedra reflected in the Debye-Waller factor of the Ni-O bond. In contrast, the JT model accounts for distortion by introducing two types of Ni-O bonds: 4 short and 2 long. The SD model considers equal proportions of two types of Ni–O₆ octahedra, short and long. For the second coordination shell (Ni-Ni), all three models use a single Ni-Ni interatomic distance. These models are illustrated in the top-left corner of the plots in Figure 6 and described in greater detail in the experimental section.

Figure 6 shows the fits of the Ni K-edge EXAFS data obtained from the SC-LNO–graphite cell in the OCV state prior to the *operando* measurements. The magnitude and real part of the Rspace are shown at the top and bottom, respectively. Although each of the models gives a visually satisfactory fit, the JT and SD models, in that order, provide a better fit according to the refinement figures of merit (R-factor and χ^2)^[57] than the conventional model. This corroborates previous works,^[2,14,24] the electronic structure of SC-LNO in its pristine state is better described by the more complex JT and SD models than the simpler conventional model. Nevertheless, considering that all three models gave a satisfactory fit, the *operando* dataset was separately fit sequentially using each of the models for an unbiased evaluation of the local structural evolution in the charged/delithiated states.

Figure 7 shows the evolution of the average Ni—O and Ni—Ni distances obtained from fitting each of the three models to the datasets for pristine and aged cells, together with the electrochemical voltage profile from the corresponding *operando* experiments. The data collected from spot two is shown here; data collected at spot one is provided in Figures S13 and S14 (Supporting Information). Comparing the fits between the models, it is evident that the conventional model provides the best overall fit, especially for the delithiated states. In the JT and SD models, the uncertainty associated with the Ni—O and Ni—Ni distances significantly increases as the cathode oxidises upon charging. The

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Figure 4. a) *Operando* Ni K-edge XANES data, with the pre-edge region magnified in the top left, from the after-formation (AF) and aged cells. b) The corresponding magnitude part of the Fourier-transformed EXAFS data, χ (R). The OCV, charged and discharged scans are highlighted in blue, red, and green, respectively. The intermediate scans are shown in grey. The NiO and BaNiO₃ data are shown as dashed and solid black lines, respectively.

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Figure 5. a) Voltage versus time profile from the *operando* Ni K-edge XAS measurements of the after-formation and aged cells. The sudden voltage drop in the aged cell data is due to the cell having to be restarted due to a faulty connection. b) The half-height energy calculated from the normalised Ni K-edge XANES data collected on the after-formation and aged cells.

same holds for the beginning of discharge, and the uncertainty only reduces toward the end when the cathode is lithiated to a certain extent. Thus, beyond a certain state of delithiation, the simpler conventional model best describes the SC-LNO data. As per this model, at the OCV state, the average Ni-O bond length is ≈ 1.94 Å, which plateaus at ≈ 1.88 Å at the fully charged state, before increasing during discharge to values close to that at OCV. Compared to the Ni-O bond length of BaNiO₃ (1.87(2) Å),^[58] it is clear that SC-LNO approaches the 3d⁸L² state upon charging, as observed in Figure 4. In the aged cell, the Ni-O bond length in the OCV state is \approx 1.915 Å, which is shorter than in the after-formation cell at the same state. This is further proof that the aged cathode is comparatively more oxidised than the one measured after formation. Similar to the operando XRD data, the Ni-O and Ni-Ni distances evolve to a comparatively smaller degree in the aged cell. Nevertheless, the values plateau toward the end of charge and are comparable to those from the afterformation operando experiment. In the JT and SD model fits, the long and short Ni-O distances begin to converge upon charging, which indicates that the effect of JT distortion reduces with delithiation. Above 4.0 V, both the Ni-O bonds become comparable, albeit with a high degree of uncertainty. Toward the end of discharge, the short and long Ni-O distances reach values close

to those at OCV. The Ni–Ni distances refine to the same values in all three models and follow the same trends, with the aged cell data showing a reduced extent of evolution compared to the afterformation cell. The data collected from spot 1 also shows identical behaviour and trends and is shown in Figure S13 (Supporting Information).

The corresponding Debye-Waller (DW) factors obtained from the operando XAS data are shown in Figure 8. This represents the local structural distortion surrounding the absorber Ni species. In the conventional model fitting, the DW factor for the Ni-O pair follows the same trend as the Ni-O bond length, confirming that the distortion in the Ni-O₆ octahedra correlates with bond length. At the beginning of charge, the magnitude of the DW factor of the Ni-O pair is approximately two times that of the Ni-Ni pair, and this reduces upon charging with both bond pairs reaching comparable values (0.004–0.005 Å²) at the fully charged state. Upon discharge, the values reach those close to the OCV state. At early stages of charging/delithiation, the Ni species exists in a distorted 3d8L state, which is susceptible to JT distortion. Upon charging, delithiation-induced oxidation brings this closer to the 3d⁸L² state, thereby reducing the local Ni–O₆ distortion in the cathode. The DW factors from the JT model fitting are shown in Figure 8c. In this case, the short and long Ni-O

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Scattering path	R [Å]	CN	DW factor [Ų]
Ni–O	1.939(7)	6.30(72)	0.0087(17)
Ni–Ni	2.878(5)	7.44(79)	0.0056(8)

Scattering path	R [Å]	CN	DW factor [Å ²]
Ni–O (short)	1.902(5)	4	0.0037(13)
Ni–O (long)	2.044(22)	2	
Ni–Ni	2.883(4)	7.39(65)	0.0055(7)

Scattering path	R [Å]	CN	DW factor [Å ²]
Ni–O (short)	1.872(11)	6	0.0000(00)
Ni–O (long)	2.006(14)	6	0.0028(22)
Ni–Ni	2.879(4)	7.27(72)	0.0054(8)

Figure 6. (Left) The OCV SC-LNO–graphite cell Ni K-edge EXAFS data fits are shown as the magnitude and real part (offset to lower magnitudes for clarity) of the R-space. The conventional, JT, and SD models are illustrated in the top-left of the plots a–c), respectively. The Ni and O species are represented in grey and red, respectively. The refinement figures of merit are also provided. (Right) Refined structural parameters for the three models. R, CN, and DW are the bond length, coordination number, and Debye–Waller factor, respectively.

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Figure 7. a) Voltage versus time profile from *operando* XAS measurements of the after-formation and aged cells. The Ni–O bond length of the Ni– O_6 octahedron and the second coordination shell Ni–Ni distances obtained from fitting b) conventional, c) JT, and d) SD models to the EXAFS data. The legend in the left panel of (c) also applies to the SD model data in (d) and represents the short and long Ni– O_6 octahedra.

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bonds are assigned the same DW factor to avoid overparameterising the data and unphysical fit values.^[59] Interestingly, the DW factor of Ni-O pair is smaller than that of the Ni-Ni pair in the OCV state, unlike in the conventional model. Thus, when structural distortion is accounted for in terms of multiple Ni-O bond lengths, the distortion represented by the DW factor diminishes. Therefore, the origin of the distortion must lie in the Ni-O bond length. Similar to the Ni-O bond lengths (Figure 7), the uncertainty associated with the Ni-O pair DW factor also increases upon delithiation, reaching unphysical negative values toward the end of the charge and beginning of discharge. The high degree of uncertainty in these Ni-O bond lengths, coupled with the negative DW factor values obtained, highlights the incompatibility of the JT model to fit the EXAFS data beyond a certain state of delithiation in the after-formation and aged cells. The SD model fitting, shown in Figure 8c, reveals similarly uncertain values for the Ni-O pair upon charging. Although a notable decrease in the Ni-O DW factor is observed at the fully charged state, the highly uncertain Ni-O bond lengths (Figure 7d) question the validity of this model. Thus, the simpler conventional model can better fit the SC-LNO EXAFS data in the delithiated states than the more complex JT and SD models. The data collected at spot 1 is shown in Figure S14 (Supporting Information) and confirms the same trends. The evolution of the EXAFS figures of merit from the operando data fitting are shown in Figures S15 and S16 (Supporting Information), and corroborates the conclusions made above: the JT model provides the best fit at the OCV and early stages of charging, with the conventional model exhibiting a better fit toward the high-voltage high-delithiation regions.

2.3. Electrochemical Degradation in the SC-LNO-Graphite System

The combination of 2.5-4.4-V voltage window and CCCV cycling protocol leads to drastic capacity fade in the SC-LNO-graphite cell, accompanied by notable impedance growth and polarisation. In the absence of any major cathode particle cracking, the performance fade is a consequence of the uncharacteristically wide voltage window, which promotes the formation of a resistive, dense Li_xNi_yO ($x + y \le 1$) rock salt-like layer (<10 nm thick) on the SC-LNO cathode surface, amongst other factors. This is directly evidenced from the O K-edge and Ni L-edge TEY spectra, which demonstrate a significant reduction has occurred at the cathode surface over the 100 cycles, which impedes the Li⁺ transport kinetics across the cathode-electrolyte interface.[60,61] Consequently, for a specific cycling rate, the cathode operates within a reduced electrochemical SOC range as it ages, which also explains the absence of any significant cycling-induced longrange crystallographic changes in the aged-cathode XRD data. The operando Ni K-edge XAS data complements the electrochemical and XRD data by providing insights into the cathode redox activity and short-range structure evolution around the Ni species. Upon aging, the cathode bulk becomes more oxidised as a function of Li⁺ loss, with no other notable local structural distortions as visible from these measurements. The aged cathode is still electrochemically active and shows comparable redox behaviour to its fresh(er) counterpart. Additionally, through multi-model EXAFS data analysis, it is shown that the electronic structure

of the cathode bulk plateaus to states resembling the 3d⁸L² configuration upon charging, before going back close to the original charge-disproportionated state on discharge. This is seen in both the after-formation and aged cathodes, although the extent of change is diminished in the latter due to its operation within a reduced SOC range, as mentioned previously. The DW factor between the after-formation and aged cathodes is similar, which implies that the short-range order has become no more disordered in the bulk after aging. The plateauing behaviour of the Ni K-edge half-height and Ni–O bond length as it reaches the 3d⁸L² state is often misattributed to the onset of O oxidation (and the end of Ni oxidation). However, several recent studies have shown that O, via ligand hole formation, is the dominant charge compensation centre during (de-)lithiation in highly covalent negative chargetransfer systems such as LiNiO₂.^[10-12] Therefore, similar to SC-LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂,^[23] ligand/O-hole mediated redox is stable in the LiNiO₂ cathode bulk. However, at the cathode surface, the ligand holes can act as reactive sites, promoting O loss and growth of the reduced surface layer, which leads to sluggish Li⁺ kinetics.

Although this study is focused on understanding how changes in the bulk and surface properties of SC-LNO cathodes affect the overall performance fade in the SC-LNO-graphite system, it is worth noting that there are also other degradation mechanisms, extending across multiple cell components, at play.^[62] While a detailed investigation of all the mechanisms is perhaps beyond the scope of any single work, it is worth summarising other plausible degradation mechanisms here to help contextualise the current work in a broader context. As mentioned previously, the overall capacity fade in the SC-LNO-graphite system has both irreversible and reversible contributions. The irreversible component predominantly involves the loss of Li⁺ inventory to the graphite SEI layer. Considering the wide operational voltage window, it is also likely that Li⁺ may be consumed through parasitic electrolyte decomposition reactions. This forms CEI layers on the cathode, which can also affect the Li⁺ diffusion properties. As experimentally demonstrated by Kaneda et al.^[18] and elaborated in other works,^[48,49] an accurate characterisation of CEI layers is difficult and requires an extensive multi-technique approach to obtain reliable results. Furthermore, spatial variations in the CEI and the cathode surface layers also make it difficult to obtain reliable, statistically significant results through conventional transmission electron microscopy techniques.[48,49,63,64] Another mechanism of note is the protonation-induced Ni dissolution that occurs during high-voltage operation.^[65,66] These phenomena can result in electrode slippage, i.e., misalignment of the electrode capacities as a consequence of cycling-induced parasitic side reactions.^[27,28] The reversible component of capacity fade is determined by factors that worsen Li-ion diffusion kinetics within the cell. In micron-sized single-crystalline cathode particles, in addition to the reduced cathode surface layer, this has also been attributed to the development of Li⁺ concentration gradients due to the comparatively longer diffusion paths.^[42,67] Kinetics-dependent capacity losses are overcome by slower cycling rates, as it can facilitate better Li⁺ diffusion kinetics within the particle and across the electrode surface layers. Quantifying the contribution of each of the mechanisms is essential to develop a complete picture of the overall cell degradation, but this task is made difficult by the sheer number of degradation modes simultaneously active in an electrochemical cell. Therefore,

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systematic, targeted, and statistically significant investigations of different cell components and their underlying degradation modes are necessary to holistically build up our knowledge in this area and devise strategies to prolong battery cycle life.

3. Conclusion

This study investigates the key performance degradation mechanisms in high-areal-capacity single-crystalline LiNiO₂ (SC-LNO)graphite pouch cells deliberately subjected to a long-term widevoltage-window (2.5-4.4 V) CCCV cycling protocol. In addition to drastic capacity fade, increased cell impedance and polarization were observed at the end of cycling, which suggests worsening Li-ion kinetics. With electron microscopy revealing no significant particle cracking, the sluggish Li⁺ transport properties were attributed to the growth of a dense reduced surface layer on the cathode, <10 nm in thickness, as revealed by soft X-ray absorption spectroscopy. Operando X-ray diffraction and X-ray absorption spectroscopy studies indicate that the SC-LNO preserves its long- and short-range structural order even after long-term high-voltage cycling, reflected in the gradually diminishing electrochemical activity of the cathode with aging. The operando measurements of the aged cell also revealed reduced electrochemical activity at the faster C/3 rate, further corroborating sluggish Li⁺ kinetics in the system. Li⁺ were also found to be trapped in the graphite, which leads to incomplete relithiation of SC-LNO during discharge. This was confirmed by spectroscopy data, which revealed the aged cathode bulk to be in a higher oxidation state with reduced electrochemical activity. A multi-model analysis of the extended X-ray absorption fine structure data using the conventional, Jahn-Teller (JT) distorted, and size disproportionated (SD) models revealed that the system undergoes a reversible transition from charge disproportionated state to 3d⁸L² in both the after-formation and aged cells, albeit to a smaller extent in the latter. Recent studies have shown this transition is not an indicator of Ni oxidation but rather ligand hole formation on the O species, which is the dominant charge-compensating mechanism in such covalent negative charge-transfer compounds. This underscores the stability of ligand hole-driven bulk redox in LiNiO2. However, at the surface, the ligand holes may promote surface reconstruction, which significantly hinders Li-ion kinetics, raising impedance and polarisation, and consequently, rate-dependent capacity degradation. This comprehensive analysis provides valuable insights into both bulk and surface degradation mechanisms in SC-LNO cathodes, aiding their development as nextgeneration Li-ion battery cathodes.

4. Experimental Section

Synthesis: The Ni(OH)₂ precursor was synthesised using a precipitation method in a stirred tank reactor. In this process, 2 M NiSO₄ solution was introduced into an NH₄OH (4 M) solution within the reactor. Simultaneously, a 2 M NaOH solution (NaOH:Ni = 2) and an NH₄OH chelating agent solution (NH₄OH:Ni = 1.2) were independently introduced into the reactor. The reaction was stirred at 1000 rpm for 20 h, to obtain pristine Ni(OH)₂ precipitate. The obtained powder was thoroughly washed in water and subsequently dried overnight at 80 °C. To achieve single-crystalline morphology, a molten-salt-assisted method was used. Ni(OH)₂ powder was finely ground in an agate mortar with LiOH.H₂O and Li₂SO₄ in the molar ratio of 1:1.5:0.25. The mixture was transferred to an alumina crucible and heated in a tube furnace under O_2 flow, first at 480 °C for 12 h, followed by 775 °C for 24 h. The resulting product was then washed with deionised water to remove residual Li species, recovered via centrifugation, and subjected to a final heat treatment at 775 °C for 6 h under an O_2 atmosphere. All heating stages were carried out with a ramp rate of 5 °C min⁻¹. The material was removed from the furnace at 200 °C and transferred to an Ar-filled glovebox for storage.

Electrode Fabrication: The slurry preparation and casting process of SC-LNO powder were carried out in a dry room (dew point of -43 °C). Approx. 2 g of SC-LNO powder, commercial-grade carbon black (C65 Imerys), and polyvinylidene fluoride (PVDF, Solef 5130) binder were combined in a Thinky mixer (ARE-250), at a weight ratio of 90:5:5, respectively. The mixing was conducted at 2000 rpm for 5 min. To achieve a uniformly mixed slurry, anhydrous N-methyl-2-pyrrolidone (NMP, 99% extra pure, Thermo Scientific Chemicals) was introduced into the slurry and again mixed for 15 min, maintaining a solid content of \approx 54 wt.%. The slurry was coated onto a 15-µm-thick aluminium foil using a 260 µm doctor blade. Finally, the coated electrodes were dried at 120 °C overnight under vacuum, achieving a coat weight of 118.2 gsm. Calendaring of the electrodes was performed with a two-roller compactor, operating at a roller speed of 1 m min⁻¹ at 85 °C, to achieve a press density of \approx 2.8 g cm⁻³ and an areal capacity of \approx 2.6 mAh cm⁻².

The graphite anode sheet was prepared by combining graphite (BTR V-H), carboxymethyl cellulose (CMC, Ashland BVH8), styrene-butadiene rubber (Zeon BM451), and carbon (Imerys C45) in a weight ratio of 95.25:1.5:2.25:1, respectively. This mixture was coated onto a 10-µm-thick copper foil and dried overnight at 50 °C, resulting in a coat weight of 93 gsm. The graphite electrode was then calendared to achieve a press density of 1.2 g cm⁻³. The estimated areal capacity of the anode was \approx 3 mAh cm⁻², resulting in a negative-to-positive electrode capacity ratio (N:P ratio) of \approx 1.15.

Pouch Cell Assembly and Electrochemical Cycling: The assembly of SC-LNO-graphite single-layer pouch cells was also carried out in a dry room environment (dew point of -45 °C). The cathode possessed a geometrical surface area of approx. 33 cm², while the anode surface area measured 35 cm². Subsequently, tabs of the current collectors were welded to the electrodes through ultrasonic welding (cathode: Al, anode: Ni-coated Cu). Afterward, the two electrodes were assembled by stacking them together with a Celgard 2325 Trilayer microporous membrane of 25 μ m thickness used as a separator. The anode–separator–cathode stack was then placed within an aluminium-laminated pouch cell and filled with electrolyte (1 g) before it was vacuum sealed. The electrolyte was 1 M lithium hexafluorophosphate in 3:7 w/w ethylene carbonate and ethyl methyl carbonate with 2 wt.% vinylene carbonate additive (Solvionic).

The cells were cycled in a testing rig sandwiched between two perspex glass plates to ensure homogeneous stack pressure. To facilitate full wetting of the electrodes, the cells were held at 1.5 V at 40 $^\circ C$ for 20 h. The cells then underwent two formation cycles, also at 40 °C, on a Maccor 4000 series cycler through constant current (CC) cycling between 2.5 and 4.4 V at a C/20 rate (1C = 220 mA g^{-1}). Electrochemical aging was carried out between the same voltage windows at a C/3 rate for 100 cycles at 25 °C following a constant current constant voltage (CCCV) protocol. The constant-voltage holds were current-limited to C/30. Following this, two additional diagnostic cycles at a C/20 rate were performed. At the afterformation and end of cycling (and aging diagnostic cycles, potentiostatic electrochemical impedance spectroscopy (PEIS) data were collected using a Biologic VMP3 potentiostat. The data was collected at 3.8 V (C/20 charge) at 25 °C between a scanning frequency range of 100 kHz to 10 mHz with a voltage amplitude of 10 mV. Afterward, the cells were discharged to 2.5 V at a C/20 rate.

Pouch Cell Disassembly: After the electrochemical cycling and *operando* studies, the pouch cells were disassembled inside an Ar-filled glovebox. The electrodes were first washed using anhydrous dimethyl carbonate (DMC, Sigma-Aldrich 99%) and then transported to the respective facilities for further characterisation without atmospheric exposure.

X-Ray Diffraction (XRD): XRD data of SC-LNO powder were collected on a Malvern Panalytical Aeries diffractometer using Cu K α radiation operated at 40 kV and 15 mA. The X-ray optics on the incident beam side included a Ni CuK β filter, a Soller slit (0.04 rad), a divergence slit (0.25°), and a 13-mm X-ray mask. On the diffracted side, an antiscatter (9 mm) and Soller (0.04 rad) slits were used. Data were collected in Bragg Brentano mode with zero-background Si holder spinning across a 10–75° (2 θ) scattering angule range, using a step size of 0.01° and an acquisition time of 150 s per step. Rietveld analysis^[68,69] was performed using the *Topas Academic* (v7) software.^[70]

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Scanning Electron Microscopy (SEM): SEM images of the SC-LNO powder were collected on a Zeiss Sigma instrument (5 kV, 1 nA). The sample was stuck onto a carbon tab for imaging. Cross-sectional images of the cathodes were collected using an accelerating voltage of 2 kV and 0.1 nA using a Thermo Fisher Scientific Scios Dualbeam using the CleanConnect inert gas transfer system. The sample preparation was identical to that in the previous work.^[55]

Operando XRD: For all the *Operando* studies, the cells were galvanostatically cycled between 2.5 and 4.4 V at a C/3 rate using a Biologic SP150 potentiostat at ambient conditions. A CV hold at 4.4 V and rest step spanning 0.5 h each was applied between charge and discharge in all cases. The experiments were carried out after formation and aging (aging + diagnostic + EIS) states.

Operando XRD studies were performed on a Malvern Panalytical Empyrean diffractometer using Mo Kα radiation ($K_{\alpha 1} = 0.7093$ Å, $K_{\alpha 2} = 0.7136$ Å) operating at 60 kV and 40 mA. A GaliPIX3D detector, with an active length spanning 4.996° was used in the scanning mode for data collection. The measurements were performed in transmission mode by using an *XYZ* stage. The incident-beam side of the setup incorporated a Zr Cu K β filter, a Soller slit with an aperture of 0.02 rad, a divergence slit set at 0.5°, and an anti-scatter slit adjusted to 0.25°. On the diffracted beam side, both an anti-scatter slit (5 mm) and Soller slit with a setting of 0.04 rad were used. Data was collected between 7.5° and 18° (2θ) with a step size of 0.028° and a counting time per step of ≈530 s, amounting to ≈15 min per scan. In situ data were collected on the pouch cells before and after the *operando* experiment under identical conditions but with a longer collection time, totalling 1 h and an extended angular range of 7.5°–32°.

Operando Ni K-Edge X-Ray Absorption Spectroscopy and Data Analysis: Operando XAS measurements were conducted on the B18 beamline at the Diamond Light Source (Didcot, UK). The cycling protocol was identical to the operando XRD experiments, except for the after-formation cell, whose post-CV-hold rest step was only 5 min due to time constraints. The sudden voltage spike in the aged cell data was due to a faulty connection. Measurements were performed directly on the pouch cell in transmission mode under ambient conditions. A Pt-coated Si 111 monochromator was used to select the desired X-ray range. The energy scans were carried out between 8250 and 8950 eV, with a step size of 0.3 eV. Ionisation chambers filled with a mixture of H₂, He, and Ar were employed to measure the intensities of the incident beam and transmitted beam during the experiment. For energy calibration, an internal Ni reference foil was simultaneously measured. The pre-edge background subtraction and post-edge normalisation of the raw XAS data were performed using the Athena program from the Demeter package.^[71]

The Ni K-edge absorption energy was determined using the half-height method, where the energy corresponding to 0.5 of the normalized intensity was taken as the Ni K-edge absorption energy. The k-space EX-AFS (extended X-ray absorption fine structure) data, weighted by k^2 , in the range of 3.1-11.8 Å⁻¹ were Fourier-transformed into R-space. Data was modeled in R-space over the range of 1-3 Å using a Python-based Larch script.^[72] Scattering paths for the modelling were generated with Feff6.^[73] The single scattering paths corresponding to the first and second coordination shells, formed by nearest-neighbour oxygen atoms and next-nearest-neighbour Ni atoms, respectively, were employed in the analysis. Three structural models-namely, the conventional, the Jahn-Teller distorted, and the size-disproportionated-were employed to model the EXAFS data.^[14] NiO and $BaNiO_3$ were used as standard structural models to get the long and short Ni-O single scattering paths, respectively. In the conventional model, LiNiO2, as the standard model, was used to get the first coordination shell Ni-O single scattering path. Ni-Ni single scattering path corresponding to the second coordination shell from the

LiNiO₂ standard was used in all three fitting models. The modelling process incorporates four EXAFS parameters: bond length (R), Debye-Waller factor, coordination number, and Fermi energy shift (E₀). The amplitude reduction factor (S_0^2) was determined from the Ni foil standard and fixed to 0.78. In the conventional model, only one Ni-O single scattering path was employed, with their corresponding bond length, Debye-Waller factor, and coordination number refined for the first coordination shell. In the Jahn-Teller model, two types of Ni-O single scattering paths-short and long-were employed to model the first coordination shell. The short and long bond lengths, with their corresponding coordination numbers fixed to two and four, respectively, were refined without any constraint. To avoid the overparameterisation of EXAFS fitting, a single Debye-Waller factor was applied to both types of bonds and refined. In the size-disproportionated model, two types of Ni-O single scattering paths were employed to represent small and large Ni–O₆ octahedrons of equal proportions. The corresponding bond lengths were refined during the data modelling. A single Debye-Waller factor was refined for each of the short and long Ni-O bond lengths. Coordination numbers were fixed at six for both small and large Ni-O₆ octahedron. The second coordination shell corresponding to the absorber-scatterer pair of Ni-Ni was modeled using a single scattering path that was consistent across all three models. The corresponding Ni-Ni interatomic distance, coordination number, and Debye-Waller factor were refined independently. A common E₀ was assigned to all single scattering paths in the fittings.

Soft X-Ray Absorption Spectroscopy: O K- and Ni L-edge soft XAS were performed in the total electron yield mode at the I09 beamline at the Diamond Light Source (Didcot, UK). Electrodes for the measurement were cycled in coin cells and disassembled in the glovebox. They were then rinsed with DMC and loaded onto sample pucks, which were then transferred to the experimental chamber. Measurements were carried out in ultra-high vacuum conditions. The O K-edge data were processed using Athena software, similar to the Ni K-edge data. Background subtraction of the Ni Ledge data was carried out using Origin software.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in Mendeley Data at https://doi.org/10.17632/t9nv93mvrp.1, reference number 0.

Keywords

cathode degradation, Ni-rich layered oxide cathodes, *operando* X-ray absorption spectroscopy, *operando* X-ray diffraction, single-crystalline LiNiO₂

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