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## Distinguishing bulk redox from near-surface degradation in lithium nickel oxide cathodes†

Lijin An,<sup>a</sup> Jack E. N. Swallow,<sup>a</sup> Peixi Cong,<sup>a</sup> Ruomu Zhang,<sup>a</sup> Andrey D. Poletayev,<sup>id ab</sup> Erik Björklund,<sup>id ab</sup> Pravin N. Didwal,<sup>ab</sup> Michael W. Fraser,<sup>ab</sup> Leanne A. H. Jones,<sup>a</sup> Conor M. E. Phelan,<sup>id a</sup> Namrata Ramesh,<sup>a</sup> Grant Harris,<sup>c</sup> Christoph J. Sahle,<sup>id d</sup> Pilar Ferrer,<sup>id e</sup> David C. Grinter,<sup>id e</sup> Peter Bencok,<sup>e</sup> Shusaku Hayama,<sup>e</sup> M. Saiful Islam,<sup>id ab</sup> Robert House,<sup>id ab</sup> Peter D. Nellist,<sup>ab</sup> Robert J. Green,<sup>id cf</sup> Rebecca J. Nicholls<sup>id a</sup> and Robert S. Weatherup<sup>id \*abe</sup>

Ni-rich layered oxide cathodes can deliver higher energy density batteries, but uncertainties remain over their charge compensation mechanisms and the degradation processes that limit cycle life. Trapped molecular O<sub>2</sub> has been identified within LiNiO<sub>2</sub> at high states of charge, as seen for Li-rich cathodes where excess capacity is associated with reversible oxygen redox. Here we show that bulk redox in LiNiO<sub>2</sub> occurs by Ni–O rehybridization, lowering the electron density on O sites, but importantly without the involvement of molecular O<sub>2</sub>. Instead, trapped O<sub>2</sub> is related to degradation at surfaces in contact with the electrolyte, and is accompanied by Ni reduction. O<sub>2</sub> is removed on discharge, but excess Ni<sup>2+</sup> persists forming a reduced surface layer, associated with impeded Li transport. This implicates the instability of delithiated LiNiO<sub>2</sub> in contact with the electrolyte in surface degradation through O<sub>2</sub> formation and Ni reduction, highlighting the importance of surface stabilisation strategies in suppressing LiNiO<sub>2</sub> degradation.

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## Broader context

Increasing the capacity of Li-ion batteries requires cathodes which can reversibly deintercalate more lithium without leading to structural instability and severe capacity fade. To this end, Ni-rich layered cathodes are under development for next-generation batteries, with LiNiO<sub>2</sub> the archetypal system for investigating their charging mechanisms. However, the role played by different redox centres in LiNiO<sub>2</sub> is still debated, and the connections with structural instabilities and associated degradation are not yet fully established. Recent reports have suggested the involvement of molecular O<sub>2</sub> in the bulk redox process at high states of charge, with direct experimental detection of O<sub>2</sub> based on techniques that probe 100–200 nm into the surface of the few μm-sized cathode particles. Here, we combine a broad suite of X-ray spectroscopies with varying information depths (10 nm to 10 μm) to separate the bulk redox from surface degradation. We reveal that trapped O<sub>2</sub> formation in LiNiO<sub>2</sub> is primarily associated with degradation at surfaces in contact with the electrolyte, rather than contributing to the bulk redox process. Interpretation of experimental spectra using theoretical calculations shows that bulk charge compensation proceeds by Ni–O rehybridization. These findings highlight the importance of using bulk sensitive techniques to understand redox, and suggests design strategies for stabilising high energy density Ni-rich cathodes.

<sup>a</sup> Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK.  
E-mail: robert.weatherup@materials.ox.ac.uk

<sup>b</sup> The Faraday Institution, Quad One, Harwell Science and Innovation Campus, Didcot OX11 0RA, UK

<sup>c</sup> Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Canada S7N 5E2

<sup>d</sup> ESRF – The European Synchrotron, 71 Avenue des Martyrs, 38000 Grenoble, France

<sup>e</sup> Diamond Light Source, Harwell Science and Innovation Campus, Didcot, OX11 0DE, UK

<sup>f</sup> Stewart Blusson Quantum Matter Institute, University of British Columbia, Vancouver, Canada V6T 1Z1

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## Introduction

Layered transition metal (TM) oxides, LiTMO<sub>2</sub> (TM = Co, Ni, Mn, etc.), are the cathode materials of choice for commercial high-energy density Li-ion batteries, reversibly intercalating Li over thousands of cycles.<sup>1,2</sup> Ni-rich stoichiometries are increasingly favoured to increase capacity, and lower Co content, which is expensive and has ethical concerns around its mining.<sup>3</sup> In the traditional picture of charge compensation, Li<sup>+</sup> removal is compensated by an increase in the formal oxidation state of the redox-active TM centres *via* a single



electron transfer. However, it is well-established that there are accompanying changes in TM–O bond covalency meaning both TM and O sites are involved.<sup>4–9</sup>

The archetypal Ni-rich cathode material, LiNiO<sub>2</sub>, undergoes several first-order structural phase transitions upon delithiation, with significant degradation observed at high potentials that has been associated with severe lattice changes,<sup>10,11</sup> structural degradation,<sup>12,13</sup> gas evolution,<sup>14,15</sup> and parasitic reactions with the electrolyte.<sup>16,17</sup> However, the causality and connections between these different modes of degradation are not yet fully established. Oxygen loss from the cathode surface and the associated formation of a reduced surface layer have been widely observed for Ni-rich cathode materials particularly above the H2–H3 transition,<sup>15,18–20</sup> and are found to depend critically on the upper cut off voltage (UCV) and electrolyte formulation.<sup>17,21–23</sup> Recently, studies of Ni-rich cathodes at high potentials ( $\geq 4.3$  V during charge) have also shown the emergence of a distinct signature in O K-edge resonant inelastic X-ray scattering (RIXS) spectra at an excitation energy of  $\sim 531.5$  eV.<sup>24–26</sup> For Li-rich materials that show excess capacity beyond TM cation redox, this signature is typically taken as evidence of the formation of molecular O<sub>2</sub> trapped in pores throughout the cathode bulk, as a result of charge compensation by non-bonding O orbitals.<sup>27,28</sup> However, the TM vacancies necessary to accommodate this are not expected in LiNiO<sub>2</sub>, with experimental samples typically containing excess Ni. Furthermore, LiNiO<sub>2</sub> does not exhibit excess capacity that might be associated with molecular O<sub>2</sub> redox. Nevertheless, bulk sensitive Ni K-edge X-ray absorption Near Edge Structure (XANES) measurements of LiNiO<sub>2</sub> have indicated a plateauing of the main edge half-height position at similarly high states of charge, which has been taken as evidence of the formal Ni oxidation state no longer changing in the bulk, and thus a change in the redox mechanism.<sup>29</sup>

Although O K-edge RIXS and the related fluorescence yield X-ray absorption spectroscopy (FY-XAS) are widely referred to as bulk-sensitive ( $\sim 200$  nm information depth), in the context of Li-ion cathode materials where typical secondary particle diameters are  $> 5$   $\mu\text{m}$ , these methods probe  $< 10\%$  of the particle volume nearest to the surface. Attribution of bulk molecular O<sub>2</sub> redox based on these methods alone is therefore ambiguous. Similar concerns have been raised around identifying oxygen redox with hard X-ray photoelectron spectroscopy (HAXPES), where typical probing depths are tens of nm.<sup>30</sup> Solid-state <sup>17</sup>O magic-angle-spinning nuclear magnetic resonance (NMR) spectroscopy provides an alternative bulk-averaged approach to estimate the amount of O<sub>2</sub> present in the lattice.<sup>31</sup> However, it does not resolve the spatial distribution of O<sub>2</sub> molecules, nor has it been reported for LiNiO<sub>2</sub> to date. Whereas, online electrochemical mass spectrometry (OEMS) can quantify the gas release associated with O-loss from the cathode surface, it does not probe molecular O<sub>2</sub> that remains trapped within the cathode.<sup>15,20,32</sup> The extent to which oxygen redox is involved in charge compensation in the LiNiO<sub>2</sub> bulk thus remains unclear, motivating approaches that can provide comparable information with surface- and bulk-sensitivity.

Here we combine complementary core-loss spectroscopies to obtain a depth-resolved (10 nm to  $> 10$   $\mu\text{m}$ ) account of the redox processes in LiNiO<sub>2</sub> and distinguish reversible bulk redox processes from near-surface degradation. X-ray Raman Spectroscopy (XRS,  $> 10$   $\mu\text{m}$  information depth) reveals that in the bulk of LiNiO<sub>2</sub> secondary particles there is a continuous change in both the Ni L<sub>3,2</sub>-edge and O K-edge spectra with state of charge (SoC) up to 4.8 V. This is consistent with charge compensation proceeding by rehybridization between the Ni and O centres, lowering the electron density on O sites but with Ni–O coordination still preserved. Features of trapped molecular O<sub>2</sub> appear at potentials of  $\geq 4.2$  V in O K-edge FY-XAS, accompanied by increased Ni<sup>2+</sup> contributions in the Ni L<sub>3,2</sub>-edge. Importantly, these changes are less pronounced in bulk-averaged XRS measurements indicating that formation of molecular O<sub>2</sub> is a predominantly surface process. Total Electron Yield (TEY)-XAS measurements ( $\sim 10$  nm information depth) confirm that a densified NiO-like layer forms in direct contact with electrolyte, whilst FY-XAS measurements are consistent with an extended cation mixing layer in which Ni<sup>2+</sup> ions have migrated to occupy Li sites. Scanning transmission electron microscopy–electron energy loss spectroscopy (STEM–EELS) further confirms this picture of a reduced surface layer (RSL) that extends  $\sim 200$  nm into the surface for LiNiO<sub>2</sub> which has been cycled to 4.8 V vs. Li/Li<sup>+</sup>. This understanding emphasises the importance of strategies to stabilise the interfaces of Ni-rich cathode materials in contact with electrolyte (*e.g.* cathode coatings/gradients, electrolyte formulation), rather than bulk stabilisation approaches (*e.g.* pillaring) that might sacrifice capacity.

## Results and discussion

### Trends in bulk chemical state

The charge–discharge profile for the 2nd cycle of the composite polycrystalline LiNiO<sub>2</sub> electrode is shown in Fig. 1(a), together with an inset showing a scanning electron micrograph (SEM) of the pristine LiNiO<sub>2</sub> active material (see ESI,† Fig. S1 for further characterisation). The  $\sim 5$   $\mu\text{m}$  diameter spheroidal LiNiO<sub>2</sub> secondary particles are composed of sub- $\mu\text{m}$  primary particles. The voltage profiles show distinct plateaus associated with the first-order structural phase transitions of LiNiO<sub>2</sub> on delithiation, apparent as maxima in the dQ/dV plots (Fig. 1(b)), at potentials consistent with prior literature.<sup>15,33,34</sup> Powder X-ray diffraction (XRD) of the pristine material (see ESI,† Fig. S1c) closely resembles the calculated pattern for LiNiO<sub>2</sub> with the R3m space group. This hexagonal H1 phase transitions to the monoclinic M phase at  $\sim 3.67$  V, then to the H2 phase at  $\sim 4.0$  V, followed by the H3 phase at  $\sim 4.2$  V. The voltage profile shows noticeable hysteresis above  $\sim 4.3$  V, with the voltage rapidly dropping from 4.8 V to  $\sim 4.2$  V on discharge. However, the capacity reached at 4.8 V is 256 mA h g<sup>−1</sup> which compares with a maximum theoretical capacity of 264 mA h g<sup>−1</sup>, based on the pristine material having  $\sim 4\%$  Ni excess as determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES).<sup>26</sup> This provides an initial indication that the full capacity





**Fig. 1** Bulk-sensitive probing of LiNiO<sub>2</sub> redox processes. (a) 2nd cycle charge–discharge profile of LiNiO<sub>2</sub> electrode cycled at a rate of C/20 between 3.0 and 4.8 V vs. Li/Li<sup>+</sup>. Inset: Scanning electron microscope (SEM) image of pristine LiNiO<sub>2</sub> particles. (b) Corresponding differential capacity plots (dQ/dV). (c), Normalised Ni K-edge XANES spectra (transmission mode) of LiNiO<sub>2</sub> at different SoC. (d) Plot of the energy shift in normalised Ni K-edge whiteline and 50% edge height positions relative to pristine LiNiO<sub>2</sub>. (e) and (f) XRS (~10 μm information depth) of the O K-edge and Ni L<sub>3</sub>-edge core-loss spectra for LiNiO<sub>2</sub> electrodes at different SoC during the 2nd charge cycle. Experimental XRS data is marked as black dots and represented with smooth solid trace lines. Charge transfer multiplet (CTM) calculations of formally Ni<sup>2+</sup> (green), Ni<sup>3+</sup> (purple), and Ni<sup>4+</sup> (pink) environments. See ESI,† Fig. S2 for fitted XRS Ni L<sub>3,2</sub>-edges.

of the electrode can be accounted for by formal Ni redox alone, without obvious excess capacity associated with molecular O<sub>2</sub> redox.

Fig. 1(c) shows normalised transmission Ni K-edge XANES spectra for the LiNiO<sub>2</sub> electrodes at different SoC ( $x$  in Li<sub>1-x</sub>NiO<sub>2</sub>) during the 2nd charge cycle. As expected, the Ni K-edge shifts to higher energies as the formal Ni oxidation state increases, with the removal of valence electrons leaving the Ni nucleus less-shielded such that it has a higher effective charge, and the core-level becomes more strongly bound. Both the energy of the fractional (normalised) edge height and the position of the white-line (intensity maximum) are routinely used as indirect measures of average oxidation state.<sup>35,36</sup> A continuous shift to higher energy in both the edge half-height and whiteline is observed up to 4.2 V,  $x = 0.22$  (Fig. 1(d)). The two trends diverge with further delithiation, with the whiteline monotonically shifting to higher energy up to the furthest measured extent of delithiation (4.8 V,  $x = 0.03$ ), while the half-height position plateaus with little variation between  $x = 0.10$  and  $x = 0.03$ . The plateau of half-height position has previously been taken as an indication that Ni is no longer involved in the redox mechanism at high SoC,<sup>24,25</sup> however the continuing shift in whiteline position would suggest otherwise. Indeed, the edge-position is known to be sensitive to other factors including bond length and ligand covalency.<sup>37</sup>

To resolve this ambiguity without introducing surface sensitivity as a confounding factor, bulk-sensitive XRS was performed to collect O K-edge (Fig. 1(e)) and Ni L<sub>3</sub>-edge (Fig. 1(f)) spectra at the same SoC as the XANES. XRS probes lower-energy O 1s → 2p and Ni 2p → 3d transitions using hard X-rays (10 keV), achieving an information depth of ~10 μm which is similar to Ni K-edge XANES. In Fig. 1(e), pristine LiNiO<sub>2</sub> exhibits a prominent asymmetric O K pre-edge feature centred at 528.8 eV associated with transitions from O 1s → O 2p-Ni 3d hybridised states, and main edge features above 535.0 eV associated with transitions from O 1s → O 2p-Ni 4s,p hybridised states. On delithiation, the pre-edge peak is seen to continuously increase in relative intensity, whilst losing its asymmetry and shifting by 0.4 eV to a higher peak energy of 529.2 eV. There is also an accompanying shift in the main edge half-height position from ~536.0 eV for pristine LiNiO<sub>2</sub> up to 539.5 eV at 4.8 V, and the shape of the main edge changes indicating a change in the O2p and Ni4s,p orbital hybridisation. Importantly, across the potentials probed, the feature arising at ~531.5 eV associated with the formation of molecular O<sub>2</sub> is not strongly pronounced.<sup>24–26</sup>

The corresponding Ni L<sub>3</sub>-edge XRS (Fig. 1(f)) for pristine LiNiO<sub>2</sub> shows a broad line shape composed of three main features at 853.6 eV, 854.9 eV, and 856.1 eV. There remains



debate over the ground state of  $\text{LiNiO}_2$  (see Supplementary Note 1, ESI†) and a variety of models based on alternating layers of  $\text{NiO}_6$  octahedra and Li have been proposed. The simplest model, in which all  $\text{NiO}_6$  octahedra are equivalent with a formal oxidation state of  $\text{Ni}^{3+}$ , is compatible with XRD data but not with measurements using more local probes.<sup>38,39</sup> As a result, more complex models involving time or spatially varying distortions of the octahedra have been proposed. These include structures with Jahn–Teller (J–T) distortions, where two different Ni–O bond lengths are present and the formal oxidation state remains  $\text{Ni}^{3+}$ ,<sup>40</sup> and spin disproportionated structures, where  $\text{Ni}^{2+}$  ( $S = 1$ ),  $\text{Ni}^{3+}$  ( $S = \frac{1}{2}$ ), and  $\text{Ni}^{4+}$  ( $S = 0$ ) octahedra coexist and interconvert dynamically at room temperature.<sup>41,42</sup> Recent temperature-dependent XAS and X-ray magnetic circular dichroism (XMCD) shows strong evidence for such disproportionation in  $\text{LiNiO}_2$ ,<sup>41</sup> which is consistent with other correlated nickelate compounds, including  $\text{AgNiO}_2$ , which show disproportionation and strong covalency between frontier O 2p and Ni 3d states.<sup>43–47</sup>

Charge transfer multiplet (CTM) calculated  $L_3$ -edges for the three Ni environments with formal oxidation states of +2, +3 and +4 are overlaid on the pristine  $\text{LiNiO}_2$  spectra in Fig. 1(f), corresponding to the three main features at 853.6 eV, 854.9 eV, and 856.1 eV seen in Ni  $L_3$ -edge XRS. Simulation parameters have been optimised based on experimental data (Supplementary Note 3, ESI†). Each simulated spectra can be thought of as a superposition of metal–ligand hole configurations,<sup>47</sup> with the formally  $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$ , and  $\text{Ni}^{4+}$  octahedra having ground-state configurations of  $0.80|3d^8\rangle + 0.19|3d^9\bar{L}\rangle + 0.01|3d^{10}\bar{L}^2\rangle$ ,  $0.25|3d^7\rangle + 0.58|3d^8\bar{L}\rangle + 0.16|3d^9\bar{L}^2\rangle + 0.01|3d^{10}\bar{L}^3\rangle$ ,  $0.04|3d^6\rangle$

+  $0.33|3d^7\bar{L}\rangle + 0.48|3d^8\bar{L}^2\rangle + 0.14|3d^9\bar{L}^3\rangle + 0.01|3d^{10}\bar{L}^4\rangle$  respectively. In CTM calculations, increasing ligand hole contributions indicate an increasing degree of Ni–O covalency for higher formal oxidation states. Linear combinations of the simulated spectra match closely to the Ni  $L_3$ -edge spectra from XRS, FY-XAS and TEY-XAS at all SoC (ESI† Fig. S2–S5), indicating that the simulated spectra for the  $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$  and  $\text{Ni}^{4+}$  environments are suitable descriptions despite the small changes in octahedral environment expected for different phases.

On cycling to higher potentials, the XRS shows a continuous growth in the intensity of the  $\text{Ni}^{4+}$  feature (see Fig. 2(d)), initially at the expense of  $\text{Ni}^{2+}$  up to 3.9 V,  $x = 0.55$ , and then  $\text{Ni}^{3+}$  up to 4.8 V,  $x = 0.03$ . This evolution of Ni species upon delithiation matches that expected from disproportionation.<sup>41</sup> At 4.8 V, the spectrum closely matches Ni  $L_3$ -edge simulations of  $\text{Ni}^{4+}$  (ESI† Fig. S6) with 4–5%  $\text{Ni}^{2+}$ . This is consistent with the excess Ni detected with ICP-OES occupying Li sites, as similarly sized  $\text{Ni}^{2+}$ , and thus preventing all sites reaching  $\text{Ni}^{4+}$ .<sup>26,48</sup> The bulk sensitivity of XRS suppresses contributions from surface layers which are otherwise seen even for inverse partial fluorescence yield (IPFY) measurements (ESI† Fig. S7), including for reference  $\text{Ni}^{4+}$  compounds.<sup>49,50</sup> Importantly this shows that charge compensation in the  $\text{LiNiO}_2$  bulk proceeds predominantly through Ni–O rehybridization across the whole cycling range, lowering the electron density on O sites, but without a significant role for molecular  $\text{O}_2$  redox. This contrasts with several reports of oxygen redox in this potential range for  $\text{LiNiO}_2$  and Ni-rich layered cathode materials, based on detection of the molecular  $\text{O}_2$  feature with less bulk-sensitive O K-edge RIXS.<sup>24–26,51</sup>



Fig. 2 Near-surface probing of  $\text{LiNiO}_2$  redox processes. (a) and (b) FY-XAS ( $\sim 200$  nm information depth) of the O K-edge and Ni  $L_3$ -edge, and (c) TEY-XAS ( $\sim 10$  nm information depth) of the Ni  $L_3$ -edge for  $\text{LiNiO}_2$  at different SoC. (d) Relative intensities of  $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$ , and  $\text{Ni}^{4+}$  components based on fitting CTM calculated spectra to XRS, FY-XAS, and TEY-XAS spectra (see fitting results in ESI† Fig. S2–S5).



## Near-surface degradation

To further investigate the origins of molecular O<sub>2</sub> reported at high SoC, the same core levels were measured using soft XAS in FY mode (Fig. 2(a) and (b)). The spectra for pristine LiNiO<sub>2</sub> closely resemble those obtained with XRS, however an additional feature is apparent at 532.3 eV in the O K-edge, and the Ni<sup>2+</sup> feature in the Ni L<sub>3</sub>-edge is more intense. These same features are seen for NiO (see ESI,† Fig. S8 for O K-edge), and correspond to a NiO-like RSL,<sup>52</sup> whose contribution is not detected in the more bulk-sensitive XRS. On delithiation, the XAS data show similar trends to the XRS until 4.1 V,  $x = 0.33$ , with the Ni L<sub>3</sub>-edge showing the Ni<sup>4+</sup> feature increasing at the expense of Ni<sup>2+</sup> and then Ni<sup>3+</sup>, and some growth in the O K pre-edge. At higher SoC there are significant deviations between FY-XAS and XRS spectra. Most notably a feature at ~531.5 eV is seen to emerge in the O K-edge, which although initially weak at 4.2 V,  $x = 0.22$ , shows significant intensity at 4.8 V,  $x = 0.03$  (see integrated peak areas in ESI,† Fig. S9). This feature corresponds to the same absorption energy as molecular O<sub>2</sub>, whose vibrational structure has been detected in LiNiO<sub>2</sub> and other conventional Ni-rich layered oxides in several recent reports.<sup>25,26</sup> Whereas this molecular O<sub>2</sub> signature and the Ni<sup>2+</sup> feature grow in FY-XAS, the O K pre-edge peak and the Ni<sup>4+</sup> feature in the Ni L<sub>3</sub>-edge are suppressed in FY-XAS compared to the XRS. This suggests a near-surface molecular O<sub>2</sub> redox process associated with RSL growth, in which Ni is reduced

toward Ni<sup>2+</sup> and molecular O<sub>2</sub> forms *i.e.*, NiO<sub>2</sub> → NiO<sub>2-x</sub> + ½xO<sub>2</sub>. Similar trends are observed with the more surface-sensitive TEY-XAS (fits shown in ESI,† Fig. S4) consistent with RSL formation proceeding from electrolyte-exposed surfaces.<sup>21,52</sup> Importantly, the bulk-sensitive XRS (Fig. 1(e) and (f)) does not detect such Ni reduction or O<sub>2</sub> formation, even after charging to 4.8 V, highlighting the key connection between the formation of trapped molecular O<sub>2</sub> and the increase in Ni<sup>2+</sup> species close to the cathode surface.

We now investigate the reversibility of this near-surface molecular O<sub>2</sub> redox process and how its extent changes with upper cutoff voltage (UCV). Fig. 3(a) shows that after discharging from a UCV of 4.8 V to 4.0 V, the molecular O<sub>2</sub> feature at ~531.5 eV disappears from the O K-edge, but a prominent RSL feature at 532.6 eV remains. On discharge to 3.0 V, the RSL feature further grows in intensity relative to the pre-edge feature, with accompanying increases in the Ni<sup>2+</sup> feature for the Ni L<sub>3</sub>-edge spectra (Fig. 3(b) and (c)). This is even more prominent in the surface-sensitive TEY-XAS (Fig. 3(c)), indicating the RSL is more densified near to the surface. Comparison to an electrode where the UCV is 4.2 V confirms that the extent of RSL formation is much greater for the UCV of 4.8 V, consistent with previous studies where significant RSL formation occurs at SoC above the H2-H3 transition in Ni-rich cathodes.<sup>20,21,52</sup> Longer-term cycling (150 cycles, ESI,† Fig. S10) further shows that the UCV of 4.8V leads to greater voltage



Fig. 3 Discharge behaviour of LiNiO<sub>2</sub>. (a), (b) FY-XAS (~200 nm information depth) of the O K-edge and Ni L<sub>3</sub>-edge, and (c) TEY-XAS (~10 nm information depth) of the Ni L<sub>3</sub>-edge for LiNiO<sub>2</sub> cycled to a UCV of 4.2 V before being discharged to (i) 4.0 V and (ii) 3.0 V, with parallel samples cycled to a higher UCV of 4.8 V and then back to (iii) 4.0 V and (iv) 3.0 V.



hysteresis and charge transfer impedance reflecting this more extensive RSL formation.

Although comparison of TEY and FY mode XAS confirms the RSL is found predominantly near the sample surface, it provides only limited insight into the depth over which it is distributed. To spatially resolve the extent of the RSL at high SoCs, STEM-EELS was performed for LiNiO<sub>2</sub> charged to 4.8 V (Fig. 4). Depth-resolved Ni L<sub>3</sub>-spectra show a decreasing proportion of the lower energy (more reduced) component (peak A1) on moving towards the bulk of the particle, stabilising at ~200 nm from surface, consistent with more Ni<sup>2+</sup> species at the surface and more Ni<sup>3+</sup> in the bulk. Similarly, the O K-edge shows a higher pre-edge intensity (peak B1) towards the bulk of the particle correlating with higher Ni oxidation state and Ni–O covalency. This extended RSL region where the Ni oxidation state is seen to vary over ~200 nm is attributable to a cation mixing layer in which Ni<sup>2+</sup> ions have migrated to occupy Li sites, and is consistent with the differences seen between TEY-XAS, FY-XAS and XRS observations. Notably, a similar extent of RSL formation is not observed at intergranular cracks away from the LiNiO<sub>2</sub> surface, presumably as electrolyte does not fully penetrate these cracks for the low cycle numbers considered here. This indicates a key role of the electrolyte in promoting RSL formation, with electrolyte infiltration into internal cracks likely proceeding over multiple cycles.

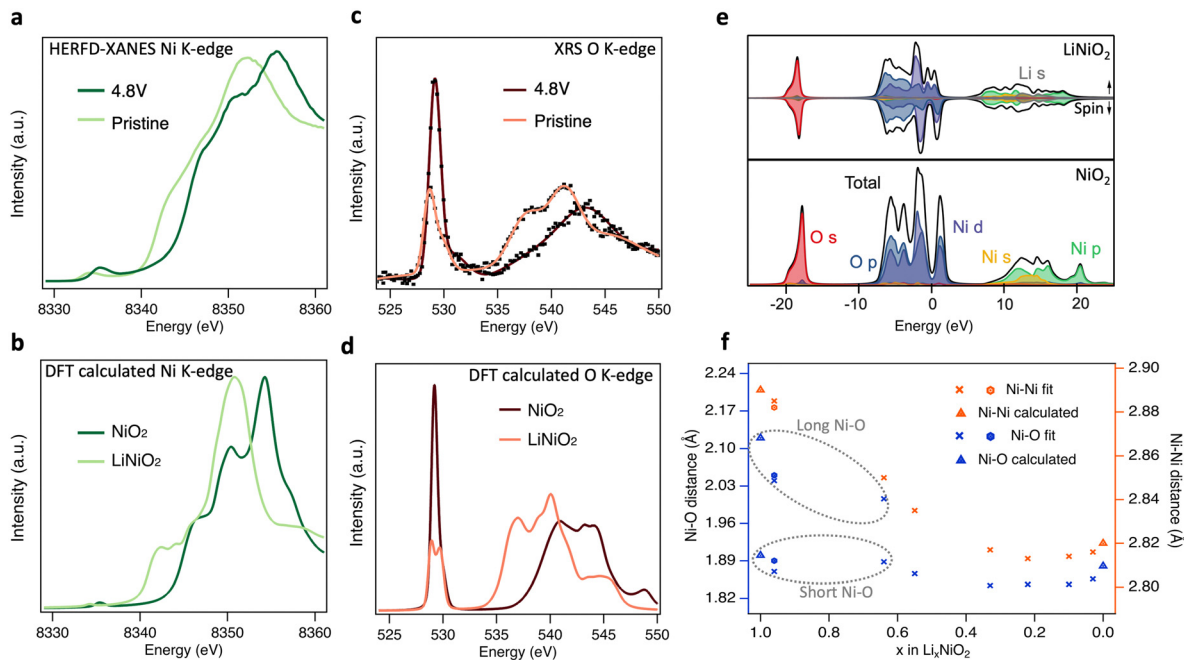
### Bulk electronic and geometric structural evolution of LiNiO<sub>2</sub>

Having shown that bulk redox in LiNiO<sub>2</sub> occurs by Ni–O rehybridization, we now consider further the associated changes in electronic and geometric structure. Fig. 5(a) shows high-energy-resolution fluorescence detection (HERFD)-XANES Ni K-edge spectra of pristine LiNiO<sub>2</sub> and after cycling to 4.8 V. Notably the main edge half-height position is shifted ~2.1 eV higher compared to LiNiO<sub>2</sub>, a more distinct change than seen in the transmission mode measurements of Fig. 1(c) (~1.5 eV), as a result of the fine-structure features along the rising edge now being better resolved. Fig. 5(c) compares the similarly bulk-sensitive O K-edge XRS spectra of the same samples. Since we anticipate that differing Ni–O bond lengths yield distinct signatures in the O K pre-edge in any model of the material, we chose the zigzag J–T *P2<sub>1</sub>/c* structure for LiNiO<sub>2</sub> spectral calculations. More complex time-varying LiNiO<sub>2</sub> model structures are computationally prohibitive for spectral calculations and although the *P2<sub>1</sub>/c* structure has a formal oxidation state of Ni<sup>3+</sup>, this will predominantly affect the Ni 3d states, which only weakly influence the main features of the Ni and O K-edge spectra. Density functional theory (DFT) calculated Ni and O K-edge spectra for LiNiO<sub>2</sub> and NiO<sub>2</sub> (Fig. 5(b) and (d)), reproduce the features of the experimental spectra extremely well, showing the same pre-edge peaks, number of fine structure features, and similar trends in intensity and linewidths across the whole spectral range. The relative energy shifts are also captured well,



Fig. 4 (a) Cross-sectional scanning electron microscopy (secondary electron detection) of LiNiO<sub>2</sub> particle from an electrode charged to 4.8 V. (b) Selected STEM-EELS scan area of 1.5 μm from surface to bulk (left to right) of the particle. (c) and (d) Fitted peak ratios of depth-resolved Ni L<sub>3</sub>- and O K-edge EELS spectra using a simplified two peak fit in each case (see ESI,† Fig. S11). Insets: Examples of EELS spectra.





**Fig. 5** Electronic and geometric structural changes of  $\text{LiNiO}_2$  upon delithiation. (a) Experimental HERFD-XANES and (b) core-hole calculated Ni K-edge spectra of pristine and charged  $\text{LiNiO}_2$ . (c) Experimental XRS with smooth trace lines and (d) core-hole calculated O K-edge spectra of pristine and charged  $\text{LiNiO}_2$ . (e) Ground-state partial and total density of states for  $\text{LiNiO}_2$  (top) and  $\text{NiO}_2$  (bottom). Fermi energies are set to zero. (f) Ni–Ni and Ni–O distances determined from the Fourier-transformed EXAFS spectra (details in ESI,† Table S1 and Fig. S12, S13). Note that the short/long Ni–O lengths of pristine (hexagons), 3.0 V and 3.8 V (crosses)  $\text{LiNiO}_2$  are related to the disproportionated model applied for EXAFS fitting. Bond lengths for the geometry optimised structures from DFT calculations used in (b), (d), (e) are shown as triangles in f.

giving confidence in the sufficiency of the chosen structure models ( $P2_1/c$  for  $\text{LiNiO}_2$ , and  $R\bar{3}m$  for  $\text{NiO}_2$ ).

The origin of the spectral features can be understood by comparison to ground-state partial density-of-states (pDOS) shown in Fig. 5(e), and consideration of the allowed spectroscopic transitions. The first unoccupied states in both  $\text{LiNiO}_2$  and  $\text{NiO}_2$  lie just above 0 eV, showing mixed O 2p and Ni 3d orbital character and giving rise to the pre-edge peaks in the experimental Ni ( $\sim 8335$  eV) and O ( $\sim 529$  eV) K-edges. A sizable gap separates the next set of unoccupied states which give rise to the main edges in the Ni ( $\geq 8340$  eV) and O ( $\geq 535$  eV) K-edges, and have Ni 4s,p character, with some Li 2s contribution also seen in this region for  $\text{LiNiO}_2$ . This gap widens by  $\sim 2.9$  eV from  $\text{LiNiO}_2$  to  $\text{NiO}_2$  which can be related to a decrease in average Ni–O bond length associated with the change in geometric structure.<sup>53,54</sup> We note that the DFT calculated Ni K-edge spectra show weaker pre-edge features than experiment, attributable to quadrupolar transitions not being considered in the calculations.<sup>55</sup>

A clear splitting of the calculated O K pre-edge peak in Fig. 5(d) for  $\text{LiNiO}_2$  resembles the asymmetric pre-edge in the XRS experimental data. The O K pre-edge becomes far more intense in the 4.8 V sample and the peak splitting seen in the calculated spectrum of  $\text{LiNiO}_2$  is lost. This corresponds with the change from  $D_{4h}$  site symmetry for the J–T distorted  $\text{Ni}^{3+}$  octahedra used in the  $\text{LiNiO}_2$  calculation, where d orbital splitting arises from the elongation of two Ni–O bonds, to  $O_h$  site symmetry for the  $\text{Ni}^{4+}$  octahedra of  $\text{NiO}_2$ , where this d

orbital splitting is lost. The growth in intensity of the O K pre-edge feature is also consistent with the CTM calculations, where the increased ligand hole contributions for the  $\text{Ni}^{4+}$  octahedra indicate an increasing degree of Ni–O covalency on delithiation. The increase of O K pre-edge intensity by a factor of  $\sim 2$  on full delithiation (see ESI,† Fig. S9) corresponds closely to the factor of  $\sim 1.8$  obtained based on the proportions of Ni species fitted to the Ni  $L_{3,2}$ -edge XRS spectra (Fig. 2(d)) and their respective electron configurations. Further evidence for increased Ni–O covalency is apparent from the emergence of more distinct fine-structure features ( $\sim 8347$  eV and 8351 eV) in the Ni K-edge, attributable to ligand-to-metal charge transfer shakedown transitions,<sup>56</sup> as well as satellite peaks in the Ni  $L_{3,2}$ -edge that are most clearly seen in FY-XAS measurements (see ESI,† Fig. S14b) and are well-reproduced in the CTM calculated  $\text{Ni}^{4+}$  spectrum. In addition, Bader charge analysis<sup>57</sup> based on the ground-state DFT calculations shows the ionic charge of the Ni only modestly changes from  $+1.41$  to  $+1.56 e^-$  between  $\text{LiNiO}_2$  and  $\text{NiO}_2$ , whilst a more significant change from  $-1.15$  to  $-0.78 e^-$  is seen for the O charges.

Fig. 5(f) shows the nearest Ni–O and Ni–Ni distances extracted by fitting to EXAFS spectra for  $\text{LiNiO}_2$  at different SoC. Since fitting with the single Ni–O bond length model showed significantly higher Debye–Waller factors at low SoC, and disproportionation is expected to persist up to 3.9 V based on Fig. 2(d), a model with two Ni–O bond lengths (ratio of short:long Ni–O bond based on the disproportionated model and associated XRS fittings) was instead used to fit pristine,





Fig. 6 Schematic representation of  $\text{LiNiO}_2$  bulk charge compensation mechanism and surface degradation processes probed by different X-ray spectroscopy techniques. The differences in  $\text{LiNiO}_2$  delithiation occurring at the surface and in the bulk, including the accommodation of trapped  $\text{O}_2$  in pores formed near the surface by  $\text{Ni}^{2+}$  species migrating to the Li layer. Continuous oxidation of Ni in bulk  $\text{LiNiO}_2$  at high SoC is distinguished from the near surface degradation.

3.0 V and 3.8 V  $\text{LiNiO}_2$  (see ESI,† Fig. S15 and Table S2). The Ni–O and Ni–Ni bond distances obtained show good agreement with both the J–T  $P2_1/c$   $\text{LiNiO}_2$  and the disproportionated structure, however, the short:long bond ratios of the disproportionated model show lower Debye–Waller factors, supporting assignment of this structure.

Similar trends in weighted average Ni–O bond lengths are seen to *operando* neutron diffraction measurements,<sup>34</sup> with Ni–O bond length gradually shrinking in line with the change in structure, increased oxidation state and increased covalency at high SoC. Notably, above the H2–H3 transition ( $x \leq 0.22$ ) a modest increase in the Ni–O bond length is observed. This has been associated with a loss of the stabilising effect of Li–O covalency at high SoC, leading to Ni–O bond elongation alongside the sudden *c*-lattice collapse related to the H2–H3 transition, and increased charge transfer from the O to Ni sites.<sup>11,58,59</sup> This changing covalency, seen as continuous spectral changes in Fig. 1(c) and (d), can account for the plateauing in half-height position of the Ni K main-edge at high SoC in transmission XANES (Fig. 1(d)). As well as highlighting the limitations of applying a single metric to assess changes in oxidation state, the limited sensitivity of the Ni K-edge fractional-edge height reflects that it arises from transitions to Ni 4s,p states, in contrast to the O K- and Ni  $L_{3,2}$ -edges which probe transitions to O 2p–Ni 3d hybridised states.

## Conclusion

In summary, bulk sensitive XRS measurements reveal that in the bulk of  $\text{LiNiO}_2$ , charge compensation occurs by Ni–O rehybridization without the involvement of molecular  $\text{O}_2$ . From an initially disproportionated structure where formally  $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$ , and  $\text{Ni}^{4+}$  octahedra coexist, the  $\text{Ni}^{4+}$  features of the Ni  $L_{3,2}$ -edge

continuously grow on delithiation, initially at the expense of  $\text{Ni}^{2+}$  and subsequently  $\text{Ni}^{3+}$  features (see Fig. 6). There is a concomitant increase in O K pre-edge intensity, consistent with significant lowering of electron density on the O sites at potentials where O loss is expected.<sup>9,50</sup> However, significant signatures of molecular  $\text{O}_2$  formation are not detected throughout the bulk suggesting its formation remains kinetically hindered.<sup>60</sup>

FY-XAS measurements reveal evidence of molecular  $\text{O}_2$  formation in the outer  $\sim 200$  nm of the cathode surface, with the growth in intensity of the  $\text{Ni}^{4+}$  feature plateauing above 4.2 V, and features of trapped molecular  $\text{O}_2$  emerging alongside increased  $\text{Ni}^{2+}$  contributions. This is consistent with molecular  $\text{O}_2$  trapped in voids formed by  $\text{Ni}^{2+}$  entering the Li layers (see Fig. 6). STEM-EELS reveals a RSL that extends  $\sim 200$  nm into the  $\text{LiNiO}_2$  surface following cycling to 4.8 V, showing a gradual change in oxidation state across its thickness. The absence of this extended RSL at internal surfaces of the secondary cathode particles, *e.g.* interparticle cracks, suggests its formation is driven by contact with the electrolyte.

The trapped molecular  $\text{O}_2$  feature disappears on discharging to 4.0 V, but a significantly increased near-surface  $\text{Ni}^{2+}$  contribution is retained. Although our results do not fully exclude some reversible molecular  $\text{O}_2$  redox, online electrochemical mass spectroscopy studies have reported  $\text{O}_2$  evolution occurring on discharge.<sup>15</sup> We therefore suggest that this may arise from the release of trapped  $\text{O}_2$  associated with structural changes, including abrupt *c*-lattice expansion and particle cracking (ESI,† Fig. S16).

Our findings highlight the importance of combining bulk- and surface-sensitive techniques to fully confirm the extent to which molecular  $\text{O}_2$  redox processes in cathode materials are bulk phenomena contributing to reversible charge compensation, rather than involved in surface degradation as revealed here for  $\text{LiNiO}_2$ . The understanding developed of the surface



instability of LiNiO<sub>2</sub> associated with rehybridisation at high SoC, emphasises the importance of strategies such as cathode coatings, composition gradients, and electrolyte formulation to stabilise Ni-rich cathode surfaces in contact with electrolyte, rather than bulk stabilisation approaches (*e.g.* pillaring) that might unduly sacrifice capacity. This study thus provides a solid basis for future exploration of molecular O<sub>2</sub> formation and Ni–O rehybridisation in Ni-rich cathodes in different electrolyte environments, and for further investigations to separate bulk redox and near-surface degradation processes in a broad range of cathode materials.

## Experimental

### Sample preparation

Commercial grade LiNiO<sub>2</sub> powder was obtained from BASF, without any deliberate doping or coating added. This was characterised by SEM (Zeiss Merlin, 2 kV, Inlens detector), XRD (Rigaku Miniflex, Cu K $\alpha$  source), and X-ray Photoelectron Spectroscopy (XPS, PHI Versaprobe III, Al K $\alpha$  source), see ESI,† Fig. S1. Free-standing electrodes were prepared by calendaring a mixture of 80 wt% LiNiO<sub>2</sub> powder, 10 wt% conductive acetylene black and 10 wt% polytetrafluoroethylene (PTFE) binder. Electrochemical tests of the LiNiO<sub>2</sub> cathodes were performed in 2032 coin cells (316 stainless steel, Cambridge Energy Solutions) using Li metal disks as negative electrodes and borosilicate glass fibre separators (borosilicate, GF/A, Whatman) soaked with 120  $\mu$ L of LP57 electrolyte (1 M LiPF<sub>6</sub> in 3 : 7 of EC : EMC). The assembled cells were charged up to 4.2 V at C/20 (calculated based on a theoretical capacity of LiNiO<sub>2</sub> of 275 mA h g<sup>-1</sup>), held for 30 min and then cycled back to 3.0 V at the same rate. This was immediately followed by a second charge at C/20 (ESI,† Fig. S1), with a voltage hold for 10 hours at the desired endpoint. The SoC of delithiated Li<sub>x</sub>NiO<sub>2</sub> is calculated based on the charge–discharge capacity curve presented in Fig. 1(a), starting from  $x = 0.96$  for pristine and 3.0 V LiNiO<sub>2</sub> (based on the  $\sim 4\%$  Ni excess). All potentials mentioned in this work are referenced to Li/Li<sup>+</sup>. For *ex situ* measurements, cathodes were recovered from the cycled coin cells by disassembly in a glove box under Ar atmosphere (O<sub>2</sub> < 1 ppm, H<sub>2</sub>O < 1 ppm). Recovered cathodes were washed in dimethyl carbonate (anhydrous,  $\geq 99\%$ , Sigma Aldrich) solvent and dried before heat-sealing in aluminised mylar (Fresherpack, 130  $\mu$ m) pouches for XANES, EXAFS, and XRS, or transferring in a vacuum suitcase for XAS, XPS.

### Electron microscopy

A Thermo Scientific Helios G4 CXe Plasma FIB (PFIB) was used to prepare the STEM lamellae. For lift-out, a thin Pt layer was deposited onto the surface region of interest (ROI), trenches were patterned around the ROI to make 4  $\mu$ m-thick lamellae. A W needle was then used to lift each lamella and place them on a FIB lift-out grid (Cu, Agar Scientific). Each lamellae was then thinned down to around 50 nm thick for STEM-EELS and polished with a low dose, low energy beam (<0.3 nA, 5 keV)

to minimise ion beam damage. Inert transfer between PFIB and an Ar glovebox was achieved using a Gatan iLoad system.

Spatially resolved EELS of the lamellae was performed using a JEOL ARM200F equipped with cold field emission gun operated at 200 keV and spherical aberration probe corrector. Dual EELS was acquired using a Gatan GIF Quantum 965 ER with energy resolution of around 1 eV at 0.25 eV per channel dispersion. Inert transfer between glovebox and STEM was achieved using a JEOL double-tilt vacuum transfer holder.

Given LiNiO<sub>2</sub> is less stable when highly delithiated, radiation damage should be considered when evaluating the oxidation state of Ni in EELS. The energised Xe ion beam in PFIB and electron beam in STEM can both induce reduction of LiNiO<sub>2</sub> and NiO<sub>2</sub> towards NiO.<sup>61</sup> The absolute A<sub>2</sub>/A<sub>1</sub>, and B<sub>2</sub>/B<sub>1</sub> ratios seen in the LiNiO<sub>2</sub> bulk reflect some degree of ion/electron beam induced reduction. Nevertheless, equal acquisition time and constant electron beam current during the EELS scans ensure a consistent radiation dose ( $3 \times 10^3 \text{ e}^- \text{ \AA}^{-2}$ ) such that the trends in EELS spectra and the spatial variations seen near their surface are still representative.

### X-ray spectroscopy

Transmission Ni K-edge XANES and EXAFS spectra were collected with a laboratory-based easyXAFS300+ spectrometer (easyXAFS, WA, US). X-rays are generated with a liquid-cooled Ag anode X-ray tube, before monochromation by a Si (551) spherically bent crystal analyser. A helium-filled box with polyimide windows is placed in the beam path for better X-ray transparency while a steel plate with a 9  $\times$  3 mm slot is placed after each sample to lower the background. The transmitted intensity is measured with a silicon drift detector (KETEK, Munich, Germany) placed behind the sample. Each acquisition was performed over 45 min and 30 scans were collected for each sample to obtain good statistics. NiO reference spectra were also collected for each batch of measurements for energy calibration. Data pre-processing was performed with the EasyXANES package to convert the measured intensity into linear attenuation coefficient,  $\mu$ . Data reduction and analysis were performed using the Demeter package (version: 0.9.26).

*In situ* HERFD-XANES was performed at Diamond Light Source's beamline I20 with aluminised mylar (Fresherpack, 130  $\mu$ m) pouch cells containing free-standing LiNiO<sub>2</sub> cathodes, with Li metal disks as negative electrodes and a Celgard 2325 separator soaked with 80  $\mu$ L of LP57 electrolyte (1 M LiPF<sub>6</sub> in 3 : 7 of EC : EMC). The cells were held at the desired potentials, and measured through the cathode side of the pouches using an X-ray emission spectrometer equipped with three Si(444) analyser crystals.<sup>62</sup> The spectrometer was set to the maximum of the Ni K $\beta_{1,3}$  line (8266 eV), and the incident energy was scanned using the four-bounce Si(111) monochromator. The spectrometer was calibrated using a Ni foil, measuring the K $\beta$  line with the incident energy tuned +300 eV from the Ni K-edge.

TEY- and FY-XAS measurements were performed at ES-2 of beamline B07-B at Diamond Light Source, with the exit slits set to 50  $\mu$ m in the dispersive direction, yielding a flux of between



$1 \times 10^{11}$  (O K-edge) and  $2 \times 10^{11}$  (Ni  $L_{3,2}$ -edge) photons  $s^{-1}$ . All samples were measured with the incident beam normal to the electrode surface, yielding a beam footprint of  $150 \times 100 \mu\text{m}$ . FY-XAS measurements were acquired using an Al coated Si photodiode directed at the sample with its surface normal at  $\sim 45^\circ$  to incident beam direction. Simultaneous TEY-XAS measurements were obtained using a SR570 low-noise current amplifier (Stanford Research Systems) to collect the current between the sample plate and an isolated steel washer in front of the sample biased to +90 V. Separate IPFY-XAS measurements of the Ni  $L_{3,2}$ -edge were acquired using a Vortex silicon drift detector (Hitachi) at the I10 beamline at Diamond Light Source, with FY and TEY mode measurements simultaneously acquired. All spectra are divided by the drain current measured from the last X-ray mirror, to correct for variations in incident photon flux. The photon energy scale is calibrated using a NiO sample.<sup>63</sup> O K-edge spectra are background-subtracted using a straight line fitted to the pre-edge region, followed by intensity normalization to the post-edge region at 550 eV. Ni  $L_{3,2}$ -edge spectra are normalized to the intensity at 867 eV after removal of a linear background.

XRS measurements were performed at the European Synchrotron Radiation Facility at the ID20 beamline.<sup>64</sup> X-rays are generated from three U26 revolver undulators, before being collimated, and then monochromated by a liquid-nitrogen cooled double-crystal Si(111) pre-monochromator. The beam from a second Si(311) channel-cut post-monochromator is focussed onto a  $\sim 20 \times 20 \mu\text{m}^2$  spot at the sample position by a mirror in Kirkpatrick-Baez geometry. The sample surface was positioned at a grazing angle of  $\sim 1^\circ$  relative to the incident beam direction, to maximise the illuminated area and the sample was scanned over a region of  $\sim 10 \text{ mm}$  during the 4-hour measurement to minimise beam-induced changes. Inelastically scattered photons were recorded using 72 spherically bent Si(660) crystal analysers with energy loss events in the vicinity of both O K-edge and Ni  $L_{3,2}$ -edge. O K- and Ni  $L_{3,2}$ -edges were recorded at momentum transfers of  $q = 6.9 \pm 0.5$ , and all data extraction and treatment were performed as described in ref. 65.

### Charge-transfer multiplet calculations

Ni  $L_{3,2}$ -edge multiplet simulations were performed at the ligand field level of theory using the many-body code, Quanty.<sup>66</sup> This was implemented using the same single-cluster  $\text{NiO}_6$  Hamiltonian as Green *et al.*,<sup>47</sup> where Ni 2p, Ni 3d ligand shells are explicitly included (see Supplementary Note S3, ESI<sup>†</sup>). Parameters used in  $\text{Ni}^{2+}$  calculation (eV):  $\Delta = 5.5$ ,  $10D_q = 0.71$ ,  $V_{\text{eg}} = 2.627$ ,  $V_{\text{t2g}} = 1.524$ . Parameters used in  $\text{Ni}^{3+}$  calculation (eV):  $\Delta = -0.5$ ,  $10D_q = 0.93$  with Jahn-Teller splitting of  $\Delta_{\text{eg}} = 0.15$  and  $\Delta_{\text{t2g}} = 0.10$  where  $\Delta_{\text{eg}}$  is the difference between the  $x^2 - y^2$  and  $3x^2 - r^2$  onsite energies and  $\Delta_{\text{t2g}}$  is the difference between the xy and xz/yz onsite energies,  $V_{3x^2 - r^2} = 2.43$ ,  $V_{x^2 - y^2} = 3.33$ ,  $V_{xz/yz} = 1.41$ ,  $V_{xy} = 1.93$ . Parameters used in  $\text{Ni}^{4+}$  calculation (eV):  $\Delta = -6.5$ ,  $10D_q = 0.78$ ,  $V_{\text{eg}} = 3.456$ ,  $V_{\text{t2g}} = 2.004$ .

### DFT spectral calculations

Density functional theory (DFT) calculations were carried out using the plane wave pseudopotential code CASTEP<sup>67</sup> and the

Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation functional,<sup>68</sup> with the addition of the G06 semi-empirical dispersion correction<sup>69</sup> to better account for van der Waals forces. The zig-zag J–T  $P2_1/c$  structure for  $\text{LiNiO}_2$ , and the  $R\bar{3}m$  structure for  $\text{NiO}_2$  were used for pristine  $\text{LiNiO}_2$  and fully delithiated materials respectively.<sup>33</sup> Each structure was initially geometry optimised using appropriate plane wave cut-off energies (900 eV) and  $k$ -points ( $0.03 \text{ \AA}^{-1}$   $k$ -point spacing) determined *via* convergence of the total energy. The geometry of the system was considered optimized when the maximum forces on the ions were below  $0.001 \text{ eV \AA}^{-1}$  for  $\text{NiO}_2$  and  $0.01 \text{ eV \AA}^{-1}$  for  $\text{LiNiO}_2$  consistent with other studies.<sup>33,70</sup> Calculations of the pDOS and core-hole spectra were subsequently performed. The energy scale of the ground-state pDOS assumes the material is an insulator and sets the Fermi energy,  $E_f$ , to zero. Since core orbitals are not treated explicitly in the pseudopotential method, a unique pseudopotential is generated for an excited atom possessing a core-hole. For O and Ni K-edges, a core-hole is placed on the O 1s or Ni 1s orbitals respectively. A supercell is generated to prevent interactions between neighbouring core-holes. For spectral calculations, the plane wave energy cut-off,  $k$ -point sampling and cell size were increased until no visible effect on the spectrum was seen. Spectral calculations were handled using the OptaDOS programme.<sup>71</sup> Lorentzian broadening was performed using full widths at half maximum of 0.14 and 0.8 eV for the O and Ni K-edges respectively, which should reflect the lifetimes of radiative and non-radiative transitions.<sup>72,73</sup> The Gaussian component was then adjusted as a free parameter to match the experimental data, but remained fixed for the same edges to allow for comparison. The Lorentzian component is given energy dependence to account for the energy dependence of the lifetime. This was done by summing the set width with a factor that varies linearly with energy as implemented in Optados. The calculated spectra were rigidly shifted to align with the first absorption peaks of the experimental data to allow better comparison. In cases where the system under investigation possessed more than one inequivalent excitation site, separate spectra were generated, energy aligned<sup>74</sup> and combined before rigidly shifting.

## Author contributions

LA, JENS and RSW conceived the study. LA performed electrode preparation and electrochemical testing, with assistance from RAH. MWF performed SEM. LA, JENS, CJS and RSW performed the XRS. LA, AP, EB, PND, MWF, LAHJ, CMPEP and RSW performed the soft XAS with support from DCG, PF and PB. LA, JENS, AP, CJS, and RSW performed XAS and XRS analysis. LA and PC performed the lab-based XANES and EXAFS, with analysis performed by PC. LA, JENS, EB, PND and RSW performed HERFD-XANES with support from SH. JENS, NR and RJN performed DFT calculations. RZ and PDN performed PFIB, STEM-EELS and related analysis. GH and RJG performed CTM calculations. LA, JENS, PC and RSW wrote the paper with contributions from all authors.



## Data availability

The data supporting this article have been included as part of the ESI.† The corresponding data sets are available from the ORA repository, <https://doi.org/10.5287/ora-ypnqgero>.

## Conflicts of interest

The authors declare that there are no conflicts of interest.

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