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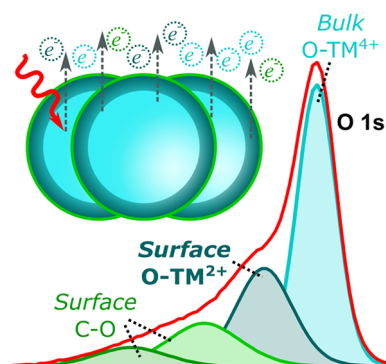
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How Bulk Sensitive is Hard X-ray Photoelectron Spectroscopy: Accounting for the Cathode–Electrolyte Interface when Addressing Oxygen Redox

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ABSTRACT: Sensitivity to the “bulk” oxygen core orbital makes hard X-ray photoelectron spectroscopy (HAXPES) an appealing technique for studying oxygen redox candidates. Various studies have reported an additional O 1s peak (530–531 eV) at high voltages, which has been considered a direct signature of the bulk oxygen redox process. Here, we find the emergence of a 530.4 eV O 1s HAXPES peak for three model cathodes—Li₂MnO₃, Li-rich NMC, and NMC 442—that shows no clear link to oxygen redox. Instead, the 530.4 eV peak for these three systems is attributed to transition metal reduction and electrolyte decomposition in the near-surface region. Claims of oxygen redox relying on photoelectron spectroscopy must explicitly account for the surface sensitivity of this technique and the extent of the cathode degradation layer.



Alkali-rich oxides have gained significant attention as next-generation battery cathodes in recent years, achieving reversible capacities beyond 270 mAh/g.^{1–3} In comparison to conventional layered oxides (LiMO₂), alkali-rich cathodes deliver excess capacity beyond what is expected from traditional transition metal (TM) redox couples that is widely attributed to oxygen redox.^{3,4} Interest in utilizing oxygen redox capacity has generated research into a variety of novel 3d, 4d, and 5d compounds^{3,5–7} and intercalation structures.^{7,8} Li- and Mn-rich Ni/Co/Mn layered oxides (LR-NMC) remain at the forefront of this field for achieving high performance^{9,10} and for investigating the fundamental electrochemistry of alkali-rich oxides.^{11–13} Indeed, recent studies focusing on LR-NMC cathodes have revealed mechanisms that contribute to the large hysteresis^{11,13} and voltage decay¹² found across anionic redox compounds.^{3,6} Direct insight into oxidized oxygen has primarily relied on two techniques: X-ray photoelectron spectroscopy (XPS) at the O 1s region^{14–16} and resonant inelastic X-ray scattering (RIXS) at the O K-edge.^{11,17,18} Unlike RIXS which requires a bright variable energy X-ray synchrotron source, XPS is a common lab-based technique resulting in its extensive use for studying oxygen redox candidates.^{5,15,19–25}

Lab-based XPS is inherently surface-sensitive (probing depth <5 nm) with a large portion of the signal coming from electrolyte decomposition species at the cathode surface. Hard X-ray photoelectron spectroscopy (HAXPES) has been used to

overcome this limitation with probing depths >20 nm that allow for increased sensitivity to the “bulk” oxygen core orbitals.^{16,26,27} In these measurements, the emergence of an O 1s peak in the same binding energy window (530–531 eV) as common peroxides, e.g., Na₂O₂²⁸ and Li₂O₂,²⁹ has been considered a signature of oxygen redox. This method has to this point been seen as a quantitative probe of bulk oxidized oxygen states for identifying the onset and reversibility of oxygen redox.

In this study, we focus on HAXPES O 1s measurements to address this interpretation for three layered oxide cathodes: Li₂MnO₃,³⁰ Li[Li_{0.144}Ni_{0.136}Mn_{0.544}Co_{0.136}]O₂ (LR-NMC),³¹ and LiNi_{0.4}Mn_{0.4}Co_{0.2}O₂ (NMC 442).³² All three systems (Li-rich and conventional) show the emergence of an additional HAXPES O 1s peak (530.4 eV peak) that is found to be inconsistent with the expected oxygen redox contribution. Indeed, a stronger 530.4 eV O 1s peak is observed for a conventional layered oxide cathode (NMC 442) than for LR-NMC at high states of charge. When accounting for the surface sensitivity of HAXPES, our results reveal how a

combination of electrolyte decomposition species and near-surface TM-reduction contribute to the evolution of a 530.4 eV peak for oxide cathodes.

For our focus on the O 1s core region, we utilized photon-dependent XPS at 0.8, 1.5, and 6 keV with electron inelastic mean free paths (IMFPs) of 0.8, 1.6, and 7.8 nm, respectively, calculated using the TPP-2 M method³³ from the NIST electron IMFP database.³⁴ The corresponding attenuation profiles³⁵ (photoelectron signal versus depth) for these three photon energies are given in Figure 1a. The 0.8 and 1.5 keV

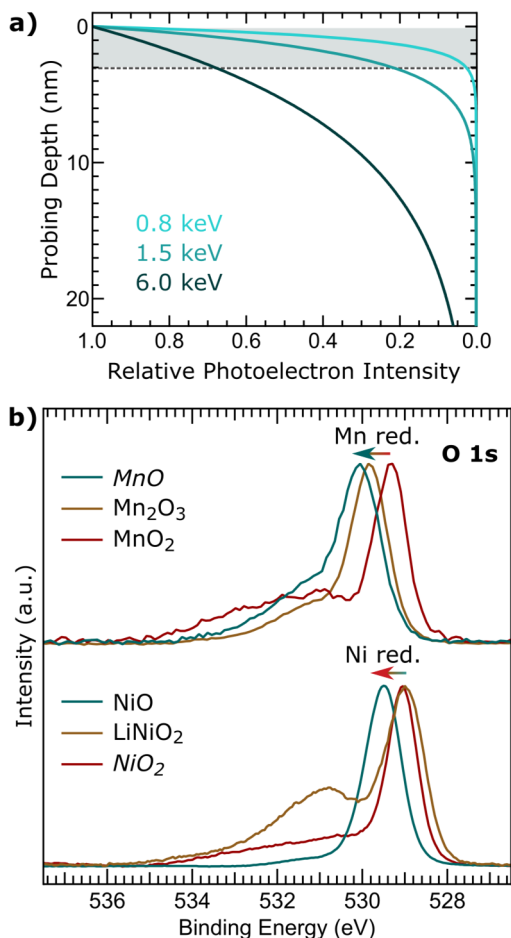


Figure 1. (a) Relative photoelectron signal versus depth at 0.8, 1.5, and 6 keV. The gray shaded region highlights the contribution from the top 3 nm. (b) HAXPES O 1s spectra for manganese (MnO, Mn₂O₃, and MnO₂) and nickel (NiO, LiNiO₂, and NiO₂) oxide references. Manganese and nickel oxides were measured at 1.5 and 6 keV, respectively.

measurements are highly surface-sensitive as over 85% of the signal originates from the top 3 nm. For 6 keV HAXPES, the contribution from the top 3 nm is reduced to 30% and the overall probing depth is ~23 nm (3× the IMFP), the region in which 95% of the signal originates from. Yet, these HAXPES measurements still have a significant contribution from the cathode–electrolyte interface given that electrolyte decomposition and TM-reduction/densification is often on the order of a few nanometers for oxide cathodes.^{36–40}

Beyond considering the attenuation profile, we explicitly examined the O 1s spectra for manganese and nickel oxide references (Figure 1b). The lattice oxygen peaks for commercial MnO (Mn²⁺), Mn₂O₃ (Mn³⁺), and MnO₂

(Mn⁴⁺) are found at 530.05, 529.8, and 529.35 eV, respectively, matching with previously reported values.^{41,42} The MnO reference may be partially oxidized (Figure S1) resulting in only a small shift of the O 1s peak beyond Mn₂O₃.⁴³ Nickel references consisted of a NiO (Ni²⁺) epitaxial film and LiNiO₂ electrodes charged to 3.6 V (LiNiO₂) and 4.75 V (NiO₂). The first charge of LiNiO₂ resulted in a charge capacity of 286 mAh/g, suggesting the material is near full delithiation (Figure S2). The nickel references were measured with HAXPES to minimize the contribution of carbonates that tend to form on lithiated nickel-rich oxides.^{44,45} The Ni–O peaks for NiO, LiNiO₂, and NiO₂ are found at 529.5, 529.0, and 529.05 eV, respectively. From these reference measurements, we find the lattice O 1s peak shifts to higher binding energies as a direct result of the reduction of surrounding TMs. Additional discussion of the fundamental contributions to the core orbital peak position^{46,47} is given in supplementary note 1.

Following these insights, we turn to HAXPES characterization of Li-rich and conventional layered oxide cathodes. Electrode preparation and cell testing details are given in the Supporting Information along with scanning electron microscopy images of pristine materials (Figure S3). First, we focus on Li₂MnO₃ that displays first charge and discharge capacities of 336 and 168 mAh/g, respectively (Figure 2a). In our recent study, this high charge capacity was found to primarily originate from oxygen loss and side reactions with limited contribution from reversible oxygen redox.³⁰ Indeed, highly charged Li₂MnO₃ displays no RIXS features associated with the formation of stabilized oxidized oxygen states.^{30,48} HAXPES measurements were conducted on pristine Li₂MnO₃ and three electrodes, beginning of charge (4.55 V), end of charge (5.00 V), and end of discharge (2.00 V), prepared with 75% active material, 15% carbon black (CB), and 10% PVDF binder. The Li 1s and Mn 3p regions for these samples are given in Figure 2b. The Li 1s peak at 54.3 eV is associated with lithium in the lattice and increases (decreases) during charge (discharge). This peak is detectable at 5.00 V, indicating some lithium remains in the lattice at the end of charge. In the Mn 3p, there is an increase in the lower binding energy shoulder at 48 eV between the pristine material and 4.55 V electrode. Ilton et al.⁴³ identified the main Mn 3p peak for Mn⁴⁺, Mn³⁺, and Mn²⁺ references at 49.94, 48.79, 47.46 eV, respectively. Comparison of these values to the Li₂MnO₃ electrodes indicates that the lower binding energy shoulder is consistent with the formation of a Mn-reduced surface layer. During the first cycle, the Mn 3p line shape never fully returns to the pristine material, indicating a partially reduced Mn surface region remains throughout the throughout the first cycle. This conclusion is supported by complementary HAXPES of the Mn 2p core region (Figure S1). These results are consistent with previous observations of extensive oxygen loss^{30,49} and surface reduction^{30,39} for Li₂MnO₃.

Focusing on the O 1s core region, we conducted peak fits for each of the Li₂MnO₃ samples (Figure 2c). For pristine Li₂MnO₃, the main lattice peak is at 529.35 and there is a minor peak at ~530.4 eV. During the first cycle, higher binding energy features (>531 eV) are found to emerge that are associated with electrolyte decomposition species including C=O (531.7 eV) and C–O (533.25 eV) environments from solvent decomposition.^{50,51} These species are particularly prevalent in 1.5 keV measurements (Figure S4).

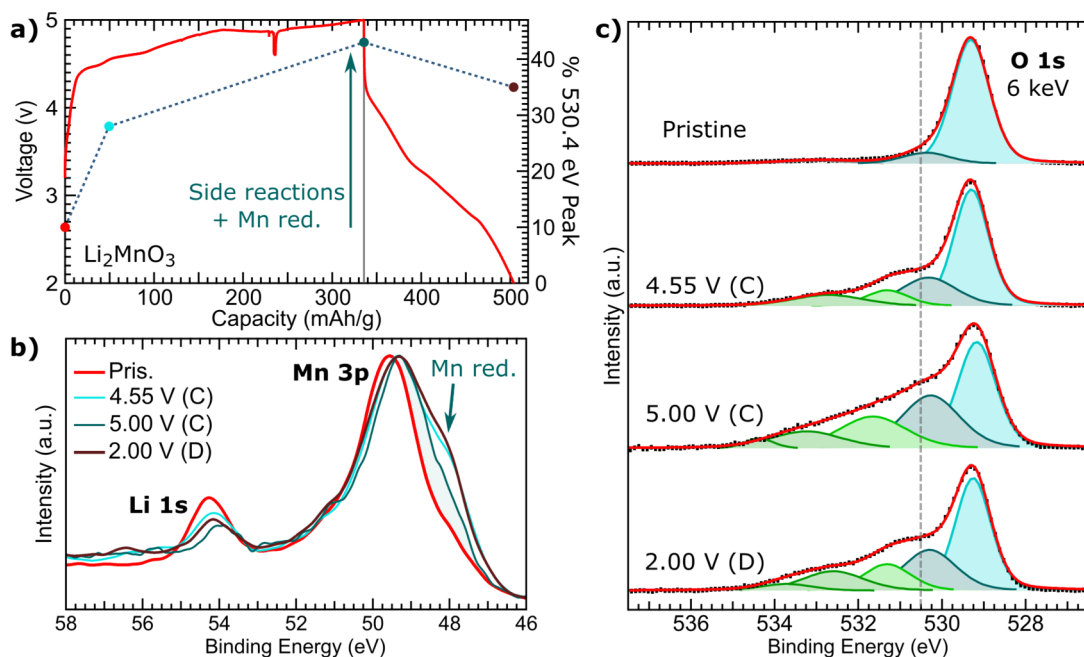


Figure 2. (a) First cycle electrochemistry for Li_2MnO_3 charged (C) to 5.00 V and then discharged (D) to 2.00 V. (b) Li 1s and Mn 3p core regions and (c) O 1s peak fits at 6 keV of pristine Li_2MnO_3 and electrodes charged to 4.55 and 5.00 V and discharged to 2.00 V. The gray line in panel c highlights the 530.4 eV peak. The variation in this peak is compared to the electrochemistry in panel a.

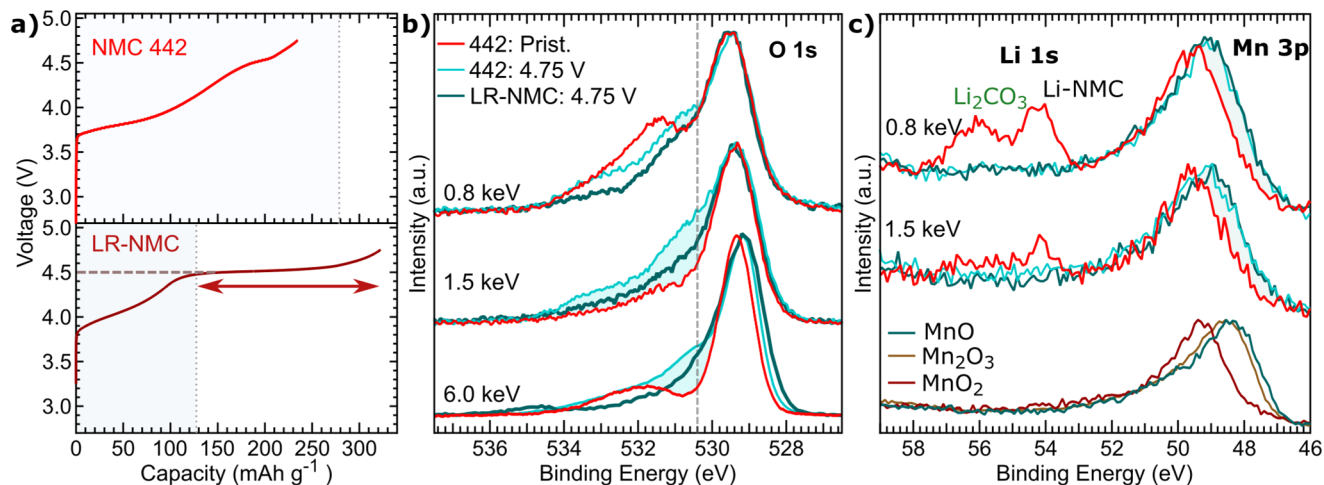


Figure 3. (a) First charge of NMC 442 and LR-NMC to 4.75 V. (b) O 1s measured at 0.8, 1.5, and 6 keV and (c) Li 1s and Mn 3p core regions at 0.8 and 1.5 keV for NMC 442 and LR-NMC 4.75 V electrodes compared to a pristine NMC 442 electrode. For the O 1s, the shading indicates the additional 530.4 eV peak that is present at high voltages for the LR-NMC and NMC 442. For the Mn 3p, reference Mn–O (Mn^{2+}), Mn_2O_3 (Mn^{3+}), and MnO_2 (Mn^{4+}) spectra relate the Mn-valence to the Mn 3p peak position.

Of particular interest is the evolution of the 530.4 eV peak at the same binding energy as assigned to “peroxo-like” oxygen redox features in other systems.^{15,16,26} The percentage of this peak versus the main lattice oxygen peak [$\text{O}_{530.4}/(\text{O}_{530.4}+\text{O}_{529.35})$] is plotted alongside the electrochemistry in Figure 2a. This peak increases at the start of charge (4.55 V) and after charging to 5.00 V but shows only a small decrease after discharge. The limited reversibility, combined with the extensive near-surface Mn-reduction (Figure 2b) and absence of oxidized oxygen RIXS features,^{30,48} suggest the 530.4 eV peak is not associated with lattice oxygen redox for Li_2MnO_3 . One possible assignment for this peak is surface Mn-reduction given its similar binding energy to lattice $\text{Mn}^{3+}/\text{Mn}^{2+}$ O 1s peaks (Figure 1b), concurrent increase with Mn-reduction at

4.55 V, and limited reversibility. There is a continued increase of the 530.4 eV peak above 4.55 V with no concurrent increase in Mn-reduction, suggesting that electrolyte decomposition species may also contribute. This could include O–H groups^{28,41} that have been assigned around this binding energy for other battery materials.⁵² The formation of hydroxide species would not be unexpected for Li_2MnO_3 .⁵³ These results indicate that a combination of electrolyte decomposition and TM-reduction account for the evolution of the 530.4 eV peak for Li_2MnO_3 .

While Li_2MnO_3 is a clear example of a 530–531 eV peak that cannot be attributed to oxidized oxygen, Li_2MnO_3 was tested with a high cutoff voltage (5.00 V) and undergoes more extensive oxygen loss/TM-reduction than Li-rich and conven-

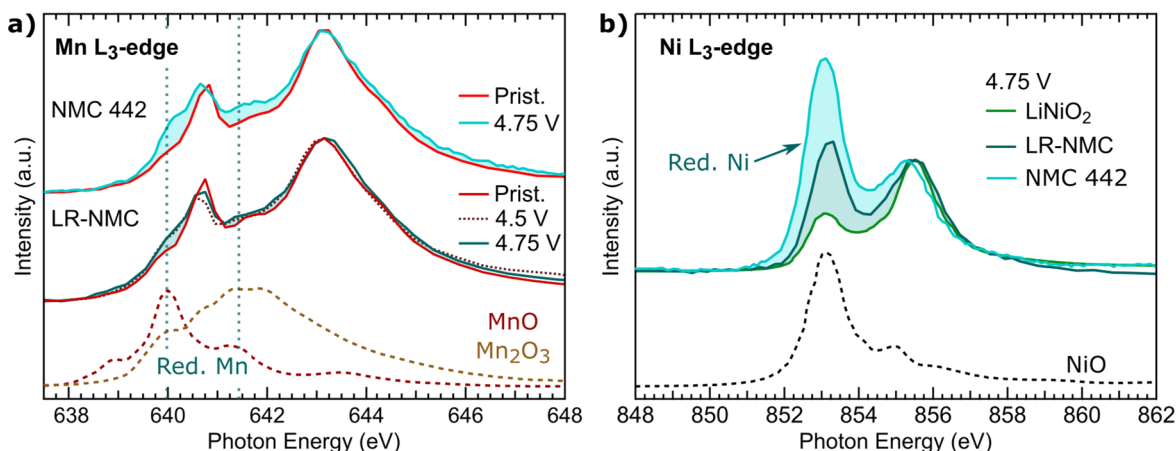


Figure 4. (a) Mn L-edge and (b) Ni L₃-edge in total electron yield (TEY) mode for NMC 442 pristine and 4.75 V, and LR-NMC pristine, 4.5 V, and 4.75 V electrodes. Mn L₃-edge spectra for MnO and Mn₂O₃ and Ni L₃-edge spectra for a NiO epitaxial thin film and LiNiO₂ 4.75 V electrode (Ni⁴⁺) are included for reference. Shadings in panels a and b highlight changes that result from TM-reduction.

tional NMC layered oxides.^{30,49,54} As such, we conducted additional HAXPES measurements on Li-rich NMC and NMC 442 cathodes. For these systems, minimal additives (CB/PVdF) were used compared to Li₂MnO₃ (see the [Supporting Information](#)) that did not compromise the electrochemistry. This will improve the direct sensitivity of the measurements to the active material. The electrochemical curves of the first charge of NMC 442 and LR-NMC to 4.75 V (vs Li-metal) at 10 mA/g and at room temperature (RT) are given in [Figure 3a](#). NMC 442 exhibits a charge capacity of 234 mAh/g that is attributed to traditional Ni/Co redox couples (gray shading). The LR-NMC exhibits the typical first charge activation plateau of oxygen redox cathodes and a higher capacity of 322 mAh/g. Although O K-edge RIXS studies have demonstrated the emergence of oxidized oxygen states in LiMO₂ cathodes at high degrees of delithiation,⁵⁵ more prominent RIXS features are observed for LR-NMC where the capacity is twice what is expected from traditional TM redox couples alone. Our previous study conducted on this LR-NMC system displayed clear O K-edge RIXS features at 4.75 V associated with oxidized oxygen states.³¹

Photon-dependent XPS measurements of the O 1s, Li 1s, and Mn 3p core regions at 0.8, 1.5, and 6 keV of these two systems are shown in [Figure 3b,c](#). The O 1s region is normalized to the main O-NMC lattice peak (529.0 to 530 eV). For the pristine electrode, initial O and Li 1s peaks at 531.4 and 56 eV, respectively, in the 0.8 keV measurements are associated with a thin Li₂CO₃ layer, a typical contaminant on oxide cathodes that breaks down during electrochemical testing.^{44,45,54} This accounts for the loss of these O 1s/Li 1s peaks after charging to 4.75 V. The lower-energy Li 1s peak in the pristine material at 54.2 eV is associated with lattice lithium.⁵¹ This peak is below our detection limit after charge directly reflecting delithiation of the NMC electrodes. Compared with Li₂MnO₃ ([Figure S4](#)), the LR-NMC and NMC 442 electrodes display minimal higher binding energy C–O/C=O (>531.5 eV) O 1s peaks.^{50,51} Instead, the main difference for the electrodes charged to 4.75 V is the formation of a new peak at 530.4 eV. The NMC 442 4.75 V electrode has a stronger 530.4 eV peak than the LR-NMC 4.75 V electrode at all photon energies, including the more bulk-sensitive HAXPES measurements.

Corresponding O 1s peak fits for the NMC electrodes are given in [Figure S5](#) and [Table S1](#). For the 6 keV measurements, the percentage of the 530.4 eV peak relative to the main lattice oxygen peak is 35% and 17% for the NMC 442 and LR-NMC 4.75 V electrodes, respectively. This is opposite what would be expected if this new O 1s peak was solely attributed to oxygen redox. In addition, this peak is partially formed by 4.0 V for NMC 442 ([Figure S5](#)), indicating it is not just a high-voltage phenomena. Turning to the manganese environment, we find the Mn 3p shifts to a lower binding energy for the high state of charge (SOC) NMC electrodes compared to the pristine electrode. From comparison with the manganese oxide references, we find that this shift to lower binding energy is consistent with Mn-reduction at the cathode surface. HAXPES measurements of the Ni and Mn core regions show additional evidence of an extended reduced layer forming after charge ([Figure S7](#)).

To further gauge the extent of TM reduction, we conducted complementary soft X-ray absorption spectroscopy (sXAS) measurements of the Mn and Ni L₃-edges in electron mode that are well-known to be highly sensitive to the TM oxidation state in the near-surface region.^{56,57} For the Mn L₃-edge ([Figure 4a](#)), high SOC NMC electrodes are compared to corresponding pristine powders. The pristine compounds are nominally Mn⁴⁺ with the shading in [Figure 4a](#) indicating the extent of Mn-reduction found at higher SOC. For the LR-NMC electrodes, the Mn-reduction increases up to 4.5 V (start of the high voltage plateau) and shows limited changes along the plateau. A larger increase in the Mn surface reduction is found for the NMC 442 system for the 4.75 V electrode compared to Li-rich NMC. Corresponding fits of the oxidation state are given in [Figure S8](#). For the Ni L₃-edge ([Figure 4b](#)), the NMC electrodes are compared to a NiO (Ni²⁺) reference and a LiNiO₂ electrode charged to 4.75 V that nominally matches the Ni⁴⁺ line shape.¹¹ The NMC electrodes show a strong Ni²⁺ surface component based on the increase in the Ni L₃-edge peak at 853.1 eV relative to the peak at 855.5 eV (shading in [Figure 4b](#)) with the NMC 442 showing more Ni-reduction than LR-NMC. From these sXAS measurements, we found that NMC 442 displays more surface TM reduction than the LR-NMC. This trend matches with the higher O 1s 530.4 eV peak observed for the NMC 442 than for LR-NMC, further

supporting that this O 1s peak forms as a result of surface TM-reduction during the first charge.

From comparison of three layered oxide cathodes, we identified how electrolyte decomposition and TM-reduction can contribute to the evolution of an O 1s peak between 530 and 531 eV. The presence of this peak at 4.0 V for NMC 442 is consistent with the onset of TM surface reduction around 3.9 V identified indirectly with differential electrochemical mass spectroscopy (DEMS).⁵⁸ This onset was found to coincide with the loss of Li₂CO₃ identified from CO₂ gas release and post-titration measurements.⁵⁸ These are just two of the changes in the cathode–electrolyte interface composition during the first cycle that have been identified with DEMS and XPS/HAXPES^{31,54,58} that need to be accounted for when addressing bulk redox mechanisms with techniques that are inherently surface-sensitive.

Our interpretation of the O 1s spectra may account for previous observations for alkali-rich oxides. For example, Uchimoto et al.²⁶ reported a strong additional peak in their O 1s HAXPES spectra of LR-NMC before the start of the high-voltage plateau that persisted after discharge, showing no clear correlation to the expected oxygen redox capacity. This HAXPES O 1s evolution is in contrast to bulk-sensitive STXM and RIXS techniques, where assignments of oxidized lattice oxygen do correlate with capacity.^{11,18} Our work highlights the importance of linking structural and electronic probes with the electrochemistry in order to establish a technique as a reliable oxygen redox probe.

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Notes

The authors declare no competing financial interest.

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