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Direct quantification of anionic redox over long cycling of Li-rich NMC via HAXPES

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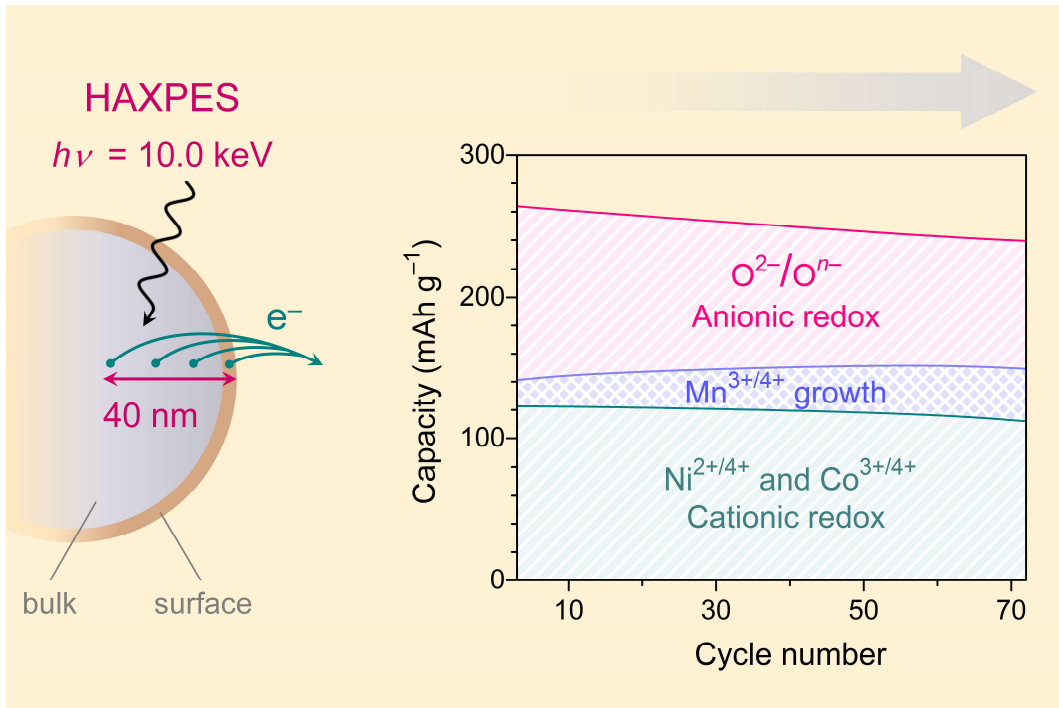
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Abstract

1 Cumulative anionic/cationic bulk redox processes are responsible for the outstanding specific
2 energy (1000 Wh kg⁻¹) of Li-rich Mn-based layered oxides as positive electrodes for lithium-ion
3 batteries. Previous attempts to quantify redox processes in these materials were either limited to initial
4 cycles or relied solely on the transition metals. It thus remains unclear to what extent does oxygen
5 redox persist over cycling. This study provides an answer via synchrotron-based bulk-sensitive hard
6 X-ray photoemission spectroscopy (HAXPES) by directly following the changes in electronic state
7 of lattice oxygen over gradually increasing cycles. We find that oxygen redox contribution stabilizes
8 after initial cycles in Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O₂ (Li-rich NMC) and even after 70 cycles, it accounts for
9 more than one-third of the overall capacity. Consequently, from the quantification of Mn spectra, we
10 observe a gradual but limited growth of Mn^{3+/4+} redox instead of a complete activation. Partial
11 degradation of the Ni^{2+/3+/4+} redox is also observed. This fundamental study generates optimism for
12 the concept of anionic redox in long-cycling batteries, and also highlights the capability of HAXPES
13 for understanding bulk vs. surface effects in energy materials.

Keywords. *Batteries, Li-rich NMC, anionic redox, HAXPES*

TOC Graphic



1 Anionic redox in transition-metal oxides has lately emerged as a promising concept of solid-
2 state electrochemistry to design materials for energy storage and conversion.¹ It has unlocked the
3 possibility to reversibly and repeatedly perform (de)intercalation reactions via the redox activity of
4 bulk oxide anions, in addition to the conventionally utilized transition-metal redox. The energy
5 storage limit of such oxide cathodes for rechargeable batteries has thus been increased and the
6 materials design space has also been widened.² Subsequent to our group's fundamental investigations
7 on 'model' materials based on 4*d* and 5*d* transition-metal layered oxides³, several studies⁴⁻¹¹ have
8 now proven that lithium-rich manganese-based layered oxides, such as $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ (Li-
9 rich NMC) that is derived from Li_2MnO_3 , also exhibit combined anionic/cationic redox activity to
10 deliver reversible capacities above 270 mAh g^{-1} and approach 1000 Wh kg^{-1} of specific energy at the
11 material level.¹²⁻¹⁸ These attributes, along with the limited use of scarce cobalt and nickel, make the
12 Li-rich NMC family a strong competitor of today's Ni-based layered oxides¹⁹ (NMCs) that are
13 derived from LiNiO_2 . NMCs are also undergoing rapid innovation owing to their promise of up to
14 800 Wh kg^{-1} at the material level.^{2,12} Therefore, for Li-rich cathodes to stay relevant in this duel²,
15 several obstacles need to be eliminated – namely insufficient electrode density¹², large voltage
16 hysteresis^{8,20}, sluggish kinetics^{8,21}, and voltage decay upon ageing²².

17 In this study, we focus on the ageing behavior of Li-rich NMC, particularly on how the
18 anionic/cationic redox activities evolve over cycling, which is essential for the fundamental
19 understanding of degradation mechanisms. Most reports on anionic redox in these materials were
20 limited to the investigation of charge-compensation in the first couple of cycles.⁴⁻¹¹ Although a recent
21 study reported redox evolutions over long cycling, it relied on transition metals' spectra since the
22 direct quantification of oxygen spectra was not possible.²³ Among the spectroscopic techniques that
23 have been adopted by the battery community specifically for the direct characterization of oxygen
24 redox², two particular classes of techniques, based respectively on X-ray absorption spectroscopy
25 (XAS) and X-ray photoemission spectroscopy (XPS), have been particularly successful in

1 demonstrating oxygen redox activity in Li-rich NMC, as summarized below.

2 Initial soft-XAS measurements in bulk-sensitive fluorescence yield mode at the O K-edge⁴
3 were later repeated^{6,7} and changes in the pre-edge intensity were assigned to changes in the electronic
4 state of bulk oxygen. By switching to transmission mode later on, a much sharper absorption feature
5 around 531 eV was observed and assigned to oxidized oxygen.⁹ Such a hypothesis was complemented
6 by obtaining O K-edge resonant inelastic X-ray scattering (RIXS) maps wherein a unique and sharp
7 absorption–emission feature appeared on charge and disappeared on discharge.^{7,9} This is now
8 believed to be a signature of oxidized lattice oxygen.²⁴ RIXS was also used to show that oxygen
9 remains active after long cycling, but further quantification could not be performed.⁹ Concerning
10 XPS-based results on the other hand, initial O 1s XPS spectra showed the appearance of oxidized
11 lattice oxygen upon charging Li-rich NMC⁵ but doubts remained due to the surface-sensitivity of
12 standard XPS technique using Al K α X-ray source. We overcame this shortcoming by moving to
13 synchrotron-based hard X-ray photoemission spectroscopy (HAXPES) for accessing bulk
14 information and systematically explored the complete anionic/cationic charge compensation
15 mechanism of Li-rich NMC in the first two cycles.⁸

16 The results from both types of direct oxygen spectroscopies have converged^{8,9} – an important
17 mutual conclusion being, apart from the reversibility of oxygen redox, the correct assignment of the
18 differential capacity (dQ/dV) discharge peak at low potential to anionic redox. The remaining task
19 now is to investigate the effect of ageing, for which we extend herein our investigation of Li-rich
20 NMC using HAXPES over long cycling. Taking advantage of this technique's bulk-sensitivity and
21 quantitative nature²⁵, we investigate the reversibility of oxygen redox during ageing and also quantify
22 the evolution of cationic redox processes, especially Mn^{3+/4+}. Our results present optimistic insights
23 on the cyclability of anionic redox, and further elucidate the ageing mechanism of these practically
24 important materials.

25 $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ (Li-rich NMC) powders were synthesized by annealing co-

1 precipitated carbonates, as described in detail elsewhere.^{8,17} These materials, mixed with 10 %
2 conductive carbon, were used as positive electrodes in Swagelok-type Li half-cells. No polymeric
3 binders were used in order to avoid decreasing the intensity of XPS signals from the active material.
4 The electrodes exhibit, as per the 1st cycle voltage vs. composition curve recorded at 20 mA g⁻¹
5 (**Figure 1a**), a staircase-like charging process followed by a sloped discharge in which the capacity
6 is 270 mAh g⁻¹. Such an electrochemistry is typical for a good batch of Li-rich NMC. A series of
7 identical cells was prepared and after the first activation cycle discussed above, they were continued
8 at 40 mA g⁻¹ (circa C/6) for making long-cycled samples with gradually increasing levels of ageing.
9 Such a relatively low C-rate is expected to uniformly age the particles and was chosen to simulate
10 realistic ageing conditions, in contrast to fast cycling (e.g. at 1C) that may lead to non-uniform ageing
11 besides inflating the total cycle number⁹ and lowering the overall run-time which is known to be an
12 important variable concerning the degradation of Li-rich NMC^{8,26}. Fully charged and discharged
13 samples in cycles 2, 13, 57, and 72 were thus obtained for *ex situ* HAXPES analysis, extending our
14 previous study on only the first two cycles.⁸ Note that a lower current of 20 mA g⁻¹ was used in the
15 final cycle (see Experimental Methods in the Supp. Info. for further sample preparation details).
16 **Figure 1b** shows the capacity retention for the longest cycled cell (at 40 mA g⁻¹, circles) along with
17 the decay of average voltage (triangles). The same graph also shows the respective capacities obtained
18 during the final sample preparation cycles (at 20 mA g⁻¹, stars). It is clear from **Figure 1b** that the
19 main issue concerning the cyclability of this class of materials is the gradual fading of voltage rather
20 than capacity retention, as we furthermore highlighted in a recent review article.² The voltage
21 instability can also be visualized via the evolution of voltage profiles and their respective dQ/dV plots
22 in **Figure 1c–e**. These panels also highlight the adequate repeatability with this cell configuration
23 over the cycling durations studied herein.

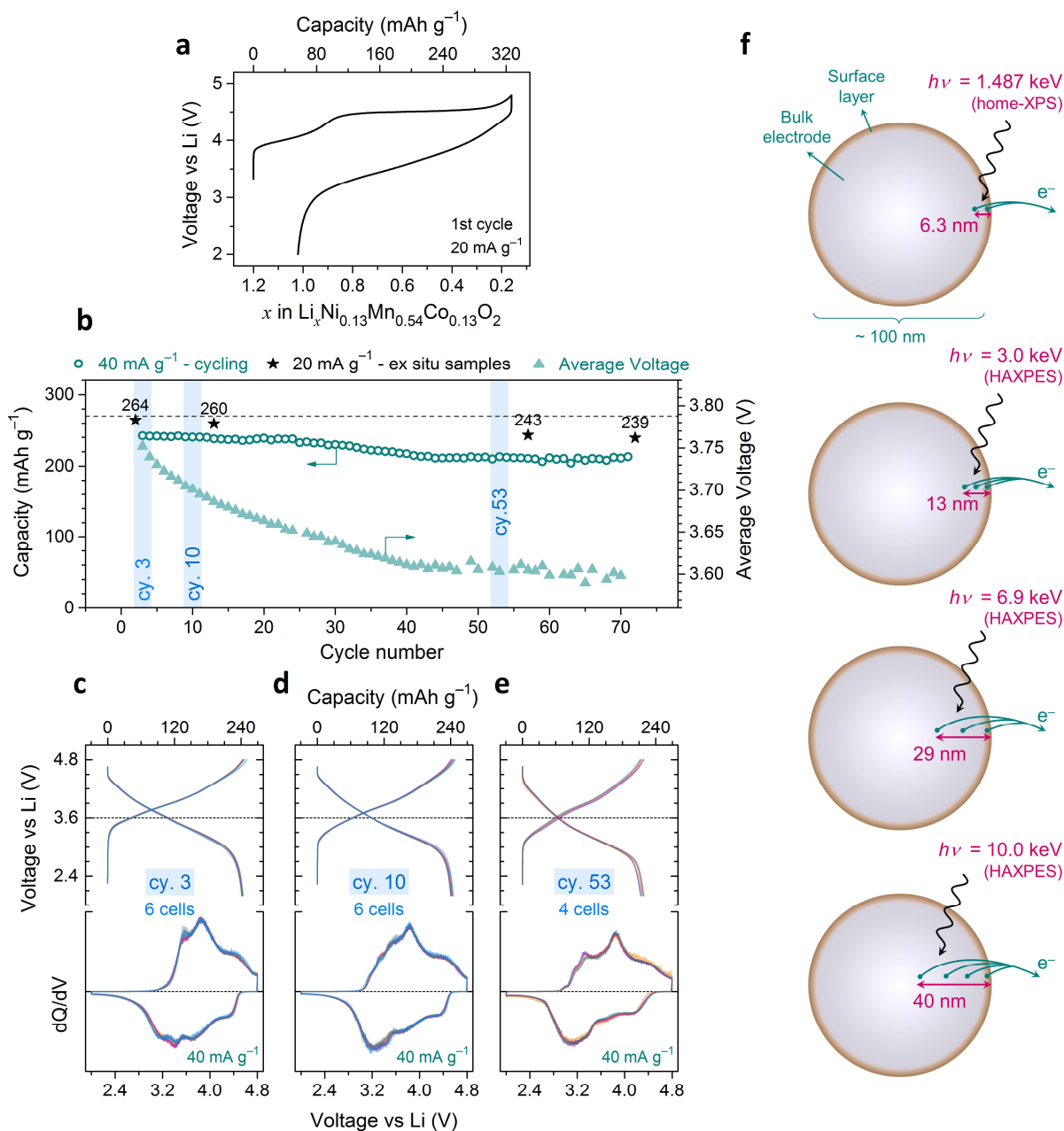


Figure 1. Electrochemical performance of Li-rich NMC and schematic view of HAXPES probe depths. (a) Voltage vs. composition profile in the first cycle. (b) Capacity retention (left axis) and average voltage (right axis) over long cycling. Average voltage is defined as the mean of the average charge and discharge voltages. The stars with corresponding values denote the capacities obtained during the *ex situ* sample preparation cycles. Voltage profiles and dQ/dV plots are shown for the six cells in cycle 3 (c) and 10 (d), and for the four cells in cycle 53 (e). (b) Schematic illustration of the photoelectron escape depth for surface-sensitive standard XPS ($\text{Al K}\alpha$ X-ray source) compared with bulk-sensitive HAXPES. The primary particles are $\sim 100 \text{ nm}$ in diameter, as characterized in the preceding work.⁸ The probe depths, defined as three times the photoelectron inelastic mean free path²⁷, are calculated for the O 1s core peak (calculation details in previous work⁸ and in Supp. Info. Note S1).

1 To study the evolution of cationic and anionic redox processes over cycling, the samples were
2 characterized with HAXPES. As schematized in **Figure 1f**, the use of high energy synchrotron
3 radiation leads to probe depths of up to 29 nm at 6.9 keV and 40 nm at 10.0 keV, making HAXPES
4 a bulk-sensitive technique. The O 1s HAXPES spectra are shown in **Figure 2a** for samples charged
5 to 4.8 V and **Figure 2b** for samples discharged to 2.0 V as the cycle number increases, allowing us
6 to directly monitor the changes in electronic state of lattice oxygen. We have previously shown that
7 the O 1s spectrum after the first charge (**Figure 2a**, top) is characterized by an asymmetric main peak,
8 which can be modelled by two types of lattice oxygen environments⁸. These are, respectively,
9 classical lattice O²⁻ at a binding energy (BE) of 529.5 eV and oxidized lattice oxygen Oⁿ⁻ ($n < 2$, pink
10 component at BE of 530.5). Furthermore, their ratio can be reliably quantified (% Oⁿ⁻ = 33 %) thanks
11 to HAXPES that leads to a diminution of polluting signals from oxygen containing surface deposits.
12 These surface species, which arise from electrolyte and salt decomposition at the cathode electrolyte
13 interface, are usually observed at BEs from 531.5 to 534 eV²⁸⁻³⁰ and are represented by the low
14 intensity grey peaks in **Figure 2a,b**. An additional satellite peak corresponding to the active material
15 is also overserved (yellow) at BE = 535 eV. The main peak becomes symmetric upon discharge
16 (**Figure 2b**, top), thus signifying the electrochemical reduction of Oⁿ⁻ to give back O²⁻. Additionally,
17 the satellite peak also disappears. For comparison, the O 1s spectra of the same samples were recorded
18 in standard laboratory conditions (in-house XPS with $h\nu = 1.487$ keV, Supp. Info. Figure S1). These
19 spectra display, as expected at lower photon energy, much higher contributions of surface species
20 relative to the lattice O²⁻ and Oⁿ⁻ components.

21 The 6.9 keV HAXPES spectrum of the charged sample after cycle 2 is very similar to cycle
22 1, but with slightly less amount of oxidized oxygen (% Oⁿ⁻ = 28 %). Oⁿ⁻ reduces back to O²⁻ after the
23 second discharge. This back-and-forth appearance of Oⁿ⁻ on charge and its disappearance on
24 discharge demonstrates the reversibility of the anionic redox process. Note that the results obtained
25 on cycle 2 in this study are nearly identical to our previous report⁸, thus underscoring the high

1 reproducibility in sample preparation and analysis. By increasing the photon energy from 6.9 keV to
2 10.0 keV herein, a further suppression of the signal from surface species is achieved for both the
3 charged and discharged samples. Although the O^{n-} shoulder at BE 530.5 eV is visually less evident
4 in the charged state due to the slightly lower energy resolution at 10.0 keV, the value of % O^{n-} remains
5 unchanged. Over long cycling, O^{n-} continues to be observed in the charged samples (**Figure 2a**),
6 without any drastic decline in the value of % O^{n-} that stays at 25, 23, and 23 % in cycles 13, 57, and
7 72 respectively. O^{2-} re-forms on the respective discharges (**Figure 2b**), with % O^{n-} always reducing
8 to 9 %. Note that the contribution of surface species tends to increase after long cycling, especially
9 on the discharged samples, which is further confirmed by in-house XPS that offers higher surface
10 sensitivity (O 1s and C 1s in Supp. Info. Figures S1 and S2). The increase of such electrolyte / salt
11 decomposition products upon cycling is expected to cause impedance rise and hence capacity fade
12 under fixed current cycling. However, the exact quantification of these surface effects is not the main
13 aim of the present study. Interestingly, the 535 eV satellite also continues to appear on charge and
14 disappear on discharge in all pairs of long-cycled samples characterized with HAXPES. Although the
15 fundamental origin of this satellite is yet to be understood, we believe that it might be concomitant
16 with the O^{n-} species, especially because the same phenomenon is observed in another Li-rich oxide
17 – $Li_{2-x}Ru_{0.75}Sn_{0.25}O_3$.³¹ Further research is therefore needed to conclude whether the satellite can be
18 ascribed as a general spectroscopic signature of oxidized oxygen. On the basis of these results that
19 are summarized in **Figure 2c**, it can be concluded that reversible oxygen redox activity stabilizes after
20 a few cycles and continues to persist over long cycling in Li-rich NMC. This should alleviate the
21 apprehensions about cyclability of anionic redox in real-world batteries.

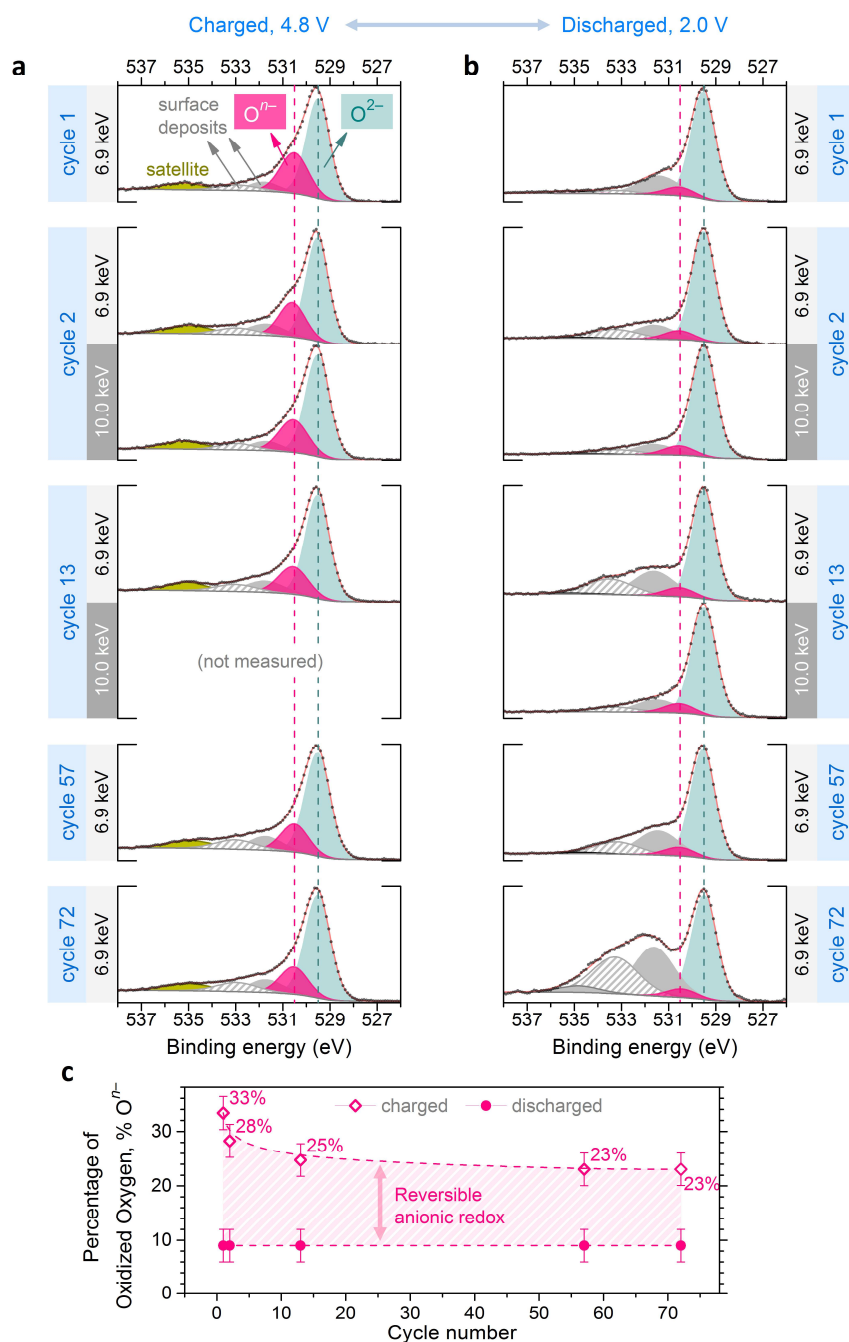


Figure 2. Evolution of the anionic redox process over cycling. O 1s HAXPES spectra recorded at 6.9 keV and 10.0 keV photon energies along with their respective fits for (a) the samples charged to 4.8 V and (b) discharged to 2.0 V with gradually increasing cycle numbers. The spectra for cycle 1 are the same as our previous work⁸, whereas the rest were measured in the present study. (c) The percentage of oxidized oxygen or % Oⁿ⁻ ($n < 2$) is plotted as a function of cycle number. It is based on the ratio of the amounts of Oⁿ⁻ with respect to (O²⁻ + Oⁿ⁻) that are estimated from the fits using integrated peak areas. % Oⁿ⁻ is 9% for all discharged samples. The absolute error bars of $\pm 3\%$ arise from the uncertainty in the fitting procedure that is described in detail in the preceding work.⁸

1 Turning now to the transition metals for understanding cationic redox, the Mn $2p_{3/2}$ HAXPES
2 spectra recorded at 6.9 keV are shown in **Figure 3a** for the charged and **Figure 3b** for the discharged
3 samples. The as-synthesized material is in Mn⁴⁺ state, which cannot be further oxidized on charge.
4 We have previously shown with 3.0 keV HAXPES that on the subsequent discharge to 2.0 V, only a
5 partial reduction of Mn⁴⁺ takes place giving only 10 % Mn³⁺ after the first discharge.⁸ Herein, the use
6 of 6.9 keV provides a higher probing depth as well as a better energy resolution (due to the change
7 of monochromator). The spectrum after charging in cycle 2 (**Figure 3a**, top) is again characteristic of
8 Mn⁴⁺. On the second discharge (**Figure 3b**, top), a clear shoulder appears on the lower BE-side of the
9 main peak, which can be ascribed to 11 % Mn³⁺ (purple component).³² The spectra of the charged
10 samples do not evolve much over long cycling, except for a broadening of the fine doublet structure
11 of the main peak that may be because of gradually increasing disorder. Therefore, all spectra of
12 charged samples are characteristic of Mn⁴⁺. On the other hand for the discharged samples, the Mn³⁺
13 shoulder gradually becomes more apparent with cycling, albeit the signal from Mn⁴⁺ is still
14 predominant. It can thus be concluded that Mn^{3+/4+} redox activity gradually augments over cycling,
15 and quantitatively-speaking reaches 14, 21, and 22 % in cycles 13, 57, and 72 respectively, as
16 summarized in **Figure 3c**. This systematic quantification is utilized later in the paper for determining
17 the capacity contributions from each redox process.

18 Concerning nickel, which is the main redox-active cation in Li-rich NMC, it starts as Ni²⁺ in
19 the pristine material and is known to undergo the multi-electron Ni^{2+/3+/4+} redox process over charge
20 and discharge. Ni $2p_{3/2}$ HAXPES at 6.9 keV was performed, as shown in **Figure 3d**, to characterize
21 the evolution of this process. In cycle 2, a clear shift in the main peak's position can be observed
22 between the charged to the discharged states. Moreover, the intensity and shape of the shake-up
23 satellite can additionally be used, along with the main peak's shift, as a signature to follow the
24 Ni^{2+/3+/4+} process.³³ The charged-discharged pairs of spectra continue to display these signatures over
25 long cycling, indicating the repeated occurrence of the Ni^{2+/3+/4+} process. However, the charged

1 samples for cycles 57 and 72 show slight signs of reduced nickel on the main peak as well as on the
2 satellite feature, suggesting a small under-completion of the cationic redox process after ageing of
3 the electrodes. We exclude the possibility of significant signal contribution from reduced Ni at the
4 surface as such reduction is limited to the first couple of nanometers^{34,35}, which is much lower than
5 the HAXPES probe depth. Although the signal to noise ratio is not enough for exact quantification,
6 qualitative capacity estimation is presented later in the paper. Lastly for cobalt, the Co $2p_{3/2}$ HAXPES
7 spectra were recorded at 6.9 keV (Supp. Info. Figure S4) but the main peak's position remains
8 unchanged, since it is known to be independent of Co^{3+/4+} redox as previously shown for Li_{1-x}CoO₂.³⁶
9 Therefore, we rely on our previous finding based on soft-XAS⁸ that Co^{3+/4+} occurs concomitantly
10 with Ni^{2+/3+/4+} in Li-rich NMC, and assume the same herein.

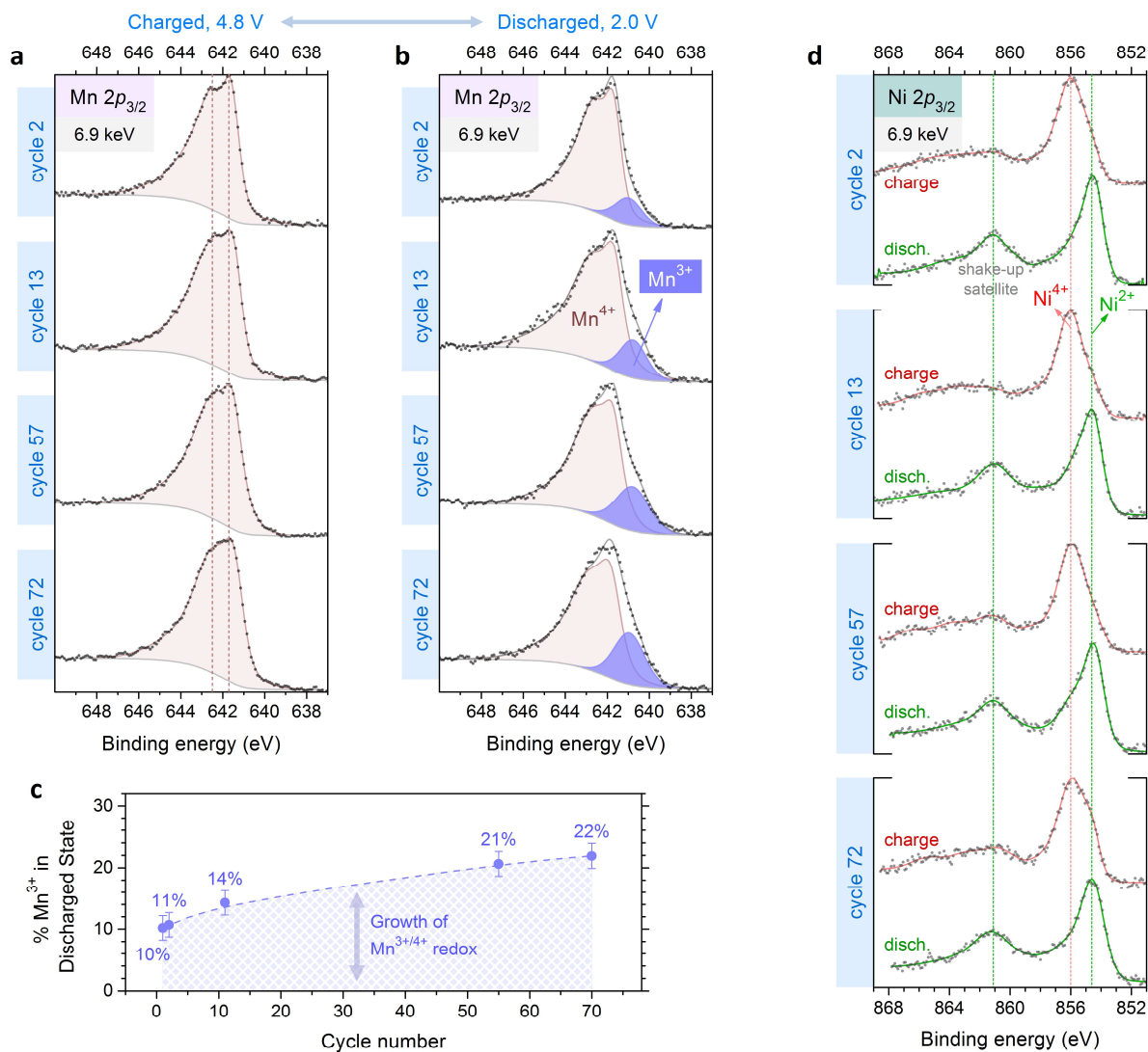


Figure 3. Evolution of the cationic redox processes over cycling. The Mn $2p_{3/2}$ HAXPES spectra for (a) the samples charged to 4.8 V and (b) the samples discharged to 2.0 V. Each Mn $2p_{3/2}$ spectrum has been fitted with two components, the first one being the spectrum of the corresponding charged sample as a reference for the Mn^{4+} shape and the second one accounting for the presence of Mn^{3+} at low binding energy (purple component around 641 eV). (c) The estimated amount of Mn^{3+} in the discharged state is plotted as a function of cycle number. (d) The Ni $2p_{3/2}$ HAXPES spectra are shown as charged-discharged pairs with increasing cycle number. All spectra in this Figure are recorded at 6.9 keV photon energy.

1 We now discuss the implication of our HAXPES results on the cyclability in Li-rich NMC,
2 further dividing this issue in two parts – namely capacity retention (**Figure 4a**) and voltage fade
3 (**Figure 4b**). Capacity-wise, out of the 264 mAh g⁻¹ delivered in the second cycle, transition metals
4 can account for a maximum possible capacity of 141 mAh g⁻¹, with 123 mAh g⁻¹ from the main
5 cationic processes of Ni^{2+/3+/4+} and Co^{3+/4+} (complete oxidation assumed) along with 18 mAh g⁻¹ from
6 the 10 % activity measured for Mn^{3+/4+}. Therefore, reversible redox of bulk lattice oxygen (denoted
7 by O^{2-/Oⁿ⁻}), which we have unambiguously demonstrated at probe depths of up to 40 nm
8 (corresponding to 10.0 keV incident energy), compensates for 123 mAh g⁻¹, i.e. nearly half of the
9 measured capacity. We also provide direct spectroscopic proof that reversible anionic redox remains
10 active over long cycling. Although lesser % Oⁿ⁻ is detected in the charged state after 72 cycles, the
11 capacity associated with it is still circa 90 mAh g⁻¹ and therefore well above one-third of the total
12 capacity (conversion ratio to get capacity from change in % Oⁿ⁻ is assumed same as that in cycle 2).
13 At the same time, the growth of Mn^{3+/4+} to 22 % corresponds just to 37 mAh g⁻¹ and the remaining
14 capacity from nickel and cobalt (112 mAh g⁻¹) turns out to be lower than their corresponding
15 contribution in the initial cycles. This observation is in agreement with the evidence of incomplete
16 nickel oxidation after long cycling (**Figure 3d**).

17 Our quantification of the long-cycling reversibility of anionic redox directly from oxygen
18 spectroscopy is consistent with a recent study²³ relying on transition-metal K-edge XAS to quantify
19 long cycling evolutions of cationic redox. The quantitative differences between the two studies likely
20 arise from differences in the studied materials (composition or morphology), with our material
21 showing lesser voltage fading. Nevertheless, the different techniques employed in the two works, and
22 hence the different quantification approaches used (HAXPES on oxygen herein vs. XAS on transition
23 metals in ref.²³), make them complementary to each other. These new works provide a systematic
24 evolution of redox processes in Li-rich NMC materials, which was only partially understood in
25 previous literature dealing with the analysis of cycled samples using techniques mainly focused on

1 transition metal redox.^{34,37-42} In **Figure 4a**, the diminution in oxygen capacity appears to be
2 compensated by the buildup of $\text{Mn}^{3+/4+}$. This is consistent with the gradual irreversible loss of lattice
3 oxygen, either as O_2 or via chemically attacking the electrolyte, leading to material densification as
4 the local stoichiometry partially changes from $\text{Li}_2\text{Mn}^{4+}\text{O}_3$ -like ($\text{O}/\text{Mn} = 3$) to $\text{LiMn}^{3+}\text{O}_2$ - and
5 $\text{LiMn}^{3+}_2\text{O}_4$ -like ($\text{O}/\text{Mn} = 2$) wherein $\text{Mn}^{3+/4+}$ is possible.^{6,7,40,43,44} This also has implications on voltage
6 fade, as discussed next.

7 **Figure 4b** shows the evolution of dQ/dV profiles with ageing. In general, the redox features
8 at higher potential become less intense over cycling with the simultaneous appearance and growth of
9 low potential processes, explaining the gradual fade in average voltage. In light of the correct redox
10 assignments of these dQ/dV features that were performed recently^{8,9}, we can observe the growth of
11 low potential $\text{Mn}^{3+/4+}$ (denoted by ‘M’) as well as a degradation in the voltage of both cationic
12 (denoted by ‘C’) and anionic (denoted by ‘A’) redox process. Voltage fade can thus be envisaged to
13 be a consequence of irreversible changes in the material’s overall bulk, and not simply due to surface
14 effects, which is also supported by model-based dQ/dV analyses of up to 500 cycles⁴⁵ as well as long-
15 term *in situ* diffraction data⁴⁶. Eliminating voltage fade therefore calls for a paradigm-shift in
16 designing mitigation strategies, especially since conventional strategies of surface-coating and cation-
17 doping have only been partially effective in Li-rich NMC.¹²

18 In summary, by using bulk-sensitive HAXPES with up to 10.0 keV incident energy for
19 directly following the changes in the electronic state of lattice oxygen, we have quantified the
20 reversibility of oxygen redox to show its persistence over long cycling in Li-rich NMC. Oxygen redox
21 compensates for almost half of the measured capacity in the initial cycles and even after the ageing
22 duration studied for the material herein, more than one-third of the capacity still comes from
23 reversible oxygen redox. Consequently, we observed only a gradual but limited growth of $\text{Mn}^{3+/4+}$
24 redox which was systematically quantified as well. A slight degradation of the $\text{Ni}^{2+/3+/4+}$ redox was
25 also observed. Capacity-wise, our findings serve as an optimistic prospect for the relatively nascent

1 concept of anionic redox chemistry, which can now without skepticism be envisaged for long-cycling
 2 high-energy batteries. On the other hand, the issue of voltage fade still plagues Li-rich NMC and
 3 appears to be bulk-related. Unconventional ideas are therefore needed to find meaningful materials'
 4 strategies for fully eliminating voltage fade.

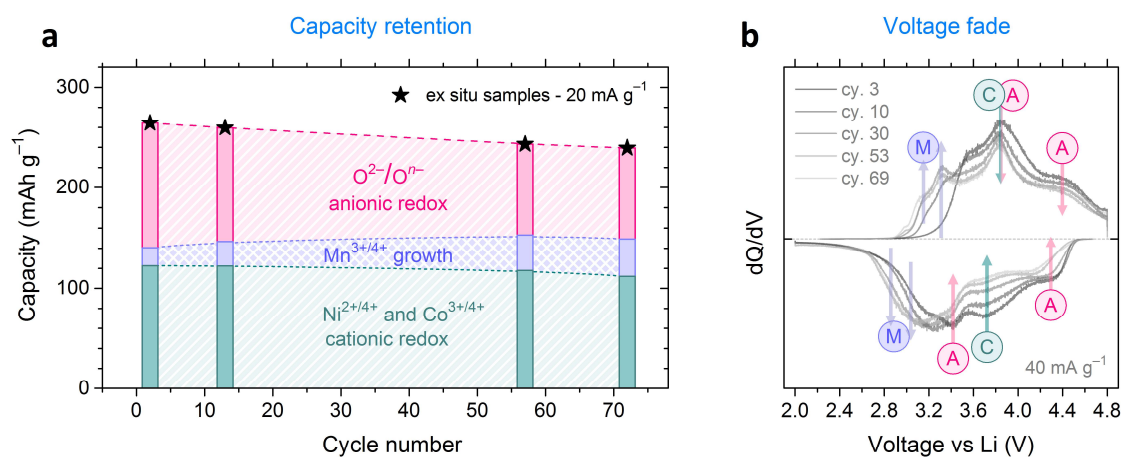


Figure 4. Evolution of capacity and voltage of cationic and anionic redox processes over long cycling. (a) The capacity from different redox couples is estimated from the qualitative and quantitative analysis of HAXPES spectra. (b) The evolution of different features in the dQ/dV curves is assigned to cationic 'C', or anionic 'A', or $Mn^{3+/4+}$ 'M' redox processes.

Associated Content

1 **Supporting Information Available.** Experimental Methods, Details of HAXPES probe-depth
2 calculations, HAXPES spectra for Co $2p_{3/2}$, and in-house XPS ($h\nu = 1.487$ keV) spectra for O 1s,
3 C 1s and F 1s.

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5 experiments were performed on the GALAXIES beamline^{47,48} at SOLEIL Synchrotron, France under
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Author Contributions

9 G.A and J.M.T. conceived the project. R.D. designed the HAXPES experiments. G.A.
10 prepared the samples and performed the electrochemical measurements. G.A., A.I. and R.D. carried
11 out the HAXPES experiments. R.D. analyzed the spectra. G.A. wrote the manuscript, which was
12 discussed by all authors.

Competing Financial Interests

13 The authors declare no competing financial interests.

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Direct quantification of anionic redox over long cycling of Li-rich NMC via HAXPES

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Supporting Information

Experimental Methods

1 **Material synthesis and characterization.** $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ (Li-rich NMC) powders
2 were synthesized with a two-step process involving carbonate co-precipitation followed by heat
3 treatment.¹ Note that we used the same batch of material as in our previous paper.² First,
4 stoichiometric Ni-Mn-Co carbonate was co-precipitated from an aqueous solution of transition-metal
5 sulphates by introducing in it an aqueous solution of sodium carbonate (2 M) and ammonia (0.2 M).
6 This was carried out in a controlled manner (pH = 8, T = 55 °C, stirring speed = 1000 rpm) by using
7 a continuously stirred tank reactor (Bioflow 320, Eppendorf) to regulate the morphology and
8 homogeneity of particles. The resulting Ni-Mn-Co carbonate powders were heat treated with Li_2CO_3
9 at 850°C for 12 hours to obtain the Li-rich NMC powders with a primary particle size of ~100 nm as
10 characterized by SEM (FEI Helios NanoLab 650). The crystal structure was confirmed with X-ray
11 diffraction (BRUKER D8 Advance diffractometer with $\text{Cu K}\alpha$ radiation) and the targeted elemental
12 composition was verified with inductively coupled plasma – mass spectrometry.

13 **Ex situ sample preparation.** Li half-cells having Li-rich NMC powders hand mixed (to
14 preserve morphology) with conductive Carbon Super P in a 90:10 ratio at the positive electrode (total
15 weight kept ~12 mg for each cell to ensure repeatability) and Li metal foil at the negative electrode
16 were assembled in Swagelok-type cells in an Argon glovebox ($\text{O}_2 < 0.1$ ppm, $\text{H}_2\text{O} < 0.1$ ppm). The
17 positive and negative electrodes were separated with two layers of Whatman GF/D borosilicate glass-
18 fiber sheets along with two layers of Cellguard separators soaked with an electrolyte – LP100 (Merck)
19 having 1 M LiPF_6 dissolved in ethylene carbonate : propylene carbonate : dimethyl carbonate in a 1
20 : 1 : 3 weight ratio. Note that Swagelok cells were preferred to coin-cells due to the possible risk of
21 short-circuit during the coin-cell disassembly process that could lead to artificial reduction of the
22 positive electrode. All cells were rested for 2 hours before testing. The first charge-discharge cycle
23 was performed at a constant specific current of 20 mA g^{-1} . Then, long cycling was performed at 40
24 mA g^{-1} (circa C/6). After achieving the desired number of cycles, the final sample preparation cycle
25 was performed at a lower specific current of 20 mA g^{-1} to reach either the full charged (4.8 V) or the
26 full discharged (2.0 V) states.

27 Upon achieving these states, the Swagelok cells were carefully disassembled in the glovebox
28 (ensuring no short circuiting) and as soon as possible (to prevent self-discharge under open circuit).
29 The positive electrode powders were rinsed thoroughly three times with anhydrous dimethyl
30 carbonate (DMC) to get rid of the electrolyte and soluble surface deposits. DMC was evaporated by
31 leaving the samples in vacuum (using the glovebox antechamber) for at least 1 hour. Note that our *ex*
32 *situ* electrode samples were recovered as loose powders that were thoroughly mixed. This averaged

1 out any concentration gradients which can bias XPS results if slurry-electrodes are used instead.

2 **Sample handling and transfer.** Great attention was paid to preserve the samples from air
3 and moisture exposure during transfer and handling. They were constantly maintained in dry argon
4 atmosphere or in vacuum. Inside the glovebox, the recovered *ex situ* powders were pasted on carbon
5 tapes stuck on a sample holder. For HAXPES, they were transferred from the on-site argon glovebox
6 to the beamline introduction chamber (that was kept under vacuum) via a specially-designed
7 detachable stainless-steel vacuum transfer system ('suitcase'). The samples were first sealed in this
8 'suitcase' inside the glovebox and then transferred to the beamline within 15 minutes.

9 **Hard X-ray Photoemission Spectroscopy (HAXPES).** HAXPES measurements were
10 carried out at the GALAXIES^{3,4} beamline of SOLEIL synchrotron facility in France. Photon
11 excitation energies $h\nu = 6.9$ and 10.0 keV were obtained from the third order reflection of the Si(111)
12 double-crystal monochromator. Photoelectrons were analyzed by a SCIENTA EW4000 spectrometer,
13 and the obtained energy resolution from the Au Fermi edge was 0.14 eV for 6.9 keV and 0.22 eV for
14 10.0 keV photon energy. No charge neutralizer was used. The analysis chamber pressure was
15 maintained around 10^{-8} mbar during the measurements. The binding energy scale was calibrated to
16 match the in-house XPS spectra on the same samples.

17 **In-house X-ray Photoemission Spectroscopy (XPS).** XPS measurements were performed
18 with a Kratos Axis Ultra spectrometer, using a focused monochromatized Al $K\alpha$ radiation ($h\nu =$
19 1486.6 eV). The analyzed area of the samples was $300 \mu\text{m} \times 700 \mu\text{m}$. Peaks were recorded with
20 constant pass energy of 20 eV. For the Ag $3d_{5/2}$ line, the full width at half maximum (FWHM) was
21 0.58 eV under the recording conditions. No charge neutralization was required and the pressure was
22 maintained around 10^{-8} mbar. The binding energy scale was calibrated from the C $1s$ core peak at
23 284.4 eV coming from Carbon Super P added to the positive electrode materials.

Supplementary Note S1

1 **Calculation of XPS and HAXPES probe depths.** The probe depths are defined as three
2 times the photoelectron inelastic mean free path (IMFP), and were estimated from the TPP-2M model
3 developed by Tanuma *et al.*⁵ This model uses four parameters: (1) the formula molecular weight, (2)
4 the density, (3) the number of valence electrons per formula, (4) the band gap. Given the composition
5 of the material $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$, its molecular weight is 85.29 g mol^{-1} and the number of
6 valence electrons is 19.45 per formula. The density is 4.18 g cm^{-3} . The band gap is unknown, but this
7 parameter has only little influence on the final result (for example, the calculated probe depth for $h\nu$
8 = 6900 eV is 29 nm using band gap = 0 eV and 30 nm using band gap = 5 eV). The band gap was
9 fixed to 2 eV for the calculations. The calculated values are as follows:

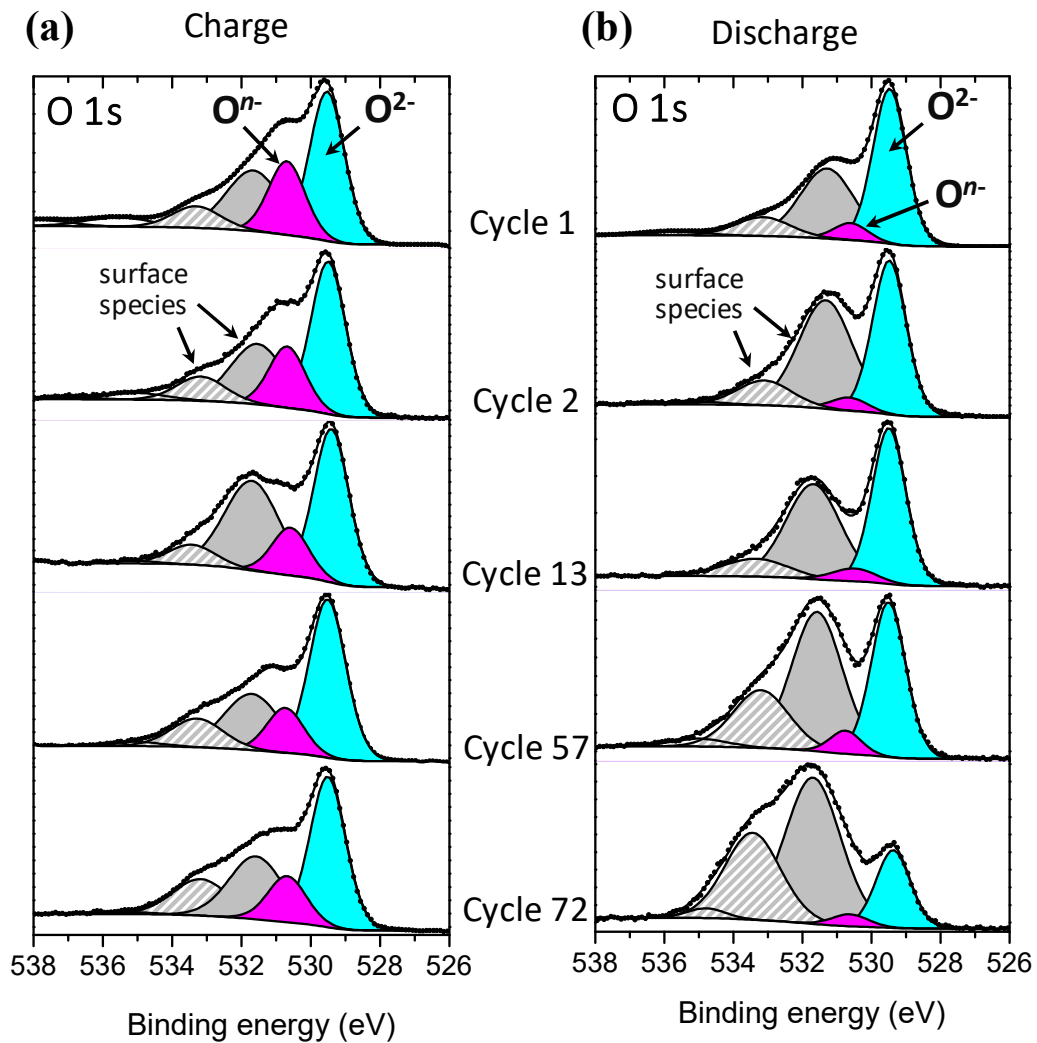
10

Photon energy (keV)	Probe depth (nm)			
	O 1s	Mn 2p	Co 2p	Ni 2p
1.487	6.3	5.7	5.0	4.6
3.0	13	13	12	12
6.9	29	28	28	28
10.0	40	40	39	39

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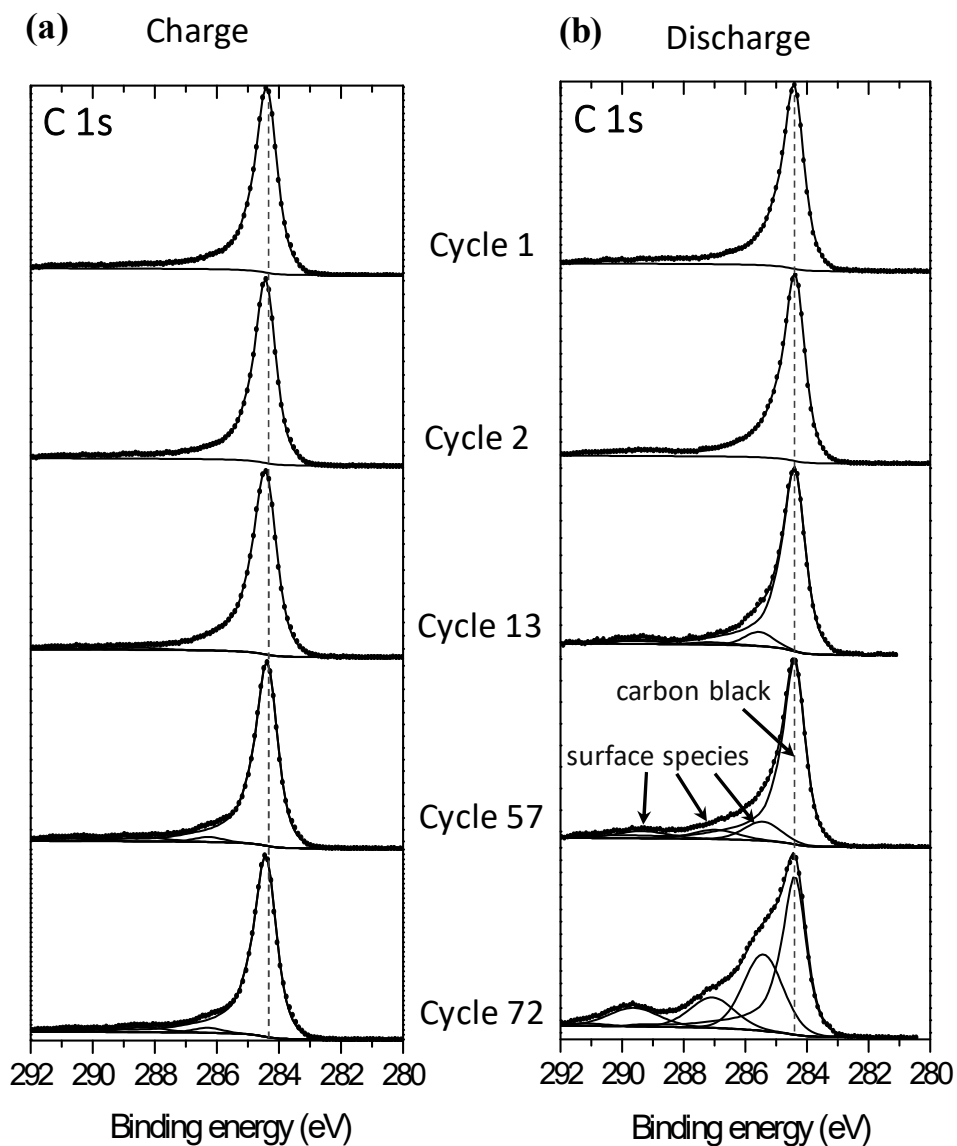
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Supplementary Figure S1



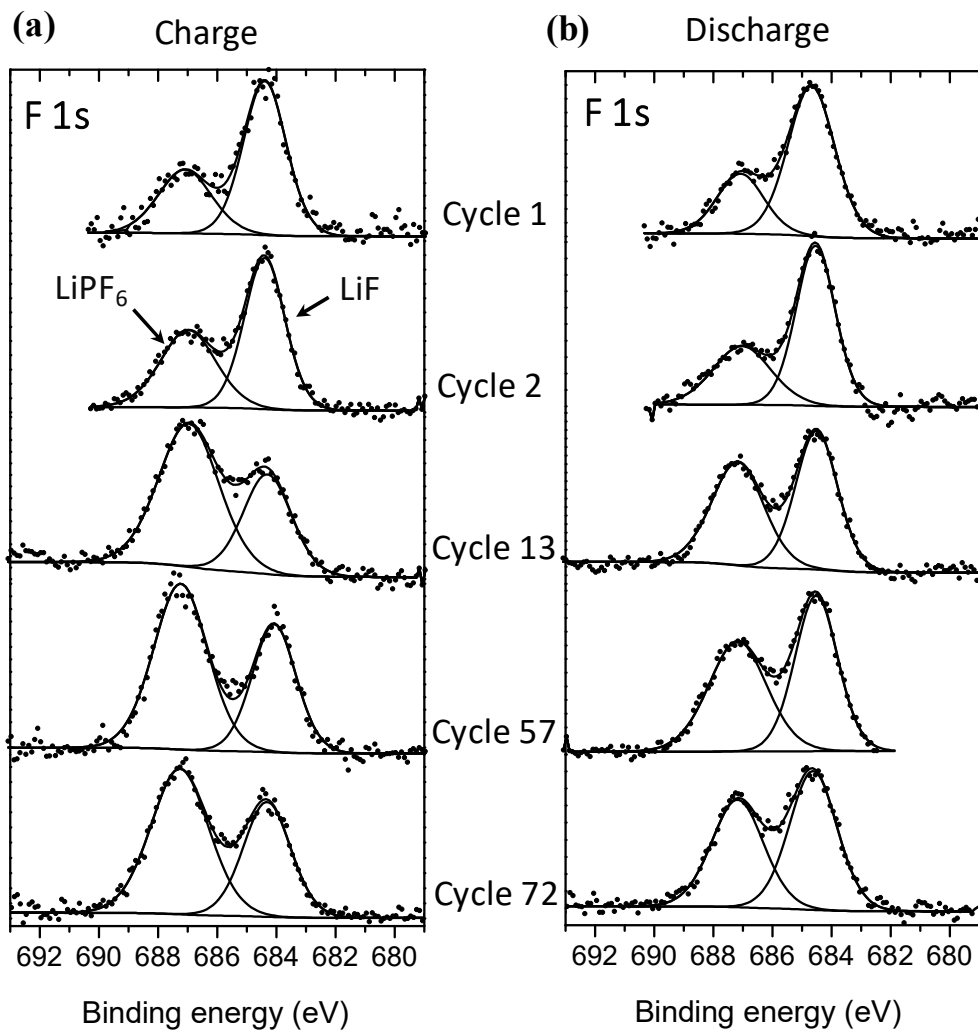
1 **Evolution of the anionic redox process over cycling.** O 1s in-house XPS spectra recorded at
2 1.487 keV: (a) samples charged to 4.8 V and (b) samples discharged to 2.0 V with gradually
3 increasing cycle numbers.

Supplementary Figure S2



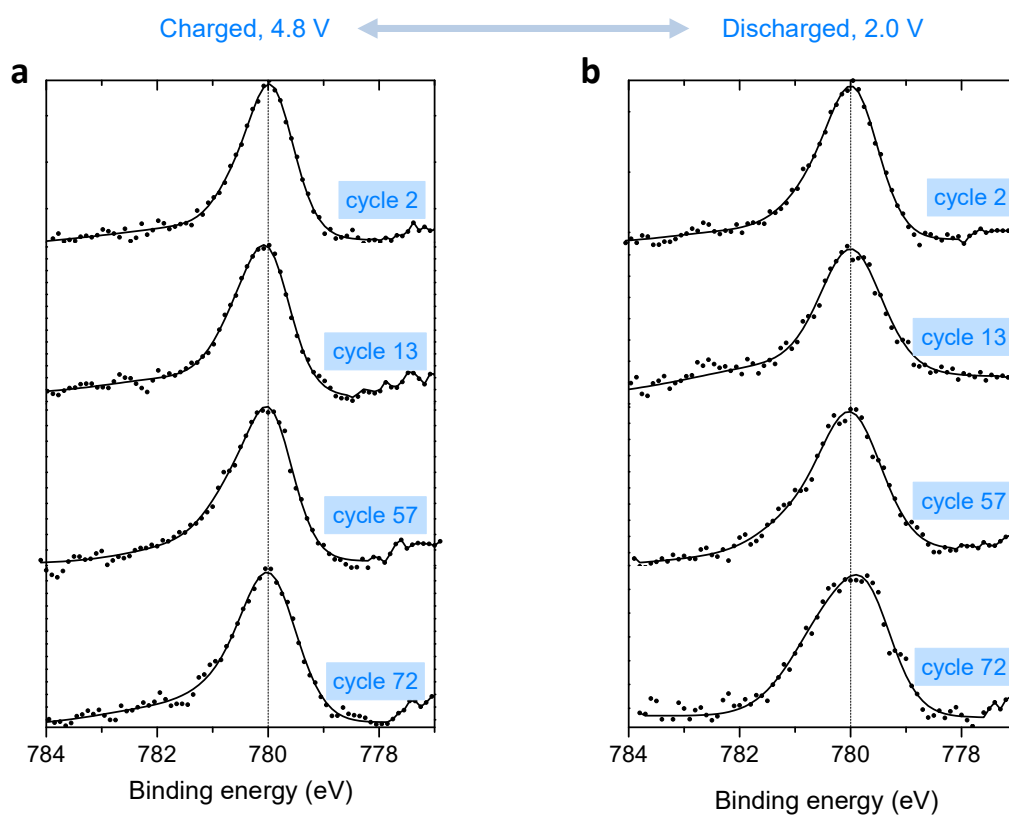
C 1s in-house XPS spectra recorded at 1.487 keV: (a) samples charged to 4.8 V and (b) samples discharged to 2.0 V with gradually increasing cycle numbers. The position of the carbon black peak at 284.4 eV was taken as reference for binding energy calibration.

Supplementary Figure S3



F 1s in-house XPS spectra recorded at 1.487 keV: (a) samples charged to 4.8 V and (b) samples discharged to 2.0 V with gradually increasing cycle numbers.

Supplementary Figure S4



Evolution of Co $2p_{3/2}$ over cycling. The main peak of Co $2p_{3/2}$ HAXPES spectra recorded at 6.9 keV for (a) the samples charged to 4.8 V and (b) the samples discharged to 2.0 V. There is no shift in the main peak's position between charge and discharge. However, this cannot be interpreted as an absence of participation of cobalt to the redox process, since the main peak binding energy is the same for Co^{3+} and Co^{4+} , as shown previously for $\text{Li}_{1-x}\text{CoO}_2$.⁶

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Supporting References

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