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Supporting information for

Pristine surface of Ni-Rich layered transition metal oxides as a premise of surface reactivity

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1. STEM-EELS experimental conditions

The use of the direct detection camera (Gatan K2 Summit) allows, together with the excited monochromator, achieving an energy resolution of ≈ 0.1 eV as given by the zero loss peak (ZLP) full width at half-maximum. Monochromated conditions were only used for detailed analysis of fine structures at Ni and O edges. The energy dispersion was chosen to be 0.25 eV/pixel in order to obtain a 927.5 eV range allowing a O-K edge to Ni L_{2,3} edge simultaneous analysis. Convergence and collection semi-angles were respectively 29.1 and 34.1 mrad and the camera

length was set at 29.5 mm. Thanks to the high performance of the used spectrometer configuration, it was possible to perform very fast acquisitions, exposing each pixel for only 20 ms. The current and the exposition time were chosen in such a way as to prevent the sample from electron beam degradation.

2. Second Derivative Method for elemental quantification of transition metals

Considering the proximity of transition metal edges, especially those of Co and Ni, the extraction of their characteristic signal is difficult and unreliable. The background extraction is indeed highly dependent on the model, the local thickness and the statistics achieved for data acquisition. The method of the second derivatives exploits the fact that such background removal is unnecessary.¹ Acquisition of Spectrum Images (SI) were performed with the surface aligned with the y vertical axis (easy in STEM-HAADF mode). Only surfaces with sufficient rectilinear lengths in this direction were chosen (at least roughly 50 nm corresponding to about 170 pixels). The first step consists in binning data along the y direction to obtain a sufficient S/N ratio even at the surface, where the signal for Co and Mn elements can be really low due to their small amount (Figure S1). The second derivative can then be calculated for all spectra in the SI. Two reference spectra for each edge (one taken in the bulk, far from the surface, and one corresponding to noise only) can then be extracted directly from the SI and be implemented in the Multiple Linear Least Square fitting routine of DM.² The fit ranges for all edges (O-K edge, L_{2,3} edges of TMs) were chosen by taking into account both the extend of EEL signal and the noise appearing in the second derivatives. Since the pre-peak at the oxygen K edge is known to be very sensitive to the oxidation state and site environment, it was not included in the fit. Likewise, the ratio of L₃/L₂ edges of TM are known to be sensitive to oxidation states, so fits were only performed based on their L₃ edge.

Slight energy shifts at the L_3 edges have in fact no effect considering the energy resolution we used for the quantification. The method showed a remarkable robustness whatever the analyzed particles.

The fit coefficients obtained for the four MLLS fits (one for each edge) represent the relative contributions of the two reference spectra within each binned pixel. The relative amount of each element can thus be calculated as a function of the distance from the surface. We decided to take Ni as reference since its signal is less prone to be influence by noise. Ratio values in the bulk (far from the surface) are set to the expected nominal values (1/8 for Co and Mn and 2.5 for O).

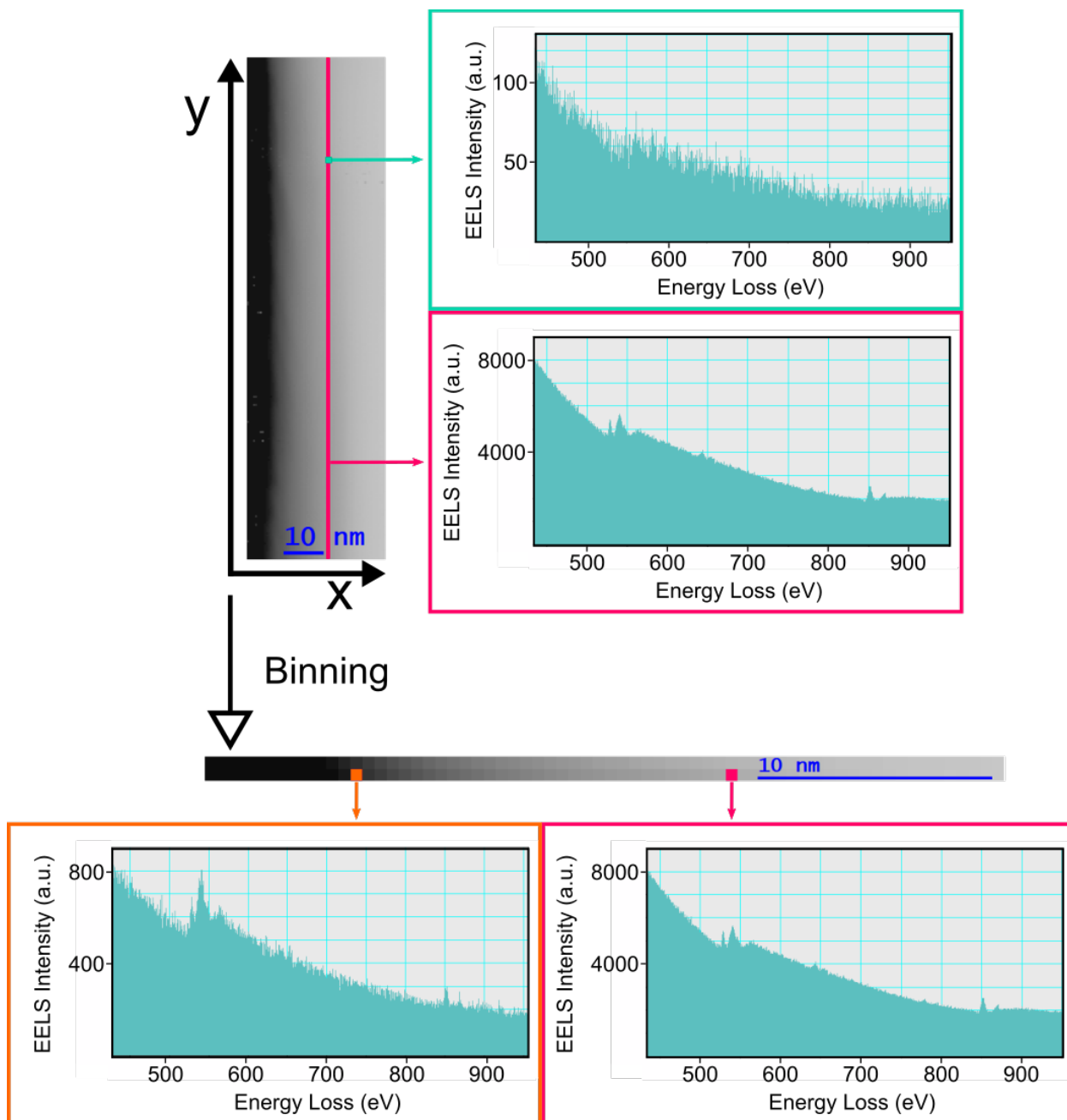


Figure S1. Example of the effect of the binning step on the S/N ratio. The spectra corresponding to a single bulk pixel of the original SI (green line) and of the binned SI (pink line) are compared. The spectrum in the orange box represents the spectrum of one pixel at the surface after binning.

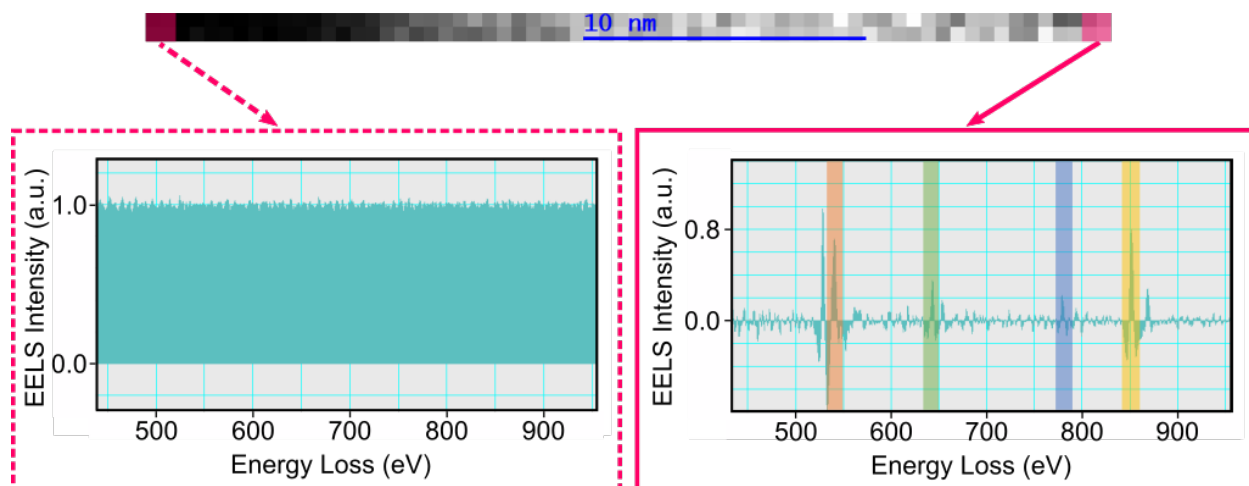


Figure S2. Reference spectra used for the MLLS fitting. The noise only reference is represented in the pink dotted box, while the bulk one in the full pink line.

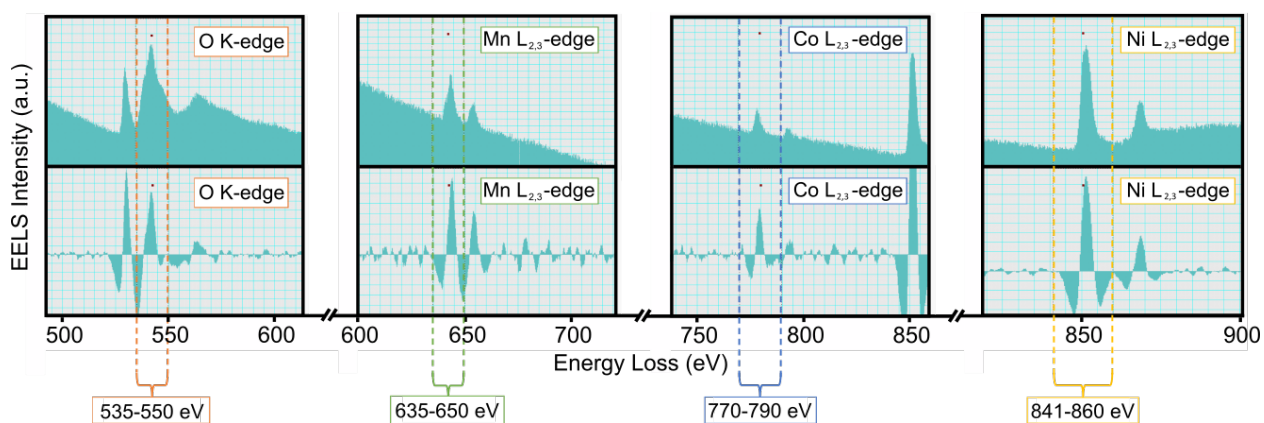


Figure S3. Chosen MLLS fitting ranges for each edge.

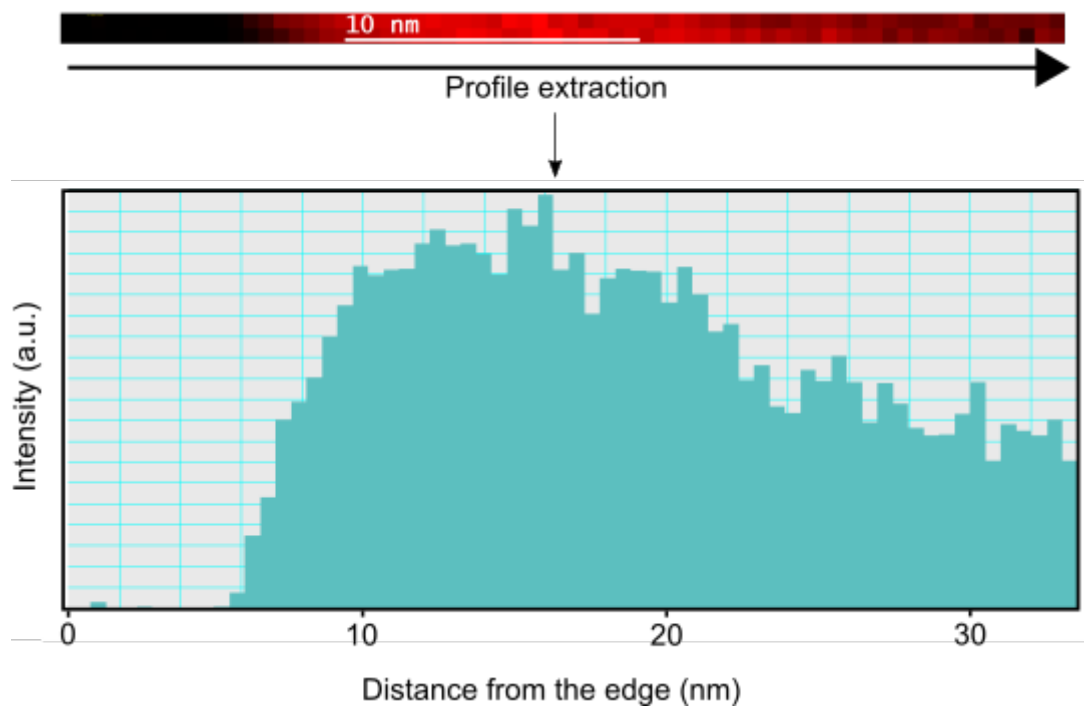


Figure S4. Fit coefficient map obtained for the MLLS fitting of the O K-edge on one of the analyzed particles and its extracted profile. The same map was obtained for each element and the fit coefficient values extracted the same way. The decrease of the coefficient for distances superior to 15 nm in this example is a consequence of the thickness increase. Performing ratios compensate for this effect.

3. Quantification results on various primary particles

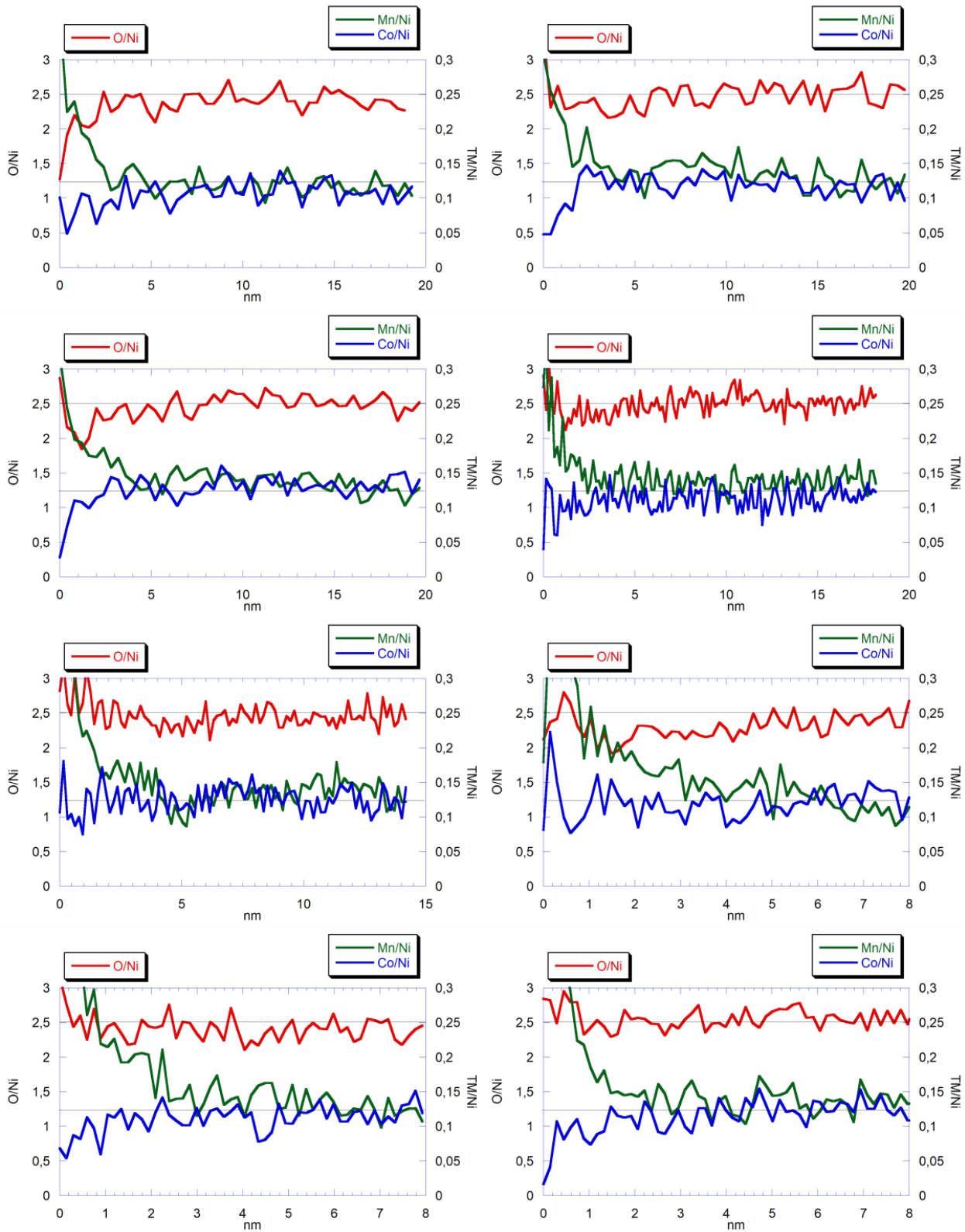


Figure S5. Quantification results obtained by STEM-EELS on various primary particles using the

second derivative method. Ratios O/Ni (in red), Mn/Ni (in green) and Co/Ni (in blue) are presented. A Mn enrichment is proven to occur over the first ~3 nm from the surface. Different pixel sizes were used and can explain the different amount of noise in the data.

4. ⁷Li MAS-NMR quantification method

In order to quantify the lithium contained in the contamination layer at the surface of the NMC811 samples, a calibration curve was needed. For this purpose, eight samples were prepared by mixing NMC811 with different quantities of LiF in a planetary ball miller for 2 x 30 minutes to guarantee the best possible intimacy between the paramagnetic material and the LiF. By using a recycle delay (D1) of 50 s the acquisition of quantitative spectra was assured.

⁷Li integrated intensities were determined by using spectral simulation (DMFit Software³) after performing a numerical fit of each set of peaks corresponding to a chemical compound. The so obtained integrated intensities were normalized considering the mass of the sample contained in the NMR rotor, the number of scans and the received gain.⁴

5. XPS compounds quantification method

A full-width-at-half-maximum (FWHM) of 1.4 eV and peak positions were initially fixed according to internal references of Li₂CO₃, LiOH and pristine NMC for each component of the Li 1s peak.

Following Grissa et al., fits were performed by imposing the integrated areas of peaks assigned to identified compounds (by means of the peak position) to be proportional to the amount of the other elements involved into the considered compounds based on their formula.⁵ For instance, once sulfates (here considered as Li₂SO₄) were identified on the S 2p peak, a component corresponding to this compound was added to the O 1s fit around 532.2 eV) with an integrated area accounting

for 4 times that of sulfur (after normalization by the relative sensibility factors). Once acceptable fits were obtained, constraints on FWHMs and positions were removed and fits were proven to be stable and consistent. The phase quantification was deduced from the addition of all element percentages involved in the same compound.

6. XPS reference spectra (LiOH & Li₂CO₃), XPS spectra for A2 sample and example of background for the XPS Li 1s region

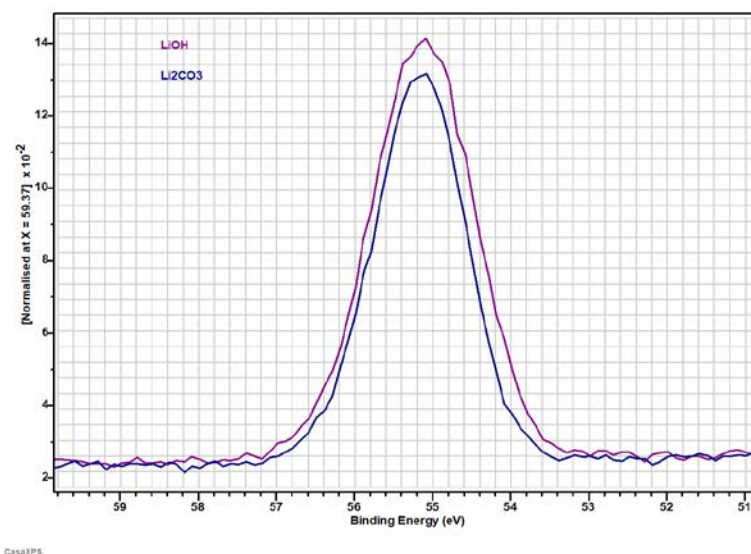


Figure S6. Experimental Li 1s XPS reference spectra for LiOH (in purple) and Li₂CO₃ (in blue) showing that the two compounds have similar peak positions. Spectra were acquired in the same conditions as the samples in the main text.

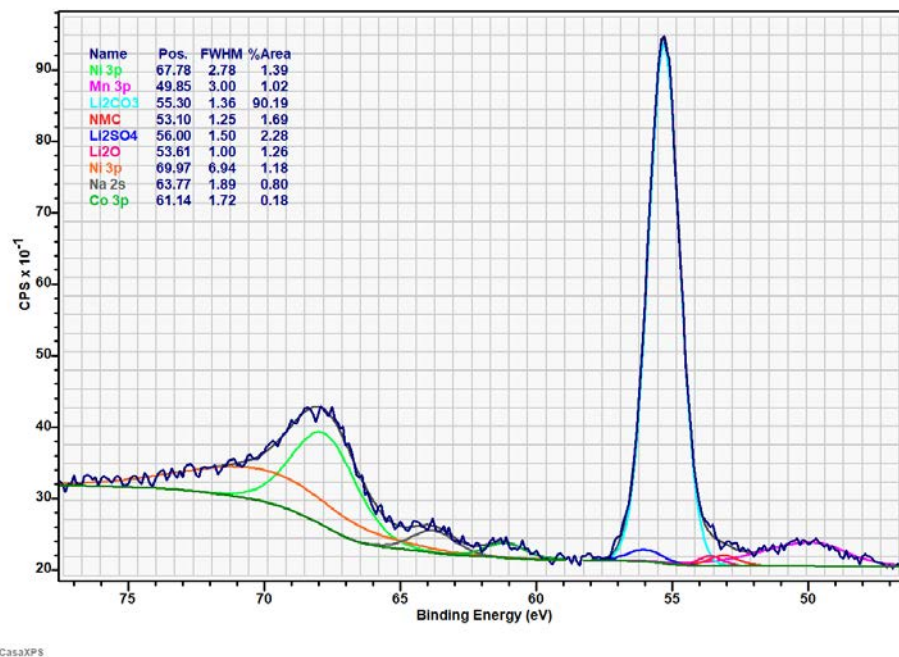


Figure S7. Li 1s XPS spectrum obtained for sample A2 (after 2 days in RH = 30%) showing that almost only Li₂CO₃ can be detected as a lithiated species after aging in these conditions.

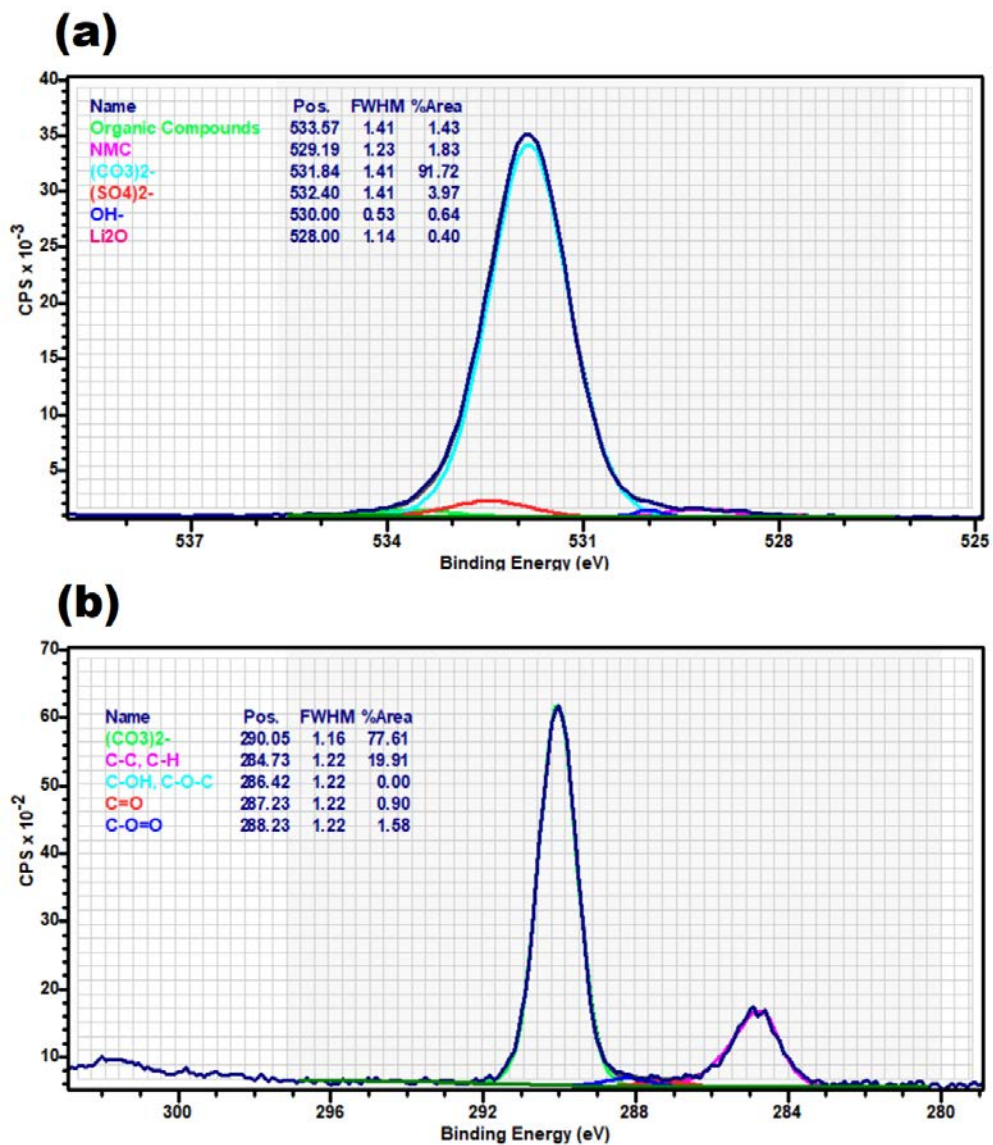


Figure S8. O 1s (a) and C 1s (b) XPS spectra obtained for sample A2 (after 2 days in
RH = 30%)

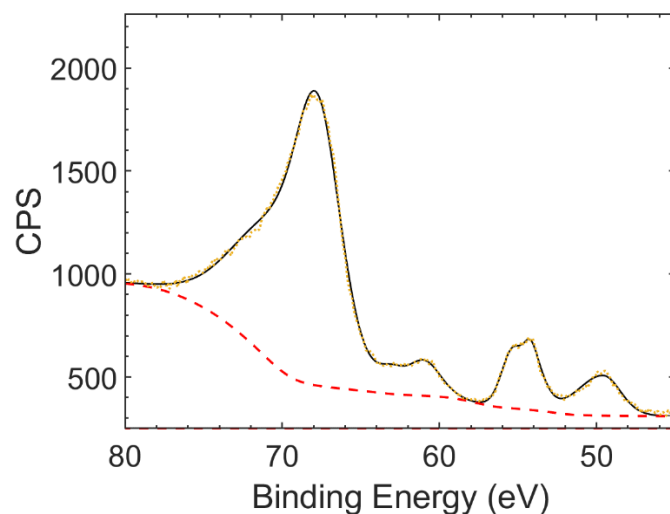


Figure S9. Example of the background developed for the Li 1s XPS region.

References

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