Supporting Information

The Role of Manganese in Lithium- and Manganese-rich Layered Oxides Cathodes

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1. 5-Gaussian model fit

Fig. S1 shows the localization in charge-discharge profiles of the charge points investigated. The Mn and O K-edge absorption spectra recorded at different states of charge exhibit a double pre-edge peak which is generally attributed to electronic transitions from the 1s to either 3d $t_{2g}$ or $e_g$ orbitals. In Fig. S2 we compare the O and Mn pre-edge peak features for the charge point P08 and P12/P16. The Mn K-edge spectra (black) have been shifted in energy for comparison. Mn and O K-edge absorption pre-peak of uncoated and VO$_x$-coated Li$_{1.2}$Mn$_{0.56}$Ni$_{0.16}$Co$_{0.08}$O$_2$ at different charge states have been modelled with a 5 Gaussian fit. In both sets of fits (Fig. S3 and S4) the energy positions of features (I) and (V) have been found after several iterations over the full set of data and then fixed to the obtained values. Similarly, the 5 Gaussian widths have been empirically determined by iterative fitting and finally fixed to constant values.
Fig. S1. Voltage profile of uncoated Li$_{1.2}$Mn$_{0.56}$Ni$_{0.16}$Co$_{0.08}$O$_2$, where the charge points corresponding to samples P01, P03, P04, P05, P08, P12, and P16 have been indicated.

Fig. S2 O and Mn pre-edge peak once subtracted the rising edge modeled by a pseudo-Voigt tail for the charge points P08 (a) and P12/P16 (b). The Mn K-edge spectra (black) have been shifted in energy (of around 6012 eV) and the O K-edge pre-peak have been rescaled in intensity (by around a factor 40) for comparison. The full and open symbols correspond to the uncoated and VO$_x$-coated samples, respectively.

The fitted parameters are reported in Fig. S5 and Table S1. The energy position of feature (IV) as a function of the charge reveals a similar behaviour for both the Mn and O K-edge data sets, with the partially or totally charged (P03, P04, and P05) VO$_x$-coated samples showing systematically lower values, suggesting a minor or less distorted Ni$^{2+}$ phase compared with the pristine samples. In fact the Ni$^{2+}$ component in the O spectra is expected around 532 eV.\textsuperscript{[S1]} Between P03 and P04, for the three considered O K-edge spectral features, (II), (III), and (IV), a shift towards higher energy is present, but to different extents, while no marked tendency is evident in the corresponding Mn K-edge features.
Fig. S3. Mn K-edge absorption pre-peak of uncoated and VOₓ-coated Li₁.2Mn₀.56Ni₀.16Co₀.08O₂ at different charge states once subtracted the rising edge background modelled by a pseudo-Voigt line tail together with the corresponding 5-Gaussian fits.

Fig. S4. O K-edge absorption pre-peak of uncoated and VOₓ-coated Li₁.2Mn₀.56Ni₀.16Co₀.08O₂ at different charge states once subtracted the rising edge background modelled by a pseudo-Voigt line tail together with the corresponding 5-Gaussian fits.
It is reasonable to assume that this discrepancy originates from the presence of the Ni$^{2+}$/Ni$^{4+}$ and Co$^{3+}$/Co$^{4+}$ redox reactions, only visible in the O K-edge absorption spectra, where the Ni$^{2+}$, Co$^{3+}$, and Co$^{4+}$ contributions are expected to be all between 530.5 and 532 eV and then masked by the much stronger Mn contribution.\[S2, S1\] Instead, the integrated intensity of features (II) and (IV) decrease, while that of feature (III) increases upon charging in a not fully reversible way. After the first charge, feature (III) seems to change in a reproducible way, while features (II) and (IV) constantly lose intensity in the first 3 cycles. This suggests a progressive deterioration in the structure of the Mn$^{4+}$ phase as a function of cycling, corresponding to a progressive reduction of the Mn 3d - O 2p hybridization. The error bars are of the order of the symbols dimensions. The full and open symbols correspond to the uncoated and VO$_x$-coated (V) samples, respectively. We excluded the evolution of the feature (V) intensity since affected by the rising edge background subtraction, and the evolution of the intensity of feature (I) for the Mn K-edge data since, in this case, we believe it is just a tail of feature (II).

Fig. S5. Fitted parameters as a function of the charge state obtained by a 5-Gaussian model representing the O and Mn K-edge absorption pre-peak, once subtracted the rising edge. a,b
Energy positions of features (II), (III) and (IV) corresponding to the Mn and O pre-edge peak, respectively. c Integrated intensity of features (II), (III), (IV), and of the full pre-edge peaks for the Mn K-edge data set. d Integrated intensity of features (II), (III), and (IV) for the O K-edge data set. Charge states 1 to 16 in horizontal axis correspond to the P01 to P16 sample notation.

Table S1. 5-Gaussian fits results obtained fitting the Mn and O absorption K-edge pre-peaks of uncoated and VO₅-coated (V) Li₁₁₂Mn₀.₅₆Ni₀.₁₆Co₀.₀₈O₂ at different charge states once subtracted the rising edge.

| O | K-edge | E1 (eV) | σ₁ (eV) | I1 | E2 (eV) | σ₂ (eV) | I2 | E3 (eV) | σ₃ (eV) | I3 | E4 (eV) | σ₄ (eV) | I4 | E5 (eV) | σ₅ (eV) | I5 | E6 (eV) | σ₆ (eV) | I6 | S1 |
| P01 | 0.38 | 0.0045 | 6541.01 | 0.38 | 0.0377 | 6542.22 | 0.42 | 0.0011 | 6541.09 | 0.56 | 0.0270 | 6544.93 | 0.38 | 0.0013 |
| P03 | 0.38 | 0.0069 | 6541.11 | 0.38 | 0.0475 | 6542.10 | 0.42 | 0.0087 | 6543.14 | 0.56 | 0.0350 | 6544.93 | 0.38 | 0.0032 |
| P04 | 0.38 | 0.0099 | 6541.08 | 0.38 | 0.0579 | 6542.11 | 0.42 | 0.0204 | 6543.17 | 0.56 | 0.0415 | 6544.93 | 0.38 | 0.0049 |
| P05 | 0.38 | 0.0122 | 6541.07 | 0.38 | 0.0618 | 6542.15 | 0.42 | 0.0297 | 6543.22 | 0.56 | 0.0480 | 6544.93 | 0.38 | 0.0082 |
| P08 | 0.38 | 0.0097 | 6541.10 | 0.38 | 0.0554 | 6542.25 | 0.42 | 0.0144 | 6543.19 | 0.56 | 0.0359 | 6544.93 | 0.38 | 0.0046 |
| P12 | 0.38 | 0.0101 | 6541.08 | 0.38 | 0.0597 | 6542.14 | 0.42 | 0.0277 | 6543.23 | 0.56 | 0.0492 | 6544.93 | 0.38 | 0.0098 |
| P15 | 0.38 | 0.0111 | 6541.04 | 0.38 | 0.0576 | 6542.17 | 0.42 | 0.0240 | 6543.23 | 0.56 | 0.0426 | 6544.93 | 0.38 | 0.0065 |
| P01 | 0.38 | 0.0044 | 6541.10 | 0.38 | 0.0405 | 6542.21 | 0.42 | 0.0019 | 6541.10 | 0.56 | 0.0303 | 6544.93 | 0.38 | 0.0015 |
| P04 | 0.38 | 0.0085 | 6541.06 | 0.38 | 0.0545 | 6542.17 | 0.42 | 0.0151 | 6543.13 | 0.56 | 0.0377 | 6544.93 | 0.38 | 0.0039 |
| P05 | 0.38 | 0.0111 | 6541.02 | 0.38 | 0.0596 | 6542.08 | 0.42 | 0.0285 | 6541.12 | 0.56 | 0.0456 | 6544.93 | 0.38 | 0.0058 |
| P08 | 0.38 | 0.0102 | 6541.05 | 0.38 | 0.0452 | 6542.25 | 0.42 | 0.0138 | 6543.18 | 0.56 | 0.0312 | 6544.93 | 0.38 | 0.0047 |

3. Mn oxidation state evaluation

Alternative estimation of the mean Mn oxidation state based on the Mn K-edge pre-edge peak centre of mass and its comparison with reference materials, which has been proposed in the past,[S3] fails in the present case because of variations on the local magnetic properties and site symmetries. In Fig. S6 we report the Mn K-edge pre-edge peak centre of mass compared with the values expected for the Mn⁢³⁺, Mn⁢⁴⁺, and Mn⁢⁵⁺ references. In the case of the VO₅-coated samples the Mn K-edge pre-edge peak centre of mass appears to decrease slightly as a function of charge, being always very close to the value for the Mn⁢⁴⁺ references, while in the uncoated samples it seems instead to slightly increase, suggesting different scenarios for the two sets of systems. We believe that the pre-edge centroid energy method[S3] cannot be applied in the present case, since distortions or Mn local magnetic variations, both detected in the present work, should invalidate it. The comparison of the Mn and O K-edge absorption pre-peaks (Fig. 4) and the Mn L-edge spectra reported in Fig. S7 confirm this claim. In fact, the Mn L-edge first feature shift in energy together with the increase of spectral weight around 641 eV (Fig. S7 b) look to confirm the partial reduction of Mn detected by comparing the O and Mn K-edge absorption data (Fig. 2 b), in agreement with the spectra reported in Ref. 38 for the Mn₃O₅ (Mn³⁺) and MnO₂ (Mn⁴⁺) reference spectra.
Fig. S6. Mn K-edge pre-edge peak centre of mass for VOₓ-coated (V) and uncoated samples compared with the values expected for the Mn³⁺, Mn⁴⁺, and Mn⁵⁺ references. Charge states 1 to 16 in horizontal axis correspond to the P01 to P16 sample notation.

Fig. S7. (a) Mn L-edge absorption spectra collected on Li[Li₀.₂Ni₀.₁₆Mn₀.₅₆Co₀.₀₈]O₂ uncoated and VOₓ-coated pristine samples (P01). Panel (b) reports a zoom over the Mn L₃-edge, where it
is possible to appreciate a shift of the A feature towards lower energy by charging, both in uncoated and VO_x-coated samples. The evolution of the A feature as a function of the charge state is reported for uncoated (c) and VO_x-coated (d) samples.

4. Mn local magnetic properties

The local Mn magnetic moment, $\mu_{\text{Mn}}$, has been quantified with the IAD method by comparing the reported spectra to the MnO and MnO_2 references. Also the energy position of the K\(_{\beta_{1,3}}\), E\(_{K\beta_{1,3}}\), provides information on the spin state, reflecting the effective number of unpaired 3d electrons. The evolution of $\mu_{\text{Mn}}$ and E\(_{K\beta_{1,3}}\) as a function of the charge state is reported in Fig. S8. The similar trends shown by the two quantities ($\mu_{\text{Mn}}$ and E\(_{K\beta_{1,3}}\)) as a function of the charge state strengthen the results, and the smaller error bar for the energy values even suggest the possibility of more detailed discussions of the evolution from one sample to the other.

![Fig. S8](image.png)

**Fig. S8** Evolution of the energy position of the Mn K\(_{\beta_{1,3}}\) emission line (a) and of the extracted average Mn local magnetic moment ($\mu_{\text{Mn}}$) by the IAD method once compared the spectra to the MnO and MnO_2 references (b) as a function of the charge state. The full and open symbols correspond to the uncoated and VO_x-coated samples respectively. The error bars have been estimated by considering the mean square deviation over the analysis results of 3 individual scans. Charge states 1 to 16 in horizontal axis correspond to the P01 to P16 sample notation.

The strong $\mu_{\text{Mn}}$ drop upon charge in the uncoated material seems to corresponds to the formation of a Mn environment corresponding to that of layered rhombohedral r-LiMnO\(_2\), where theoretical calculations predict the Mn\(^{3+}\) in the low spin (LS) configuration (ref. 47). Interestingly, the theoretical simulation of this phase predicts several potential advantages for a good electrochemical activity and agrees with the reported results. In particular, a strong hybridization between Mn e\(_g\) and O 2p should favor a larger reversible Li fraction extraction, i.e. a larger capacity. Moreover, the partially reduced O ions could function as the electron acceptor upon discharge as seen experimentally, which ensures that doping with other M ions can be used to optimize the material without damaging the electrochemical properties (ref. 50). In addition,
LS Mn$^{3+}$ is expected not to be Jahn Teller active, and to stabilize the structure upon cycling. The structural and electronic rearrangements expected with $r$-LiMnO$_2$ formation could induce clear XANES changes. However, in LS Mn$^{3+}$ all three $t_{2g}$ orbitals are occupied while the $e_g$ are empty. Its electronic structure looks similar to that of HS Mn$^{4+}$ ion but different from HS Mn$^{3+}$ ion. Thus, it is reasonable to predict the XANES spectra of $r$-LiMnO$_2$ similar rather to that of HS Mn$^{4+}$ ion (Li$_2$MnO$_3$) than to HS Mn$^{3+}$ ion in the typical manganites ($\alpha$-LiMnO$_2$). The suggested formation of Mn$^{3+}$ in LS configuration in Li-rich NMC cathodes also explains the shift of the main Mn K-edge absorption feature towards higher energy during the charge, generally associated to oxidation, while Mn is actually partially reducing.

5. Local structure

The Fourier transforms (FTs) of the Mn K-edge EXAFS spectra are reported in Fig. S9. The FTs show two main features at around 1.5 and 2.5 Å corresponding to the Mn-O and Mn-M bond distances, respectively.
The intensity of the FT Mn-O peak decreases, highlighting an increasing disorder in the Mn-O shell, as a function of charge, in agreement with the literature \[S6\]. The occurrence of coexisting different Mn sites by charge is expected to globally increase the local structural disorder and local distortions. The partially irreversible formation of Mn\(^{3+}\) in the charge state is in agreement with the not completely reversible evolution of the local structure by charging. The Mn-O bond length looks to not change as a function of charge despite the Mn reduction. Most likely this is because the first shell peak is containing several contributions which can’t be easily deconvoluted by eyes and a modelization is necessary to extract quantitative information on the interatomic distances. Instead, the strains induced by the \(\text{VO}_x\)-coating strongly affect the Mn local structure in the pristine compound. The \(\text{VO}_x\)-coating is estimated to be around 3% of the full material \[S11\]. We have identified isolated particles of around 300-150 nm in diameter. A 3 wt% coating of a 150 nm particles accounts for a \(\text{VO}_x\) shell of less than 2 nm of average thickness. The EXAFS spectral variation are most likely coming by the strain induced even if affecting only a portion of the nanoparticles, the one closer to the surface. Interestingly the \(\text{VO}_x\)-coating induced strains relax during the first charge cycle. From our results it is tempting to hypothesize that, while the coating increases the extent of the Mn\(^{3+}\) HS formation, it is as well suppressing the detrimental Jahn-Teller distortions that would be expected with the HS configuration and are naturally absent in the Mn\(^{3+}\) LS. In fact, the FTs first shell intensity of P05 and P08 is the same for the two systems, highlighting a similar averaged Mn local structure.

The EXAFS oscillations show a good signal to noise ratio until \(k=15\ \text{Å}^{-1}\). This implies that it is not reasonable to model the spectra considering the 3 different Mn sites which have been detected (Mn\(^{4+}\) HS, Mn\(^{3+}\) LS, and Mn\(^{3+}\) HS) being the maximum number of independent parameters in an EXAFS fit limited by the formula \(N = (2 \cdot \Delta k \cdot \Delta R ) / \pi\). In the present case \(N\) is equal to 15 or 7, including or not the second shell.

Taking into account such constrains and by following the literature \[S6\] we tentatively fit the EXAFS oscillation by a simplified model. We considered, as in the past \[S6\] an equimolar solid solution of monoclinic (C2/m) \(\text{Li}_2\text{MnO}_3\) and hexagonal layered (R3m) \(\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2\). The EXAFS analysis was performed using the GNXAS package \[S7-S8\] which is based on the multiple scattering (MS) theory. The method uses the decomposition of the EXAFS signals into a sum of several contributions, namely the n-body terms. In the reported fits we used four different two-body terms related to pairs of atoms, i.e., the selected photoabsorber and surrounding atoms located in consecutive shells. Even though all the MS signals are rather important in determining the total one, the most significant contributions are those deriving from the interaction with the first and second shell, i.e., Mn-O and Mn-Mn, respectively. The strains induced by the \(\text{VO}_x\)-coating, strongly affecting the Mn-O local structure in the pristine compounds (Fig. S9), has been parametrized by the asymmetric coefficient \(\beta\). Indeed, the total number of parameters used in the fitting procedure was 11, including bond distances and Debye Waller factors for the two considered shells (4 per shell) plus \(\beta\), \(E_0\), and \(S_0\)^2 \[S6, S9\].

Figure S10 reports the MS contributions to the EXAFS signal in the case of P05 sample for both uncoated and \(\text{VO}_x\)-coated.
The results of the fitting of the EXAFS spectra, in terms of first- and second-shell bond lengths, and Debye-Waller factors are reported in Fig. S11 and Table S2. Within the error bars the presented results are consistent with the previous ones reported for the uncoated compound in the literature. The fitting results look scattered and the corresponding error bar are probably underestimated because coming only from the fitting procedure, i.e. no taking into account the spline which was not trivial due to the limited data quality.

While detailed variations in bond lengths and Debye-Waller are not extractable because too small inside their error bars, and clear differences are difficult to be highlighted between the two systems, uncoated and VO$_x$-coated samples show clearly distinct asymmetric coefficient $\beta$. More in details, only for the coated samples (especially in P01) this parameter significantly differs from zero. This finding reflects the spectral differences shown in Fig. S9 (bottom-left panel) and suggests again an existent strain in the VO$_x$-coated samples. Instead, in the charged state (P05) $\beta$ tends to 0 on both systems, in agreement with the similarity observed on the FTs relative to uncoated and VO$_x$-coated samples (Fig. S9, bottom-right panel), confirming a release of that strains during the charge.

**Fig. S10.** MS contributions to the experimental signal for both P05 uncoated (left) and P05 VO$_x$-coated (right) samples.
Fig. S11. EXAFS fitting results: Mn-O and Mn-Mn distances (a, b) and relative Debye-Waller factors (c, d) for both uncoated and VO$_x$-coated datasets. Charge states 1 to 8 in horizontal axis correspond to the P01 to P08 sample notation.

Table S2. Relevant EXAFS fitting results for both uncoated and VO$_x$-coated datasets. Interatomic Mn-O and Mn-Mn distances and relative Debye-Waller factors are presented, together with the $\beta$ asymmetry parameter for the Mn-O first shell. The value for the amplitude reduction factor, $S_0^2$, was initially fitted and then kept fixed to 0.69, accordingly to the literature.$^{[S9]}$ The estimated parameter errors are indicated in parentheses. They have been obtained by contour plots.$^{[S10]}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Uncoated</th>
<th>VO$_x$-coated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P01</td>
<td>P03</td>
</tr>
<tr>
<td>Mn-O / Å</td>
<td>1.890(4)</td>
<td>1.876(3)</td>
</tr>
<tr>
<td>$\sigma^2$(Mn-O) / Å$^2$</td>
<td>0.0027(4)</td>
<td>0.0033(5)</td>
</tr>
<tr>
<td>Mn-Mn / Å</td>
<td>2.901(5)</td>
<td>2.881(6)</td>
</tr>
<tr>
<td>$\sigma^2$(Mn-Mn) / Å$^2$</td>
<td>0.0067(8)</td>
<td>0.007(1)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>$S_0^2$</td>
<td>0.69 FIX</td>
<td>0.69 FIX</td>
</tr>
</tbody>
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$\chi^2$-like residual ($10^{-6}$) | 5.29 | 7.32 | 4.21 | 4.59 | 4.18 | 5.02 | 7.32 | 4.21 | 4.59 | 4.18 |
6. Soft X-ray elemental maps

Spatially resolved energy scan at O-K and Mn L-edge allow the determination of the total variation of the absorbance across the corresponding absorption edge with spatial resolution around 25 nm. In figure S12 some examples of these maps at the O-K edge are reported both for the uncoated and the VO$_x$-coated samples at different charge points.

![Fig. S12. Total absorbance variation across the O – K edge. Only pixels with S/N ≥ 2 are considered while pixels with smaller S/N are white and are assumed to be free of oxygen. (a) P01 uncoated, (b) P05 uncoated, (c) P04 coated and (d) P08 coated sample. Each pixel corresponds to 10 nm.](image)

The absorbance signal in the maps is proportional to both the thickness and the concentration of the selected element, i.e. Oxygen in this case. Only pixels with a S/N ≥ 2 are considered, where the Noise is defined as the average single pixel spectra standard deviation in the pre-edge energy region (< 526 eV) and the Signal is defined as the difference between the absorbance average value in the post edge energy region (> 544 eV) and the average value in the pre-edge energy region. Pixels with smaller S/N are white and are assumed to be free of O. This criterion defines the particles edge and allows for the spectral comparison between particles borders and bulk reported in Fig. S15. An S/N threshold equal to 1 was too weak, selecting pixels clearly well
outside the sample material. Also, spatially resolved energy scan allows mapping the ratio between different components with spatial resolution, as it is explained in the caption of Fig. 5. In this case the average of 3 images around the selected energies was used to calculate the final map.

For the V L-edge the selection of the pixels based on the total absorbance variation was in general not possible, because of the weak signal corresponding to just few nm thicknesses, and the proximity to the O – K edge. Also the selection of V signal using the V L₃ peak maximum was subject to noise artefacts due to the small number of points available on the peak and its small S/N in the single pixel spectrum. Therefore the V distribution overlapped on the Mn signal in the inset Fig.1f is just indicative. An alternative approach to visualize the distribution of the VOₓ-coating at the particles border relied on the V L₃-edge peak maxima. Figure S13 (a), (b) shows binary maps of the coated sample at charge point P01 and P08 respectively. The red pixels have V L₃-edge peak maxima bigger than half the total absorbance variation across the O-K edge, as graphically explained in figure S13 (f). This criterion selects pixels only at the borders of the particles. In figure S12 (c) - (e) are reported zooms on some particles from figure S13 (a).

Being few nm the expected thickness of the VOₓ-coating (3% of the full material mass [S11]), one order of magnitude below our spatial resolution, we can only appreciate the actual distribution of the coating. We confirm a VOₓ-shell-like distribution, which dimension is apparently not uniform, possibly because of different surface roughness of the coated particle.

**Fig. S13.** VOₓ-distribution (red) at the borders of electrode particles (white) for the pristine sample (a) and charge point P08 (b), full field of view. In (c), (d) and (e) are reported some isolated particles from (a), scale bar is 200 nm. Pixels where selected comparing the total absorbance variation at the O-K edge with the absorbance intensity at the L₃ peak maxima of V L-edge, as graphically explained in (f): only pixels with a V L₃ peak maximum equal or bigger
than half of the total absorbance variation at O-K edge are displayed with red colour in the images, i.e. only the pixels for which the black dashed line intercept the V L₃ peak.

7. Soft X-rays energy stack pre-treatment

Each image of the energy stack (I(x,y), where I is the transmitted intensity by the sample, and x and y are the 2D coordinates of a generic pixel) is firstly normalized to unity dividing by the corresponding Flat Field image (I₀(x,y), being I₀ the incident intensity on the sample), taking into account the value of the electron current in the storage ring, and then aligned taking as reference the first image. The alignment is done by a homemade software (SW) selecting a suitable region of interest (ROI). The ROI of a single image is compared with the ROI of the first image and thanks to the Python library of cv2 (Open Computer Vision: OpenCV) the SW uses the normalized cross-correlation of both ROIs to detect the best matching between them (the function used is 'cv2.matchTemplate()'). Once this best matching is detected, the image is shifted by the number of pixels calculated in the precedent operation. This process is repeated for each image of the energy stack. Normally this operation reduces the effective field of view of about 10%-15%, i.e. from 10 µm × 10 µm to ≈ 9 µm × 9 µm. The described method, if performed on the suitable ROI, assures an alignment with an error within ± 1 pixel. An additional manual alignment step was performed before doing image calculations to assure an optimal alignment which avoids misalignment artefacts, particularly in ratio images (see Fig. 5). For this double check, a manual alignment was realized only on the average images corresponding to the selected energies, using the manual alignment option of EFTEM-TomoJ[S12]. In all the cases the additional applied shift respect with the automatic alignment described before and performed on the full energy stack, was zero or ± 1 pixels.

8. Soft X-rays spectra experimental error

A repetition of 3 energy scan on the uncoated pristine sample P01 was performed to evaluate the spectra experimental error. The error was calculated as the average deviation:

\[(|AVG - S1| + |AVG - S2| + |AVG - S3|)/3\]

With AVG average normalized spectrum and S1, S2 and S3 the individual normalized spectra from the measured ones. Results are reported in figure S14. Average error value is 0.005 and its maximum value is 0.018 located at 528.8 eV.
Fig. S14. (a) Normalized absorbance signal extracted from the field of view of 3 consecutive transmission image energy stacks acquired on the uncoated pristine sample P01 with the corresponding calculated deviation in magenta. (b) A zoom on the calculated deviation. The variation of the error as function of the energy is apparent. The biggest values are in the steepest energy region, between 528 eV and 543 eV.

9. O K-edge spectral differences along isolated particles: border vs bulk

In Fig. S15 are shown the averaged O K-edge pre-edge regions corresponding to the bulk and the border of isolated particles. We considered border a particle thickness of about 30 nm from the edge, accordingly with the experimental spatial resolution. The pre-peak averaged spectral intensity is generally higher in the bulk of the uncoated system, while above 532 eV the difference of the normalized spectra looks negligible in the error bar. Being the spectra normalized with respect to the oxygen absorption jump, the decreased intensity of the O K-edge pre-peak most likely corresponds to a lower 3d M contribution, i.e. to a higher content of oxygen that is not bound to transition metals. This reflects again the presence of some surface oxygen compounds, which is also in agreement with the work of G. Assat and coworkers [S13]. Interestingly, this surface-bulk difference is smaller with VO
\_\text{X}\_-
-coating, which would support some hindered SEI formation from reaction with the electrolyte, much more significant with the uncoated samples. However, it is not possible to exclude that the general smaller size of the VO
\_\text{X}\_-
-coated particles, which is increasing the surface contribution anyway present in the bulk spectra, is affecting the comparison. Fig. S15 g plots the difference of bulk and border spectra integral around the pre-edge region as a function of the charge state. It is interesting to evidence the presence of a more than 100% jump at the end of the voltage plateau only for the uncoated system. This jump strongly suggests formation of compounds with the oxygen expected to be released at the end of the voltage plateau in the uncoated material, but which seems suppressed by the VO
\_\text{X}\_-
-coating [S14].
**Fig. S15**  a-f  O K-edge absorption spectra normalized to the atomic absorption corresponding to the bulk (red squares) and border (blue circles) of isolated particles. The figures report a zoom over the pre-edge region. Each spectrum corresponds to the average over 5 isolated particles. It has been considered border the particle region distant less than 30 nm from the edge. The upper and middle row report the data collected on uncoated and VO\textsubscript{x}-coated sample at representative charge states, respectively.  

**g** Difference of the normalized spectra integral around the pre-peak region (526-532 eV) corresponding to the bulk and the borders of the particles. Above 532 eV the difference of the normalized spectra (bulk vs. border) looks negligible. Charge states 1 to 8 in horizontal axis correspond to the P01 to P08 sample notation.

**References**


