

Supporting Information

Sodium Containing Surface Film Formation on Planar Metal Oxide Electrodes with Potential Application for Sodium-Ion and Sodium-Oxygen Batteries

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Raman spectroscopy: The Raman spectra of $\text{TiO}_{2-x}\text{-A}$ and $\text{TiO}_{2-x}\text{-R}$ shown in **Figure S1**, containing 5 spectra each, measured at different positions/areas on the electrode. The vertical, black lines indicate the mean wavenumber of the peak maxima.

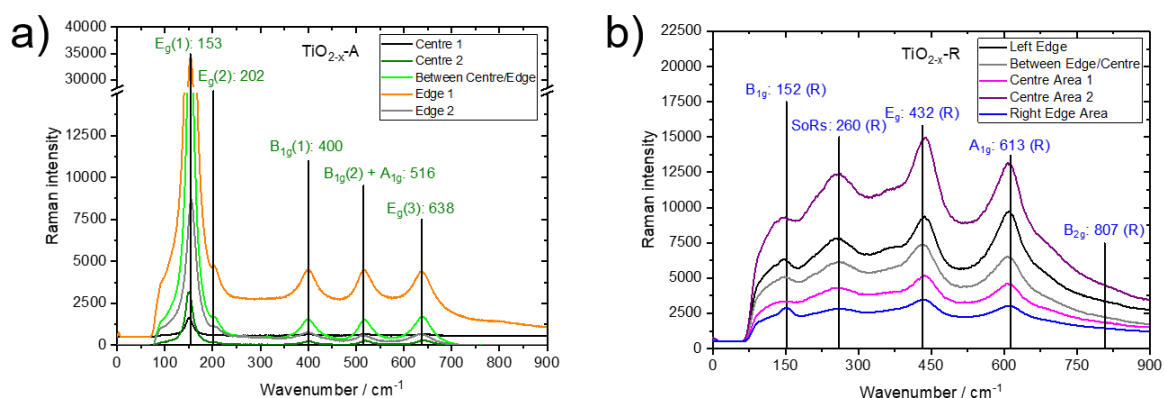


Figure S1: Measured Raman spectra of a) $\text{TiO}_{2-x}\text{-A}$, and b) $\text{TiO}_{2-x}\text{-R}$ at various measurement points on the sample surface, pristine (after synthesis).

All $E_g(1)$ peaks in the spectra of the $\text{TiO}_{2-x}\text{-A}$ electrode shown in **Figure S1a**, show maxima around 153 cm^{-1} , whereas the theoretical peak maximum is between 143 and 146 cm^{-1} . [1] Also,

the Eg(2) peak maxima are not in the theoretical peak range of 186-196 cm^{-1} , but slightly shifted to higher wavenumbers of 202 cm^{-1} . Thus, both peaks show a positive shift of about 710 cm^{-1} and 616 cm^{-1} , respectively, compared to the literature values.[1] This indicates a possible inaccuracy during the measurement, possibly caused by a slightly misaligned focus. The three other peaks at 400 cm^{-1} , 516 cm^{-1} and 638 cm^{-1} are in agreement with the theoretical values for Ti_{16}O_2 . [1] Additionally, the Raman intensity is high, indicating a thick oxide layer, which leads to a conclusive result. However, even if deviations can be detected, the evaluation clearly proves that the synthesis was successful, because only the peaks from the anatase phase can be seen and no peaks at other positions, which might indicate a mixed phase of additional rutile or other phases.

The various Raman spectra of the $\text{TiO}_{2-x}\text{-R}$ electrode are shown in **Figure S1b**. The maximum of the B_{1g} peak should be at 152 cm^{-1} but is slightly shifted to 147 cm^{-1} for all spectra except the one of right edge area. Similar behaviour can be observed for the remaining peaks of the different spectra where all peak positions with a maximum deviation of 5 cm^{-1} correspond to the values in the literature. [1] In summary, both spectra in **Figure S1** show, that the synthesis of the $\text{TiO}_{2-x}\text{-A}$ and $\text{TiO}_{2-x}\text{-R}$ was successful.

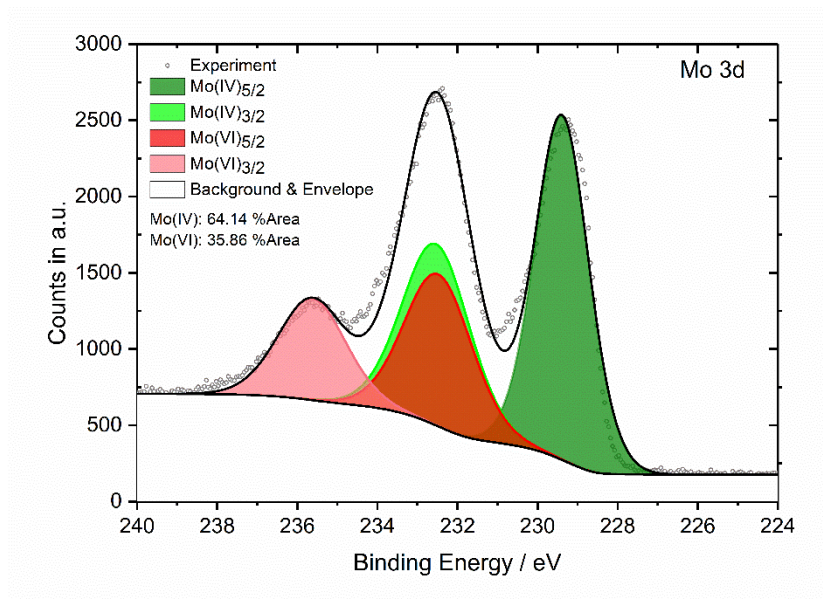


Figure S2.: Mo 3d spectra of the initial MoO_{2+x} sample including relative mass distribution.

Figure S2 shows the high-resolution Mo 3d XPS spectra of MoO_{2+x} . As expected, the MoO_{2+x} sample consists of a phase mixture of Mo(IV)-oxide and Mo(VI)-oxide, which may originate from the instability of the Mo(IV)-oxide in the presence of oxygen. The Mo(IV)_{5/2} peak maximum (**Figure S2**, dark green) is located at 229.4 eV, the Mo(IV)_{3/2} peak maximum (**Figure S2**, light green) at 232.5 eV, respectively. Since the spectra are shifted with respect to the C1 peak, the molybdenum peaks are not exactly at the theoretical positions, however, the deviation is small with 0.3 ± 0.9 eV for Mo(IV)_{5/2} and also for Mo(IV)_{3/2}, compared to the literature values given in **Table S1**. The Mo(VI)_{5/2} peak maximum (**Figure S2**, dark red) at 232.5 eV and the Mo(VI)_{3/2} peak maximum (**Figure S2**, light red) at 235.6 eV also show a deviation, which amounts to 0.65 ± 0.2 eV compared to the theoretical peak position at 233.15 eV. Other oxides, such as Mo(V)-oxide, were not considered in this evaluation, as it is not expected that such oxides are present in our sample. In conclusion, it can be said that the synthesis of MoO_{2+x} was successful.

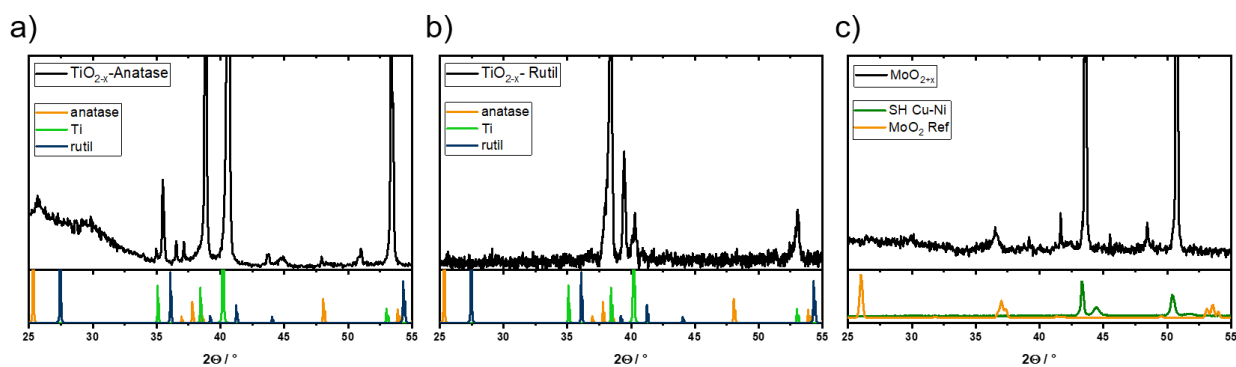


Figure S3.: X-ray diffractograms (XRD) of a) $\text{TiO}_{2-x}\text{-A}$, b) $\text{TiO}_{2-x}\text{-R}$ and c) MoO_{2+x} electrodes. Reference data taken from [2].

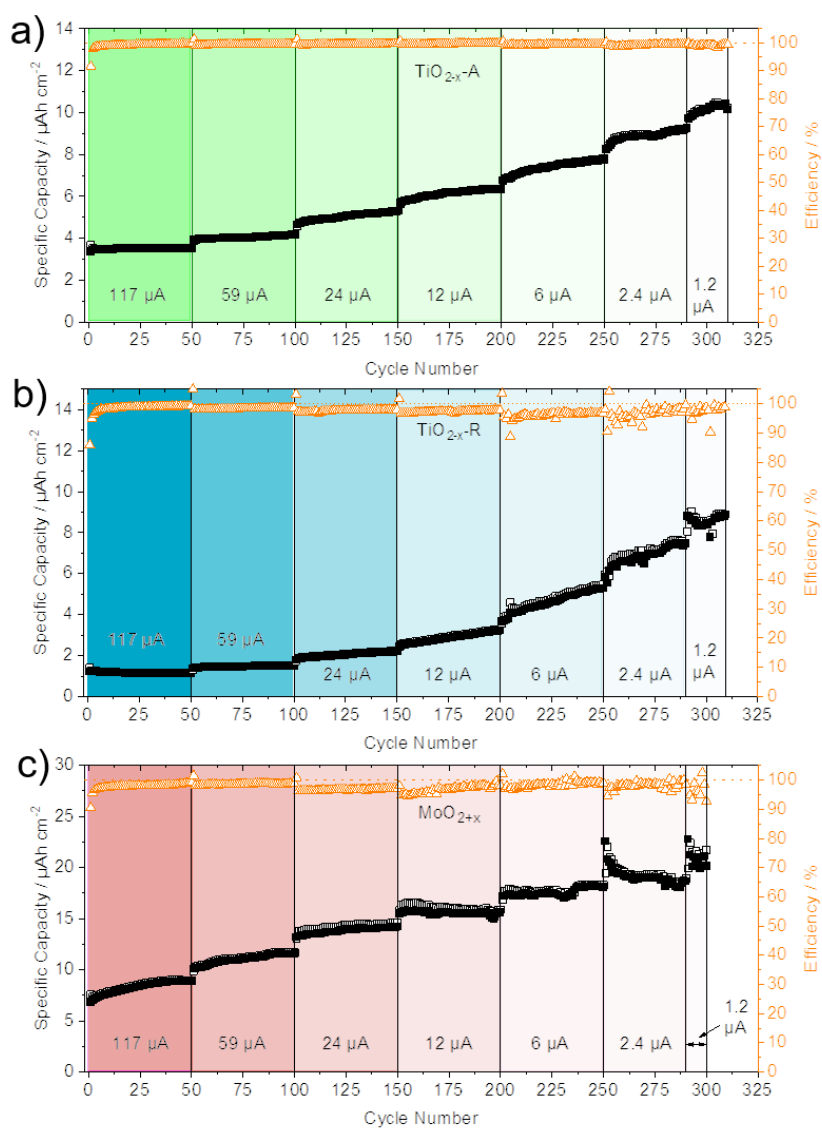


Figure S4: The specific area normalized capacities (black squares) with respect to the cycle number and corresponding Coulombic efficiencies (orange triangles) of a) $\text{TiO}_{2-x}\text{-A}$, b) $\text{TiO}_{2-x}\text{-R}$ and c) MoO_{2+x} . Closed squares relate to charge (desodiation) and open squares.

Impedance spectroscopy: To understand the electrochemical processes within the battery cells, potential dependent electrochemical impedance spectroscopy (PEIS) was performed. Measurements at open cell voltage (OCV) were carried out before the CV and before and after 310 GCPL cycles (see **Figure S5**) to investigate the impedance characteristics of the battery half-cells after long-term cycling, shown in **Figure S4**.

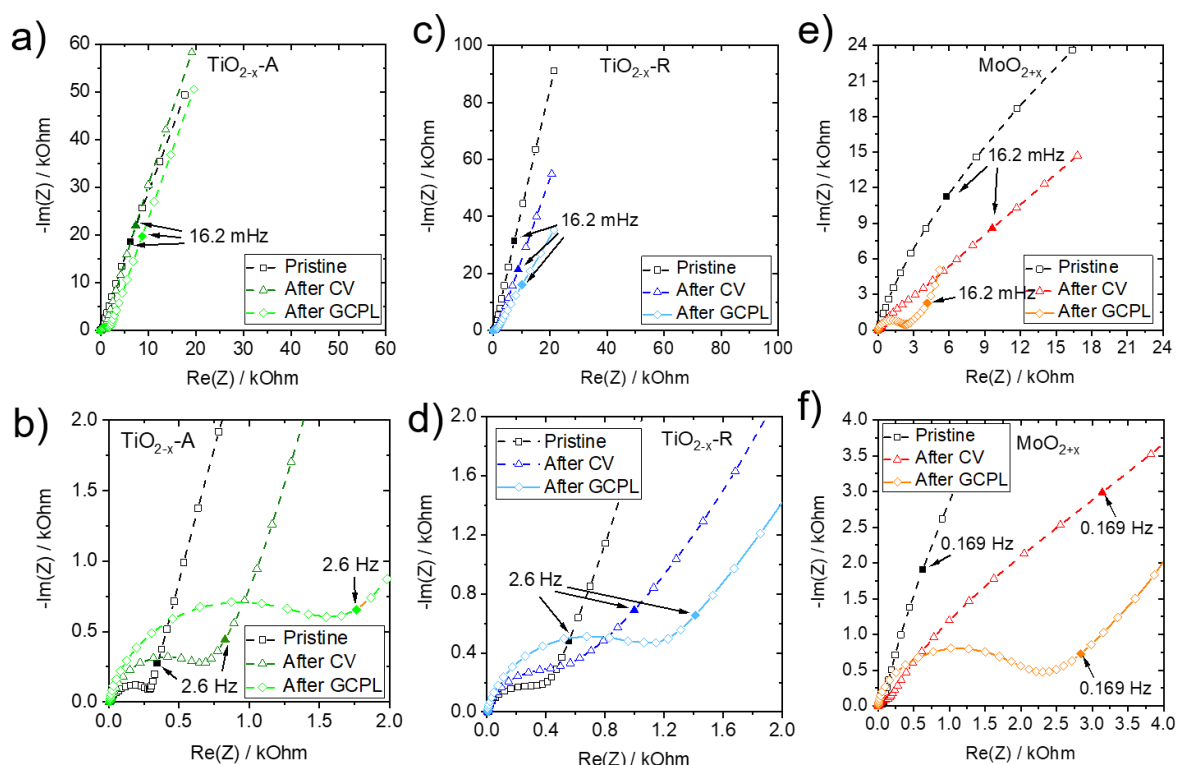


Figure S5: Nyquist plots of $\text{TiO}_{2-x}\text{-A}$ a) overview and b) zoom, $\text{TiO}_{2-x}\text{-R}$ c) overview and d) zoom and MoO_{2+x} e) overview and f) zoom from 10 kHz to 5 mHz before CV, after CV, before GCPL and after GCPL measurements (300 cycles).

The distance on the real axis between the origin of the graph and the measuring point with the highest frequency represents the ohmic resistance, more precisely the resistance of the electrolyte and the contact resistance of the cell.[3] The semicircle formed in the frequency region until 8 Hz for the spectra after CV and until 4 Hz for the spectra after the GCPL is related to charge transfer processes which take place at the electrode interface. This charge transfer process represents the solid/electrolyte interface including the electrolyte double-layer capacitance and the corresponding Na ion transfer parameters. The increasing radius of the semicircle after long term galvanostatic cycling is attributed to the formation of the surface film

causing the increasing impedance and charge transfer resistance.[4][3] The straight line at low frequencies (below 2.6 Hz) is related to the diffusion of Na ions in electroactive particles, either within the formed surface film, or in the subjacent anatase bulk structure.[3]

The different Nyquist plot of MoO_{2+x} are shown in **Figure S5e,f**. The detailed explanation of the semicircle at middle frequencies and the straight slope at low frequencies have been declared in previous publications.[3,4] The radius of the semicircle of the pristine electrode amounts about $25\ \Omega$ and is increasing to a radius of $1\ \text{k}\Omega$ for the semicircle after the GCPL measurement. Compared to the semicircles of the $\text{TiO}_{2-x}\text{-A}$, shown in **Figure S5a,b** and $\text{TiO}_{2-x}\text{-R}$, shown in **Figure S5c,d**, the radius of the semicircles of the MoO_{2+x} depicted in **Figure 5e,f** have approximately the same radius, which suggest that the surface film should have the same thickness, which however the SEM measurements whose results are subsequently discussed will not confirm.

X-ray photoelectron spectroscopy: In

Table S1, the XPS peak binding energies of all components presumed at the surfaces of the WE are listed. The evaluation was done by CasaXPS, using a Shirley background setting and GL(30) as the line shape. For the necessary charge correction of the spectra, which was performed before the fitting, the Na 1s peak was set to 1071.4 eV, because the peak is sharp and its full width at half maximum (FWHM) is small compared to the FWHMs of the other components. In addition to the surface measurements, depth profiles were made after the electrochemical characterisation to check the composition inside the surface film.

Table S1: XPS peak binding energies of all surface film components of $\text{TiO}_{2-x}\text{-A}$ and MoO_{2+x} .

TiO_{2-x}-A	Peak [eV]	FWHM [eV]	Peak [eV]	FWHM [eV]	Reference
	Ti 2p _{3/2}		Ti 2p _{1/2}		
Ti(IV)-oxide	458.59 ± 0.00	1.04	+5.72	1.98	[5]
Ti(III)-oxide	457.30 ± 0.70		+5.20		[6]
Ti(II)-oxide	455.50 ± 0.60		+5.60		[6]
Ti(0)	453.74 ± 0.02	0.69	+6.05	0.83	[5]
O 1s					
Na ₂ O ₂	530.90 ± 0.00	1.10			[7]
Na ₂ O	529.70 ± 0.00				[8]
Na ₂ CO ₃	531.30 ± 0.30	2.11			[9]
C=O*	531.80 ± 0.40				[10]
C 1s					
C-C, C-H	285.00 ± 0.00	1.2			[11]
C-O-C*	286.50 ± 0.20	1.2			[11]
CO ₃ ²⁻	289.30 ± 0.6	2.1-2.2			[11]
Na 1s					
Na	1071.40 ± 0.5				[12]
Na Auger	536.00 ± 1.00				[13]
MoO_{2+x}	Peak [eV]	FWHM [eV]	Peak [eV]	FWHM [eV]	Reference
	Mo 3d _{5/2}		Mo 3d _{3/2}		
Mo(IV)-oxide	229.70 ± 0.9		+3.15		[6]
Mo(VI)-oxide	233.15 ± 0.20	0.86	+3.15	0.9	[6] [‡]
Mo(V)-oxide	231.75 ± 0.15				[14]
O 1s					
Lattice IV	530.50 ± 0.50				[6]
Lattice VI	530.60 ± 0.40				[6]
H ₂ O	534.40 ± 1.80				[15]

* Adventitious carbon, [‡]shift C1s to 284.8

The survey of the $\text{TiO}_{2-x}\text{-A}$ sample, shown in **Figure S6a**, contains peaks of the S 2p at 169 eV, the N 1s at 399 eV and the F 1s at 638 eV, which can be assigned to the electrolyte, even if it was largely removed when the test cell was disassembled by rinsing the sample several times in dimethyl carbonate (DMC). The weak signals of the Ti 2p and Ti 2s further suggest that the surface film forms a closed layer on top of the oxide. The survey of the MoO_{2+x} sample is shown in **Figure S6c**. The peaks of S 2p, N 1s and F 1s, can again be assigned to the electrolyte. The distinctly visible Mo 3d signal, compared to the weak Ti 2p signal shown in **Figure S6a,b** at 233 eV suggests that the surface film does not form a closed layer on the oxide. The post mortem SEM analysis show that both oxide layers do not have a uniform coating.

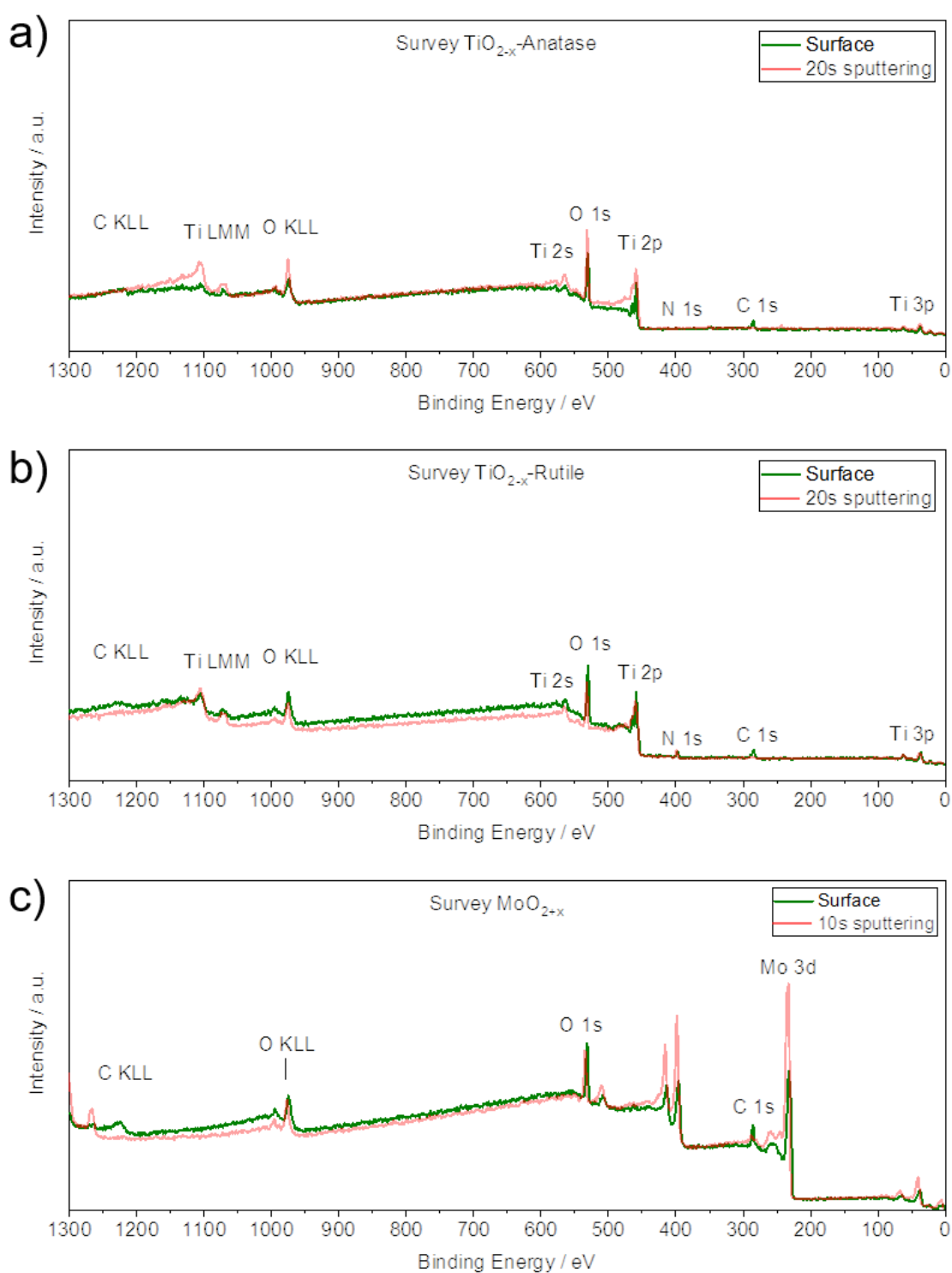


Figure S6: Pristine (after synthesis) XPS survey spectra of a) TiO_{2-x} -A, b) TiO_{2-x} -R and c) MoO_{2+x} of the surface (green line) and after 20 seconds of sputtering (orange line).

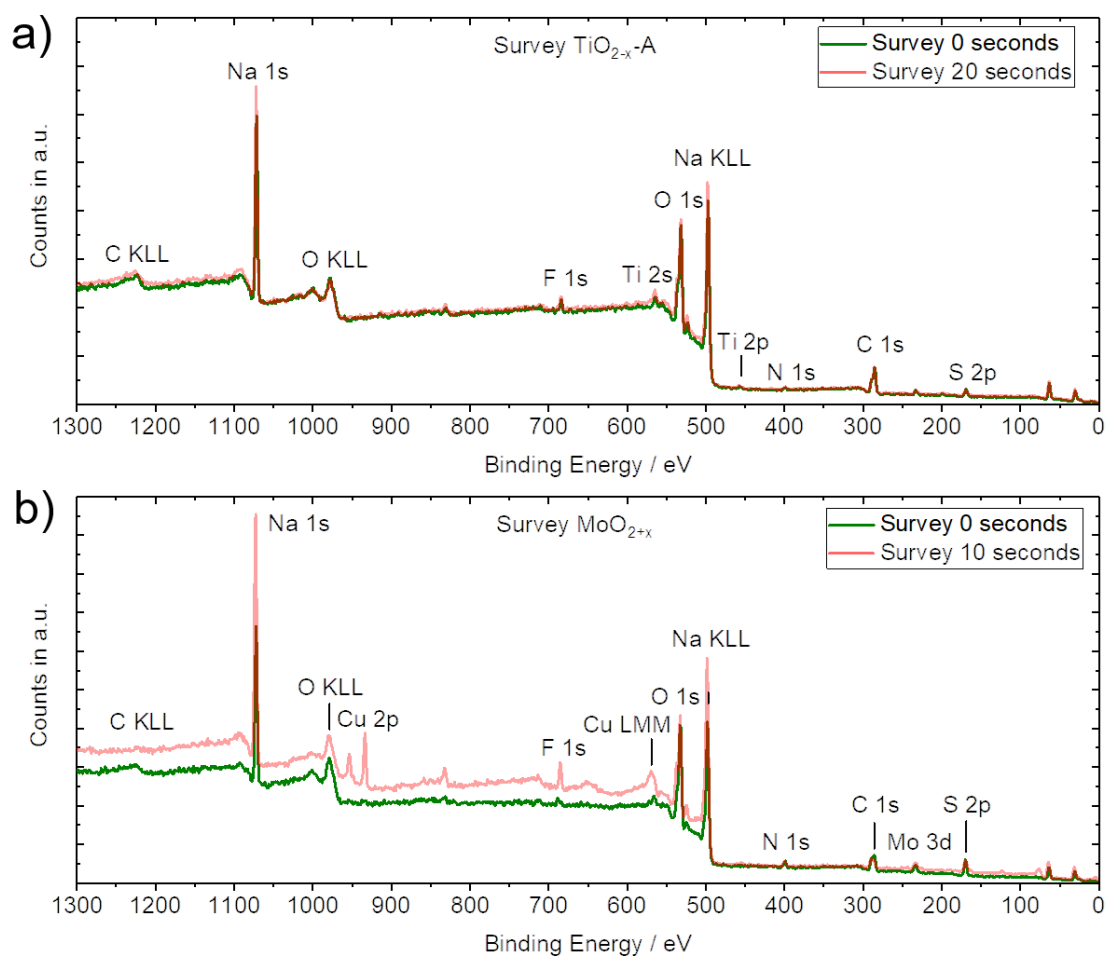


Figure S7: Post mortem XPS survey spectra of a) $\text{TiO}_{2-x}\text{-A}$ and b) MoO_{2+x} of the surface (green line) and after 20 seconds of sputtering (orange line).

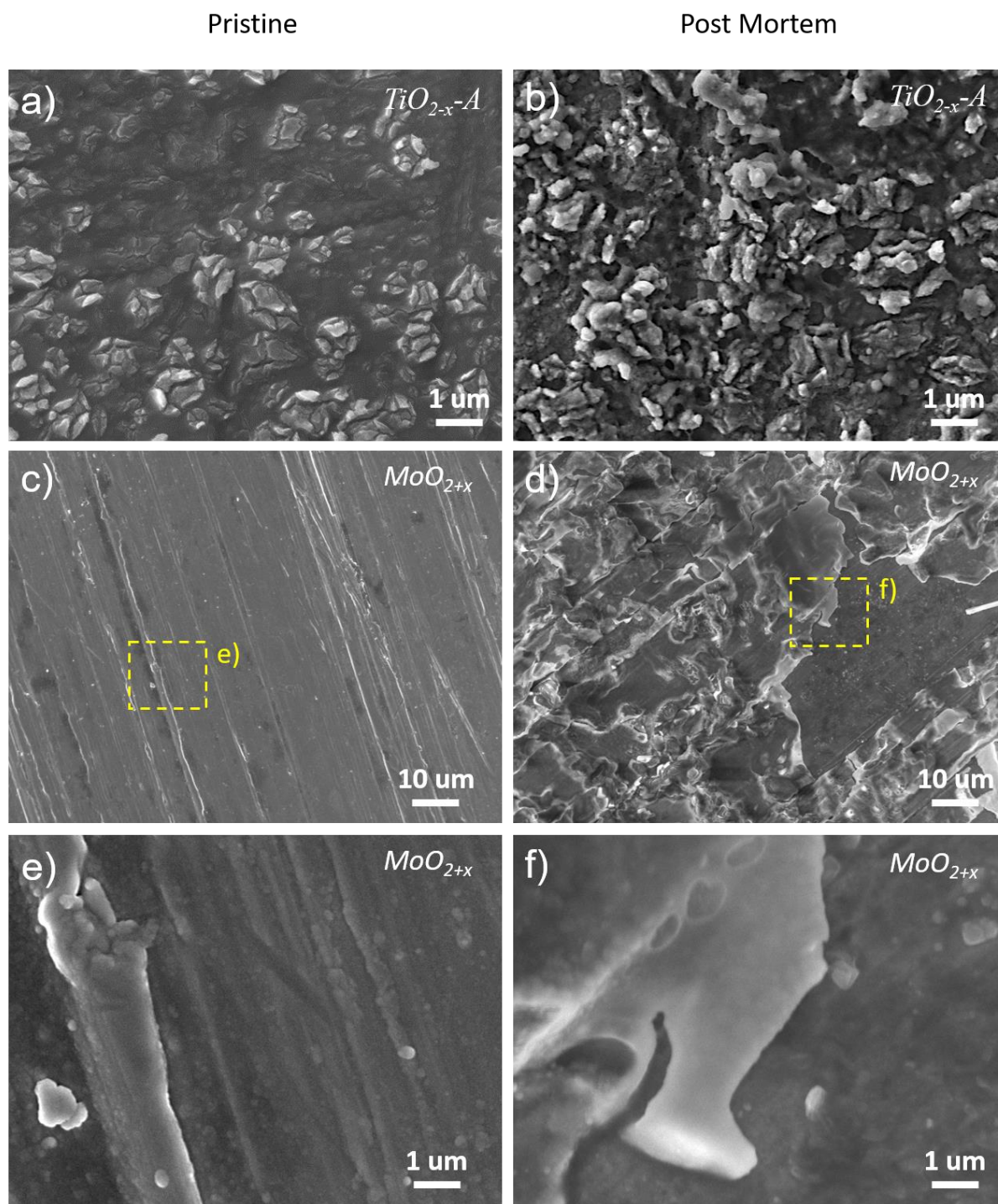


Figure S8: SEM images of TiO_{2-x-A} (a,b) and MoO_{2+x} (c-f) electrodes, pristine (a,c and e) and sodiated (at 0.1 V) after 290 GCPL cycles at various scan rates between 117 μA and 2.5 μA (b,d and f). The highlighted, yellow areas in c) and d) are magnified in e) and f), respectively.

Ex-situ SEM and EDX: To investigate the composition and the properties of the surface film of the aged $\text{TiO}_{2-x}\text{-A}$ and MoO_{2+x} samples, post mortem SEM pictures with additional energy-dispersive X-ray spectrometry (EDX) measurements were acquired (**Figure S9**). Therefore, the aged test cells were discharged to a voltage of 0.1 V and were then immediately disassembled. For all post mortem SEM measurements, it is possible that air impurities changed the composition of the surface film due to the high reactivity of the sodium with oxygen. The contact with air could not be prevented because of the transfer to the SEM setup.

The EDX analyses of two electrode materials, $\text{TiO}_{2-x}\text{-A}$ and MoO_{2+x} , were performed at the areas marked in **Figure S9a,b**. Area 1 in both figures is representative for the supposedly not or low sodiated part of the electrode and area 2 is representative for the protrusion clusters. The EDX spectra contain the signal cps in eV in respect to the energy in keV. The spectra of area 1 of the $\text{TiO}_{2-x}\text{-A}$ (**Figure S9c**) shows a high oxygen peak (12 eV) at 0.5 keV, a sodium peak (5 eV) at 1 keV and three titanium peaks with a signal of 8 eV at 0.4 keV, 14 eV at 4.2 keV, and 2 eV at 5 keV. A carbon peak can also be located with a signal of 2.5 eV at 0.3 keV. This indicates that the main part of this area 1 contains $\text{TiO}_{2-x}\text{-A}$ and only a small part is sodium oxide and sodium carbonate.

The measurement of area 2 (**Figure S9e**) shows a different composition. The oxygen peak can be located at 0.5 keV with a signal of over 30 eV. The three titanium peaks at 0.4 keV, 4.2 keV and 4.8 keV are smaller compared to the signals of area 1 with signal values of 5 eV, 4 eV and 1 eV. The sodium peak at an energy of 1 keV amounts 29 eV, which is also higher compared to the value at area 1. The carbon peak at 0.3 keV also increases to 7 eV. The higher sodium and oxygen values are an indicator that these clusters consist mainly of sodium oxide.

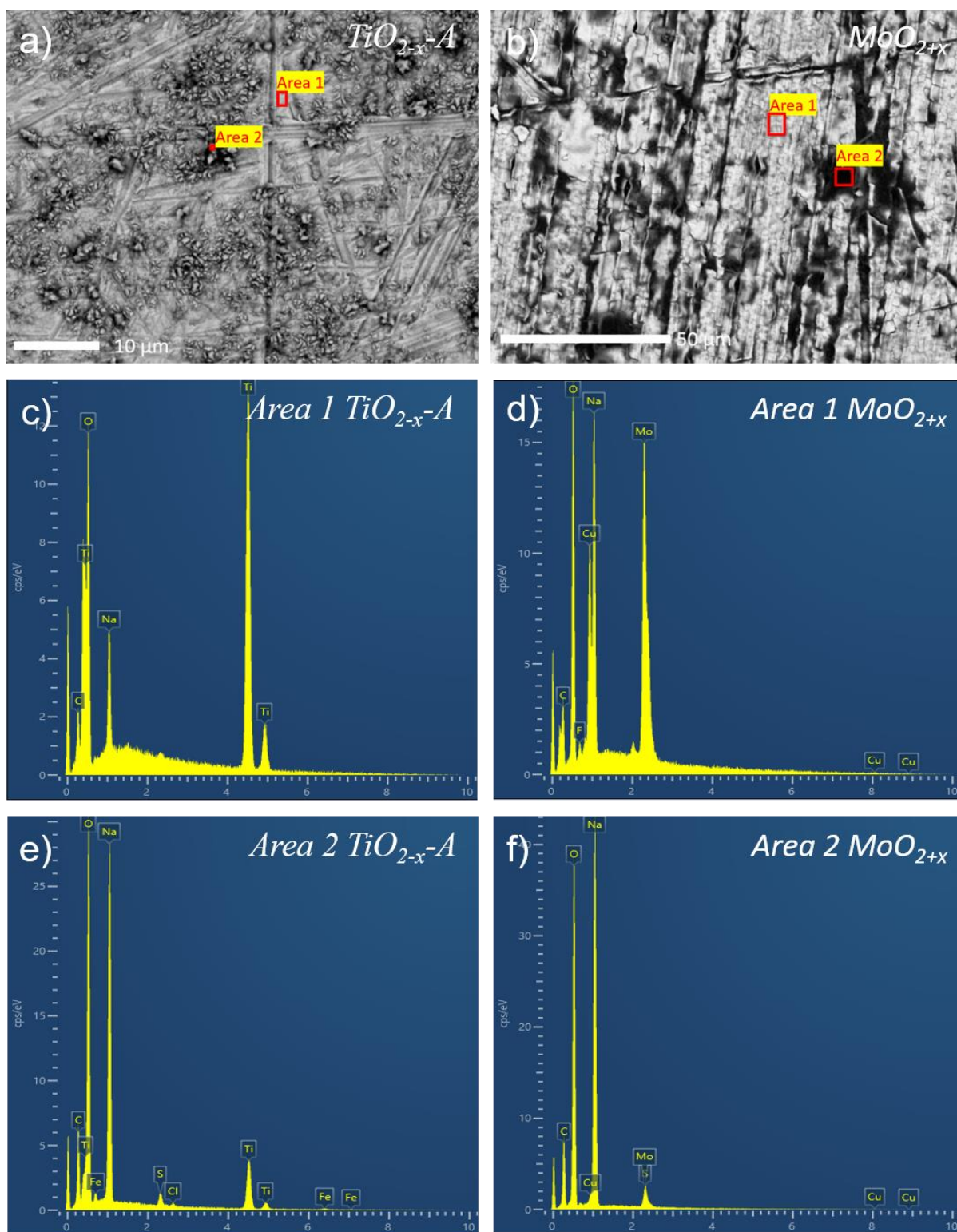


Figure S9: Post mortem SEM images of the surface of a) $\text{TiO}_{2-x}\text{-A}$ and b) MoO_{2+x} , with two marked areas where EDX measurements (c-f) are recorded.

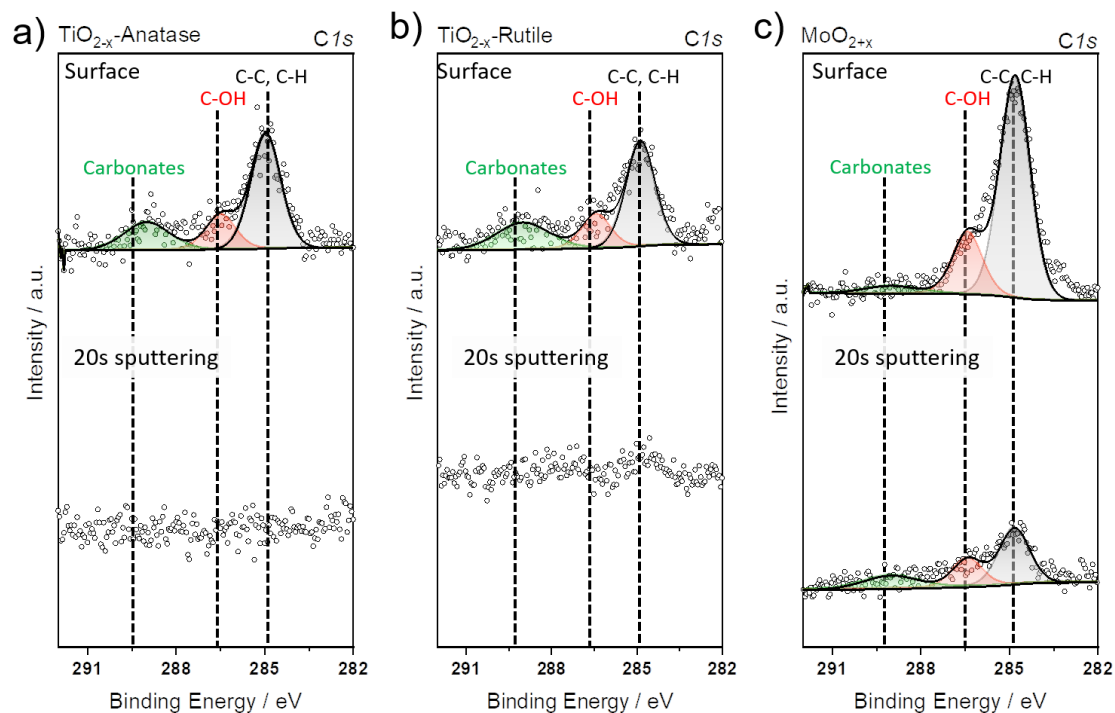


Figure S10: High resolution C1s XPS spectra of pristine a) TiO_{2-x} -A, b) TiO_{2-x} -R and c) MoO_{2+x} before (Surface) and after 20 seconds of argon sputtering.

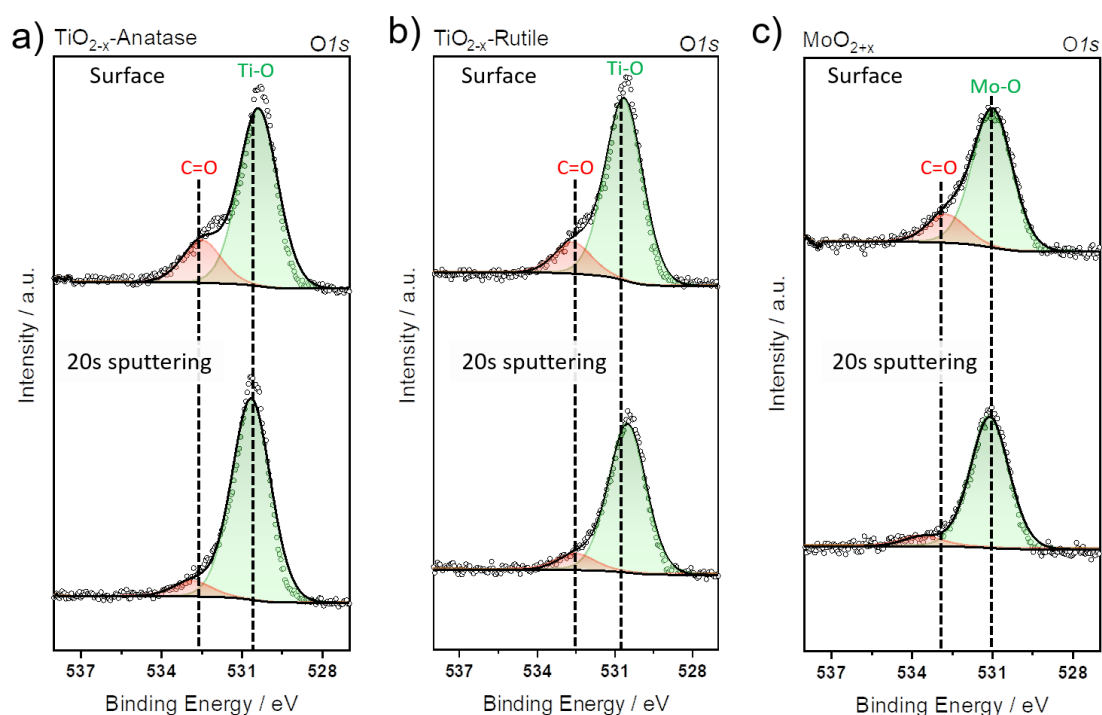


Figure S11: High resolution O1s XPS spectra of pristine a) TiO_{2-x} -A, b) TiO_{2-x} -R and c) MoO_{2+x} before (Surface) and after 20 seconds of argon sputtering.

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