Insights into the electronic structure of Fe-Ni thin-film catalysts during oxygen evolution reaction using operando resonant photoelectron spectroscopy

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A. Setup and Procedures for Operando Measurements

Electron analyzer and X-ray source: The SOL³PES experimental setup is equipped with a SCIENTA OMICRON R4000 HiPP-2TM hemispherical electron analyzer. Due to three differential pumping sections that separate the detector (kept at <10⁻⁸ mbar) from the experimental chamber, the electron-analyzer is capable of detecting photoelectrons at elevated pressures of up to 10 mbar water vapor around the sample inside the chamber. A similar differential pumping system is used to compensate for the pressure difference between the interaction chamber and the ultra-high vacuum (<10⁻⁹ mbar) within the beamline. The distance between the electron analyzer entrance pinhole and the focal point of the soft X-ray beam was set to approximately 1 mm, allowing us to align the beam on the flow cell membrane and at the same time minimize electron scattering caused by the water vapor inside the chamber. The angle between the polarization axis of the incoming X-ray beam and the electron analyzer was set to 54.7° (so called magic angle) to prevent any photoelectron angular distribution effects. The photon energy at the oxygen K-edge was determined by calibration on the O₂ gas feature at 531 eV ¹.

The 0.1 M KOH liquid-reference was measured at the P04 Beamline at the PETRA III synchrotron facility at DESY in Hamburg, Germany² with the EASI experimental setup described in detail by Malerz et al.³.



Figure S1: Sketch of the operando PES flow-cell setup. (A) Flow-cell as implemented in the analysis chamber. Wires from the electrodes are connected to the potentiostat. The electrolyte tubes are connected to the reservoir and waste located at different heights outside the interaction chamber to facilitate gravitation-driven electrolyte flow through the cell. (B) Cross-sectional view of the flow-cell, showing the three-electrode assembly including the leak-free reference electrode (RE) and the Pt-counter electrodes (CE). (C) Closer cross-sectional view of the working electrode (WE) assembly that shows the coated ionomer-membrane sealed against the ITO-coated Titanium cover. (D) Schematic representation of the catalyst coated membrane assembly covered with two monolayers (ML) of graphene.

<u>Wetting control and formation of the confined electrolyte</u>: As in more detail discussed in section E, the graphene cap on top of the catalyst coated ionomer membrane acts as an evaporation barrier, which is partially permeable for water vapor. This promotes the formation of confined electrolyte on the surface of the catalyst. As the graphene is attached to the catalyst surface after deposition, the electrolyte primarily fills cavities between the ionomer and the catalyst coating, which are covered by the graphene. Such cavities are provided by the nano-roughness of the catalyst film, as demonstrated by AFM (see Figure S3 and corresponding discussion). The amount of confined electrolyte formed within the

graphene covered cavities can be tuned by adjusting the water-gas partial pressure within the vacuum chamber. Increasing the water-gas partial pressure inside the vacuum chamber shifts the equilibrium further toward condensation.^{4–6} Without backfilling the vacuum chamber with water vapor, we observed insufficient electrolyte contact of the catalyst. In our experience, sufficient wetting is achieved with a water-gas partial pressure of 0.4 - 0.5 mbar within the vacuum chamber. Further raising the water-gas partial pressure leads to increasing water signal contributions to the O K-edge XAS.⁶ With increasing wetting we did not observe any shifts of measured redox-potentials or decreased electrochemical current signals. This indicates that the contact between the catalyst and the graphene layer is not influenced by the increasing amount of liquid. Furthermore, we were always able to see the resonant Auger electrons at the Ni L-edge originating from the catalyst ($E_{kin} \approx 800 - 850 \text{ eV}$, inelastic mean free path ~ 2 nm). This demonstrates that no bulky water film is formed between the catalyst and the graphene on top of the graphene layer. To maintain a constant water-gas pressure within the vacuum chamber, we connected a test tube filled with Milli-Q water (degassed by two freeze-pump-thaw cycles) to the vacuum chamber, that is heated up to 40°C. A needle valve is used to adjust the water gas flow into the chamber. The flow rate of the vacuum pump attached to the analysis chamber is controlled with a motorized gas regulating valve (PFEIFFER EVR 116[™]). This valve is operated by a proportional-integral-derivative controller (PFEIFFER RVC300[™] pressure gauge) to maintain the chamber pressure at the desired value.

<u>Details about the ionomer Membrane</u>: We used the ionomer membrane Fumasep FAD[™] 55 (FUMATECH) as catalyst support in our operando studies (compare with Figure S1 D). This membrane is designed to be non-permeable for oxygen gas. This allows us to keep the electrolyte behind the membrane at ambient pressure (1 bar) without degassing or inert-gas purging. According to the manufacturer, Fumasep FAD[™] 55 is permeable for anions as well as small cations. Our measurements demonstrate that potassium ions, although exhibiting a relatively large ionic radius, can easily trespass this ionomer membrane.

<u>Electrochemistry</u>: The three-electrode setup allows the application of a well-defined potential, which was kept constant during the spectroscopic measurements. The potential of the leakage-free reference electrode against the reversible hydrogen electrode (RHE) was determined prior to all measurement series against a commercial RHE (GASKATEL). Thus, we can exclude fluctuations of the reference potential between the measurements. Using two counter electrodes, one in the electrolyte upstream and one in the downstream, minimizes possible fluid-flow induced ion-drift overpotentials.

To transform Ni_{0.75}Fe_{0.25}O_y into Ni_{0.75}Fe_{0.25}(OH)₂, we performed 100 CV cycles prior to the operando-PES measurements in the range of 0.55-1.65 V vs RHE at 100 mV/s, which was designed to be a more time-efficient activation procedure compared to the galvanostatic conditioning used by Trotochaud et al.⁷. During spectroscopic measurements we applied chronoamperometric potentials. We started with a reducing potential of 0.95 V vs RHE close to the open circuit potential, followed by an oxidizing potential of 1.75 V vs RHE in the OER regime, followed by the same reducing potential again to examine reversibility.

<u>PES-data collection</u>: The X-ray photoelectron spectra were energy-calibrated using the graphene C 1s feature of sp²-hybridized carbon at a 284.8 eV binding energy.^{8–10} Spectral shifts caused by the applied potential have been corrected by aligning the K 3p-peaks in the valence band region or the K 2p-peaks in the C 1s region. We used Gaussian fit functions to determine the K 2p-peak positions at different applied potentials. The obtained shifts reveal overpotentials < 0.1 V. The signals of the core-level XPS peaks were normalized to their maximum after a Shirley-type background was subtracted. Especially in the case of the operando-spectra, the O 1s and C 1s peaks were normalized to their maximum under applied reductive electrode potential. Spectra measured on oxidizing electrode potentials are not normalized but shown with the same scaling factor as the associated one on a reductive potential to demonstrate reversible intensity changes. PEY-XAS data is obtained by integrating individual valence-band PE spectra measured at photon energies around the absorption edge of interest.

B. Pre-Characterization of the Catalyst

Prior to our operando studies, we have thoroughly pre-characterized the sputtered Ni_{0.75}Fe_{0.25}O_V films. Electron-diffraction images show distinct diffraction patterns, and the measured intensity maxima can be assigned in good agreement to the cubic NiO lattice, which is of rock salt structure type with Fm3m symmetry (see Figure S2A). The absence of a distinct amorphous ring indicates high crystallinity. In addition to the reflections of the rock salt structure, no other diffraction peaks appear. Consequently, the sample consists of a single phase. This finding is also confirmed by X-ray diffractograms, which also show exclusively reflections of the rock salt structure (Figure S2C). We determined the mean value of the lattice parameter calculated from the individual values obtained at each diffraction peak to be 4.24 \pm 0.02 Å, which is about 1.5% larger than the literature value of iron-free NiO (a = 4.1771 Å)¹¹. These deviations and lattice distortions are caused by the defect structure associated with the incorporation of iron into the NiO lattice. ^{12–14} Due to the small size of the coherently scattering regions, the Bragg reflections are distinctly broadened. We estimated the structural coherence length to be of the order of 4.2 nm based on the Scherrer equation. Appropriately, based on the DF-TEM images, the average crystallite size was found to be 4.52 \pm 0.13 nm.



Figure S2: Structural characterization of the $Ni_{0.75}Fe_{0.25}O_y$ -catalyst. (A) Electron diffraction image and peak assignment according to the cubic NiO-structure on a radial cut of the diffraction pattern. (B) Exemplary high-resolution TEM image (C) X-ray diffractogram with the NiO reflection-positions assigned to it. A polynomial background has been subtracted. The feature marked by the black arrow originates from the glass substrate.

On the scale of the HR-TEM images, the material appears crystalline, showing a roughness of the order of the extent of the coherent scattering regions. AFM images of the Ni_{0.75}Fe_{0.25}O_y-surface deposited on FAD show island-like height differences of the order of the film thickness (see Figure S2A). In contrast, the surface of the uncoated FAD-membrane does not show this island-like quality. The root mean square roughness is 1.0 ± 0.1 nm on the coated and 0.28 ± 0.02 nm on the uncoated membrane. Due to the small height differences, the Ni_{0.75}Fe_{0.25}O_v layers are ideally suited to be sealed by graphene, which is jeopardized (risk of getting shredded) if the covered surface is too rough. At the same time, the nanoroughness of the catalyst provides cavities for condensation and additionally an increased surface area for the catalytic processes to take place. Importantly, small pores in the film deposited on the ionomer are necessary to provide ionic contact between the membrane and the condensed water film on top of the sample. Furthermore, EELS measurements show that the iron content x = n(Fe)/(n(Fe)+N(Ni)) in the Ni_(1-x)Fe_xO_y layers is equal to $x = 0.271 \pm 0.011$. Quantitative evaluations of the Ni and Fe 2p XPS peaks measured on the pristine, dry samples by contrast yield an iron content of $x = 0.196 \pm 0.011$ at the surface. The differences between these two values may be caused by systematic errors arising from matrix-corrections or differences in the surface and bulk composition. We anyhow refer the formal value of x = 0.25

to the samples in this article, which is the expected value based on the composition of our sputtering target and lies between both experimental results.



Figure S3: AFM Images of the FAD membrane coated with (A) Ni0.75Fe0.25Oy and (B) the uncoated FAD membrane. The color scale on the right reflects the height of the structures shown.



Figure S4: Crystalite Size distribution for (A) the number density and (B) the volume fraction. The number density can be approximated with a gaussian shape und the volume fraction seems to be approximately logarithmic normal distributed.

C. Electrochemical Activation of the Catalyst



Figure S5: Exemplary set of cyclic voltammograms measured during activation.

D. Operando Measurements of the Oxygen 1s XPS

Figure S6 shows the operando measured O1s signal at a reducing potential of 0.85 V vs RHE in the non-catalytic regime and at an oxidizing potential of 1.75 V vs RHE in the OER regime after activation. For better comparability, the contributions of the H₂O gas originating from the chamber atmosphere were removed by subtracting a Gaussian peak obtained from fitting. More details on the fitting procedure are given in the supporting information in the caption of Figure S7, showing a raw spectrum. We observe distinct peaks in the valence band and in the C 1s region, which can be attributed to the K 3p (~17 eV binding energy) and 2p splitted spin-orbit levels (~293 eV and 296 eV binding energy), respectively (compare Figure 3 and Figure S9). Due to the low potassium concentration of 0.1 M in the electrolyte, we assume these signals to originate predominantly from the catalyst layer, as potassium is known to incorporate into the active y-phase. Despite the positive working electrode potentials applied in the OER-regime, the positively charged potassium ions accumulate in the interlayer space of the catalyst to compensate the negative charges of the (predominantly) deprotonated MO₂-slabs.^{15–17} Therefore, we expect the shift in the K 2p signal to be a good measure of the potential applied to the catalyst. To correct the O 1s spectra for the energy shift caused by the applied potential and to consider possible diffusion overpotentials, we determined the emergent shift at the K 2p peaks from potential dependent spectra-sets measured directly afterwards under the same conditions. The obtained shift is in good agreement with the applied potentials, with overpotentials being smaller than 0.1V. The potential-related changes, which occur after we applied the correction and which are reflected in the difference of the O1s peaks (see Figure S6), turn out to be completely reversible. However, the membrane assembly investigated operando contains oxygen in several components. In order to classify the observed changes, it is necessary to

distinguish the contributions of all individual components that are superimposed to yield the overall peak. Beside the Ni_(1-x)Fe_xOOH_y, the graphene layer contains oxygen as it becomes partly oxidized, if high electrode potentials are applied. Furthermore, the confined water located below the graphene-layer also contributes significantly to the oxygen signal. The ionomer membrane also contains oxygen. It is however reasonable to assume that only a few characteristic photoelectrons reach the detector from the ionomer located below the 5 nm thick catalyst layer and the 2 monolayers of graphene due to their low escape depth (kinetic energy $E_{kin} \approx 740 \text{ eV}$, inelastic mean free path ~2 nm¹⁸). Figure S6 shows spectra of the significantly contributing oxygen species obtained from measuring reference samples. The O1s spectrum of graphene (Figure S6A) is composed of two contributions: Oxygen species that form a single bond to carbon (binding energy $E_B \approx 532.9$ eV), and oxygen species that form a double bond between carbon and oxygen (E_B ≈ 531.9 eV).^{19,20} The 0.1 M KOH spectrum shown in Figure S6B is measured from a liquid microjet. Using the calibration according to Thürmer et al.²¹, yielding a value of $E_B \approx 532.8$ eV for the binding energy of free liquid water, which is also in agreement with the findings of Löytty et al. for thin aqueous electrolyte films using the dip and pull method.²² We have complemented our fit by corresponding to the H₂O gas evaporating from the liquid microjet and OH⁻ species resulting from the alkaline conditions. We note, that the OH⁻ species doesn't contribute significantly to our fit due to their low concentration. We have added this component based on the results presented by Brown et al. using the binding energy they evaluated as fixed parameter in our fit.²³ Figure S6C shows the O 1s spectrum of the pristine, dry catalyst without graphene coverage. Since iron-nickel oxides always form a surface-hydroxide layer in contact with air^{24,25}, the spectrum also contain an oxide ($E_B \approx 529.6 \text{ eV}$) and a hydroxide contribution ($E_B \approx 531.3 \text{ eV}$) as well as the inevitable adventitious carbon contributions (see Figure S6C).^{24–26}



Figure S6: Changes of the oxygen 1s XPS signals during operando measurements and oxygen 1s reference spectra of the separated membrane-assembly components measured with an excitation energy of 1270 eV. For the reference-spectra Gaussian fitting-model components are also included. The sum of these components is shown as dashed black line. A: Free-standing graphene layer on a holey Si₃N₄-membrane under high vacuum conditions (C-O/C=O = Oxygen with a single/double bond to carbon), B: 0.1 M KOH measured in liquid microjet (g = water gas, I = liquid water, OH⁻ = Hydroxide ions shown scaled 5x), C: Ni_{0.75}Fe_{0.25}O_y under high vacuum conditions. (adv. C-O = adventitious carbon oxides, M-O = metal oxide, M-OH = metal hydroxide) E: NiFe-catalyst at 1: 0.85 V vs RHE and 2: 1.75 V vs RHE and difference spectrum obtained by subtracting the spectrum measured at 0.85 V vs RHE from the spectrum measured at 1.75 V vs RHE. Sum: Sum of the fits.

The difference between the two spectra measured at different applied electrode potentials, Figure S6D, reveals an increase of the measured signal around $E_B \approx 534.0 \text{ eV}$ and a decrease around $E_B \approx 531.6 \text{ eV}$, which does not match any of the signals of the species under consideration (see Figure S6D). The changes cannot be directly attributed to an increase or decrease in the individual components either. However, although according to the findings of Löyty et al. an increase of the oxide signal would be expected (related to the transition Ni_(1-x)Fe_x(OH)₂ \rightarrow Ni_(1-x)Fe_xOOH_y)²², this is not detected in our data. Since the effect is rather small, it might be obscured by the counting statistics and the superposition with other potential-induced spectral changes in our experiment. Another conceivable scenario would be the

oxidation of the graphene layer, which would lead to an increase in the intensity of the graphene peaks at $E_B \approx 532.9$ eV and at $E_B \approx 531.9$ eV, presumably at the expense of the water contribution at $E_B \approx 532.8$ eV. Due to the superposition of the increasing graphene oxide and decreasing water signals, in total one would expect a rather subtle increase caused by the double-bonded graphene oxide, which is also not visible in our spectra.



Figure S7: Exemplary O 1s XP-spectrum of the membrane assembly including the catalyst layer at reducing potential (0.85 V vs RHE). Four gaussian components were chosen to fit the peak: iron nickel oxide, iron nickel hydroxide, liquid water (as well as adventitious carbon oxides, C-O, exhibiting approximately the same binding energy as liquid water) and water gas. The peak-positions of the first three components were fixed at values obtained from the reference spectra shown in Figure S6. The peak widths of the first three components were constrained to be equal. The gas peak contribution was then subtracted to yield the spectrum presented in Figure S6.

We propose the potential-induced spectral changes to predominantly arise from a local inhomogeneity of the applied electrode potential between different parts of the membrane assembly. For example, fractions of the confined water further away from the catalyst experience a lower potential due to the potential drop across the Helmholtz-layer.⁴ This would lead to a broadening of the water signal at the flank of high binding energies and consequently could explain the spectral change of the O 1s. We conclude that the position and shape of the operando measured spectra can be well explained by the superposition of the expected components. It is important to notice that the core levels of the catalyst, whose energetic positions are quite distant from those of the graphene and the water, remain unchanged within the experimental detection statistics. Especially, no additional features arise on binding energies lower than the binding energy of the oxidic contributions of the pristine catalyst. We will come back to this aspect when constructing the oxygen p-DOS.

E. Characterization of the Graphene-Covered Catalyst-Membrane Assembly: Carbon-Species and Graphene Oxidation

The wet transfer method we used to deposit bilayers of graphene on the catalyst coated ionomer membranes (see materials section in the main manuscript) potentially influences the graphene quality. This aspect has previously been investigated by Falling et al. using Raman spectroscopy, who applied the same deposition procedure to equivalent graphene bilayers from Graphenea[™]. According to their results, the wet transfer leads to deposition of graphene layers with overall good structural integrity. Small deviations of the spectroscopic parameters with respect to a HOPG reference, which they obtained in their measurements, can be explained by strain and doping (C-oxidation) induced by the transfer.⁶ Accordingly, an exemplary C1s XPS spectrum measured on a free-standing graphene layer deposited on a holey Si₃N₄ membrane based on the wet transfer method is dominated by the spectral contributions sp²-hybridized carbon species (see Figure S8 and discussion below). Smaller contributions of oxidized carbon species probably originate partly from heteroatom (C,N) containing moieties within the graphene layers, and partly from adventitious carbon. Based on the results of Falling et al. and based on the XPS characterization, it seems likely that functional groups and defects are incorporated in the pristine Graphene membrane after wet transfer. Defect-free graphene has been shown to be almost non-permeable for gases.²⁷ Defective graphene, in contrast, is permeable for gases like O₂ and water vapour.^{28,29} Consequently, as our pre-characterization suggests the graphene membrane to be not defectfree, it seems likely that mass exchange through can occur through the graphene layers of the membrane electrode assembly.

Mom, Falling & Velasco-Velez and coworkers have studied the impact of a graphene bilayer on the wetting of a catalyst coated ionomer membrane within a vacuum chamber with different water-gas background pressures present. Their results clearly demonstrate that the graphene layer acts as barrier for evaporation. Without additional water-vapor supply a water-gas partial pressure of 0.05 to 0.15 mbar was achieved in their vacuum chamber with the wetted, graphene covered membrane inside.^{4–6} This finding once more indicates that the graphene does not fully block evaporation, but rather acts as a partially permeable barrier. This would be in line with the proposed permeability resulting from the defects within the graphene layers deposited by the wet transfer method we also applied.



Figure S8: C 1s XPS at 528 eV excitation energy of free-standing graphene bilayer (grey) compared with the membrane assembly including the catalyst layer (green) and with the membrane assembly without catalyst layer (blue). The dots represent the measured datapoints and the lines are the result of the 5component fit discussed below. The insets show the relative intensity of the fitted components (the farther to the right, the higher the center binding energy of the feature). The numbers assigned to the features correspond to the labeling in Table ST1.

Figure S8 compares the C1s spectrum of the free-standing graphene bilayer to the C1s spectrum of the membrane assembly with and without the Ni_{0.75}Fe_{0.25}OOH layer, respectively. To analyze the different signal contributions to the C1s spectrum in more detail, we assumed a model with 5 components. These correspond to carbon species oxidized to different degrees depending on their bonding partner, namely: sp² hybridized carbon, sp³ hybridized carbon, carbon single bonded to an electronegative partner (C-O / C-N), C double bonded to an electronegative partners (O-C-O / C=O) and carboxylic or ester groups (O=C-OH / O=C-O-C). This is inspired by similar fitting models

known from literature ^{8,26,30,31}. After subtracting a Shirley-type background, we fitted the components, each represented by a Gaussian function. For this, we assumed the peak width to be the same for all components and we kept the binding energy distances between the Gaussians constant based on literature values. The literature peak-positions were used as starting values and are summarized in the following table:

Label	Component	BE-Position (from ref ³¹)	Difference to next [eV]	
		[eV]		
1	sp ²	284.4	-	
2	sp ³	285.2	0.7	
3	C-O, C-N	286.1	0.9	
4	0-C-O, C=O	287.5	1.4	
5	0=C-OH, 0=C-O-C	288.8	1.3	

Table ST1: Fitting model parameters of C 1s peak components.

As a result of the fits, the relative proportions of the 5 components are shown in the insets, in order of increasing oxidation state. This demonstrates that, as expected, free-standing graphene contains relatively few highly oxidized groups and is strongly dominated by the sp²-hybridized graphene-carbon. If the graphene is positioned on the membrane assembly without a catalyst, the membrane is directly underneath it and a distinct signal contribution from the membrane is observed. This is characterized by a rather high fraction of functionalized carbon groups, especially quaternary N groups, which carry the positive countercharge to the mobile hydroxide ions in the membrane, but also by higher oxidized carbon-oxygen groups.

In contrast, the C 1s spectrum of the membrane setup with catalyst shows only a small increase of oxidized species compared to the free-standing graphene. This clearly shows that the signal from the membrane contributes only very slightly to the overall measured signal due to the limited information-depth of the photoelectrons.

Moreover, we studied the operando effects of oxidizing potentials on the C 1s signal of the membrane assembly. In Figure S9 three C 1s spectra are shown: before applying oxidizing potentials on 0.85 V vs RHE, in the oxidizing region on 1.75 V vs RHE and afterwards again on 0.85 V vs RHE. The spectrum is clearly changed on the oxidizing potential, but it is completely reversible. We investigated this in more detail based on the fit model described above. In contrast to the procedure above, we only specified the distance between sp²-carbon and sp³-carbon and otherwise left the positions free to move. The inset in Figure S9 shows the resulting relative proportions of the carbon components in the three spectra. From this, it is evident, that while oxidizing potentials the fraction of sp²-hybridized carbon decreases and only the fraction of sp³-hybridized carbon increases, while the fractions of all other components remain constant. This is also reflected in the difference shown in Figure S8 below. Apparently, the graphene is oxidized without the participation of oxygen. We hypothesize that the applied oxidizing potentials trigger the formation of carbenium ions, which can be stabilized by emerging sp³ hybridizations in the graphene.

However, this reversible, oxygen-free oxidation contradicts the changes observed on the O K PEY-XAS, which indicate irreversible oxidation of graphene with the participation of oxygen. There may be several explanations for these different findings: First, a C 1s measurement takes about 3 min, while a PEY-XAS measurement takes about 11 min. Thus, it might be possible that the oxygen-induced oxidation is very slow and therefore only becomes significantly visible if the measurement duration is long. In addition, perhaps the XAS could be more sensitive to carbon oxide formation because of resonant enhancement leading to the spectral features in XAS. On the other hand, oxygen is resonantly excited to a high extent when oxygen absorption is measured, which is not the case if C 1s XPS is measured. This creates excited oxygen species that may react with the graphene layer to create functional oxygen groups, as long as oxidizing potentials favor this process.³²It is likely, that the graphene becomes slightly more oxidized over time, when dwelling on high electrode potentials. The higher defect density of the oxidized graphene layers could potentially lead to a loss of electrical connection of the catalyst as well as a higher permeability for water gas. The latter causes a higher evaporation rate and thus a decreased amount of confined electrolyte to be present at the interface. Both effects of graphene oxidation primarily cause quantitative electrode potential dependent spectral changes. Dry and electrically unconnected regions of the catalyst are electrochemically inactive and do not contribute to the potential dependent changes. Therefore, it is unlikely that the qualitative potential dependent changes we focused on in this work are affected by graphene degradation. Moreover, in the timescale of our experiments we did not observe indications for a decrease of wetting or of electrical contact.



Figure S9: Operando C 1s XPS at 850 eV excitation Energy on different applied electrode potentials, while normalized to the under the peak. Below: Curves on high and low potentials with their spectral difference. Above: The same C1s-peaks fitted with 5 components that represent different oxidation states of the Carbon. The dots represent the measured data-points, and the lines are the result of the 5-component fit, which is discussed below. The inset shows the relative intensity of the fitted components (the farther to the right, the higher the center binding energy of the feature) on the different potentials, color coded according to the colors of the plot. The numbers assigned to the features correspond to the labeling in Table ST1.

F. Oxygen K-Edge XAS and Pre-Peak Resonance of Reference Materials



Figure S10: Oxygen PEY XAS of different membrane components in comparison with the operando measured spectra.



Figure S11: Oxygen PEY XA-spectra the membrane assembly without catalyst coating measured under operando conditions. No pre-peak occurs upon oxidizing electrode potentials. The features between 529.5 eV and 534 eV originate from overlapping graphene oxide contributions and oxygen group contributions from the ionomer membrane.



Figure S12: Resonant PES-signals of Oxygen species in Ni^{3*} -compounds on the excitation energy of the pre-peak feature. Green: Operando measured active phase of $Ni_{0.75}Fe_{0.25}OOH$, Red: $LiNiO_2$ -reference, Blue: Sputter deposited NiO_x with excess Oxygen implemented in the lattice.

Oxygen gas detection: With our system, we were not able to detect the O₂ gas generated in the OER-regime at the catalyst electrolyte interface. With a Faradic current of about $100\mu A$ reached in the activated state, 0.02 μ mol O₂ is generated per minute along the whole membrane electrode assembly in our operando cell. It may be possible, that a small fraction of this gas is accumulated between the graphene layer and the catalyst electrolyte interface. However, the cavities are of the order of several nm³ (compare with Figure S3A), and the volume of the gas is by 5-8 orders of magnitude smaller (~2*10⁻⁸ mol/mL at 0.5 mbar at 25°C or ~4*10⁻⁵ mol/mL at 0.5 mbar at 25°C) compared to the molar volume of the condensed phase (1 mol/mL). Therefore, we expect XPS and XAS signals originating from trapped O₂ to be by 5-8 orders of magnitude lower compared to the signals of the liquid and the solid phases, we assume their contribution to the interaction volume to be equal. So, we don't expect to detect trapped O₂ gas spectroscopically. The largest part of the generated O₂ gas most probably escapes through the partially oxidized graphene layers into the vacuum chamber. The overall volume of our vacuum chamber is about 55 L and with a pump-rate of about 7 L/s at 0.5 mbar the chamber atmosphere is on average fully exchanged within about 8 s. Assuming all the O_2 gas generated within this time span is equally mixed with the H_2O gas within the chamber, its concentration would be around 2 ppm in the chamber atmosphere. This may would be enough to be detected by mass spectrometry methods (detection limits between 1 and 0.02 ppb can be reached³³), but the XPS signal of equally distributed O_2 is expected to be 6 orders of magnitude lower compared to the signal of the water-gas peak (see Figure S7). This is much lower than the noise level. Now, this assumption of an equal O₂

gas distribution is not very realistic. Probably the O_2 gas is locally enriched around the membrane electrode assembly. A detailed calculation of the local concentration involves the diffusion and convection rate of the gases and is not trivial. As a simple estimation we assume the closest volume of 1 cm³ around the membrane electrode assembly to become enriched with the whole amount of O_2 generated in the time span, in which the chamber volume is exchanged one time on average (8 s). Under this assumption, the oxygen molecules represent about 10% of the gaseous species within the interaction volume around the membrane electrode assembly. Consequently, the XPS-signal of the O_2 is expected to be about ten times smaller compared to the signal of H₂O even in the case of this strong enrichment, which is in the same order of magnitude as the noise level. Overall, with the uncertain extent of O_2 enrichment in mind, it seems plausible that we were not able to clearly identify the signatures of O_2 in our O 1s XPS and O K PEY-XAS spectra.

	C1	C1_sigma	C2	C2_sigma	Chi^2	ΔChi^2 [%]
Ni ³⁺ RES	0.493	0.012	1.130	0.015	1323748	
Ni ²⁺ RES2	0.602	0.015	1.311	0.012	2079812	
Ni ⁴⁺ RES	0.307	0.007	0.387	0.017	584579	
Ni ³⁺ RES*	0.428	0.010	0.411	0.018	1432774	+ 8.2
Ni ⁴⁺ RES*	0.362	0.008	1.133	0.015	659451	+ 12.8

G. Fitting Values of the Resonant Ni-Valence Band Difference Fits

Table ST2: Values obtained from fitting the resonant nickel valence band of the oxidized catalyst.



H. Potential Dependency of the Off-Resonant Valence Band

Figure S13: Off-resonant valence band signal on an excitation energy of 850 eV on different electrode potentials. There are barely no potential-caused changes visible, excepting a small negative contribution slightly below the band edge. As discussed in the main text, this most probably corresponds to a potential caused shift of different membrane constituents against each other, rather than a decreasing off-resonant signal caused by the Ni-Oxidation. This is illustrated by the calculated off-resonant Ni-signal by Tanaka et al., which is shown enhanced by a factor of 100.

Tanaka et al. (34)

I. Certainty of the Energetic Levels in the Derived Oxygen p-DOS

To discuss the certainty of energetic levels in the derived p-DOS, errors in the Fermi level and photon energy calibration must be considered. The energy calibration of the beamline based on the assumption, that the oxygen gas $O \ 1s \rightarrow \pi^*$ resonance is located at 531 eV, has an uncertainty of about ± 0.2 eV due to different results presented in the literature.^{35–40} Moreover, the resonant valence band spectrum at 528.9 eV photon energy was calibrated while reducing the electrode potential based on the C 1s peak-position of graphene. The shift caused by the applied electrode potentials was accounted for by aligning the K 3p peaks in the valence band (Details given in the experimental section). As discussed in the main text, this procedure accounts for possible diffusion overpotentials, as the potassium signal mainly originates from interlayer-cations present in Ni_{0.75}Fe_{0.25}OOH_y. Moreover, it requires the Fermi level in the graphene layer and the catalyst to be equilibrated. This condition should be well fulfilled in the oxidized state, where the catalyst is highly conductive, but may be not well fulfilled in the reduced state, where the catalyst is an insulator.⁴¹ However, as the observed shifts of the K 3p peaks match quite well with the applied potential, we assume these errors of Fermi level mismatch to be not larger than the observed overpotentials, which are < 0.1 V. The core level binding energies in contrast, could not be determined directly, but were estimated to be the same as an oxidic reference. This probably constitutes the leading contribution of systematic errors and can also not be quantified. As the assumed oxidic peak position is on the low-energy end of the O 1s peak of the active phase, the Fermi level position relative to the unoccupied states derived here is also rather a lower bound. We conclude that the presented energy values should not be taken with higher significance than \pm 0.2 eV and especially the unoccupied density of states reflect an upper bound position in energy, based on the choice of oxidic core level binding energy. This makes our data well suitable for qualitative considerations.

J. Influence of Beam Damage on our Results

Irradiating the sample with the X-ray beam potentially has an impact on the structure of the solid-liquid interface on the membrane electrode assembly. To mitigate radiation damage, we have reduced the photon flux during the experiments to a value of about 10¹⁰ photons/s by using the 4th instead of the first diffraction order of the U49/2-PGM-1 monochromator, and by enhancing the constant fix-focus. Moreover, we have restricted the energy ranges of the potential dependent measurements to the necessary minimum. Each set of potential dependent spectra was recorded on a fresh spot.

To evaluate the influence of sample irradiation, we calculate the radiation dose absorbed by the sample, which is defined as the amount of absorbed radiation energy per mass unit. We assume that the beam is fully absorbed by the membrane electrode assembly. We first calculate the dose/time using the photon flux F (~10¹⁰ 1/s), photon energy E_{ph} (~530 eV for the O K edge or ~850 eV fo the Ni L-edge), the density ρ of the membrane (~2 g/cm³), the thickness of absorption d within the membrane electrode assembly (~5 µm) and the dimensions of the irradiated area A (~150 µm x 100 µm):

$$dose/time = \frac{F * E_{ph}}{\rho * A * d}$$

We then multiply the results with the respective irradiation times. This yields 29 MGy, 16 MGy, 11 MGy, 8 MGy, 24 MGy and 5 MGy for the set of three measurements (under noncatalytical, catalytical and on catalytical conditions) of the Ni L₃-edge PEY-XAS, the resonant valence band spectra at the nickel L₃-edge, the O K-edge PEY-XAS, the resonant valence band spectra at the O K-edge, the O 1s XPS and C 1s XPS, respectively. It is worth noting that these dose values represent averages over all components of the membrane electrode assembly. We expect that the graphene, for example, receives a higher radiation dose compared to the ionomer membrane below. Based on their experience with X-ray studies of ionomer supported catalysts, Falling et al. have suggested a threshold value for the radiation time, below which the membrane electrode assembly is not significantly affected by radiation damage. Above this threshold, they found clear indication for a reduced mass transport through ionomer membrane within the interaction volume.⁶ To compare our calculated radiation dose values with the reported threshold, we have recalculated the dose the samples received within this time. With the beam parameters given in their publication⁶, a membrane density of 2 g/cm³ and an absorption depth of 5 μ m, this is equal to a radiation-dose threshold of 36 MGy. This value is by a factor of about 10⁸ larger compared to the dose threshold value reported by Falling et al. themselves as they have used an unrealistic density of 2*10⁶ g/cm³ and they assumed an absorption depth of 183 µm representing the whole membrane. The latter overestimates the absorption depth by a factor of about 35, as nearly all radiation is absorbed within the first \sim 5 μ m. All radiation dose values reached in our experiments are well below the recalculated threshold. Consequently, we expect that the ionic contact of the catalyst is not significantly influenced by radiation damage in our experiments. Moreover, we did not observe differences of the catalyst features measured under non-catalytical conditions before and after the measurement in the OER-regime. This makes us confident, that the qualitative changes of the catalyst-electrolyte interface we have evaluated and discussed in this work, are also not influenced by radiation damage. The only irreversible spectral change, which we observe in the potential dependent 3-step measurements can be attributed to the oxidation of the graphene layer. As discussed in Section E, the oxidation process may be favored by the resonant excitation of oxygen species when the photon energy is swept over the O K-edge. Such a degradation of the graphene layer cannot be avoided on oxidizing potentials. This effect may lead to a decrease of the sample area, which is electrically connected by the graphene layer, and a decreased water film on top of the membrane electrode assembly. Therefore, the graphene degradation overall lowers the electrochemically active areas und the quantitative but not on the quantitative spectral changes of the catalyst features between catalytical and non-catalytical conditions. As we did not draw conclusions from quantitative spectral changes, the graphene degradation does not influence the validity of our results.

Supplementary Sources

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