Supporting information

Nickel-iron catalysts for electrochemical water oxidation – redox synergism investigated by *in-situ* X-ray spectroscopy with millisecond time resolution

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Table S1. Quantification of the deposited metals by Total Reflection X-ray Fluorescence. The electrodeposited NiFe oxides were dissolved in acid and the metal content of the catalyst film was determined using a standard procedure.

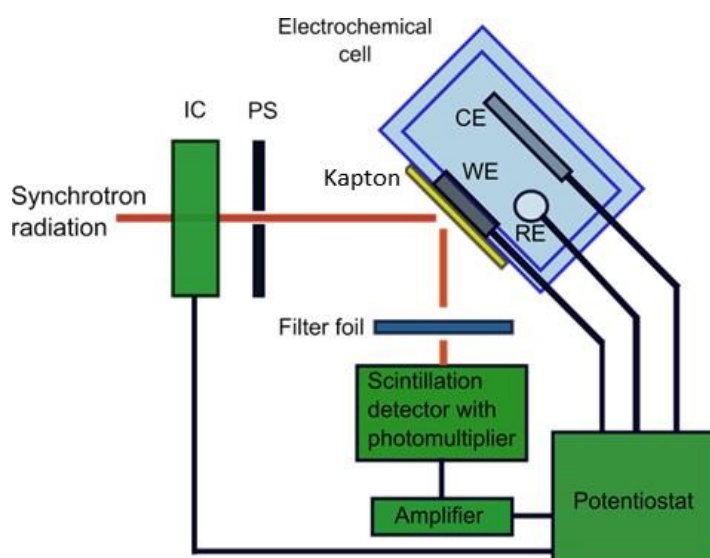| Deposition time (s)	Deposited material (nmol cm^{-2})	Ni:Fe ratio
1	199.1 Ni + 131.4 Fe	1.5
20	2623.5 Ni + 1508.5 Fe	1.7

Figure S1. Simplified schematic representation of the experimental setup of the time-resolved X-ray absorption measurements. Monochromatic synchrotron radiation passes through an ionization chamber (IC, for recording the variations in the incoming beam intensity) and a photoshutter (PS) before hitting the catalyst film. The film is deposited on a carbon-paper working electrode (WE) in a standard 3-electrode electrochemical setup, with a reversible hydrogen electrode as a reference electrode (RE) and a platinum mesh serving as counter electrode (CE). The cell is filled with 1 M KOH. Kapton tape covers a side window in the electrochemical cell, thereby supporting the thin carbon working electrode regarding mechanical stability. The excited Fe and Ni X-ray fluorescence passes through the Kapton window and then through a 10 μm metallic Mn or Co foil that filters out the majority of the scattered light. The fluorescence is monitored perpendicular to the incident beam by a scintillation detector. The detector consists of a scintillating crystal and a fast photomultiplier operated at 0.9kV. The signal from the photomultiplier passes through a 1 MΩ resistor for current-to-voltage conversion and is read by an amplifier. The amplified signal is finally recorded by A/D converters of the potentiostat that also operates the electrochemical cell and records the signal from the reference ionization chamber (IC).

Supporting Text - EXAFS Fourier-transforms and EXAFS simulations

The extracted EXAFS spectrum was weighted by k^3 and simulated in k-space. All EXAFS simulations were performed using in-house software (SimX3) after calculation of the phase functions with the FEFF program (version 8.4, self-consistent field option activated). Phase functions were calculated using a fragment of a layered transition metal oxide with 10 metal atoms and 32 oxygen atoms as shown in Figure S2. As usually observed, the EXAFS phase functions did not depend strongly on the details of the used model. Cosine windows covering 10% at the low-k and high-k side of the spectra were applied before calculation of the Fourier transforms. An amplitude reduction factor (S_0^2) of 0.7 was used for both metals. The data range used in the simulation was 29–549 eV (2.76–12 Å^{-1}). In order to minimize the number of free parameters and to improve the significance of the simulation results, a joint fit approach was used where the interatomic distances were kept the same for all spectra of one data set. The Debye-Waller parameters for all shells were fixed to 0.063 Å to avoid over-parameterization, and to emphasize the changes in coordination number of the samples. The EXAFS simulation was optimized by a minimization of the error sum obtained by summation of the squared deviations between measured and simulated values (least-squares fit). The fit was performed using the Levenberg-Marquardt method with numerical derivatives. The error ranges of the fit parameters were estimated from the covariance matrix of the fit; they indicate the 68 % confidence intervals of the corresponding fit parameters. The fit error was calculated as in ref [1]. For calculation of the Fourier-filtered error (described in ref. [2]), the range from 1 to 3.5 Å on the reduced distance scale was used.
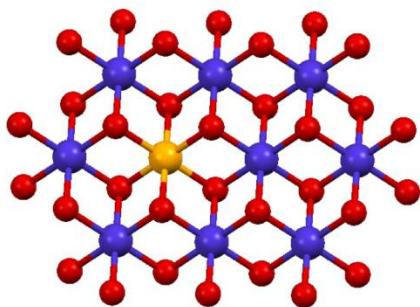

Figure S2. Structural model used for calculation of phase functions for the NiFe catalyst (oxygen – red, transition metal (Ni or Fe) – blue, Ni or Fe absorber – orange).
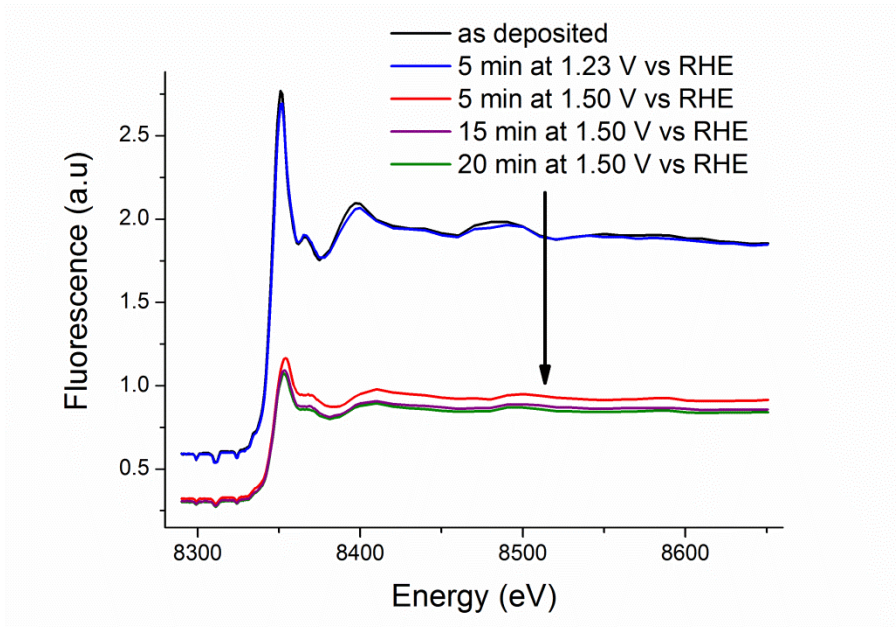
Figure S3. *In-situ* XAS measurements at the Ni K-edge in 1 M KOH for NiFe catalyst films cathodically electrodeposited on carbon paper (at 250 mA cm^{-2} for 5 s). Note that the here shown spectra are *not* normalized. With exception of the "as deposited" spectrum, all shown spectra were collected such that during data collection a constant potential of 1.23 V$_{RHE}$ was applied. The following color code is used: black, sample as deposited; blue, sample measured with 1.23 V$_{RHE}$ potential applied; red, sample measured with 1.23 V$_{RHE}$ applied after conditioning at 1.50 V$_{RHE}$ for 5 min; purple, sample measured with 1.23 V$_{RHE}$ applied after conditioning at 1.50 V$_{RHE}$ for 15 min, and green, sample measured with 1.23 V$_{RHE}$ applied after conditioning at 1.50 V $_{RHE}$ for 20 min. We observed that the fluorescence at the Ni K-edge decreases to about half of the initial value during conditioning at 1.50 V$_{RHE}$. However, this decrease reaches a stable steady state after about 20 minutes. After a conditioning of 20 min at 1.50 V$_{RHE}$, it was possible to employ the samples for further measurements that provide stable, fully reproducible data.
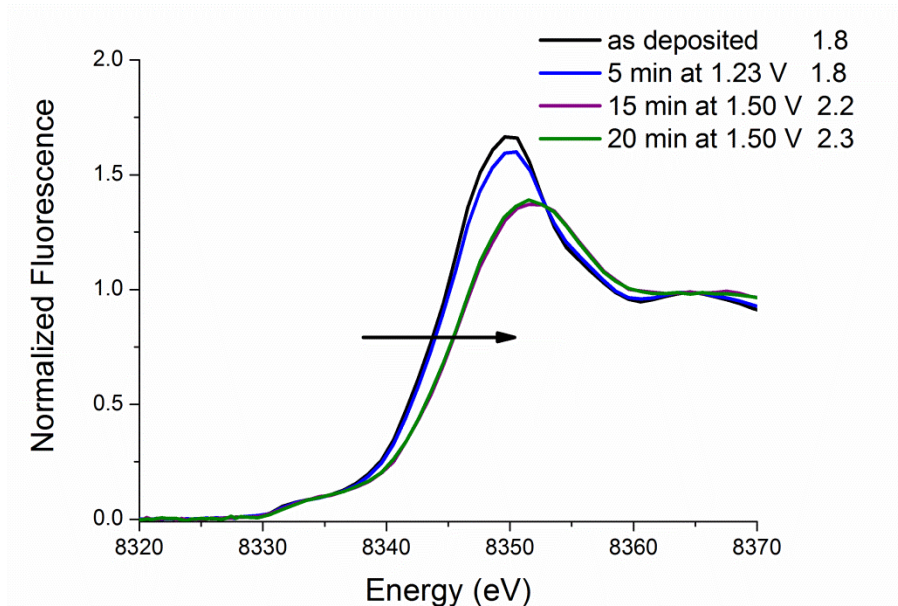
Figure S4. *Normalized in-situ* XANES at the Ni K-edge in 1 M KOH of the NiFe catalyst deposited on carbon paper for 5 s. The color code corresponds to: black, sample as deposited; blue: sample measured with 1.23 V_{RHE} potential applied; red: sample measured with 1.23 V_{RHE} applied after conditioning at 1.50 V_{RHE} for 5 minutes; purple: sample measured with 1.23 V_{RHE} applied after conditioning at 1.50 V_{RHE} for 15 minutes and green: sample measured with 1.23 V_{RHE} applied after conditioning at 1.50 V_{RHE} for 20 minutes. The number shown in the legend corresponds to the estimated oxidation state of the sample. Figure S4 shows the normalized XANES spectra from Figure S3. It can be observed that the sample as deposited and after applying 1.23 V_{RHE} has a very similar Ni oxidation state (of 1.8). However, when 1.50 V_{RHE} is applied for 15-20 minutes and the edge is measured at 1.23 V_{RHE}, the Ni-edge position remains at a higher oxidation state than the initial one measured in the as-deposited sample. This suggests that after operation at catalytic potential some of the Ni metal centers are trapped in a higher oxidation state. As it can be observed in Figure S5 the initial low oxidation state (around 1.8) can be slowly restored, but only after to 1.23 V_{RHE} for extended time periods (more than 1 hour).
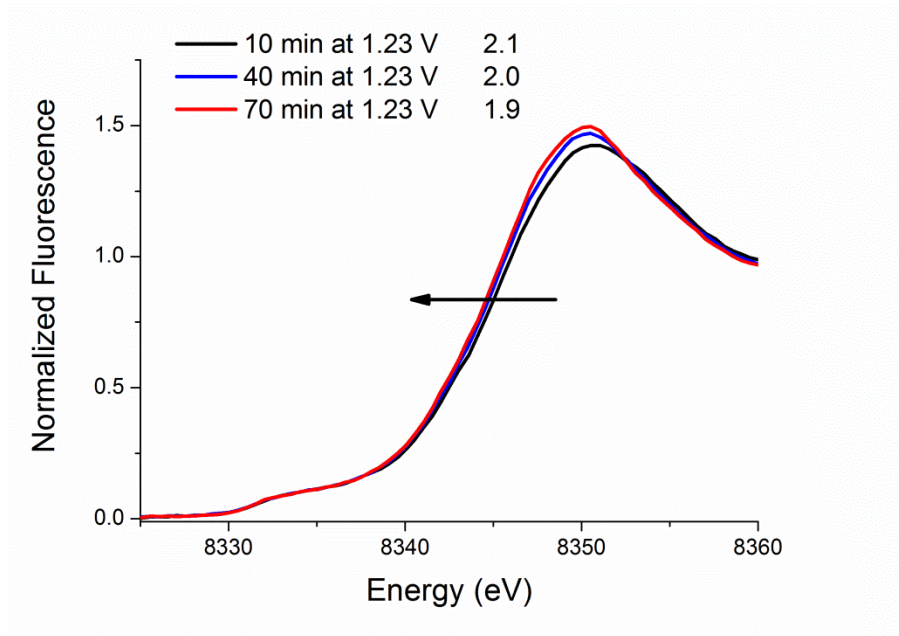
Figure S5. Normalized *in-situ* XANES at the Ni K-edge in 1 M KOH of the NiFe catalyst deposited on carbon paper for 5 s. The NiFe catalyst was exposed to 1.55 V_{RHE} for 2 hours, then 1.23 V_{RHE} was applied for 10 to 70 minutes, and simultaneously Ni K-edge spectra were recorded. The number shown in the legend corresponds to the estimated oxidation state of the sample.
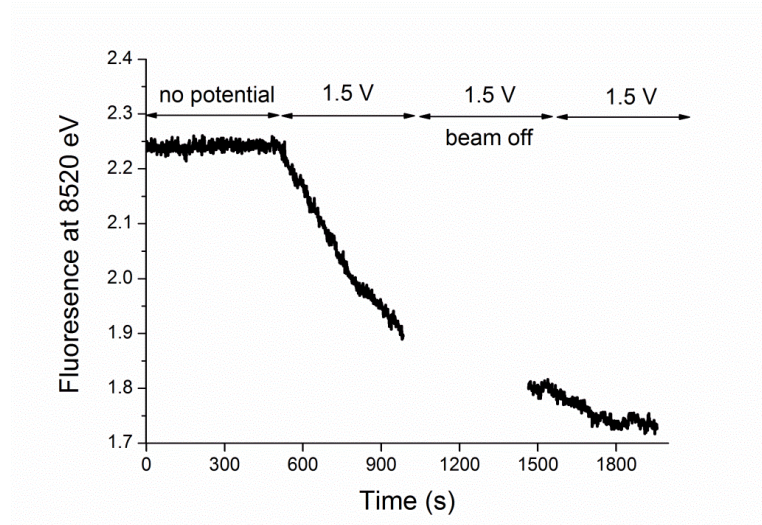

Figure S6. Stability of the NiFe catalyst (deposited on carbon paper for 5 s) towards radiation damage in 1 M KOH. The film was first kept with no potential applied with the X-ray beam at an energy after the Ni K-edge (8520 eV). After that 1.50 V_{RHE} was applied. After about 500 s, the X-ray beam was switched off and then switched on again. The time course reflects the loss of catalyst material within the first 20 min of exposure to 1.5 V_{RHE}. It is obvious that the material loss is unrelated to X-ray exposure.
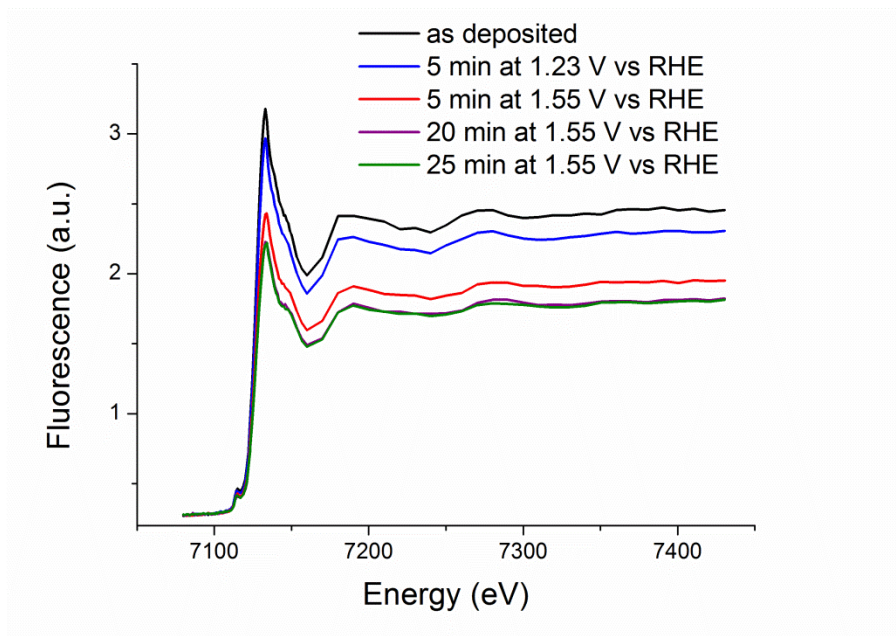
Figure S7. *In-situ* XANES spectra at the Fe K-edge in 1 M KOH of the NiFe catalyst deposited on carbon paper for 5 s (without normalization). The color code corresponds to: black, sample as deposited; blue: sample measured with 1.23 V_{RHE} potential applied for 5 minutes; red: sample measured with 1.55 V_{RHE} applied for 5 minutes; purple: sample measured with 1.55 V_{RHE} applied for 15 minutes and green: sample measured with 1.55 V $_{RHE}$ applied for 20 minutes. The decrease in the fluorescence reaches steady state after 20 min operation.
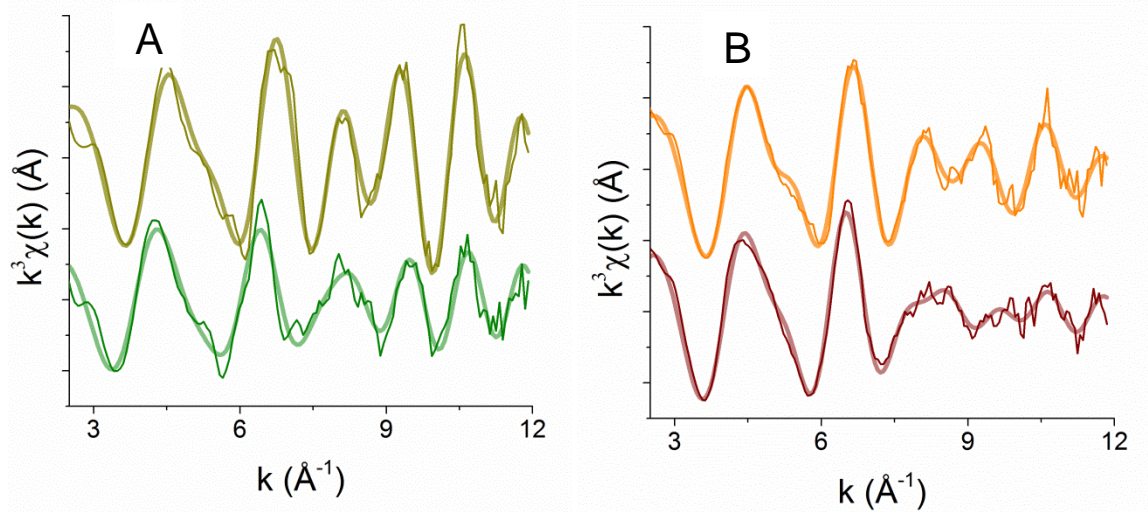
Figure S8. Fourier-transformed k^3-weighted EXAFS spectra at the Ni K-edge **(A)** and at the Fe K-edge **(B)** of the NiFe catalyst (deposited on carbon paper for 5 seconds in 1 M KOH) at 1.23 V_{RHE} and at 1.55 V_{RHE} with the corresponding simulations (a cosine window covering 10% of the left and right side of the EXAFS spectra was used to suppress the side loops in the Fourier transforms). The data was simulated after subtracting a 10 % of metal contribution at the Ni edge. The simulation parameters are provided in Table 1.
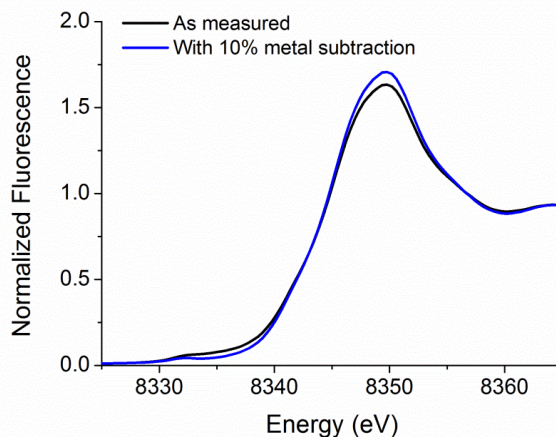
Figure S9. Nickel K-edge of the NiFe catalyst during in-situ XANES (no potential applied) before (black) and after correction with a 10 % metallic contribution (blue). The metallic contribution in the extended X-ray absorption fine structure (EXAFS) spectrum was corrected for by subtracting a weighted metal spectrum from the sample spectrum according to the following formula:

$$corrected\ spectrum = \frac{1}{1-\alpha} * (sample\ spectrum - \alpha * metal\ spectrum)\ with\ \alpha < 1,$$

where α represents the fraction of the metallic contribution. The correction factor was chosen such that features in the XANES and EXAFS spectra know to arise from metallic contributions were minimized (using a qualitative trial-and-error approach). This kind of corrections have been used before for cobalt based catalysts.[5] An example of the effect of the correction in the XANES and EXAFS spectra for the NiFe catalyst is shown in Figures S9 and S10, where α was 0.1.
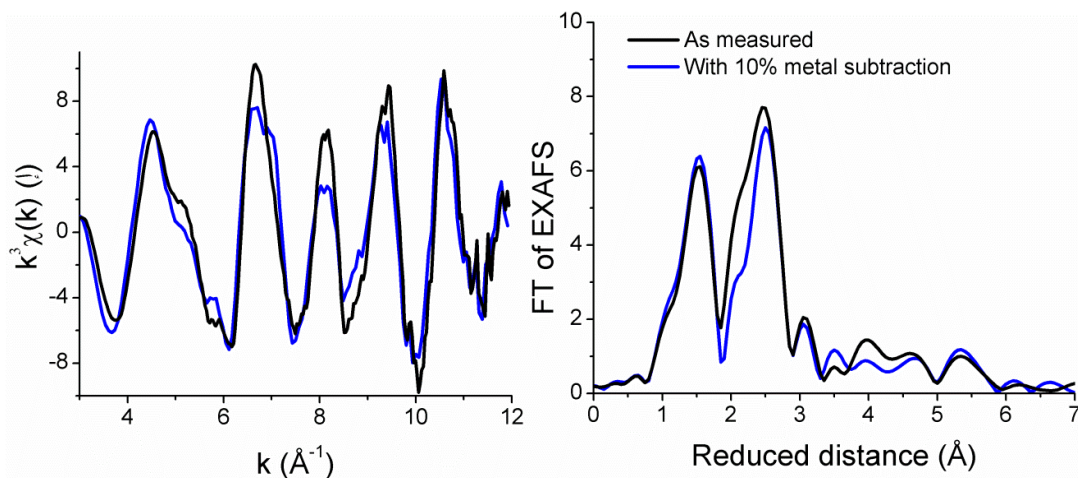

Figure S10. k^3-weighted EXAFS spectra (left) and FT of EXAFS for the NiFe catalyst at 1.55 V_{RHE} before (black) and after correction for a 10 % metallic contribution (blue).

Table S2. Simulation parameters for the fitting the fluorescence time courses (potential steps between 1.55 V_{RHE} and 1.23 V_{RHE}, see Figure 4C and 4D, according to Eq. 1 in the main article. The number in parenthesis corresponds to the uncertainty in the last digit.

Parameter	Ni Oxidation	Ni Reduction	Fe (Oxidation)	Fe (Reduction)
A / a.u.	1.3353(1)	1.3863(3)	1.7273(1)	1.7497(6)
B / a.u.	0.0331(8)	-0.0188(4)	0.012(3)	-0.0113(9)
C / a.u.	0.0135(7)	-0.0291(2)	0.007(3)	-0.0092(4)
t_1 / s	0.44(1)	0.27(1)	0.46(9)	0.13(2)
t_2 / s	2.4(1)	5.0(2)	1.7(4)	5.2(8)

Table S3. Alternative simulation parameters for the fitting the fluorescence time courses (protocol of step potentials between 1.55 V_{RHE} and 1.23 V_{RHE}) for Figure S14. The number in parenthesis corresponds to the uncertainty in the last digit. The value marked by an asterisk (*) were fixed in the simulation to the corresponding value of the Ni time courses upon stepping to a reductive potential. Visual inspection of the below figure and comparison to figure 5D reveals that the agreement between experimental and simulated time courses is equally good for the two alternative simulation approaches.

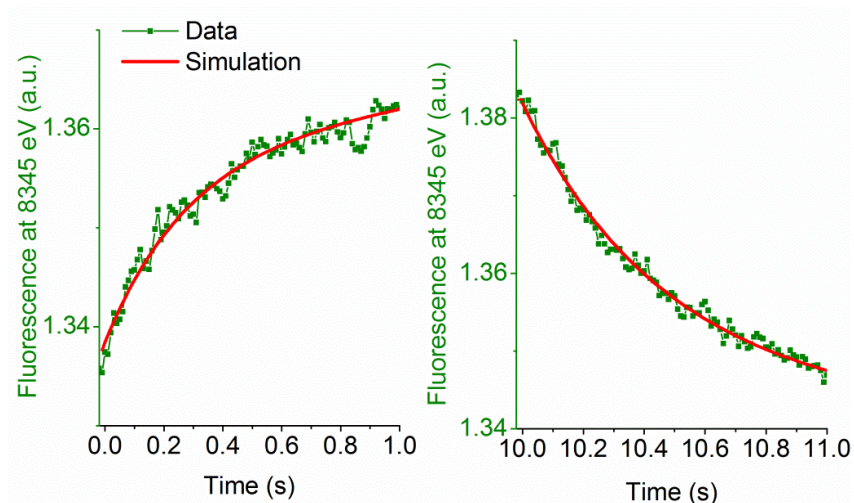| Parameter	Fe (Oxidation)	Fe (Reduction)
A / a.u.	1.7273(1)	1.7497(6)
B / a.u.	0.012(3)	-0.0113(9)
C / a.u.	0.007(3)	-0.0092(4)
t_1	0.46(9) s	0.27* s
t_2	1.7(4) s	5.0*
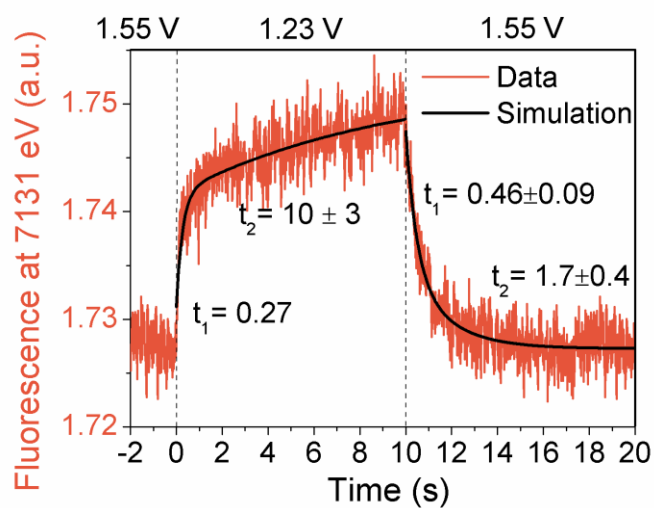
Figure S11. X-ray fluorescence time courses during *in-situ* XAS with step potential protocol for the NiFe catalyst. Magnification of the data shown in Figure 4C between 0 and 1s after the potential pulse. We stepped the potentials 90 times between 1.55 V_{RHE} and 1.23 V_{RHE} with the X-ray energy set at the middle of the Ni K-edge (8345 eV). The data shown is the average of 90 measurements in each case. The measurements were performed with 30-40 ms time resolution. The data was simulated using two exponential functions for the reduction and oxidation processes as described in Table S2.
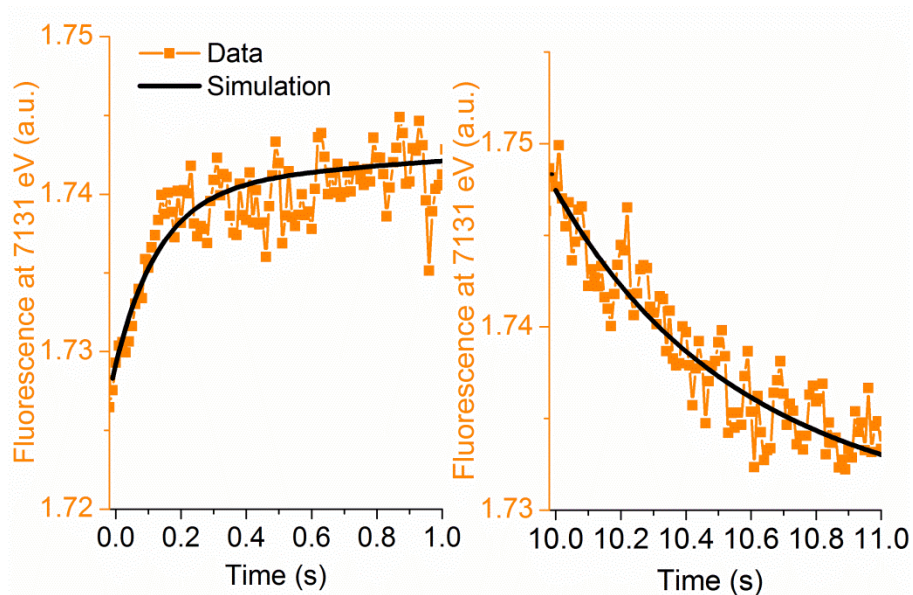

Figure S12. Fluorescence time courses during in-situ XAS with step potential protocol for the NiFe catalyst. Magnification of the data shown in Figure 4D between 0 and 1s after the potential pulse. We stepped the potentials 90 times between 1.55 V_{RHE} and 1.23 V_{RHE} with the X-ray energy set at the top of the Fe K-edge (7131 eV). The data shown is the average of 90 measurements in each case. The measurements were performed with about 30 ms time resolution (determined by the low-pass filter of the used amplifier; data point were sampled every 10 ms). The data was simulated bi-exponentially with parameters provided in Table S2.