Electronic Supplementary Information

Delving into Fe-Content Effects on Surface Reconstruction of Ba_{0.50}Sr_{0.50}Co_{1-x}Fe_xO_{3-δ} for the Oxygen Evolution Reaction

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Detailed Methods

XRD: Reference patterns

The following reference patterns were used to assign the present phases of the as-synthesized powders (ICSD collection code or PDF number are given in brackets): c-Ba_{0.5}Sr_{0.5}CoO_{2.5} (163669),¹ c-Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃ (185122),² c-Ba_{0.5}Sr_{0.5}Co_{0.5}Fe_{0.5}O_{2.36} (191511),³ c-BaFeO₃ (29096),⁴ c-SrFeO_{2.5580} (154942),⁵ c-Ba_{0.75}Sr_{0.25}(NO₃)₂ (00-026-0185), c-Ba_{0.5}Sr_{0.5}(NO₃)₂ (00-026-0186), o-Ba_{0.8}Sr_{0.2}CO₃ (00-047-0223), o-Ba_{0.5}Sr_{0.5}CO₃ (00-047-0224), c-Ba_{0.504}Sr_{0.496}O (44798),⁶ rs-CoO (9865),⁷ β -CoOOH (22285),⁸ sp-Fe₃O₄ (26410),⁹ and c-Fe_{0.95}O (67197).¹⁰ The proposed unit cells with the edge-sharing polyhedra (esp) with the chemical formula of Ba_{0.5}Sr_{0.5}CoO₂ and Ba_{0.5}Sr_{0.5}FeO_{2.5} were generated using the following parameters: Tetragonal (crystal system), P4/mmm (space group), 3.01 Å for esp-Ba_{0.5}Sr_{0.5}CoO₂ and 3.07 Å for esp-Ba_{0.5}Sr_{0.5}FeO_{2.5} (lattice parameter a = b), 7.35 Å for esp-Ba_{0.5}Sr_{0.5}CoO₂ and 7.2 Å for esp-Ba_{0.5}Sr_{0.5}CoO₂ and O1_{0.75} 0.5/0.5/0.2 for esp-Ba_{0.5}Sr_{0.5}FeO_{2.5}, and O2₁ 0/0/0.5. The software CrystalMaker[®] X Version 10.7.3 was used to generate the unit cells and to calculate the XRD patterns of esp-Ba_{0.5}Sr_{0.5}CoO₂ and esp-Ba_{0.5}Sr_{0.5}FeO_{2.5}.

K-edge and L₃-edge XAS: Commercial standards

The following materials were used as standards to assign the approximate Co and Fe bulk oxidation state: Cobalt(II) oxide (CoO, \geq 99.99%, Sigma-Aldrich), cobalt(II,III) oxide (Co₃O₄, 99.9985% Puratronic[®], Thermoscientific - Alfa Aesar), iron(II) oxide (FeO, 99.7%, Sigma-Aldrich), iron(II,III) oxide (Fe₃O₄, 99.999%, Sigma-Aldrich), and α -iron(III) oxide (Fe₂O₃, \geq 99.995%, Sigma-Aldrich). β -cobalt(III) oxyhydroxide (CoOOH) was synthesized as described in the Methods section in the article.

K-edge XAS: EXAFS models

The following CIF-files were used to generated the models for the fit (ICSD collection code is given in brackets): $c-Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (185122),² rs-CoO (9865),⁷ and β -CoOOH (22285).⁸ The proposed unit cell with the edge-sharing polyhedra (esp) with the chemical formula of BaCoO₃ and BaFeO₃ were generated using the following parameters: Te-tragonal (crystal system), P4/mmm (space group), 3.01 Å for esp-BaCoO₃ and 3.07 Å for esp-BaFeO₃ (lattice parameter a = b), 7.35 Å for esp-BaCoO₃ and 7.2 Å for esp-BaFeO₃ (lattice parameter c), Ba₁ 0/0/0 (x/y/z coordinate), Co₁ 0.5/0.5/0.5, O1₁ 0.5/0.5/0.25 for esp-BaCoO₃ and O1₁ 0.5/0.5/0.2 for esp-BaFeO₃, and O2₁ 0/0/0.5. The software CrystalMaker[®] X Version 10.7.3 was used to generate the unit cells and CIF-files of esp-BaCoO₃ and esp-BaFeO₃ for the FT-EXAFS spectra fitting.

L3-edge XAS: Energy calibration and normalization

The α , β , γ and δ peaks of the Co²⁺ L₃-edge XAS spectra were used to perform a relative energy calibration of all Co L₃-edge XAS spectra, whereas the β and γ peaks of the Fe³⁺ L₃-edge XAS from the Fe₂O₃ standard were used to perform the same for Fe L₃-edge XAS spectra. The relative energy calibration was necessary to align data measured during different beamtimes and/or different beamlines (X-Treme¹¹ or PHOENIX beamline of Swiss Light Source (SLS), PSI, Switzerland). The Co L₃-edge XAS spectra were normalized by dividing the averaged maximum β and δ peak intensity. The Fe L₃-edge XAS spectra were normalized by dividing the averaged maximum β and γ peak intensity.

L₃-edge XAS: Surface oxidation state and fraction estimations

The mole fraction weighted average oxidation state of the surface B-site metals was estimated by $(1-x) \cdot OS_{Co} + x \cdot 3$ assuming a surface Fe oxidation state of +3 (x in BSCo_{1-x}Fe_x and OS_{Co} = surface Co oxidation state).

The remaining surface Co^{2+} fraction, which does not contribute to the high-spin (hs) Co^{2+} in O_h -sites fraction, was estimated by $3 - sOS_{Co} - hs Co^{2+}$ in O_h -sites fraction. The equation $sOS_{Co} - 2$ was used to estimate the Co^{3+} fraction. A systematic error of ~10% is assumed in these estimations.

OER stability protocol

The OER stability protocol included the following steps: (1) Two CV cycles between 1.0 and 1.6 V_{RHE} with a scan rate of 50 mV·s⁻¹, (2) CA experiments at 1.0 (lower potential value) and 1.6 V_{RHE} (upper potential value) holding at each potential for 10 s and cycled 101 times between these two values, (3) Six CV cycles between 1.0 and 1.4 V_{RHE} with a scan rate of 50 mV·s⁻¹, (4) IS measurement with an amplitude of 10 mV at 1.2 V_{RHE} and a frequency range of 1 MHz to 1 Hz, (5) Open-circuit voltage (OCV) for 5 min, and (6) Repeating the steps (2) to (5) four times (in total 505 CA cycles between 1.0 and 1.6 V_{RHE}).

Jnet and Qnet calculations

The 25th CV cycle measured during the OER activity protocol was analyzed to calculate the Co-mass normalized net current density (J_{net}) and cumulated net charge (Q_{net}) from the pseudocapacitive (redox) processes in the pre-OER potential range (Figure S17). In general, the measured current density in the pre-OER potential range between 1 and ~1.5 V_{RHE} has only contributions from pseudocapacitive (pc) and double-layer (dl) capacitive processes. Therefore, the overall current density of the positive going potential scan (J_+) is the sum of these two contributions ($J_+ = J_{+,pc} + J_{+,dl}$), whereas the same is also valid for the negative going potential scan ($J_- = J_{-,pc} + J_{-,dl}$) as shown in Detailed Methods Figure 1. To get a J_{net} that depends only on the difference of pseudocapacitive processes between the positive and negative going potential scan ($J_{net} = J_{+,pc} - |J_{-,pc}|$), one needs to remove the current density contribution from the double-layer (dl) capacitive processes in the pre-OER potential range.

A characteristic of double-layer capacitive processes is that the generated current density is independent of the applied potential and thus creates a constant current density for a given potential scan rate during the positive going potential scan. The same constant current density is also generated during the negative going potential scan but with an opposite sign resulting in a rectangular CV if only double-layer capacitive processes are present (grey box in Detailed Methods Figure 1). However, this rectangular CV is not always perfectly aligned around the current density—axis (J = 0). For this purpose, one needs to find an optimal potential region in the CV, where the current density contribution of the double-layer capacitive processes is maximal. This optimal potential region was selected to be at 1.05 V_{RHE} due to the low redox couples in all materials of the BSCo_{1-x}Fe_x series at this potential region closer to the lower end of the CV potential scan e.g. 1 V_{RHE}. Therefore, the 25th CV cycle of each material of the BSCo_{1-x}Fe_x series was shifted on the current density—axis, as indicated with J + Δ J, until the current density of the positive and negative going potential scan are equal at 1.05 V_{RHE} (Detailed Methods Figure 1). After this shift, the current density contribution of the double-layer capacitive processes is aligned around the current density—axis so that J_{+,dl} = |J_{-,dl}|. Now, J_{net} can be simply calculated by taking the difference between the current density of the positive going potential scan (J₋) and the negative going potential scan (J₋). J_{net} = J₊ – |J₋| = (J_{+,pc} + J_{+,dl}) – (|J_{-,pc}| + |J_{-,dl}|)

 $= (J_{+,pc} - |J_{-,pc}|) + (J_{+,dl} - |J_{-,dl}|) = J_{+,pc} - |J_{-,pc}|.$ The last step is possible because $J_{+,dl} = |J_{+,dl}|$ is valid at any potential after applying the shift (ΔJ) and aligning the double-layer capacitive processes box around J = 0. Therefore, the current density contribution of the double-layer capacitive processes (DL) are canceled out in J_{net} so that J_{net} depends only on the difference of the pseudocapacitive processes ($J_{net} = J_{+,pc} - |J_{-,pc}|$).

Finally, the Co-mass normalized cumulated net charge (Q_{net}) was calculated by dividing J_{net} with the scan rate of 10 mV·s⁻¹ and integrating it between 1.05 and 1.5 V_{RHE} . J_{net} and Q_{net} are both not corrected by the contribution from the non-capacitive faradaic process (OER) so that the values above ~1.45 V_{RHE} have to be considered with caution.



Detailed Methods Figure 1. Current density contributions of the positive (J_+) and the negative going potential scan (J_-) in the pre-OER potential range. J_{net} is free from the double-layer (dl) capacitive processes as their contribution are cancelled out when calculating J_{net} , but only when the CV is shifted (ΔJ) so that $J_{+,dl} = |J_{-,dl}|$ at 1.05 V_{RHE} . Therefore, J_{net} is equal to the difference between the pseudocapacitive processes from the positive $(J_{+,pc})$ and the negative going potential scan $(J_{-,pc})$.

Operando K-edge XAS: Electrochemical protocol

The operando protocol included in general the following steps:

(1) XAS measurement of the as-prepared electrode

(2) XAS measurement at OCV

(3) Start of the CA experiments at 1.000, 1.100, 1.200, 1.300, 1.400, 1.450, 1.500, 1.525, 1.550 V_{RHE} in the so-called positive going potential scan and at 1.200 and 1.000 V_{RHE} in the negative going potential scan afterwards

(4) 10 CVs between 1.000 and 1.600 V_{RHE} (Figure S33a,b)

(5) IS at 1.200 V_{RHE} with a 10 mV amplitude and in a frequency range of 1 MHz to 1 Hz for the high-frequency resistance (HFR) correction.

The $BSCo_{0.80}Fe_{0.20}$ was measured only once, since the material has already been measured and published several times by the research group,¹²⁻¹⁴ whereas $BSCo_{0.60}Fe_{0.40}$ was measured several times and the XAS spectra with the best quality are shown in this manuscript.

Supplementary Information Figures



Figure S1. TEM images and EDX maps recorded in ADF-STEM mode of flame-spray synthesized BSCo_{0.80}Fe_{0.20}. (Top row) TEM images representing the agglomerated nanoparticles at the lower size range between ~5 and ~40 nm. (Middle and bottom row) Same agglomerated nanoparticles as shown in the top row, but as EDX maps from ADF-STEM revealing a homogeneous distribution of O, Fe, Co, Sr, and Ba atoms. The low signal intensity of Sr Ka in comparison to the remaining elements originates from the energy difference of the emitted X-rays: The Sr Ka emission line has a higher energy, which leads to a lower signal intensity in comparison to the other elements (Figure S3). The Sr La signal with a similar intensity in comparison to the other elements with the Si Ka signal from the background and could not be selected (Figures S8 and S9).



Figure S2. ADF-STEM images of BSCo_{0.80}Fe_{0.20}. Same agglomerated nanoparticles as shown in Figure S1 before and after the EDX mapping proving the stability of the agglomerated nanoparticles for the used conditions during the acquisition.



Figure S3. EDX spectrum of flame-spray synthesized $BSCo_{0.80}Fe_{0.20}$. Integrated EDX spectrum over the whole ADF-STEM scanning range of the EDX map in Figure S1 revealing the presence of other elements beside of the expected O, Fe, Co, Sr, and Ba signal. The remaining peaks are from the background as shown in Figures S8 and S9. Inset: Same figure but with a magnified intensity to better see the relative difference of the Fe Ka (~6.5 keV) and Co Ka (~7 keV) peaks roughly resembling the ratio as expected from $BSCo_{0.80}Fe_{0.20}$.



Figure S4. TEM images and EDX maps recorded in ADF-STEM mode of flame-spray synthesized $BSCo_{0.60}Fe_{0.40}$. (Top row) TEM images representing the agglomerated nanoparticles at the lower size range between ~5 and ~40 nm. (Middle and bottom row) Same agglomerated nanoparticles as shown in the top row, but as EDX maps from ADF-STEM revealing a homogeneous distribution of O, Fe, Co, Sr, and Ba atoms. The low signal intensity of Sr Ka in comparison to the remaining elements originates from the energy difference of the emitted X-rays: The Sr Ka emission line has a higher energy, which leads to a lower signal intensity in comparison to the other elements (Figure S6). The Sr La signal with a similar intensity in comparison to the other elements with the Si Ka signal from the background and could not be selected (Figures S8 and S9).



Figure S5. ADF-STEM images of $BSCo_{0.60}Fe_{0.40}$. Same agglomerated nanoparticles as shown in Figure S4 before and after the EDX mapping proving the stability of the agglomerated nanoparticles for the used conditions during the acquisition.



Figure S6. EDX spectrum of flame-spray synthesized $BSCo_{0.60}Fe_{0.40}$. Integrated EDX spectrum over the whole ADF-STEM scanning range of the EDX map in Figure S4 revealing the presence of other elements beside of the expected O, Fe, Co, Sr, and Ba signal. The remaining peaks are from the background as shown in Figures S8 and S9. Inset: Same figure but with a magnified intensity to better see the relative difference of the Fe Ka (~6.5 keV) and Co Ka (~7 keV) peaks roughly resembling the ratio as expected from $BSCo_{0.60}Fe_{0.40}$.



Figure S7. Averaged specific surface area of the complete flame-spray synthesized $BSCo_{1-x}Fe_x$ series from three independent measurements. The values are between 8 and 13 m²·g⁻¹ relatively similar within the materials series.



Figure S8. EDX spectrum of the background. Integrated EDX spectrum over the whole ADF-STEM scanning range of the TEM grid (without a sample) representing the background of the sample measurements as shown in Figures S3 and S6: C, O, and Cu (grid), O, F, and Si (grease), Au, Cr and small amounts of Fe and Co (instrument). Inset: Same figure but with a magnified intensity to better see the small Fe Ka and Co Ka peaks from the background.



Figure S9. ADF-STEM background images and corresponding EDX maps of the background. ADF-STEM images before and after the EDX mapping, and the corresponding EDX maps of all elements detected in the integrated EDX spectrum (Figure S8) of the TEM grid (without a sample) representing the background of the sample measurements.



Figure S10. As-synthesized bulk properties of $BSCo_{1-x}Fe_x$ series with focus on cobalt. (a) As-synthesized powder XRD of $BSCo_{0.99}(Fe_{0.01})$ measured in Bragg-Brentano mode with the assigned secondary phases. The dashed vertical lines were added for all reference materials to guide the eyes of the reader. (b) Estimated oxygen content 3- δ and oxygen vacancy concentration δ based on the oxidation state of the metal ions as a function of the Fe-content. (c) Magnitude of k^2 -weighted Fourier transformed- (FT) EXAFS from Co K-edge spectra (*k*-range from 2.7 to 12 Å⁻¹). (d) Same data as shown in (c) but magnified between 1.0 and 3.5 Å. (e) Same data as shown in (c) but stacked. Refer to 'Detailed Methods' for ICSD collection code of the reference materials shown in the XRD pattern. The color code as defined in (e) is also valid in (c) and (d). The intensities of the standards in (c) and (d) were halved (×0.5).



Figure S11. As-synthesized bulk properties of $BSCo_{1-x}Fe_x$ series with focus on iron. (a) As-synthesized powder XRD of $BS(Co_{0.01})Fe_{0.99}$ measured in Bragg-Brentano mode with the assigned secondary phases. The dashed vertical lines were added for all reference materials to guide the eyes of the reader. (b) XANES of Fe K-edge spectra. Inset (b) Same data as shown in (b) but magnified around the half-normalized intensity. (c) Magnitude of k^2 -weighted Fourier transformed- (FT) EXAFS from Fe K-edge spectra (*k*-range from 2.7 to 11.4 Å⁻¹). (d) Same data as shown in (c) but magnified between 1.0 and 3.5 Å. (e) Same data as shown in (c) but stacked. Refer to 'Detailed Methods' for ICSD collection code of the reference materials shown in the XRD pattern. The color code as defined in (e) is also valid in (c) and (d).



Figure S12. As-synthesized Co K-edge FT-EXAFS best fit. (a) Magnitude and real part of k^2 -weighted FT-EXAFS at Co K-edge for BSCo_{0.80}Fe_{0.20} (*k*-range from 3 to 11.5 Å⁻¹). (b) Magnitude and real part of k^2 -weighted FT-EXAFS at Co K-edge for BSCo_{0.60}Fe_{0.40} (*k*-range from 3 to 11.5 Å⁻¹). Refer to 'Detailed Methods' for ICSD collection code of the standards used in the fitting and to Table S3 and S4 for the fitting values.



Figure S13. As-synthesized surface Co properties of $BSCo_{1-x}Fe_x$ series. (a) Co L₃-edge TEY-XAS spectra of standard materials including as-purchased 'CoO', one-time Ar-ion sputtered 'CoO', and LiCoO₂. Inset (a) Same data as shown in (a) but magnified to proof a similar oxidation state of the Co³⁺ standards (CoOOH and LiCoO₂) as the δ peak maximum has the same position on the energy scale.¹⁵⁻¹⁷ (b) I₀ and baseline corrected Ba M_{5,4}-edge (& Co L₃-edge) TEY-XAS spectra of as-synthesized BS(Co_{0.01})Fe_{0.99} to demonstrate the barely visible surface Co signal. Inset (b) Same data as shown in (b) but magnified for the energy range of the Co L₃-edge, but only the pre-peak of the Ba M-edge is visible at 781 eV.^{18,19} (c) High-spin (hs) Co²⁺, which is octahedrally (O_h) coordinated by oxygen atoms, low-spin (ls) Co²⁺ in O_h-sites, and Co³⁺ fractions (sum of all is 100%) as a function of the Fe-content. As horizontal lines are shown the hs Co²⁺ in O_h-sites, ls Co²⁺ in 'O_h'-sites, and Co³⁺ fractions (sum of the standard materials. (d) Same data as shown in (c) but cumulated. (e) Co mole fraction weighted hs Co²⁺ in O_h-sites, ls Co²⁺ in 'O_h'-sites, and Co³⁺ fractions (sum of the Fe-content. (f) Same data as shown in (e) but cumulated. Refer to 'Detailed Methods' for the assignments of the different Co fractions.



Figure S14. As-synthesized surface properties of $BSCo_{1-x}Fe_x$ series with focus on iron. (a) Fe L₃-edge TEY-XAS spectra of standard materials including as-purchased 'FeO' and one-time Ar-ion sputtered 'FeO'. Inset (a) Same data as shown in (a) but magnified to show the oxidation state sensitivity of the γ peak position on the energy scale. (b) Fe L₃-edge TEY-XAS spectra of as-synthesized $BSCo_{1-x}Fe_x$ series. Inset (b) Same data as shown in (b) but magnified to show the γ peak position on the energy scale and thus, the oxidation state trend within the $BSCo_{1-x}Fe_x$ series. (c) I₀ corrected but not baseline corrected Fe L₃-edge TEY-XAS spectra of as-synthesized BSCo_{0.99}(Fe_{0.01}) over the whole scanning range. (d) Same data as shown in (c) but magnified around the Fe L₃-edge peak position to reveal a barely visible surface Fe signal. (e) Estimated mole fraction weighted average oxidation state (OS) of the surface B-site metals as a function of the Fe-content. The values were calculated with (1-x) $\cdot OS_{Co} + x \cdot 3$ assuming $OS_{Fe} = 3$.



Figure S15. Electrochemical characterization of BSCo_{1-x}Fe_x series. (a) Tafel plot of Co-mass (from ICP-OES) normalized OER currents and the linear fits (dotted line). The vertical and horizontal lines indicate the error bar of four independent measurements. Inset (a) U-shaped OER potentials at $10 \text{ A} \cdot \text{g}_{Co}^{-1}$ (left axis) and volcano-shaped OER current densities at 1.55 V_{RHE} (right axis) as a function of the Fe-content. (b) Cycle number of maximum OER current density change during the stability protocol as a function of the Fe-content. (c) 5th (orange dash-dotted line), 10th, 15th, 20th and 25th (red dash-dotted line) CV cycle measured with 10 mV·s⁻¹ prior to CA's measurements of the BSCo_{1-x}Fe_x series with x = 0.01, 0.10, 0.20, and 0.30. Inset (c) Same data as shown in (c) but with a magnified pre-OER potential range. (d) 5th (orange dash-dotted line), 10th, 15th, 20th and 25th (red dash-dotted line) CV cycle measured with 10 mV·s⁻¹ prior to CA's measurements of the BSCo_{1-x}Fe_x series with x = 0.40, 0.50, 0.79, and 0.99. Inset (d) Same data as shown in (d) but with a magnified pre-OER potential range. All electrochemical experiments were performed in 0.1 M KOH (saturated with synthetic air) at room temperature.



Figure S16. OER stability performance of BSCo_{1-x}Fe_x series. (a) Absolute OER current density changes in $A \cdot g_{cat}^{-1}$ at 1.6 V_{RHE} (not IR-free) as a function of the cycling number. (b) Relative OER current density changes in % at 1.6 V_{RHE} (not IR-free) as a function of the cycling number. (c) OER current density in $A \cdot g_{cat}^{-1}$ at 1.6 V_{RHE} (not IR-free) as a function of the cycling number. (c) OER current density in $A \cdot g_{cat}^{-1}$ at 1.6 V_{RHE} (not IR-free) as a function of the cycling number. (c) OER current density in $A \cdot g_{cat}^{-1}$ at 1.6 V_{RHE} (not IR-free) as a function of the cycling number. BS(Co_{0.01})Fe_{0.99} was measured once with a modified OER stability protocol, where the upper potential value was 1.7 V_{RHE} instead of 1.6 V_{RHE} due to the low OER activity. The data is compared with BSCo_{0.21}Fe_{0.79} using the standard stability protocol in (d,e). (d) Absolute OER current density changes in $A \cdot g_{cat}^{-1}$ at 1.6 V_{RHE} for BSCo_{0.21}Fe_{0.79} and at 1.7 V_{RHE} for BS(Co_{0.01})Fe_{0.99} (both not IR-free) as a function of the cycling number. (e) OER current density in $A \cdot g_{cat}^{-1}$ at 1.6 V_{RHE} for BSCo_{0.21}Fe_{0.79} and at 1.7 V_{RHE} for BSCo_{0.21}Fe_{0.79} and at 1.7 V_{RHE} for BS(Co_{0.01})Fe_{0.99} (both not IR-free) as a function of the cycling number. (f) Same data as shown in (c) but on a logarithmic scale for the absolute OER current density. The color code as defined in (f) is also valid in (a-c).



Figure S17. Electrochemically irreversible surface Co oxidation in BSCo_{1-x}Fe_x series. (a) Co-mass (from ICP-OES) normalized cumulated net charge (Q_{net}) from pseudocapacitive processes calculated for the 25th CV cycle between 1.05 and 1.475 V_{RHE}. Inset (a) Cumulated Q_{net} values up to 1.325, 1.400 and 1.475 V_{RHE} for the 25th CV cycle as a function of the Fe content. (b) Co-mass (from ICP-OES) normalized 25th CV cycle of BSCo_{1-x}Fe_x with x = 0.01, 0.10, 0.20, and 0.30. (c) Co-mass (from ICP-OES) normalized 25th CV cycle of BSCo_{1-x}Fe_x with x = 0.40, 0.50, and 0.79. The horizontal dashed grey line indicates 0 A·g⁻¹_{Co}. The net current density (J_{net}) represents the difference between the positive (orange) and negative going potential scan afterwards (red) as calculated between 1.05 to 1.475 V_{RHE} and indicated by the vertical grey lines. The values of J_{net} and Q_{net} above ~1.425 V_{RHE} has to be considered with caution as the contribution from the non-capacitive faradaic OER current density was not subtracted. Refer to 'Detailed Methods' for the approach to determine J_{net} and Q_{net}.

Figure S18. Ex situ TEY-XAS at Co L₃-edge of BSCo_{1-x}Fe_x series. (a) Total irreversible surface Co oxidation in the 'after OER' spectra relative to the 'as-synthesized' spectra as a function of the Fe-content. The total change is categorized in the two different Co²⁺ sources of ls Co²⁺ in 'O_h'-sites (left bar) or hs Co²⁺ in O_h-sites (right bar), and in the two different triggers of electrochemistry ('after OER' vs 'as-prepared') or electrode preparation ('as-prepared' vs 'as-synthesized'). The sum of the two bars (left (ls) and right (hs)) is equal to the total change as indicated with the scale bars for x = 0.79. (b) The 'as-synthesized', 'as-prepared', and 'after OER' mole fraction weighted average oxidation state (OS) of the surface B-site metals as function of the Fe-content as estimated with (1-x) · OS_{Co} + x · 3 assuming OS_{Fe} = 3. (c) The hs Co²⁺ in O_h-sites, (d) the ls Co²⁺ in 'O_h'-sites, and (e) the Co³⁺ in O_h-sites fraction for 'as-synthesized', 'as-prepared', and 'after OER' in O_h-sites fraction for 'as-synthesized', as-prepared' as function of the Fe-content. The negative value of x = 0.79 for the after OER ls Co²⁺ in 'O_h'-sites fraction lies in the assumed error range of 10%. Refer to 'Detailed Methods' for the assignments of the different Co fractions.

Figure S19. As-prepared surface of $BSCo_{1-x}Fe_x$ series with focus on cobalt. (a) TEY-XAS spectra at Co L₃-edge. (b) hs Co^{2+} in O_h-sites, ls Co^{2+} in 'O_h'-sites, and Co^{3+} fractions (sum of all is 100%) as function of the Fe content. The horizontal lines indicate the hs Co^{2+} in O_h-sites fraction of the standard materials. (c) Same data as shown in (b) but cumulated. (d) Co mole fraction weighted hs Co^{2+} in O_h-sites, ls Co^{2+} in 'O_h'-sites, and Co^{3+} fractions (sum of all is 1-x) as a function of the Fe-content. (e) Same data as shown in (d) but cumulated. Refer to 'Detailed Methods' for the assignments of the different Co fractions.

Figure S20. Surface cobalt state of $BSCo_{1-x}Fe_x$ series after OER. (a) TEY-XAS spectra at Co L₃-edge. (b) hs Co²⁺ in O_h-sites, ls Co²⁺ in 'O_h'-sites, and Co³⁺ fractions (sum of all is 100%) as function of the Fe content. The horizontal lines indicate the hs Co²⁺ in O_h-sites fraction of the standard materials. (c) Same data as shown in (b) but cumulated. (d) Co mole fraction weighted hs Co²⁺ in O_h-sites, ls Co²⁺ in 'O_h'-sites, and Co³⁺ fractions (sum of all is 1-x) as a function of the Fe-content. (e) Same data as shown in (d) but cumulated. The negative value of x = 0.79 after OER in (b-e) lies in the assumed error range of 10%. Refer to 'Detailed Methods' for the assignments of the different Co fractions.

Figure S21. Surface iron state of $BSCo_{1-x}Fe_x$ series after OER. (a-c) Fe L₃-edge TEY-XAS spectra of as-synthesized powder, as-prepared electrode, and ex situ after OER for $BSCo_{0.80}Fe_{0.20}$, $BSCo_{0.60}Fe_{0.40}$, and $BSCo_{0.21}Fe_{0.79}$, respectively. (d) Fe L₃-edge TEY-XAS spectra of 'as-prepared' $BSCo_{1-x}Fe_x$ series with x = 0.20, 0.40, and 0.79. (e) Fe L₃-edge TEY-XAS spectra of $BSCo_{1-x}Fe_x$ series with x = 0.20, 0.40, and 0.79. (e) Fe L₃-edge TEY-XAS spectra of $BSCo_{1-x}Fe_x$ series with x = 0.20, 0.40, and 0.79 ex situ after OER. Inset (a-e) Same data as shown in (a-e) but magnified to show the energy position trend of the γ Fe L₃-edge peak maximum. (f) Surface Fe oxidation state trend of 'as-synthesized', 'as-prepared' and 'after OER' $BSCo_{1-x}Fe_x$ series assigned by the energy position of the γ Fe L₃-edge peak maximum.

Figure S22. Fe and Co content change on the surface after OER process. (a) Fe L₃-edge TEY-XAS spectra of 'as-prepared' and ex situ 'after OER' BSCo_{0.99}(Fe_{0.01}). (b) Relative change of the surface Fe-to-Co ratio of the 'as-synthesized', 'as-prepared' and ex situ 'after OER' BSCo_{1-x}Fe_x series as calculated with the division of the normalization factors of the Fe L₃-edge by the value of the Co L₃-edge. Only the relative Fe-to-Co ratio of BSCo_{0.99}(Fe_{0.01}) significantly changes for the different samples: The Fe-content on the surface increases from barely visible in the as synthesized power (Figure S14c,d), to a noisy peak in the 'as prepared' and finally, to a clear peak 'after OER' (Figure S21a). Therefore, the relative surface Fe-to-Co ratio significantly increases for BSCo_{0.99}(Fe_{0.01}) in comparison to the other materials in the series. ICP-OES measurements indicated that most likely the bulk of the BSCo_{0.99}(Fe_{0.01}) particles acts as the Fe-source for the accumulation on the surface and not the 0.1 M KOH electrolyte solution, which had a Co and Fe signal below the detection limit DL of 7 ppb for Co and 6 ppb for Fe. The DL was calculated with the following equation: DL (ppm) = ((3 σ)·(C₁-C₀)) / (I₁-I₀), where σ is the standard deviation of 10 blank measurements (in units of intensity), C₁ the concentration of the lowest standard (0.2 ppm), C₀ the concentration of the blank (0 ppm), I₁ the intensity of the lowest standard and I₀ the intensity of the blank.

Figure S23. Co oxidation state in the bulk during OER process. (a) Operando XANES at the Co K-edge of $BSCo_{0.80}Fe_{0.20}$ in the positive and negative going potential scan afterwards. Inset (a) Operando change of the Co oxidation state. (b) Operando XANES at the Co K-edge of $BSCo_{0.60}Fe_{0.40}$ in the positive and negative going potential scan afterwards. Inset (b) Operando change of the Co oxidation state. (c) Same data as shown in (a) of $BSCo_{0.80}Fe_{0.20}$ but magnified in the range of the half-normalized intensity. (d) Same data as shown in (b) of $BSCo_{0.60}Fe_{0.40}$ but magnified in the range of the half-normalized intensity. (e) Several XANES at the Co K-edge of $BSCo_{0.80}Fe_{0.20}$ to show the minimal changes of Co oxidation state in the bulk triggered by the sample preparation and electrolyte. Inset (e) Same data as shown in (e) but magnified around the half-normalized intensity. (f) Several XANES at the Co K-edge of $BSCo_{0.60}Fe_{0.40}$ to show the minimal changes of Co oxidation state in the bulk triggered by the sample preparation and electrolyte. Inset (e) Same data as shown in (f) but magnified around the half-normalized intensity. The color codes for the different potentials are defined in the Insets (a) and (b) and are valid for the lines in the spectra of (a and c) and (b and d), respectively.

Figure S24. Local geometry of Co in the bulk during OER process of $BSCo_{0.80}Fe_{0.20}$. (a) Operando magnitudes of k^2 -weighted FT-EXAFS at the Co K-edge for all measured potentials in the positive going potential scan (*k*-range from 2.7 to 12 Å⁻¹). (b) Same data as shown in (a) but magnified between 1.0 and 3.5 Å to highlight the changes of the first two shells. (c) Same data as shown in (a) but stacked. (d) Operando magnitudes of k^2 -weighted FT-EXAFS at the Co K-edge for the potentials, which were measured in the positive and negative going (afterwards) scan to indicate the high degree of irreversible changes in the local geometry of Co in the bulk (*k*-range from 2.7 to 12 Å⁻¹). (e) Several magnitudes of k^2 -weighted FT-EXAFS at the Co K-edge to show the minimal local geometry changes of Co in the bulk triggered by the sample preparation and electrolyte (*k*-range from 2.7 to 12 Å⁻¹). The color code for the different potentials as defined in (c) is also valid in (a) and (b). The intensities of the standards in (a), (b), (d), and (e) were halved (×0.5).

Figure S25. Local geometry of Co in the bulk during OER process of $BSCo_{0.60}Fe_{0.40}$. (a) Operando magnitudes of k^2 -weighted FT-EXAFS at the Co K-edge for all measured potentials (*k*-range from 2.7 to 12 Å⁻¹). (b) Same data as shown in (a) but magnified between 1.0 and 3.5 Å to highlight the minimal changes of the first two shells. (c) Same data as shown in (a) but stacked. (d) Several magnitudes of k^2 -weighted FT-EXAFS at the Co K-edge to show the minimal local geometry changes of Co in the bulk triggered by the sample preparation and electrolyte (*k*-range from 2.7 to 12 Å⁻¹). The color code for the different potentials as defined in (c) is also valid in (a) and (b). The intensities of the standards in (a), (b), and (d) were halved (×0.5).

Figure S26. Magnitude and real part of k^2 -weighted FT-EXAFS best fit at Co K-edge of BSCo_{0.80}Fe_{0.20}. (a) As-prepared (*k*-range from 3 to 11.5 Å⁻¹). (b) Operando at 1.00 V_{RHE} (*k*-range from 3 to 11.5 Å⁻¹). (c) Operando at 1.55 V_{RHE} (*k*-range from 3 to 11.5 Å⁻¹). Refer to 'Detailed Methods' for ICSD collection code of the standards used in the fitting and to Tables S5-S7 for the fitting values.

Figure S27. Magnitude and real part of k^2 -weighted FT-EXAFS best fit at Co K-edge of BSCo_{0.60}Fe_{0.40}. (a) As-prepared (*k*-range from 3 to 11.5 Å⁻¹). (b) Operando at 1.00 V_{RHE} (*k*-range from 3 to 11.5 Å⁻¹). (c) Operando at 1.55 V_{RHE} (*k*-range from 3 to 11.5 Å⁻¹). Refer to 'Detailed Methods' for ICSD collection code of the standards used in the fitting and to Tables S8-S10 for the fitting values.

Figure S28. Fe oxidation state in the bulk and crystalline structure after OER of BSCo_{0.80}Fe_{0.20}. (a) Operando XANES at the Fe K-edge in the positive and negative going potential scan afterwards. Inset (a) Operando change of the energy at half-normalized intensity of the Fe K-edge. (b) Same data as shown in (a) but magnified in the range of the half-normalized intensity. The color code for the different potentials is defined in the Insets of (a) and (b) and are valid for the lines in the spectra of (a) and (b). (c) Several XANES at the Fe K-edge to show the minimal changes of Fe oxidation state in the bulk triggered by the sample preparation and electrolyte. All XANES at the Fe K-edge are measured in fluorescence except the as-synthesized power as indicated with T. Inset (c) Same data as shown in (c) but magnified around the half-normalized intensity. (d) XRD patterns of the as-synthesized powder, the as-prepared electrode (same as used for the operando XAS experiments) and ex situ after the operando XAS measurements ('after OER'). The additional peaks in the XRD patterns of the 'as-prepared' and 'after OER' originate from the sputtered Au on the electrode as indicated with the control measurement of an electrocatalyst-free (bare) electrode. The XRD patterns of all electrodes were measured in transmission, which leads to a significant decrease of the intensity and increase of the noise towards higher 2θ angles, leading to a vanishing signal after 55°. Refer to Methods and 'Detailed Methods' for ICSD collection code of the reference materials shown in the XRD pattern.

Figure S29. Fe oxidation state in the bulk and crystalline structure after OER process of BSC0_{0.60}Fe_{0.40}. (a) Operando XANES at the Fe K-edge. Inset (a) Operando change of the energy at half-normalized intensity of the Fe K-edge. (b) Same data as shown in (a) but magnified in the range of the half-normalized intensity. The color code for the different potentials is defined in the Insets of (a) and (b) and are valid for the lines in the spectra of (a) and (b). (c) Several XANES at the Fe K-edge to show the minimal changes of Fe oxidation state in the bulk triggered by the sample preparation and electrolyte. All XANES at the Fe K-edge are measured in fluorescence except the as-synthesized power as indicated with T. Inset (c) Same data as shown in (c) but magnified around the half-normalized intensity. (d) XRD patterns of the as-synthesized powder, the as-prepared electrode (same as used for the operando XAS experiments) and ex situ after the operando XAS measurements ('after OER'). The additional peaks in the XRD patterns of the 'as-prepared' and 'after OER' originate from the sputtered Au on the electrode as indicated with the control measurement of an electrocatalyst-free (bare) electrode. The XRD patterns of all electrodes were measured in transmission, which leads to a significant decrease of the intensity and increase of the noise towards higher 2 θ angles, leading to a vanishing signal after 55°. Refer to Methods and 'Detailed Methods' for ICSD collection code of the reference materials shown in the XRD pattern.

Figure S30. Local geometry of Fe in the bulk during OER process of BSCo_{0.80}Fe_{0.20}. (a) Operando magnitudes of k^2 -weighted FT-EXAFS for all measured potentials in the positive going potential scan (*k*-range from 2.7 to 11.4 Å⁻¹). (b) Same data as shown in (a) but magnified between 1.0 and 3.5 Å to highlight the changes of the first two shells. (c) Same data as shown in (a) but stacked. (d) Operando magnitudes of k^2 -weighted FT-EXAFS for the potentials, which were measured in the positive and negative going (afterwards) scan to indicate the high degree of irreversible changes in the local geometry of Fe in the bulk (*k*-range from 2.7 to 11.4 Å⁻¹). (e) Several magnitudes of k^2 -weighted FT-EXAFS to show the minimal local geometry changes of Fe in the bulk triggered by the sample preparation and electrolyte (*k*-range from 2.7 to 11.4 Å⁻¹). The color code for the different potentials as defined in (c) is also valid in (a) and (b).

Figure S31. Local geometry of Fe in the bulk during OER process of BSCo_{0.60}Fe_{0.40}. (a) Operando magnitudes of k^2 -weighted FT-EXAFS for all measured potentials (*k*-range from 2.7 to 11.4 Å⁻¹). (b) Same data as shown in (a) but magnified between 1.0 and 3.5 Å to highlight the minimal changes of the first two shells. (c) Same data as shown in (a) but stacked. (d) Several magnitudes of k^2 -weighted FT-EXAFS to show the minimal local geometry changes of Fe in the bulk triggered by the sample preparation and electrolyte (*k*-range from 2.7 to 11.4 Å⁻¹). The color code for the different potentials as defined in (c) is also valid in (a) and (b).

Figure S32. Additional information about the used methods. (a) XRD of as-synthesized CoOOH powder in Bragg-Brentano mode, which was used as Co^{3+} standard. The vertical dashed lines were added to guide the eyes of the reader for the peaks of the reference pattern. The ICSD collection code of the reference pattern is given in the 'Detailed Methods'. (b) Aligned XANES at Co K edge of all Co reference foils measured simultaneously with the as-synthesized BSCo_{1-x}Fe_x series. Inset (b) Same data as shown in (b) but magnified around the half-normalized intensity to representatively reveal the exact alignment of all shown spectra in this study. (c) Description of Ba M₅-edge correction in all Co L₃-edge XAS spectra. Inset (c) Same data as shown in (c) but magnified around the Co L₃-edge to show the minimal change of the spectra due to the correction. (d) Description of F K-edge correction in the 'as-prepared' and 'after OER' Fe L₃-edge XAS spectra. Inset (d) Same data as shown in (d) but magnified around the pre-edge of Fe L₃-edge to show the minimal change of the spectra above 700 eV due to spline correction. (e) Hg/HgO RE calibration against RHE in H₂ saturated 0.1 M KOH electrolyte solution (top inset) using a clean polycrystalline Pt disc insert (bottom inset).²⁰⁻²⁴ (f) Representative Nyquist plot of impedance spectroscopy measured during OER activity protocol to assign the uncompensated ohmic resistance.

Figure S33. Additional information about the used methods. (a) CV of $BSCo_{0.80}Fe_{0.20}$ after the operando XAS experiments at the Co and Fe K-edge inside the flow cell in 0.1 M KOH and a scan rate of 10 mV·s⁻¹. Inset (a) Same data as shown in (a) but magnified. (b) CV of $BSCo_{0.60}Fe_{0.40}$ after the operando XAS experiments at the Co and Fe K-edge inside the flow cell in 0.1 M KOH and a scan rate of 10 mV·s⁻¹. Inset (b) Same data as shown in (b) but magnified. The current densities are normalized by the electrocatalyst-mass and corrected by the high frequency resistance (HFR). The relative change of the Co and Fe K-edge jump during the operando XAS experiments at the Co and Fe K-edge of $BSCo_{0.80}Fe_{0.20}$ (c) and $BSCo_{0.60}Fe_{0.40}$ (d). Inset (c,d) Same data as shown in (c,d) but magnified. Fe K-edge XAS spectra of $BSCo_{0.80}Fe_{0.20}$ (e) and $BSCo_{0.60}Fe_{0.40}$ (f) in transmission (T) and fluorescence (F) and the required shift in energy to align the fluorescence spectra with the simultaneously measured transmission spectra as shown in the Inset (e,f).

Supplementary Information Notes

Note S1. The molar fraction of the secondary phases with carbonates/nitrates as anion was estimated to be between 7 and 23% depending on the error of the ICP-OES measurement between 10 and 0%, respectively. Possible errors of the ICP-OES result are an incorrect weighed mass of the as-synthesized materials due to adsorbed water or pieces from the filter paper, which was used to collect the powder during the synthesis, as well as the loss of metal-ions during the digestion process. The molar fraction range was calculated based on the difference between the theoretically expected oxygen total mass fraction (estimated with the average bulk metal oxidation states of Ba (+2), Sr (+2), Co (+2.25), and Fe (+3)) and the experimentally measured remaining total mass fraction called 'Rest' (neither Ba, Sr, Co, nor Fe) from the ICP-OES result (Table S1). The calculation included the assumption of a 1-to-2 molar ratio of carbonates and nitrates as secondary phases according to their presence in the XRD patterns of the as-synthesized BSCo_{1-x}Fe_x series.

Note S2. In general, the unit cell size of a cubic perovskite-type oxide is not only proportional to the average ionic radius of the metals but also on the oxygen vacancy concentration (δ), which in turn is also related to the average metal oxidation state.^{25,26} However, the broad diffraction peaks of the nanocrystalline powders as well as the secondary phases prevent to find a clear explanation for the observed unit cell expansion towards the higher Fe content materials. Particularly the Ba-to-Sr ratio is difficult to assign in the cubic perovskite-type oxide when secondary phases are present. Therefore, the possibility for an increasing Ba-to-Sr ratio towards the higher Fe-content materials in the BSCo_{1-x}Fe_x series cannot be excluded as the reason for the unit cell expansion.

Note S3. The estimated oxygen vacancy concentration (δ) from the average bulk metal oxidation state were not corrected by the secondary phases, so that these values has to be considered with caution. Particularly the rs-CoO phase in the lower Fe-content materials can lead to a lower δ in the perovskite-type oxide than estimated. However, the overall trend is still assumed to be correct as the secondary phases are estimated to be between 7 and 23% (Note S1).

Note S4. The esp-peak (~ 2.6 Å) in the Co and Fe K-edge FT-EXAFS spectra of the as-synthesized BSCo_{1-x}Fe_x series can be partially explained by the presence of rock-salt (rs) CoO or FeO as secondary phase (Figures S10c-e and S11c-e). The separation of such a secondary phase is typically for a $BSCo_{1-x}Fe_x$, particularly with high oxygen vacancy concentrations (δ) , and allows the stabilization of the cubic perovskite-type oxide structure in highly reductive environments.²⁷ However, the Co and Fe K-edge FT-EXAFS spectra of the as-synthesized $BSCo_{1-x}Fe_x$ series cannot be explained by a simple mixture of a cubic $BSCo_{1-x}Fe_x$ (with csp) and rs-Co_{1-x}Fe_xO: 1) The peak at ~1.4 Å in the Co K-edge FT-EXAFS spectra of the as-synthesized materials with x between 0.01 and 0.50 is too short for the TM-O coordination shell of cubic csp-BSCo_{1-x}Fe_x and rs-Co(Fe)O at reduced distances of ~1.6 Å and ~1.7 Å, respectively (Figure S10c-e), 2) the relative weak signal of rs-CoO in the XRD pattern of $BSCo_{0.99}(Fe_{0.01})$ further decreases for the materials with a higher Fe-content and is out of proportion to the observed esp-peak in the Co K-edge FT-EXAFS spectra (Figure 1a and Figure S10), and 3) Fe has a bulk oxidation state close to +3 in all materials indicating the small amount of rs-FeO as secondary phase and is also out of proportion to the observed esp-peak in the Fe K-edge FT-EXAFS spectra (Figure S11). Therefore, the observations in the TM K-edge FT-EXAFS spectra can only be explained by considering the presence of an additional phase with a unit cell which is connected over esp. A possible candidate for such an additional phase is a tetragonal esp-Ba_{0.5}Sr_{0.5}Co_{1-x}Fe_xO₃₋₆ (BSCo_{1-x}Fe_x) and is inspired by highly oxygen-deficient perovskite-type oxides with the chemical formula of ABO₂ as found in the literature for A = Ba/Sr and $B = Co/Fe^{.28-31}$ Key characteristics of a tetragonal $esp-BSCo_{1-x}Fe_x$ unit cell are discussed in the following section:

The unit cell of an idealized cubic perovskite-type oxide ABO₃ is connected to all neighbor unit cells in all three directions over corner-sharing polyhedra (csp) around the B-site metals (Note S4 Figure 1a). This connectivity leads to the most symmetric unit cell with the space group $Pm\bar{3}m$ and has the identical look from all three directions. Contrarily, the unit cell of an idealized tetragonal perovskite-type oxide ABO₃ is connected to the neighbor unit cells in the *ab*-plane over edge-sharing polyhedra (esp) around the B-site metals (Note S4 Figure 1b). This connectivity leads to a lower symmetric unit cell with the space group P4/mmm and has the identical look only from two directions in the *ab*-plane. The difference in the connectivity of the unit cells leads to a shrinking of the *ab*-plane for the tetragonal esp-ABO₃ relative to the cubic csp-ABO₃. Consequently, the lattice places of the oxygen-atoms on the *c*-axis in a tetragonal esp-ABO₃ can move inside the unit cell due to the missing space in the A-site metal plane, which in turn can lead to a prolongation of the tetragonal esp-ABO₃ unit cell along the *c*-axis relative to a cubic csp-ABO₃. These changes in the unit cell of the tetragonal esp-ABO₃

enables the possibility to distinguish between two oxygen lattice places: The apical position on the c-axis and the basal position in the *ab*-plane of the esp, which are indistinguishable in a cubic csp-ABO₃. The different connectivity / symmetry of the tetragonal esp-ABO₃ unit cell relative to the cubic csp-ABO₃ can also lead to changes in the electronic configuration of the B-site metals. The cubic csp-ABO₃ has B-site metals which are octahedrally coordinated by oxygen atoms (O_h). In this case, the crystal field theory distinguishes between two relevant orbitals, namely the t_{2g} at lower energy and eg at higher energy, when transition metals (TMs) with valence electrons in the 3d orbitals occupy the B-site lattice places (Note S4 Figure 2 middle).³² The same is also valid for the tetragonal esp-ABO₃ as long as the distances are identical between the TM on the B-site and all oxygen lattice places, which is most likely the case for all TMs with Jahn-Teller inactive configurations such as hs Fe^{3+} (Is is weakly active). However, the situation changes when TMs occupy the B-site of the tetragonal esp-ABO₃ with Jahn-Teller active configurations such as ls Co²⁺ (hs is weakly active). In those cases, the distance between the TM and the oxygen-atoms on the c-axis will be either elongated (Note S4 Figure 2 left) or compressed (Note S4 Figure 2 right) so that the two distinguishable oxygen lattice places will have different distances to the TM. Besides these differences between the two types of unit cells, both types also have similarities such as the possibility to have unoccupied oxygen lattice places, which is indicated in ABO_{3- δ} with δ and is also known as oxygen vacancy concentration. These oxygen vacancies have a significant influence on the unit cell size. The general trend is that a larger δ leads to a larger unit cell size. Therefore, δ has to be taken into consideration when calculating the diffraction peaks for a given unit cell. Here, the XRD pattern of a tetragonal esp-Ba_{0.5}Sr_{0.5}CoO₂ ($\delta = 1$) and esp-Ba_{0.5}Sr_{0.5}FeO_{2.5} ($\delta = 0.5$) were calculated as the extreme cases regarding δ and the Co-to-Fe ratios (Note S4 Figure 3). The calculated peaks matches quiet well with the experimental XRD patterns of as-synthesized BSCo_{0.99}(Fe_{0.01}) and BS(Co_{0.01})Fe_{0.99}, respectively. Moreover, the unit cell of the tetragonal esp-Ba_{0.5}Sr_{0.5}CoO₂, which was used to calculate the XRD pattern, has different distances between Co and the two oxygen lattice places: The distance to the apical oxygen atoms (on *c*-axis) is shorter than to the basal oxygen atoms (in *ab*-plane). Contrarily, the unit cell of the tetragonal esp-Ba_{0.5}Sr_{0.5}FeO_{2.5} has almost identical distances between Fe and the two oxygen lattice places. Refer to 'Detailed Methods' for the exact unit cell parameters. The possible presence of a highly oxygen-deficient esp-BSCo_{1-x}Fe_x is estimated to decrease towards the higher Fe-content materials as the average oxygen vacancy concentration (δ) proportionally decreases in those materials (Figure S10b). This estimation is supported by the observed decrease of the esp-peak (~2.6 Å) in Co and Fe K-edge FT-EXAFS spectra towards the higher Fe-content materials in the as-synthesized BSCo_{1-x}Fe_x series (Figures S10c-e and S11c-e). Moreover, the possible presence of a tetragonal esp-BSCo_{1-x}Fe_x cannot only be supported by observations in the XRD pattern but also in the TM K-edge FT-EXAFS spectra. Key characteristics of the FT-EXAFS spectra at the TM K-edges from a tetragonal esp-BSCo_{1-x}Fe_x are discussed in the following section:

The differences in the unit cell of a cubic csp-ABO₃ and tetragonal esp-ABO₃ have also influence on the FT-EXAFS spectra at the TM K-edges. To better understand the FT-EXAFS spectra of a tetragonal esp-ABO₃, the individual paths for the TM–O and TM–TM coordination shells were calculated for the two extreme cases of esp-BaCoO₃ and esp-BaFeO₃ (Note S4 Figure 4a,b). The unit cells of esp-BaCoO₃ and esp-BaFeO₃, which were used to calculate the FT-EXAFS spectra, were identical with the unit cells of esp-Ba_{0.5}Sr_{0.5}CoO₂ and esp-Ba_{0.5}Sr_{0.5}FeO_{2.5}, respectively, which were used to calculate the XRD patterns (Note S4 Figure 3a,b) but have only Ba on the A-site and no oxygen vacancies. The reason for this changes in the unit cells originates from the difficulties of the software 'Artemis' to calculate FT-EXAFS spectra with lattice place occupancies smaller than one.³³ The calculated FT-EXAFS spectra of esp-BaCoO₃ clearly show the splitting of the Co–O coordination shell for the apical (\sim 1.4 Å) and basal oxygen lattice places (\sim 1.8 Å). This splitting is missing in the calculated FT-EXAFS spectra of esp-BaFeO₃ due to the Jahn-Teller inactive configuration of Fe^{3+} . Moreover, one can clearly see the TM-TM coordination shell at the reduced distance of the esp-peak (~2.6 Å). Even though the oxygen vacancy concentration δ is not considered in the calculated TM K-edge FT-EXAFS spectra of esp-BaCoO₃ and esp-BaFeO₃, the coordination number for the different paths is a fitting parameter so that the value of δ can be evaluated during the fitting process. The fitting of the Co K-edge FT-EXAFS spectra from the as-synthesized BSCo_{0.80}Fe_{0.20} and BSCo_{0.60}Fe_{0.40} clearly indicated significantly lower fitted coordination numbers for the Co–O shell, thus the presence of oxygen vacancies, in comparison to the theoretical values in esp-BaCoO₃ with $\delta = 0$ (Note S4 Figure 4c,d, Note S4 Tables 1 and 2).

Overall, the proposed tetragonal esp-phase delivers not only explanation for the esp-peak (~2.6 Å) in the FT-EXAFS spectra at both edges of the as-synthesized $BSCo_{1-x}Fe_x$ series but also the observed splitting in the Co–O coordination shell (~1.4 - 1.8 Å) for the lower Fe-content materials at the Co K-edge (Figures S10c-e). However, even though the findings in the bulk properties from XRD and TM K-edge XAS support the presence of a tetragonal esp-BSCo_{1-x}Fe_xO₃₋₈ phase, the secondary phase peaks and the peak broadening due to the nanocrystals makes e.g. a proper XRD refinement challenging so that the presence of an additional esp-phase has still to be considered as an educated guess.

Note S4 Figure 1. Corner- versus edge-sharing polyhedra in perovskite-type oxides. (a) Two unit cells of a cubic perovskite-type oxide with corner-sharing polyhedra (csp). (b) Two unit cells of a tetragonal perovskite-type oxide with edgesharing polyhedra (esp). The 1st (apical) and 2nd (basal) oxygen types in the tetragonal esp-perovskite-type oxide can have different distances to the B-site metal and can be partially unoccupied.

Note S4 Figure 2. Energy level diagram for the 3d orbitals of transition metals in an octahedrally coordinated crystal field (middle) and the induced changes by the Jahn-Teller effect (left: elongated and right: compressed).³²

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Note S4 Figure 3. Tetragonal edge-sharing polyhedra (esp) in flame-spray synthesized $BSCo_{1-x}Fe_x$ series. (a) XRD pattern of the as-synthesized $BSCo_{0.99}(Fe_{0.01})$, a cubic $Ba_{0.5}Sr_{0.5}CoO_{2.5}$ reference and the calculated of esp- $Ba_{0.5}Sr_{0.5}CoO_2$. (b) XRD pattern of the as-synthesized $BS(Co_{0.01})Fe_{0.99}$, a cubic $BaFeO_3$ reference and the calculated of esp- $Ba_{0.5}Sr_{0.5}FeO_{2.5}$. Only the peaks with a relative intensity above 8% are shown for the calculated esp- $Ba_{0.5}Sr_{0.5}CoO_2$ and esp- $Ba_{0.5}Sr_{0.5}FeO_{2.5}$. Refer to 'Detailed Methods' for ICSD collection code of the reference XRD patterns and the parameters for the unit cell of esp- $Ba_{0.5}Sr_{0.5}FeO_{2.5}$.

Note S4 Figure 4. k^2 -weighted FT-EXAFS of tetragonal esp-ABO_{3-δ}. (a) The individual paths at the Co K-edge of esp-BaCoO₃ shows the splitting of the Co–O coordination shell and the characteristic esp-peak at a reduced distance of ~1.4 - 1.8 Å and ~2.6 Å, respectively (*k*-range from 3 to 11.5 Å⁻¹). (b) The individual paths at the Fe K-edge of esp-BaFeO₃ shows no splitting of the Co–O coordination shell (~1.7 Å) but the characteristic esp-peak at a reduced distance of ~2.6 Å (*k*-range from 2.7 to 11.4 Å⁻¹). (c) Magnitude and real part of k^2 -weighted FT-EXAFS best fit at Co K-edge of as-synthesized BSCo_{0.80}Fe_{0.20} (*k*-range from 3 to 11.5 Å⁻¹) including esp-BaCoO_{3-δ} as a part of the fitting model. (d) Magnitude and real part of k^2 -weighted FT-EXAFS best fit at Co K-edge of as-synthesized BSCo_{0.60}Fe_{0.40} (*k*-range from 3 to 11.5 Å⁻¹) including esp-BaCoO_{3-δ} as a part of the fitting model. Refer to 'Detailed Methods' for ICSD collection code of the standards used in the fitting and to Note S4 Tables 1 and 2 for the fitting values.

Note S4 Table 1. Co K-edge FT-EXAFS magnitude fitting values of as-synthesized BSCo_{0.80}Fe_{0.20} (inc. esp-BaCoO_{3-δ}).

Amplitude Reduction Factor Sẵ = 0.78 ± 0.04 & Energy Shift ∆E₀ = -0.8 ± 1.6 eV									
Scattering Path (Model)	Half Path Length R / Å	Theoretical Coor- dination Number N _{th} / -	Fitted Coordina- tion Number N _{fit} / -	Cumulated Coor- dination Number N _{cum} / -	Mean Square Displacement σ² / Ų	R-Factor			
Co-O₁ (esp-BaCoO₃-₀)	1.89 ± 0.03	2	1.5 ± 0.5	41114	0.004 + 0.005				
Co-O₂ (esp-BaCoO₃-ͽ)	2.09 ± 0.02	4	2.6 ± 0.9	4.1±1.4	0.004 ± 0.005	0.000			
Co-M₁ (esp-BaCoO₃-ͽ)	2.98 ± 0.04	4	3.7 ± 0.7	44.2 + 2.5	0.011 + 0.002	0.009			
Co-M ₁ (rs-CoO)	3.01 ± 0.02	12	7.6 ± 2.8	11.3 ± 3.5	0.014 ± 0.003				

Note S4 Table 2. Co K-edge FT-EXAFS magnitude fitting values of as-synthesized BSCo_{0.60}Fe_{0.40} (inc. esp-BaCoO_{3-δ}).

Amplitude Reduction Factor S_0^2 = 0.78 ± 0.04 & Energy Shift ΔE_0 = -0.7 ± 1.5 eV										
Scattering Path (Model)	Half Path Length	Theoretical Coor- dination Number	Fitted Coordina- tion Number	Cumulated Coor- dination Number	Mean Square Displacement	R-Factor				
	R/Å	N _{th} / -	N _{fit} / -	N _{cum} / -	σ^2 / Å ²	R'/-				
Co-O₁ (esp-BaCoO₃-₀)	1.89 ± 0.04	2	1.4 ± 0.4	4 1 + 1 4	0.005 + 0.005					
Co-O₂ (esp-BaCoO₃-₀)	2.08 ± 0.02	4	2.7 ± 1.0	4.1 1.4	0.005 ± 0.005	0.005				
Co-M₁ (esp-BaCoO₃-₀)	2.97 ± 0.04	4	3.7 ± 0.5	11 1 + 2 1	0.015 ± 0.002	0.005				
Co-M ₁ (rs-CoO)	3.02 ± 0.02	12	7.4 ± 2.6	11.1 ± 3.1	0.015 ± 0.005					

Note S5. Beside of the surface hs Co^{2+} in O_h -sites and Co^{3+} fraction, the analysis reveals also a Co^{2+} component, which does not contribute to the first peak at 776.5 eV in the Co L₃-edge XAS spectra (Figure S13c-f). Small distortions of the O_h symmetry towards D_{4h} are always possible, but not be distinguishable in an Co L₃-edge XAS spectra.³⁴ Therefore, the additional surface Co^{2+} component must have a significantly different electronic configuration (e.g. low-spin state^{35,36}) and/or coordination geometry (e.g. tetrahedrally shaped oxygen shell³⁷⁻³⁹) in comparison to the hs Co^{2+} in O_h -sites component. Here, this additional fraction is interpreted as low-spin (ls) Co^{2+} in O_h '-sites due to the tendency of perovskite-type oxides to have a low-spin state at room temperature,^{40,41} but without excluding the possibility of a distorted O_h -geometry towards D_{4h} (unequal Co–O bond lengths) as indicated with ' O_h '. As previously discussed in Note S4, ls Co^{2+} is Jahn-Teller active, which can lead to an elongation or compression of the Co–O bond length along the *c*-axis as shown in Note S4 Figure 2 and detected in the Co K-edge FT-EXAFS spectra of the as-synthesized low Fe-content materials in the BSCo_{1-x}Fe_x series (Figure S10c-e).

Note S6. The values for Max ΔJ and Final ΔJ does almost not change for BS(Co_{0.01})Fe_{0.99} (Figure 2b and Figure S16a,c,f). This should not be interpreted as an example for a stable OER electrocatalyst as BS(Co_{0.01})Fe_{0.99} has a relatively small OER current density at 1.6 V_{RHE}. To better evaluate the stability of BS(Co_{0.01})Fe_{0.99}, the protocol was repeated but with a higher upper CA potential value of 1.7 V_{RHE}. The data of this experiment are presented in Figure S16d,e and clearly show a decreasing OER activity trend with cycling right from the beginning. Therefore, BS(Co_{0.01})Fe_{0.99} supports also the trend that the OER stability behavior continuously decreases when the Fe-content in the BSCo_{1-x}Fe_x series is increased above 20% (x = 0.20).

Note S7. Both materials exhibit no longer secondary phase peaks of A-site metals nitrates in the ex situ after OER XRD pattern, whereas peaks assigned to A-site metals carbonates significantly increases in both materials (Figure S28d and S29d). The correlation between the two A-site metal containing phases indicates that these nitrates chemically transform to carbonates and are not washed away in alkaline electrolyte as previously predicted in the literature.^{12,14}

Supplementary Information Tables

Table S1. ICP-OES data.

	Bar	ium	Stror	Strontium		Cobalt		Iron	
Ba₃Sr♭CoℴFedO₃₅	Total mass fraction w _{Ba} / -	Metal mole fraction a / -	Total mass fraction w _{sr} / -	Metal mole fraction b / -	Total mass fraction w _{co} / -	Metal mole fraction c / -	Total mass fraction w _{Fe} / -	Metal mole fraction d / -	Total mass fraction w _{Rest} / -
Ba _{0.49} Sr _{0.50} Co _{1.00} Fe _{0.01} O _{3-δ}	0.27	0.49	0.18	0.50	0.24	1.00	0.0016	0.01	0.31
Ba _{0.49} Sr _{0.50} Co _{0.91} Fe _{0.10} O ₃₋₈	0.28	0.49	0.18	0.50	0.22	0.91	0.023	0.10	0.31
$Ba_{0.49}Sr_{0.50}Co_{0.81}Fe_{0.20}O_{3\cdot\delta}$	0.27	0.49	0.17	0.50	0.19	0.81	0.044	0.20	0.32
Ba _{0.50} Sr _{0.50} Co _{0.71} Fe _{0.30} O ₃₋₈	0.28	0.50	0.17	0.50	0.17	0.71	0.066	0.30	0.32
Ba _{0.49} Sr _{0.50} Co _{0.61} Fe _{0.40} O ₃₋₈	0.27	0.49	0.18	0.50	0.14	0.61	0.089	0.40	0.32
Ba _{0.49} Sr _{0.50} Co _{0.51} Fe _{0.50} O ₃₋₈	0.26	0.49	0.17	0.50	0.12	0.51	0.11	0.50	0.34
Ba _{0.49} Sr _{0.51} Co _{0.21} Fe _{0.79} O ₃₋₈	0.26	0.49	0.17	0.51	0.049	0.21	0.17	0.79	0.34
Ba _{0.50} Sr _{0.50} Co _{0.01} Fe _{0.99} O _{3-δ}	0.27	0.50	0.17	0.50	0.0012	0.01	0.22	0.99	0.34

The relative standard deviation including ICP-OES, weight, and volume measurement errors for the cation signals is estimated to be less than 5% for the absolute mass fractions and less than 2% for the relative mole fractions (only ICP-OES measurement errors).

Table S2. A- and B-site normalized ICP-OES data.

	Barium	Strontium	Cobalt	Iron
Ba₁₋vSrvCo₁₋xFexO₃₅	A-site metal mole fraction 1-v / -	A-site metal mole fraction v / -	B-site metal mole fraction 1-x / -	B-site metal mole fraction x / -
Ba _{0.49} Sr _{0.51} Co _{0.99} Fe _{0.01} O _{3-δ}	0.49	0.51	0.99	0.01
Ba _{0.49} Sr _{0.51} Co _{0.90} Fe _{0.10} O _{3-δ}	0.49	0.51	0.90	0.10
$Ba_{0.49}Sr_{0.51}Co_{0.80}Fe_{0.20}O_{3\text{-}\delta}$	0.49	0.51	0.80	0.20
Ba _{0.50} Sr _{0.50} Co _{0.70} Fe _{0.30} O _{3-δ}	0.50	0.50	0.70	0.30
Ba _{0.49} Sr _{0.51} Co _{0.60} Fe _{0.40} O _{3-δ}	0.49	0.51	0.60	0.40
Ba _{0.49} Sr _{0.51} Co _{0.50} Fe _{0.50} O _{3-δ}	0.49	0.51	0.50	0.50
$Ba_{0.49}Sr_{0.51}Co_{0.21}Fe_{0.79}O_{3-\delta}$	0.49	0.51	0.21	0.79
Ba _{0.50} Sr _{0.50} Co _{0.01} Fe _{0.99} O ₃₋₈	0.50	0.50	0.01	0.99

The relative standard deviation including only ICP-OES measurement errors is estimated to be less than 2% for the relative mole fractions.

Table S3. Co K-edge FT-EXAFS magnitude fitting values of as-synthesized BSC00.80Fe0.20.

	Amplitude Reduction Factor S $_{0}^{2}$ = 0.78 ± 0.04 & Energy Shift ΔE_{0} = 0.8 ± 1.6 eV										
Scattering Path (Model)	Half Path Length	Theoretical Coor- dination Number	Fitted Coordina- tion Number	Cumulated Coor- dination Number	Mean Square Displacement	R-Factor					
	R/Å	N _{th} / -	N _{fit} / -	N _{cum} / -	σ^2 / Å ²	R'/-					
Co-O ₁ (β-CoOOH)	1.87 ± 0.03	6	1.7 ± 0.7	46110	0.006 + 0.006						
Co-O ₂ (rs-CoO)	2.08 ± 0.02	6	2.9 ± 1.2	4.0±1.9	0.006 ± 0.006	0.007					
Co-M _{B1} (β-CoOOH)	2.90 ± 0.03	6	2.2 ± 0.1	0.0 + 2.0	0.012 + 0.004	0.007					
Co-M _{B2} (rs-CoO)	3.02 ± 0.02	12	7.7 ± 2.8	9.9 I 2.9	0.012 ± 0.004						

	Amplitude Reduction Factor S_0^2 = 0.78 ± 0.04 & Energy Shift ΔE_0 = 1.1 ± 1.4 eV										
Scattering Path	Half Path Length	Theoretical Coor- dination Number	Fitted Coordina- tion Number	Cumulated Coor- dination Number	Mean Square Displacement	R-Factor					
(Model)	R/Å	N _{th} / -	N _{fit} / -	N _{cum} / -	σ² / Ų	R '/-					
Co-O₁ (β-CoOOH)	1.87 ± 0.03	6	1.6 ± 0.6	40.47	0.000 + 0.005						
Co-O ₂ (rs-CoO)	2.08 ± 0.02	6	3.0 ± 1.1	4.0 ± 1.7	0.006 ± 0.005	0.008					
Co-M _{B1} (β-CoOOH)	2.90 ± 0.03	6	2.1 ± 0.0	04+24	0.013 + 0.004	0.008					
Co-M _{B2} (rs-CoO)	3.02 ± 0.01	12	7.3 ± 2.4	9.4 ± 2.4	0.013 ± 0.004						

Table S4. Co K-edge FT-EXAFS magnitude fitting values of as-synthesized BSCo_{0.60}Fe_{0.40}.

Table S5. Co K-edge FT-EXAFS magnitude fitting values of as-prepared BSCo_{0.80}Fe_{0.20}.

Amplitude Reduction Factor S $_0^2$ = 0.77 ± 0.04 & Energy Shift ΔE_0 = 0.7 ± 2.4 eV										
Scattering Path (Model)	Half Path Length	Theoretical Coor- dination Number	Fitted Coordina- tion Number	Cumulated Coor- dination Number	Mean Square Displacement	R-Factor				
	R/Å	N _{th} / -	N _{fit} / -	N _{cum} / -	σ^2 / Å ²	R'/-				
Co-O₁ (β-CoOOH)	1.89 ± 0.04	6	2.2 ± 1.3	49+29	0.006 ± 0.010					
Co-O ₂ (rs-CoO)	2.08 ± 0.02	6	2.6 ± 1.5	4.0 I 2.0	0.000 ± 0.010	0.013				
Co-M _{B1} (β-CoOOH)	2.89 ± 0.04	6	2.7 ± 0.1	70+20	0.006 ± 0.007	0.013				
Co-M _{B2} (rs-CoO)	3.03 ± 0.03	12	4.5 ± 3.1	1.2 ± 3.2	0.000 ± 0.007					

Table S6. Co K-edge FT-EXAFS magnitude fitting values of BSCo_{0.80}Fe_{0.20} operando at 1.00 V_{RHE}.

Amplitude Reduction Factor S $_0^2$ = 0.77 ± 0.04 & Energy Shift ΔE_0 = 1.4 ± 2.3 eV										
Scattering Path	Half Path Length	Theoretical Coor- dination Number	Fitted Coordina- tion Number	Cumulated Coor- dination Number	Mean Square Displacement	R-Factor				
(Woder)	R/Å	N _{th} / -	N _{fit} / -	N _{cum} / -	σ² / Ų	R'/-				
Co-O₁ (β-CoOOH)	1.89 ± 0.03	6	2.2 ± 1.2	40.000	0.000 + 0.000					
Co-O ₂ (rs-CoO)	2.08 ± 0.02	6	2.7 ± 1.4	4.9 ± 2.0	0.006 ± 0.008	0.012				
Co-M _{B1} (β-CoOOH)	2.89 ± 0.03	6	2.7 ± 0.2	67120	0.005 + 0.005	0.012				
Co-M _{B2} (rs-CoO)	3.04 ± 0.03	12	4.0 ± 1.8	0.7 ± 2.0	0.005 ± 0.005					

Table S7. Co K-edge FT-EXAFS magnitude fitting values of BSCo_{0.80}Fe_{0.20} operando at 1.55 V_{RHE}.

Amplitude Reduction Factor S $_0^2$ = 0.75 ± 0.04 & Energy Shift ΔE_0 = 4.1 ± 1.2 eV										
Scattering Path (Model)	Half Path Length	Theoretical Coor- dination Number	Fitted Coordina- tion Number	Cumulated Coor- dination Number	Mean Square Displacement	R-Factor				
	R/Å	N _{th} / -	N _{fit} / -	N _{cum} / -	σ² / Ų	R'/-				
Co-O ₁ (β-CoOOH)	1.88 ± 0.01	6	3.3 ± 0.2	47.06	0.003 + 0.001					
Co-O ₂ (rs-CoO)	2.08 ± 0.01	6	1.4 ± 0.4	4.7 ± 0.0	0.003 ± 0.001	0.005				
Co-M _{B1} (β-CoOOH)	2.86 ± 0.01	6	2.8 ± 0.8	55+15	0.001 ± 0.002	0.005				
Co-M _{B2} (rs-CoO)	3.04 ± 0.01	12	2.7 ± 0.7	0.0 ± 1.0	0.001 ± 0.002					

	Amplitude Reduction Factor S $_{0}^{2}$ = 0.77 ± 0.04 & Energy Shift ΔE_{0} = 1.2 ± 1.6 eV										
Scattering Path	Half Path Length	Theoretical Coor- dination Number	Fitted Coordina- tion Number	Cumulated Coor- dination Number	Mean Square Displacement	R-Factor					
(model)	R/Å	N _{th} / -	N _{fit} / -	N _{cum} / -	σ^2 / Å ²	R'/-					
Co-O₁ (β-CoOOH)	1.88 ± 0.03	6	1.6 ± 0.7	4.4.2.0	0.000 + 0.000						
Co-O ₂ (rs-CoO)	2.08 ± 0.01	6	2.8 ± 1.3	4.4 ± 2.0	0.006 ± 0.006	0.013					
Co-M _{B1} (β-CoOOH)	2.90 ± 0.01	6	2.1 ± 0.0	10.6 + 3.4	0.014 + 0.004	0.013					
Co-M _{B2} (rs-CoO)	3.03 ± 0.02	12	8.5 ± 3.4	10.0 ± 3.4	0.014 ± 0.004						

Table S8. Co K-edge FT-EXAFS magnitude fitting values of as-prepared BSCo_{0.60}Fe_{0.40}.

Table S9. Co K-edge FT-EXAFS magnitude fitting values of $BSCo_{0.60}Fe_{0.40}$ operando at 1.00 V_{RHE} .

Amplitude Reduction Factor S $_0^2$ = 0.77 \pm 0.04 & Energy Shift ΔE_0 = 0.8 \pm 2.4 eV										
Scattering Path (Model)	Half Path Length	Theoretical Coor- dination Number N _{th} / -	Fitted Coordina- tion Number N _{fit} / -	Cumulated Coor- dination Number N _{cum} / -	Mean Square Displacement	R-Factor				
	R/Å				σ^2 / Å ²	R'/-				
Co-O₁ (β-CoOOH)	1.87 ± 0.04	6	2.2 ± 1.3	5.8 ± 3.5	0.009 ± 0.010	0.028				
Co-O ₂ (rs-CoO)	2.08 ± 0.02	6	3.6 ± 2.2							
Co-M _{B1} (β-CoOOH)	2.90 ± 0.03	6	2.7 ± 0.1	6.1 ± 1.0	0.003 ± 0.003					
Co-M _{B2} (rs-CoO)	3.06 ± 0.03	12	3.4 ± 0.9							

Table S10. Co K-edge FT-EXAFS magnitude fitting values of $BSCo_{0.60}Fe_{0.40}$ operando at 1.55 V_{RHE}.

Amplitude Reduction Factor S $_{0}^{2}$ = 0.77 \pm 0.04 & Energy Shift ΔE_{0} = 1.6 \pm 2.3 eV										
Scattering Path (Model)	Half Path Length	Theoretical Coor- dination Number N _{th} / -	Fitted Coordina- tion Number N _{fit} / -	Cumulated Coor- dination Number N _{cum} / -	Mean Square Displacement	R-Factor				
	R/Å				σ^2 / Å ²	R '/-				
Co-O₁ (β-CoOOH)	1.88 ± 0.03	6	2.2 ± 1.2	4.9 ± 2.6	0.007 ± 0.008	0.027				
Co-O ₂ (rs-CoO)	2.08 ± 0.02	6	2.7 ± 1.4							
Co-M _{B1} (β-CoOOH)	2.90 ± 0.03	6	2.7 ± 0.1	5.9 ± 0.9	0.004 ± 0.003					
Co-M _{B2} (rs-CoO)	3.06 ± 0.03	12	3.2 ± 0.8							

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