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Electronic Supporting Information

Understanding the formation of bulk- and surface-active layered (oxy)hydroxides for water oxidation starting from a cobalt selenite precursor

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Experimental

Synthesis of $CoSeO_3 \cdot H_2O$. $CoSeO_3 \cdot H_2O$ was synthesized by a mild hydrothermal method following a reported procedure with slight modification.¹ $Co(Ac)_2 \cdot 4H_2O$ (Alfa Aesar ACS quality 98-102 %, 2.0 mmol), SeO₂ (Acros Organics, 99.8 %, 2.0 mmol) and 35 ml demineralized water were successively added into a 50 ml Teflon-lined autoclave. Subsequently, the mixture was treated under autogenous pressure at 180 °C for 15 h and cooled down naturally to room temperature. The reaction product was washed three times with 30 ml demineralized water and two times with 30 ml acetone. The product obtained after washing was dried at 60 °C in air. Purple needles with up to 0.4 mm in size were obtained.

Electrochemical measurements

A thermostat regulated the temperature to 25 °C for all measurements. A standard three-electrode (working, counter and reference) electrochemical cell in 50 ml 1 M aqueous KOH (Alfa Aesar 1.0 N standardized solution) with a potentiostat (SP-200, BioLogic Science Instruments) controlled by the EC-Lab v10.20 software package was used for measurements. Fluorine-doped tin oxide (FTO) glass plates ($2 \times 1 \text{ cm}^2$) with samples deposited ($1 \times 1 \text{ cm}^2$) served as the working electrodes, Pt wire (0.5 mm diameter \times 230 mm length; A-002234, BioLogic) as counter and Hg/HgO as the reference electrode (CH Instruments, Inc.).

Electrophoretic deposition. The materials were deposited electrophoretically by a well-established method on FTO.^{2–5} A potential difference of 10 V, using FTO as counter and reference electrode, in a mixture of iodine and acetone on a 1×1 cm² area was applied. Through keto-enol tautomerisation, acetone and iodine produce protons. The formed protons are adsorbed on the surface of the suspended particles and in consequence create a positive surface charge. The applied electric field induces the charged particles to migrate towards the cathode where they deposit. Usually, 30 mg of the catalyst powder was suspended in 8 ml acetone and sonicated at room temperature for 2 h. Subsequently, 2 mg of iodine was added, and the suspension sonicated for another 3 min. The EPD was performed with stirring at 10 V for 5 min and uniform films were obtained. The sample loading was determined by inductively coupled plasma optical absorption spectroscopy (ICP-OES) of several samples and found to be 4 µmol/cm² of CoSeO₃·H₂O with a high reproducibility. For the other Ni, Co and Fe reference compounds, the loading was determined by weighting of the samples before and after the deposition, and the loading kept to 4 µmol/cm² with an error of around 15 %.

iR compensation: The uncompensated resistance (R_u) was obtained by impedance spectroscopy at 100 MHz and a potential of 1.175 V_{RHE} prior to the measurements and usually in the range of 11 Ω . The potential was corrected by 90% of R_u .

Cyclic and linear scan voltammetry. CV and LSV was carried out without stirring and with *iR* compensation. The potentials were referenced to the reversible hydrogen electrode (RHE) through calibration, and in 1 M aqueous KOH (pH 13.8) the potential was calculated using the following equation:

 $E(RHE) = E(Hg/HgO) + 0.098 V + (0.059 \times pH) V.$

Chronoamperometry. The CA measurements were performed with stirring and an applied *iR* compensation of 90% in 1 M aqueous KOH. For the long-term measurement of *Co-V*, the electrolyte was exchanged after 24 h with fresh 1 M KOH. The main reasons for the fluctuations are bubble formation and a decreased electrolyte level caused by evaporation, which results in a reduced area of catalyst in contact with the 1 M KOH.

Steady state Tafel analysis. CA measurements for 5 min at each potential were performed to obtain the respective *i*. The Tafel slope was calculated according to the Tafel equation $\eta = b \times \log(i) + a$, where η is the overpotential in V, *i* is the current density in mA/cm², and *b* is the Tafel slope in mV/dec.

Double-layer capacitance. The C_{dl} was determined from CVs (cycled between 0.785 and 0.835 V_{RHE}) at a potential range, where no apparent faradaic process occurred. Half of the potential difference at 0.81 V_{RHE} were plotted as a function of the scan rate and from the slope the C_{dl} was attained.^{6,7} The equation ECSA = C_{dl}/C_{s} , where C_{s} can be defined as the specific capacitance of the material per unit area under identical electrolyte conditions and ECSA stands for the electrochemical active surface area, can be used to calculate the ECSA.⁸ Therefore, the ECSA is directly proportional to the C_{dl} under the approximation of a constant C_{s} .

Electrochemical impedance spectroscopy. EIS was recorded at 1.55 V vs reversible hydrogen electrode (V_{RHE}) . The amplitude of the sinusoidal wave was examined in the frequency range 100 kHz to 1 mHz. From the diameter of the semicircle in the Nyquist plots, the charge-transfer resistance (R_{ct}) was approximated.⁶ **Faradaic efficiency.** The Faradaic efficiency of *Co-V* in 1 M KOH towards the oxygen evolution reaction was measured in a two-electrode configuration where *Co-V* on FTO was used as anode and Pt wire as a cathode in a closed electrochemical cell. The electrolyte and cell were first degassed with Argon for 30 min under stirring. Afterwards, a constant current density of 50 mAcm⁻² was applied for 9 min. At the end of electrolysis, the gaseous samples were drawn from the headspace by a gas tight syringe and analysed by a GC calibrated for O₂ and H₂. The procedure was performed twice.

Characterization details

Inductive coupled plasma optical absorption spectroscopy. ICP-OES was performed on a Varian ICP-OES 715 ES. Prior to the measurements of the samples a calibration with six references in the range 1 to 100 ppm was performed. The investigated material and the references were dissolved in diluted *aqua regia*.

Powder X-ray diffraction. A Panalytical X'Pert PRO diffractometer (Bragg-Brentano geometry, $Cu-K_{\alpha}$ radiation) was used for powder XRD measurements.

X-ray photoelectron spectroscopy. The XPS measurements were performed on a Kratos Axis Ultra X-ray photoelectron spectrometer (Kratos Analytical Ltd., Manchester, U.K.) with an Al K_{α} monochromatic radiation source (1486.7 eV) and 90° takeoff angle (normal to analyzer). The pressure in the analyzing chamber was 2 × 10⁻⁹ Torr. The XPS spectra were collected for C 1s, O 1s, Co 2p and Se 3d with pass energy 20 eV and step 0.1 eV. The calibration of the binding energies was performed relative to the C 1s peak energy position at 285.0 eV. For data analyses, Casa XPS (Casa Software Ltd.) and the Vision data processing program (Kratos Analytical Ltd.) were used.

Scanning electron microscopy. SEM was carried out on a GeminiSEM500 NanoVP microscope (ZEISS) integrated with an energy dispersive X-ray (EDX) detector (Bruker Quantax XFlash® 6|60). For data handling and analysis, the software package EDAX was used. The SEM experiments were performed at the Zentrum für Elektronenmikroskopie (ZELMI) of the TU Berlin.

Transmission electron microscopy. TEM was conducted on an FEI Tecnai G2 20 S-TWIN transmission electron microscope (FEI Company, Eindhoven, Netherlands) equipped with a LaB₆ source at 200 kV acceleration voltage and on a FEI TITAN 80-300 with a field emission gun (300 mV acceleration voltage) and C_s corrector. The films were scratched off from the FTO substrate and transferred onto a carbon-coated copper grid for their investigation after catalysis. EDX analyses were achieved with an EDAX r-TEM SUTW detector (Si (Li) detector). A GATAN MS794 P CCD camera was used to collect the images. The TEM experiments were conducted at the Zentrum für Elektronenmikroskopie (ZELMI) of the TU Berlin. Exposing the less crystalline *Co-V* sample for multiple minutes to a high intensity X-ray beam leads to the formation and growth of additional crystalline domains. Nevertheless, this transformation is slow enough that images without any beam damage that are consistent with the SAED can be acquired.

Infrared spectroscopy. For IR investigations after OER, the films were scratched from off the FTO substrate and mortar ground together with 300 mg CsI. Subsequently, the substrate CsI mixture was pressed for 3 min under vacuum. The obtained pellet was measured in transmission mode with a Thermo Nicolet

Magna-IR 750 FTIR. In the wavenumber range 4000-650 cm⁻¹, a KBr beamsplitter was used, and in the range 750-250 cm⁻¹ a CsI beamsplitter.

Resonance Raman spectroscopy. RR spectra were recorded using the 458 nm emission of an Argon ion laser (Innova 70, Coherent) for excitation and a confocal RR spectrometer (Lab Ram HR-800 Jobin Yvon) equipped with a liquid-nitrogen cooled charge-coupled device CCD camera for data acquisition.. Much lower intensities were observed at 647 nm and 514 nm. The peak shifts observed at 514 nm were consistent with the ones at 458 nm. The typical laser power at the sample ranged between 2-3 mW. Initially, measurements were performed at 100 μ W to exclude beam induced damage, which resulted in similar vibration and low intensities. For all samples, measurements at three different parts of the samples were performed and consistent peak positions were obtained (see Fig. S26). Laser/heat-induced transformations of CoO_xH_y to Co₃O₄ compounds have been reported.^{9,10} Such a transformation can easily be tracked through the appearance of the characteristic A_{1g} vibration of Co₃O₄, which appears as a sharp and intense peak at approximately 690 cm⁻¹,¹¹ We could not observe such a transformation, most likely because we measured at 80 K instead of rt.^{9,10} When samples (quasi *in-situ Co-KOH-V* and *Co-V*) were heated up to rt, kept there for 2 h and subsequently measured at 80 K, we could observe the formation of a Co₃O₄ phase in the Raman spectra (see Fig. S26).

All samples for RR experiments were prepared on FTO glass substrates in analogy to the electrochemical experiments. The samples denoted quasi *in situ* were electrochemically treated for OER at a potential leading to a current response of 10 mA/cm² for 2 h in 1 M KOH solutions (CA measurement with suitable potential). After 2 h, the samples were freeze-quenched at the same potential using liquid N₂ under vigorous N₂ gas flow and stored in liquid N₂. For all samples the RR measurements were conducted at 80 K using a Linkam Cryostage THMS600 cryostat.

In situ X-ray absorption spectroscopy. The *in situ* XANES/EXAFS spectra were collected at the BESSY synchrotron radiation source operated by the Helmholtz-Zentrum Berlin. The KMC-3 bending-magnet beamline at 20 K in a helium-flow cryostat (Oxford-Danfysik) was used to conduct the measurements. A Si(111) double-crystal monochromator was used to select the incident beam energy. The measurements at the cobalt *K*-edge were conducted in in fluorescence mode using a 13-element energy-resolving Ge detector (Canberra). The XANES edge position was determined by the integration method.¹² The extracted spectra were weighted by k^3 and simulated in *k*-space ($E_0 = 6547$ eV). All EXAFS simulations were conducted using in-house software (SimX) after calculation of the phase functions with the FEFF program (version 8.4, self-consistent field option activated).^{13,14} The EXAFS simulations between measured by a minimization of the error sum acquired 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 approximated from the covariance matrix of the fit. Further details are given elsewhere.^{15,16}

All samples for XAS experiments were prepared on FTO glass substrates in analogy to the electrochemical experiments. The samples were electrochemically treated for OER at a potential leading to a current response of 10 mA/cm² for 2 h in 1 M KOH solutions (CA measurement with suitable potential). After 2 h, the samples were freeze-quenched at the same potential using liquid N₂ under vigorous N₂ gas flow and stored in liquid N₂ until XAS measurements were conducted. For *Co-V*, additional samples at 0.9 V_{RHE} and 1.27 V_{RHE} were freeze quenched after 5 min of continuous operation at the respective potential. The *ex situ* sample was kept for 2 h at room temperature in air and subsequently stored in liquid nitrogen until measurement.

Synthesis of reference compounds

Co₃O₄. Was purchased from Alfa Aesar. pXRD revealed a pure Co₃O₄ phase (JCPDS 42-1467).

Synthesis of β-**Co(OH)**₂.¹⁷ Into 80 mL of 0.05 mol/l Co(NO₃)₃ solution 50 mL of 0.1 mol/l NaOH solution was added dropwise. After stirring at 45 °C for two hours a pink precipitate formed. The precipitate was separated by centrifugation and washed with deionized water (3×50 ml) and dried in air at 60 °C. pXRD revealed a pure β-Co(OH)₂ phase (JCPDS 30-443).

Synthesis of β -CoOOH.¹⁷ The as prepared β -Co(OH)₂ was dispersed in 30 ml 4 M KOH solution. This solution was slowly heated up to 45 °C. Subsequently, 2 mL of 30% H₂O₂ was added dropwise at 45 °C for 18 h. The brown precipitate was separated by centrifugation, washed three times with deionized water (3×50 ml) and dried at 60 °C overnight in air. pXRD revealed a pure β -CoOOH phase (JCPDS 7-169).

Synthesis of β -Ni(OH)₂.¹⁸ To a solution of 291 mg of Ni(NO₃)₂.6H₂O and 10 mL deionized water 15 ml of NaOH (0.1 M) was added dropwise. After stirring for 30 min a bright green solid precipitated which was separated by centrifugation and washed three times with deionized water (3×50 ml), before drying at 60 °C. pXRD revealed a pure β -Ni(OH)₂ phase (JCPDS 14-117).

Synthesis of NiOOH.¹⁷ The as-prepared Ni(OH)₂ was dispersed in 30 mL 4 M KOH solution. This solution was slowly heated up to 45 °C. Subsequently, 2 mL of 30% H_2O_2 was added dropwise at 45 °C for 18 h. The solid was separated by centrifugation, washed three times with deionized water (3×50 ml) and dried at 60 °C overnight in air. pXRD revealed a fully amorphous phase.

Synthesis of Fe(OH)₃,¹⁹ Amorphous iron(III) hydroxide ((Fe(OH)₃) was prepared by a precipitation method. To an aqueous solution of Fe(NO₃)₃.9H₂O (205 mg in 10 mL), 1.6 mL of KOH (1 M) was added dropwise, and the solution was stirred at room temperature. A dark brown precipitate was separated by centrifugation and washed with deionized water (3×50 mL) and dried in air at 60°C. pXRD revealed a fully amorphous phase.

Synthesis of FeOOH.¹⁹ The as-synthesized $Fe(OH)_2$ was first dispersed in 30 mL (4 M) KOH solution which was then heated slowly up to 45 °C. 2 mL of 30% H_2O_2 solution was then added dropwise and was kept at the same temperature for 18 h. The final brown precipitate was filtered and washed with deionized water three times (3×50 mL), then dried at 60 °C overnight in air. pXRD revealed a pure FeOOH phase (JCPDS 27-713).



Figure S1. Pourbaix diagram of cobalt (10^{-7} mol/l) ,²⁰ nickel (10^{-6} mol/l) ,²¹ and iron (10^{-6} mol/l) .²²



Figure S2. Light microscope (top) and scanning electron microscope (SEM, bottom) images of as prepared $CoSeO_3$ ·H₂O.



Figure S3. SEM energy dispersive X-ray (EDX) spectrum of as prepared CoSeO₃·H₂O. A referring SEM/EDX



mapping is shown in the main text in Figure 3 on the right. The Si comes from the sample holder.

Figure S4. Powder X-ray diffraction (pXRD) pattern of $CoSeO_3 \cdot H_2O$ that was not mortar ground. The material has a preferred orientation due to its needle like morphology as reported previously.^{1,23} ICP-OES results are in accordance with the expected stoichiometry.



Figure S5. X-ray photoemission spectra (XPS) of as prepared $CoSeO_3 \cdot H_2O$. The orange peaks in the Co 2p spectrum are the typical Co^{2+} satellites and spin-orbit level energy spacing of the deconvoluted red peaks is typical for Co^{2+} .^{4,24} Two peaks were obtained from the deconvolution of the O 1s spectra: one refers to oxygen of water and the other one to oxygen of selenite.^{4,24,25} The Se 3d spectrum is in agreement with reported cobalt selenites.²⁵



Figure S6. Transmission electron microscopy (TEM) images of mortar ground $CoSeO_3$ ·H₂O and the referring selected area diffraction pattern (SAED, right bottom). The purple rings refer to the distances (miller indices in brackets in agreement with JCPDS 88-1510) 3.41 nm (040), 2.82 nm (012), 2.46 nm (200),



2.28 nm (060), 1.90 nm (-212) and 1.73 nm (-123) from the smallest to the largest ring.

Figure S7. SEM/EDX spectrum of $CoSeO_3 \cdot H_2O$ deposited on FTO.



Figure S8. SEM images of CoSeO₃·H₂O deposited on FTO and EDX mapping. The deposited CoSeO₃·H₂O particles no longer have a needle-like morphology and vary in size from 0.1 to 10 μ m.



Figure S9. (a) image showing an as deposited $CoSeO_3 \cdot H_2O/FTO$ electrode and another one after one CV. A drastic color change can be observed. (b) first cyclic voltammogram (CV) of a fresh $CoSeO_3 \cdot H_2O/FTO$ with 5 mV/s sweep rate and second CV with the same scan rate. The first CV shows a strongly pronounced redox feature that we assign to the oxidation of the Se^{IV} and Co^{III}. The second CV shows the Co^{III/III} and Co^{III/IV} redox couples. These redox couples remained unchanged when the catalyst was transferred into a fresh 1 M KOH solution. (c) A CoSeO₃·H₂O/FTO before and after 60 s of KOH exposure. (d) pXRD of CoSeO₃·H₂O/FTO after 1 h and after 60 s of KOH exposure.



Figure S10. (a) CV of *Co-V* (CoSeO₃·H₂O/FTO transformed by direct application of the potential 1.56 V_{RHE} in 1 M KOH solution for 1 h) with the arrows implicating the potentials chosen for the CA experiments presented in (b) of this figure. (b) CA current responses $CoSeO_3 \cdot H_2O$ on FTO at pH 14 at different potentials. (c) current response of $CoSeO_3 \cdot H_2O/FTO$ at pH 13. (d) Current response of $CoSeO_3 \cdot H_2O/FTO$ at pH 12 and different potentials. (e) current response at an applied potential of 1.24 V_{RHE} of $CoSeO_3 \cdot H_2O$ on FTO. The integrated area is marked in grey and yields the number electrons involved in the catalyst oxidation (3.1 electrons per formula unit). (f) integration of the current responses at 1.56 V_{RHE} of $CoSeO_3 \cdot H_2O/FTO$ that was exposed to 1 M KOH before for 1 h (referred to as *Co-KOH-V*).



Figure S11. Integration of the Co^{II/III} and Co^{III/"IV"} redox features of *Co-V* (red curves) and *Co-KOH-V* (green curves).



Figure S12. Plot of the peak current of the Co^{II/III} redox couple plotted against the sweep rate for *Co-V* (red line) and *Co-KOH-V* (green line). For both electrodes, a linear relationship was obtained revealing that a capacitive process takes place that is not influenced by transport limitations.^{26,27}



Figure S13. CVs of *Co-KOH-V* (a) and *Co-V* (b) used for the determination of the double-layer capacitance (C_{dl}) . The shape of the CVs deviates from the rectangular form characteristic for pure capacitive regions with hydroxide migration into the C_{dl} . The closest pseudocapacitive process that could interfere is the Co^{II/III} redoxcouple located at a 200 mV higher potential. Measurements in other potential regions were

also performed but led to larger current densities/ C_{dl} indicating that additional processes occur in these regions. (c) Estimation of the C_{dl} by plotting the current density variation ($\Delta i = (i_a - i_c)/2$), acquired from (a) and (b) at 0.81 V_{RHE}, against the scan rate (ν). At low ν , a linear correlation is observed, but at higher ν , iis a function of the square root of ν . Such a square root relationship indicates that mass/charge transport phenomena limit the capacitive process of hydroxide migration into the double-layer. For small ν , the transport limitations should be the lowest and reasonable linear fits were obtained ($R^2 > 0.99$) and the C_{dl} was estimated to be 870 and 82 μ F/cm² for *Co-KOH-V* and *Co-V*, respectively.

Recently, Abel Chuang and co-worker proposed a method to extrapolate a total C_{dl} for an infinite small scan rate, which, as a result, should be less affected by transport limitations.^{28,29} To do so, a C_{dl} for every

$$=\frac{\int_{E_1}^{E_2} |i| dE}{2 \int_{E_1}^{E_2} |i| dE}$$

 $C_{v} = \frac{2}{2v(E2 - E1)}$ (E1 and E2 are the cut-off potentials of the CVs). The reciprocal of the obtained capacitance for a certain $v(C_{v})$ is then plotted against the square root of v. Linear extrapolation gives the intercept for v = 0. The smallest v should be used for the extrapolation, as they are least influence by the transport limitations. These graphs are shown for *Co-KOH-V* (d) and *Co-V* (e). In both cases, a linear relation could be obtained. As expected, the total C_{dl} is in both cases larger in both than the one determined in plot (c).

For all measurements presented here, the C_{dl} of Co-KOH-V is significantly larger than the one of Co-V. This trend was also obtained for measurements in different potential windows. Co-V shows a more pronounced $Co^{II/III}$ redox feature and it is located closer to the for the C_{dl} investigated region than the one of Co-KOH-V. Therefore, it is not likely that a pseudocapacitive contribution is causing the apparently larger C_{dl} of Co-KOH-V. The higher C_{dl} of Co-KOH-V. The higher C_{dl} of Co-KOH-V is consistent with the in the SEM/TEM observed morphologies of the two samples: nanoplates for Co-KOH-V and chunks of several micrometers for Co-V.

The observation that *Co-KOH-V* has a larger C_{dl} , but 15 times less redox active cobalt sites is uncommon. It can be understood when the differences in the required electrolyte access is considered. An electrically wired cobalt site on the surface of a particle can be redox active and contribute to the C_{dl} . However, a cobalt within the particle can be redox active, as it might have access to potassium and hydroxide through the large, electrolyte-filled interlayer space. Nevertheless, the latter situation is barely contributing to the C_{dl} , as hydroxide migration into the interlayer is limited by its small volume compared to the electric double-layer (several nanometers)²⁸ and probably also electrostatic restrictions. Thus, in our case, the C_{dl} (or the proportional electrochemical active surface area) is only a measure of the outer surface of the material and is unsuitable for an approximation of catalytically active sites.



Figure S14. (a) Electrochemical impedance spectroscopy *Co-V* (red squares) and of *Co-KOH-V* (green circles). (b) Determination of the Faradaic efficiency (FE) from the gas volumes evolved in a closed two-electrode setup with Pt wire as HER and *Co-V* on FTO as OER electrode and the charge (*Q*) passed during the OER experiment.



Figure S15. TEM/SAED patterns taken from an area with around 2 μ m diameter of CoSeO₃·H₂O/FTO after 1 h of 1 M KOH exposure (referred to as *Co-KOH*, a), of *Co-KOH-V* (b) and of *Co-V* (c). In the corner at the right bottom, the refereeing distances and miller indices of the diffraction rings are shown. The two distances in (c) are assigned in Fig. 8 of the main text.



Figure S16. XPS spectra of *Co-KOH* (top), *Co-KOH-V* (middle) and of *Co-V* (bottom). The orange peaks marked with a * are the Co satellite peaks. The three different oxygen species belong to a cobalt hydroxide as well as physi- and chemisorbed water.^{4,24} Interestingly, no peaks below 530 eV are present, where cobalt oxides are usually reported to appear.^{4,24}



Figure S17. Transmittance infrared (IR) spectroscopy of *Co-KOH* (orange), of *Co-KOH-V* (green) and of *Co-V* (red) with a zoom into the OH stretching vibration of *Co-V* as inset.



Figure S18. SEM images at various magnifications of *Co-KOH* (top and middle) and SEM/EDX mapping of the same sample (bottom). No meaningful potassium mapping could be obtained, due to the strong overlap of its peak with tin in the EDX spectrum (see Fig. S21).



Figure S19. SEM images at various magnifications of *Co-KOH-V* (top and middle) and SEM/EDX mapping of the same sample (bottom). No meaningful potassium mapping could be obtained, due to the strong overlap of its peak with tin in the EDX spectrum (see Fig. S21).



Figure S20. SEM images at various magnifications of *Co-V* (top and middle) and SEM/EDX mapping of the same sample (bottom). No meaningful potassium mapping could be obtained, due to the strong overlap of its peak with tin in the EDX spectrum (see Fig. S21).



Figure S21. SEM/EDX spectra of *Co-KOH* (top), of *Co-KOH-V* (middle) and of *Co-V* (bottom). Potassium was not included in the quantification, due to the strong overlap of its peak with tin in the EDX spectrum (see Fig. S21).



Figure S22. TEM images at various magnifications of *Co-KOH*. The high resolution (HR) images at the bottom were Fourier transformed and the obtained distances assigned to lattice planes of β -Co(OH)₂ JCPDS [30-443].



Figure S23. TEM images at various magnifications of *Co-KOH-V*. The high resolution (HR) images at the bottom were Fourier transformed and the obtained distances assigned to lattice planes of β -CoOOH JCPDS [7-169].



Figure S24. TEM images at various magnifications of *Co-V*. The high resolution (HR) images at the bottom were Fourier transformed. However, no periodicity could be observed.



Figure S25. HR-TEM images at various magnifications of *Co-V* acquired with a field emission gun TEM with a spatial resolution of 75 pm. The insets are the Fourier transformed of the whole images or the white square if present. The obtained distances could be assigned to lattice planes of edge sharing $[CoO_6]$ octahedra layers.



Figure S26. SEM images of a Co-V samples after 48 h under OER conditions at 10 mA/cm².



Figure S27. TEM images of a *Co-V* samples after 48 h under OER conditions at 10 mA/cm² together with an SAED pattern.



Figure S28. (a) Resonance Raman spectrum of quasi *in situ Co-KOH-V* (dark green). The light green spectrum is of the same sample after 2 h of air exposure at room temperature. Resonance Raman spectrum of quasi *in situ Co-V* (dark red). The light red spectrum of the same sample after 2 h of air exposure at room temperature. For both samples, after 2 h of air exposure, the formation of a Co_3O_4 phase can be observed consistent with the reported reversible transformation of amorphous CoO_xH_y to Co_3O_4 .³⁰ (b) and (c) Raman measurements of quasi *in situ Co-KOH-V* (different shades of green) and quasi *in situ Co-V* (different shades of red) measured at different locations of the respective samples. The formation of Co_3O_4 , the reported beam damage for such phases, cannot be observed in any case.^{9,10}



Figure S29. For increased oxidation states, the XANES edge position shifts to higher energies. To quantify the clear differences of the edge positions, they were converted into single numbers using the integral method.³¹ The obtained values were plotted and converted to oxidation states in a linear regression (blue line) based on the reference compounds (see compounds written in blue).



Figure S30. XANES spectra collected at the cobalt *K*-edge of *Co-V* freeze quenched *in situ* at three different potentials and after 24 h of air exposure at room temperature. The oxidation states in the table were determined analogously to the ones of Figure S27.



Figure S31. Original *k*³-weighted extended X-ray absorption fine structure (EXAFS) spectra. The black lines are the simulated spectra.



Figure S32. Fourier-transformed *K*-edge EXAFS spectra (top) and original k^3 -weighted EXAFS spectra (bottom). *Co-V* was freeze quenched *in situ* at three different potentials and after 24 h of air exposure at room temperature. The black lines are the simulated spectra.

EXAFS tables

N represents the *EXAFS* coordination number, *R* the absorber-backscatter distance and σ the Debye-Waller parameter. The amplitude reduction factor, $s_0^2(k)$, was 0.9 in all refinements. The Debye-Waller factors were restricted as joined-fit in order to reduce the number of variables. The errors represent the 68% confidence interval of the respective fit parameter. The values marked with * were fixed to crystallographic values and not fitted.

Table S1. Simulation parameters for as prepared $CoSeO_3 \cdot H_2O$ powder. The obtained R_f value of the fit is 14.5%, which corresponds to a mean deviation between data and simulation of 14.5% in the distance range of interest (0 - 6 Å of reduced distance).³¹

| shell | N | error | <i>R</i> [Å] | error [Å] | σ [Å] | error [Å] |
|-------|----|-------|--------------|-----------|--------------|-----------|
| Co-O | 6* | | 2.07 | 0.04 | 0.087 | 0.021 |
| Co-Se | 2* | | 2.94 | 0.10 | 0.106 | 0.025 |
| Co-Se | 2* | | 3.33 | 0.16 | 0.106 | 0.025 |
| Co-Se | 4* | | 3.63 | 0.09 | 0.106 | 0.025 |
| Co-Co | 4* | | 4.10 | 0.12 | 0.106 | 0.025 |

Table S2. Simulation parameters for $CoSeO_3 \cdot H_2O$ deposited on FTO. The obtained R_f value of the fit is 12.7%.

| shell | N | error | <i>R</i> [Å] | error [Å] | σ [Å] | error [Å] |
|-------|----|-------|--------------|-----------|--------------|-----------|
| Co-O | 6* | | 2.07 | 0.04 | 0.085 | 0.020 |
| Co-Se | 2* | | 2.93 | 0.08 | 0.103 | 0.024 |
| Co-Se | 2* | | 3.34 | 0.14 | 0.103 | 0.024 |
| Co-Se | 4* | | 3.64 | 0.08 | 0.103 | 0.024 |
| Co-Co | 4* | | 4.09 | 0.11 | 0.103 | 0.024 |

| shell | N | error | <i>R</i> [Å] | error [Å] | σ [Å] | error [Å] |
|-------|------------------|-------|--------------|-----------|--------------|-----------|
| Co-O | 1.8 [#] | 0.6 | 1.90 | 0.04 | 0.061 | 0.020 |
| Co-O | 4.2 [#] | 0.6 | 2.10 | 0.024 | 0.061 | 0.02 |
| Co-Co | 1.5 | 0.6 | 2.85 | 0.02 | 0.057 | 0.006 |
| Co-Co | 4.5 | 0.6 | 3.17 | 0.01 | 0.057 | 0.006 |
| Co-Co | 2.4 | 2.5 | 4.11 | 0.06 | 0.057 | 0.006 |
| Co-Co | 1.7 | 2.8 | 4.26 | 0.100 | 0.057 | 0.006 |
| Co-O | 7.8 | 8.8 | 4.66 | 0.08 | 0.057 | 0.006 |
| Co-O | 8.8 | 9.8 | 4.92 | 0.07 | 0.057 | 0.006 |
| Co-O | 5.2 | 11.0 | 5.26 | 0.14 | 0.057 | 0.006 |
| Co-Co | 7.1 | 3.4 | 5.56 | 0.030 | 0.057 | 0.006 |

Table S3. Simulation parameters for *Co-KOH*. The obtained R_f value of the fit is 12.4%. The fit was performed based on the crystallographic data of β -Co(OH)₂ (JCPDS 30-443). The parameters marked with a # were fixed to give six in total based on the crystal structure.

Table S4. Simulation parameters for *Co-KOH-V* freeze quenched at a current density of 10 mA/cm². The obtained R_f value of the fit is 14.5. The fit was performed based on the crystallographic data of β -Co(OH)₂ (JCPDS 30-443) and β -CoOOH (JCPDS 7-169). From the ratio of the first and second Co-O coordination shell, the fraction of the β -Co(OH)₂ to β -CoOOH phase was determined. It was assumed that the population of the first and second Co-O coordination shell for β -Co(OH)₂ is identical to the one in table S3. The fraction was found to be 40% β -Co(OH)₂ and 60% β -COOH. The parameters marked with a # were fixed to give six in total.

| shell | N | error | <i>R</i> [Å] | error [Å] | σ [Å] | error [Å] |
|-------|------------------|-------|--------------|-----------|--------------|-----------|
| Co-O | 4.5 [#] | 0.2 | 1.90 | 0.01 | 0.069 | 0.004 |
| Co-O | 1.5 [#] | 0.2 | 2.16 | 0.02 | 0.069 | 0.004 |
| Co-Co | 2.6 | 0.5 | 2.84 | 0.00 | 0.046 | 0.011 |
| Co-Co | 1.1 | 0.3 | 3.16 | 0.02 | 0.046 | 0.011 |
| Co-O | 2.4 | 0.8 | 3.43 | 0.03 | 0.046 | 0.011 |
| Co-O | 1.9 | 1.0 | 3.77 | 0.03 | 0.046 | 0.011 |
| Co-O | 4.5 | 2.0 | 4.66 | 0.03 | 0.046 | 0.011 |
| Co-Co | 0.9 | 0.6 | 4.92 | 0.03 | 0.046 | 0.011 |
| Co-Co | 3.5 | 1.0 | 5.56 | 0.01 | 0.046 | 0.011 |
| Co-Co | 1.0 | 0.9 | 5.87 | 0.04 | 0.046 | 0.011 |

Table S5. Simulation parameters for *Co-V* freeze quenched at a potential of 1.56 V_{RHE}. (identical to *Co-V* quasi *in situ*). The obtained R_f value of the fit is 16.6%. The fit was performed based on the structural model shown in Figure 10 of the main text. Simulation of EXAFS oscillations referring to the longest Co-Co distance (about 5.6 Å) includes multiple-scattering (ms) contributions. The 2-leg, 3-leg, and 4-leg path phase functions were calculated with FEFF as well. In the ms-shell, *N* is constraint to the value of the 5.65 Å Co-Co-shell, *R* is constraint to the value of the first Co-Co-shell at about 2.83 Å, and σ is constraint to the value of the value of the Co-Co-shells.

| shell | N | error | <i>R</i> [Å] | error [Å] | σ [Å] | error [Å] |
|-------|-----|-------|--------------|-----------|--------------|-----------|
| Co-O | 5.3 | 0.4 | 1.88 | 0.00 | 0.056 | 0.005 |
| Co-Co | 5.0 | 0.4 | 2.83 | 0.00 | 0.053 | 0.004 |
| Co-O | 4.5 | 1.1 | 3.40 | 0.02 | 0.056 | 0.005 |
| Co-Co | 2.5 | 0.8 | 4.92 | 0.02 | 0.053 | 0.004 |
| Co-Co | 2.7 | 0.4 | 5.65 | | 0.053 | 0.004 |

Table S6. Simulation parameters for *Co-V* freeze quenched at a potential of $1.27 V_{RHE}$. The obtained R_f value of the fit is 15.6%. The fit was performed based on the structural model shown in Figure 10 of the main text. Simulation of EXAFS oscillations referring to the longest Co-Co distance (about 5.6 Å) includes multiple-scattering (ms) contributions. The 2-leg, 3-leg, and 4-leg path phase functions were calculated with FEFF as well. In the ms-shell, *N* is constraint to the value of the 5.65 Å Co-Co-shell, *R* is constraint to the value of the first Co-Co-shell at about 2.83 Å, and σ is constraint to the value of the Co-Co-shells.

| shell | N | error | <i>R</i> [Å] | error [Å] | σ [Å] | error [Å] |
|-------|-----|-------|--------------|-----------|--------------|-----------|
| Co-O | 5.7 | 0.4 | 1.88 | 0.00 | 0.053 | 0.004 |
| Co-Co | 5.4 | 0.4 | 2.83 | 0.00 | 0.046 | 0.003 |
| Co-O | 5.2 | 1.1 | 3.41 | 0.01 | 0.053 | 0.004 |
| Co-Co | 2.4 | 0.6 | 4.92 | 0.01 | 0.046 | 0.003 |
| Co-Co | 3.0 | 0.4 | 5.66 | | 0.046 | 0.003 |

Table S7. Simulation parameters for *Co-V* freeze quenched at a potential of 0.9 V_{RHE} . The obtained R_f value of the fit is 20.0%. The fit was performed based on the structural model shown in Figure 10 of the main text. Simulation of EXAFS oscillations referring to the longest Co-Co distance (about 5.6 Å) includes multiple-scattering (ms) contributions. The 2-leg, 3-leg, and 4-leg path phase functions were calculated with FEFF as well. In the ms-shell, *N* is constraint to the value of the 5.65 Å Co-Co-shell, *R* is constraint to the value of the first Co-Co-shell at about 2.83 Å, and *s* is constraint to the value of the Co-Co-shells.

| shell | N | error | <i>R</i> [Å] | error [Å] | σ [Å] | error [Å] |
|-------|-----|-------|--------------|-----------|--------------|-----------|
| Co-O | 5.3 | 0.4 | 1.90 | 0.00 | 0.052 | 0.005 |
| Co-Co | 4.7 | 0.4 | 2.85 | 0.00 | 0.057 | 0.004 |
| Co-O | 4.3 | 1.1 | 3.43 | 0.02 | 0.052 | 0.005 |
| Co-Co | 2.9 | 0.9 | 4.97 | 0.02 | 0.057 | 0.005 |
| Co-Co | 3.0 | 0.5 | 5.69 | | 0.057 | 0.004 |

Table S8. Simulation parameters for *Co-V* exposed to air at room temperature for 24 h. The obtained R_f value of the fit is 16.8%. The fit was performed based on the structural model shown in Figure 10 of the main text. Simulation of EXAFS oscillations referring to the longest Co-Co distance (about 5.6 Å) includes multiple-scattering (ms) contributions. The 2-leg, 3-leg, and 4-leg path phase functions were calculated with FEFF as well. In the ms-shell, *N* is constraint to the value of the 5.65 Å Co-Co-shell, *R* is constraint to the value of the first Co-Co-shell at about 2.83 Å, and *s* is constraint to the value of the Co-Co-shells.

| shell | N | error | <i>R</i> [Å] | error [Å] | σ [Å] | error [Å] |
|-------|-----|-------|--------------|-----------|--------------|-----------|
| Co-O | 5.4 | 0.3 | 1.88 | 0.00 | 0.051 | 0.005 |
| Co-Co | 5.2 | 0.4 | 2.82 | 0.00 | 0.049 | 0.004 |
| Co-O | 4.8 | 1.0 | 3.41 | 0.01 | 0.051 | 0.005 |
| Co-Co | 1.5 | 0.7 | 4.91 | 0.02 | 0.049 | 0.004 |
| Co-Co | 2.4 | 0.4 | 5.65 | | 0.049 | 0.004 |

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