

## Electronic Supplementary Information

### Brownmillerite-type $\text{Ca}_2\text{Fe}_{0.75}\text{Co}_{1.25}\text{O}_5$ as a Robust Electrocatalyst for Oxygen Evolution Reaction in Neutral Conditions

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## **Experimental**

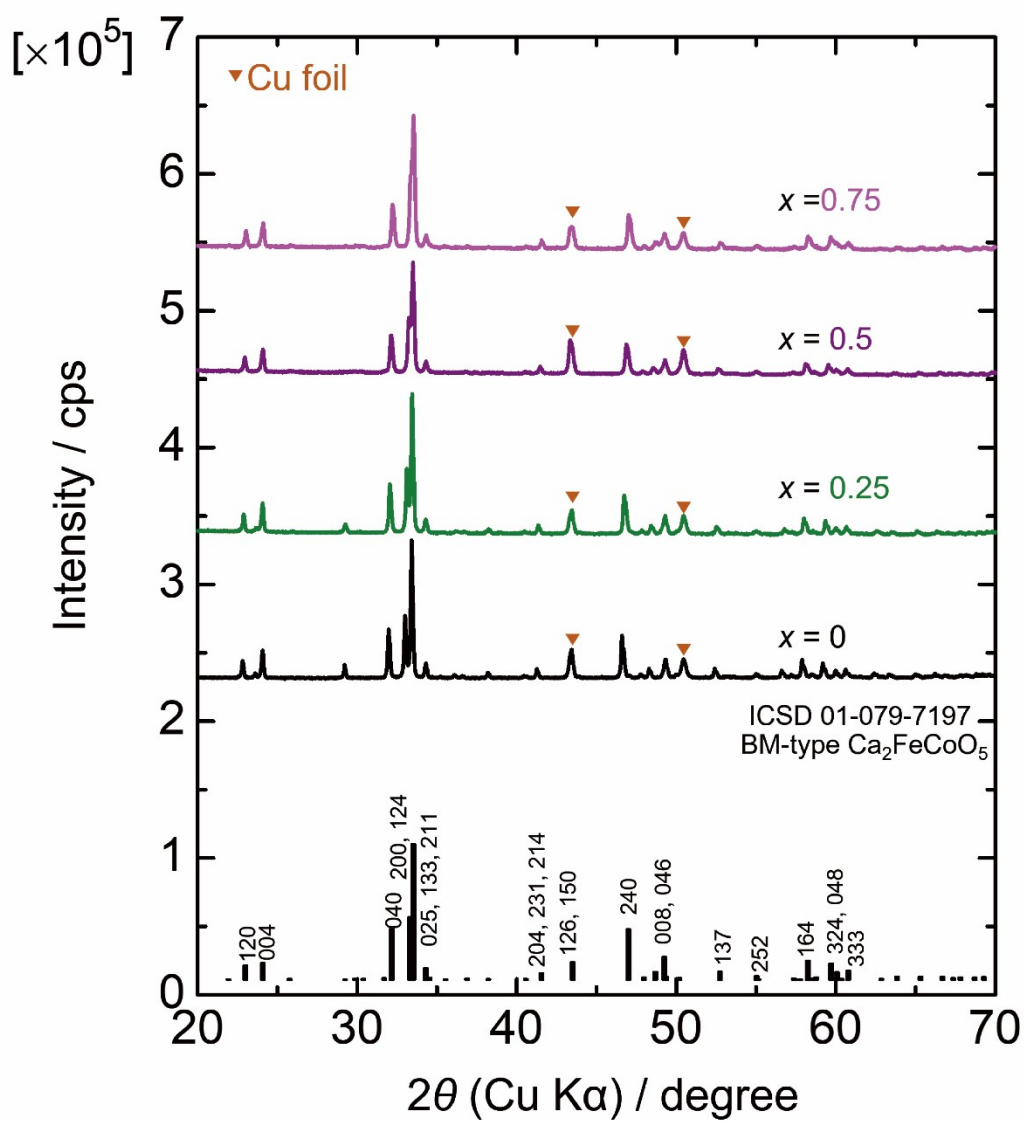
**Synthesis of  $\text{LaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$ :**  $\text{LaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$  was synthesized by a citric acid sol-gel method.<sup>S1,S2</sup>  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (FUJIFILM Wako Pure Chemical Corp., 99.9%),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (FUJIFILM Wako Pure Chemical Corp., 99.0%),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (FUJIFILM Wako Pure Chemical Corp., 98.0%) and citric acid monohydrate (FUJIFILM Wako Pure Chemical Corp., 99.5%) were dissolved in 30 mL of ion-exchanged water, and the amounts of employed raw materials were adjusted to have La : Fe : Co : citric acid molar ratio = 2 : 1 : 1 : 4. The obtained solutions were stirred and heated at 363 K to promote polymerization. The product was heated at  $0.17 \text{ K s}^{-1}$  up to 723 K, pre-calcined at 723 K temperature for 1 h in air to remove the organic compounds, grounded for 30 min in a mortar, re-heated at  $0.17 \text{ K s}^{-1}$  up to 1073 K and calcined at 1073 K for 6 h in air. The calcined product was ground for 30 min in a mortar.

$\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$  was synthesized by ethylenediaminetetraacetate (EDTA) -citric acid sol-gel method.<sup>S3</sup>  $\text{Sr}(\text{NO}_3)_2$  (FUJIFILM Wako Pure Chemical Corp., 98.0%),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , EDTA (FUJIFILM Wako Pure Chemical Corp., 99.0%) and citric acid were dissolved in 30 mL of ion-exchanged water, and the amounts of employed raw materials were adjusted to have Sr : Fe : Co : EDTA : citric acid molar ratio = 2 : 1 : 1 : 4 : 8. A 10 % aqueous ammonia solution (FUJIFILM Wako Pure Chemical Corp.) was added with stirring until pH increased up to 7. The obtained solutions were stirred and heated at 363 K to promote polymerization. The product was heated at  $0.17 \text{ K s}^{-1}$  up to 523 K, pre-calcined at 523 K temperature for 5 h in air to remove the organic compounds, grounded for 30 min in a mortar, re-heated at  $0.17 \text{ K s}^{-1}$  up to 1073 K and calcined at  $1073 \text{ K s}^{-1}$  for 6 h in air. The calcined product was ground for 30 min in a mortar.

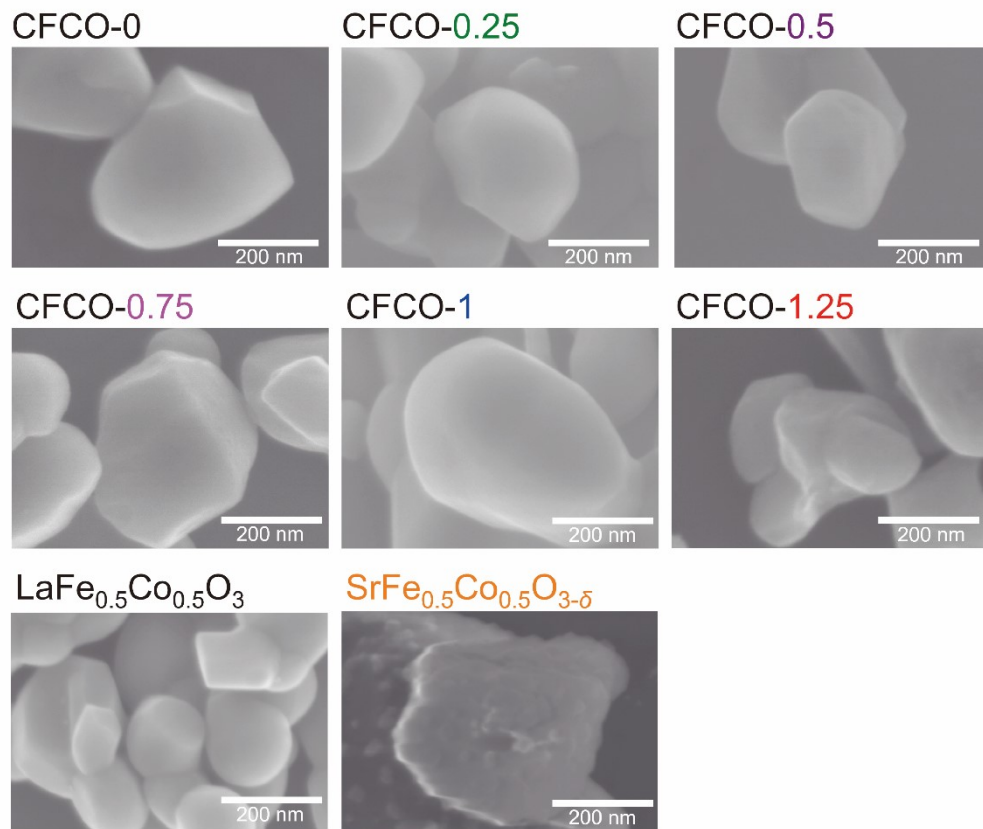
**XPS analysis:** The chemical compositions of the sample surfaces were investigated using X-ray photoelectron spectroscopy (XPS; JEOL JPS-9200) with Mg K $\alpha$  line (1253.6 eV). The binding energies of the elements were calibrated by the C1s peak at 284.8 eV. After smoothing, background was removed using the Shirley method, and the peaks were fitted using 5 : 1 mixture of Gaussian and Lorentz functions.

**Measurement of water adsorption capacity:** CFCO-1 or LaFe<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub> (20 mg) was pressed at 200 kgf cm<sup>-2</sup> for 1 min to prepare a 10 mm diameter disc (wafer). The disc was placed in an IRMS-TPD analyser (MicrotracBEL Corp.) and evacuated, then heated to 823 K at 0.17 K s<sup>-1</sup> with O<sub>2</sub> flowing and kept for 1 h. The temperature was lowered to 323 K in vacuum, and the disc was exposed to water vapor to adsorb water. Ar was used to replace the gas in the cell, and the ion current at  $m/z=18$  was measured by MS while the temperature was increased at 0.17 K s<sup>-1</sup> in 0.15 mmol s<sup>-1</sup> of Ar flow.

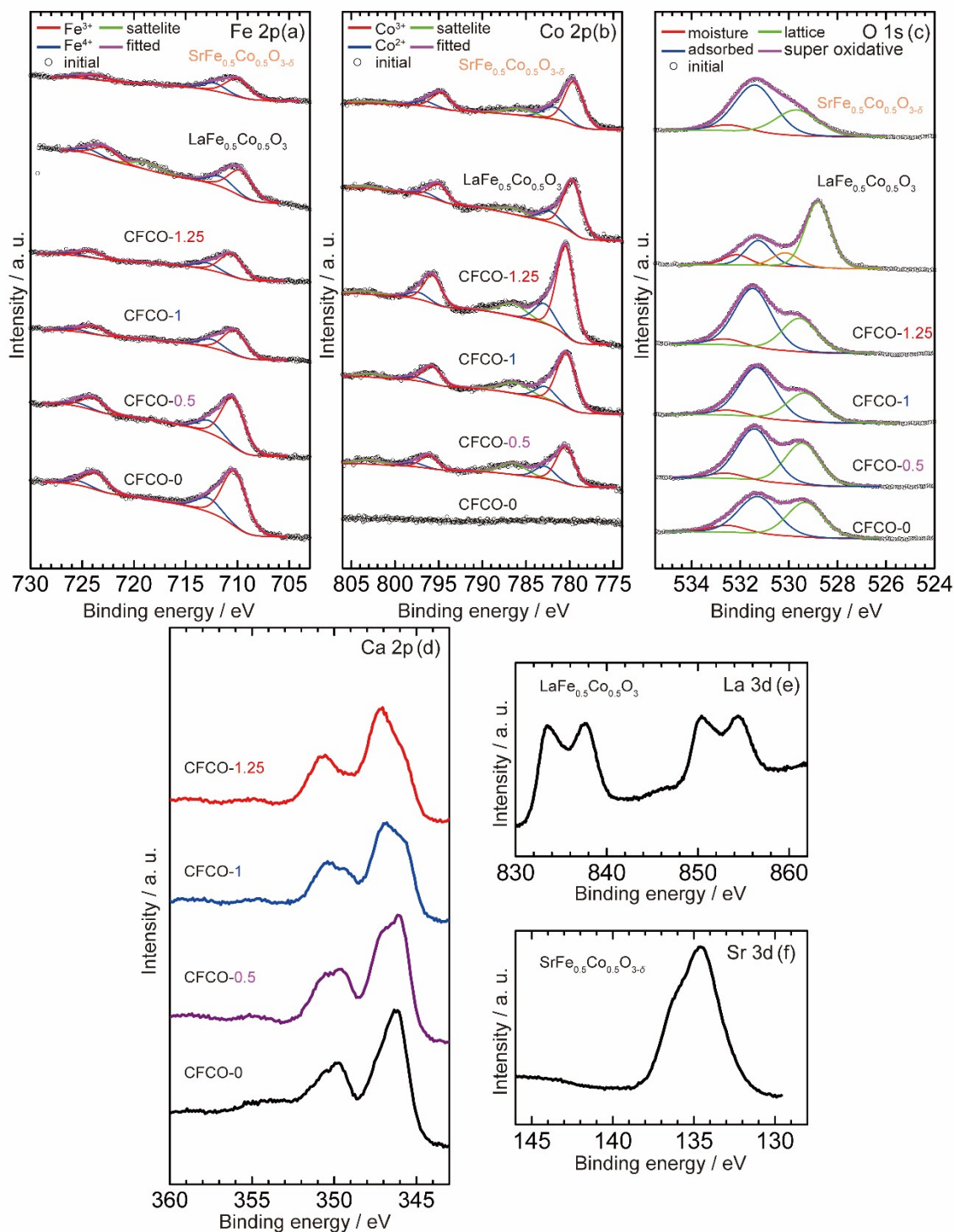
**Measurement of Faradic Efficiency:** An H-type cell (EC FRONTIER CO., LTD, VB11A) in which the anode and cathode sides are separated by an anion exchange membrane (AGC Engineering CO., LTD, SELEMION<sup>®</sup> AMVN) was used to measure the oxygen yield. Using the same electrodes and electrolyte as in the durability measurement, the cell was sealed after bubbling with Ar for at least 30 minutes, and a constant potential of 1.7 V vs. RHE was applied for 20 hours. Gaseous phase was extracted 1 mL from the anode side with a gas tight syringe after a constant potential measurement and analysed by gas chromatograph equipped with a TCD detector (Shimadzu Corp., GC-8A4).



**Figure S1.** X-ray diffraction of CFCO- $x$  ( $0 \leq x \leq 0.75$ ). All oxides were synthesized by citric acid sol-gel method using nitrate and citric acid at 1073 K calcination. It was consistent with XRD pattern of brownmillerite-type  $\text{Ca}_2\text{FeCoO}_5$  (orthorhombic  $Pbcm$ ) reported in the past.<sup>S2</sup>



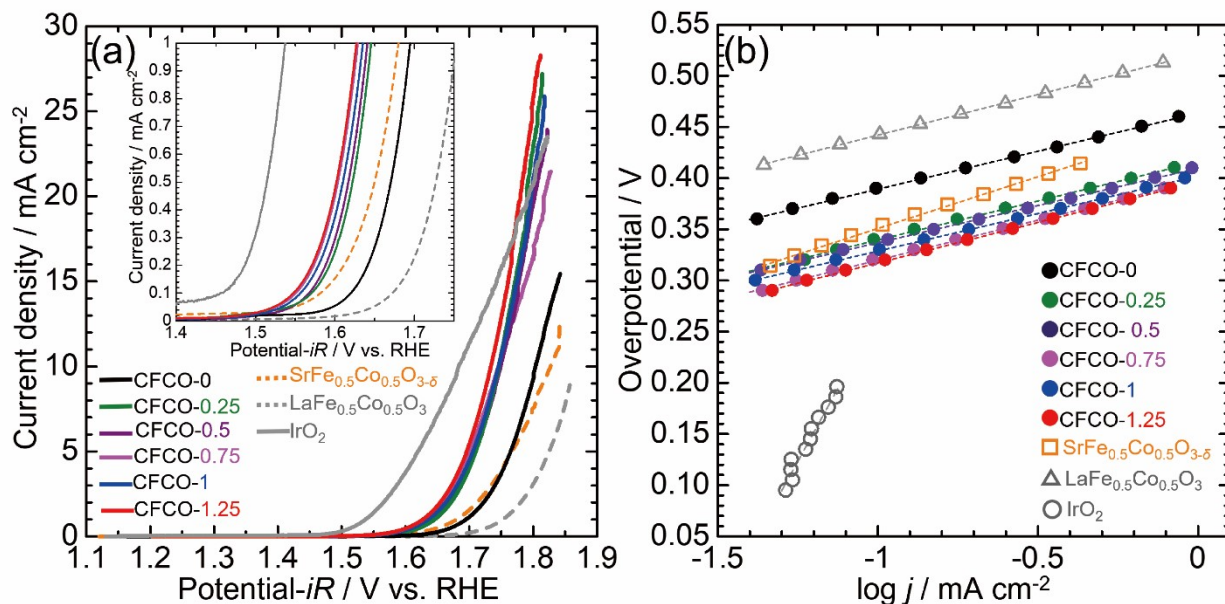
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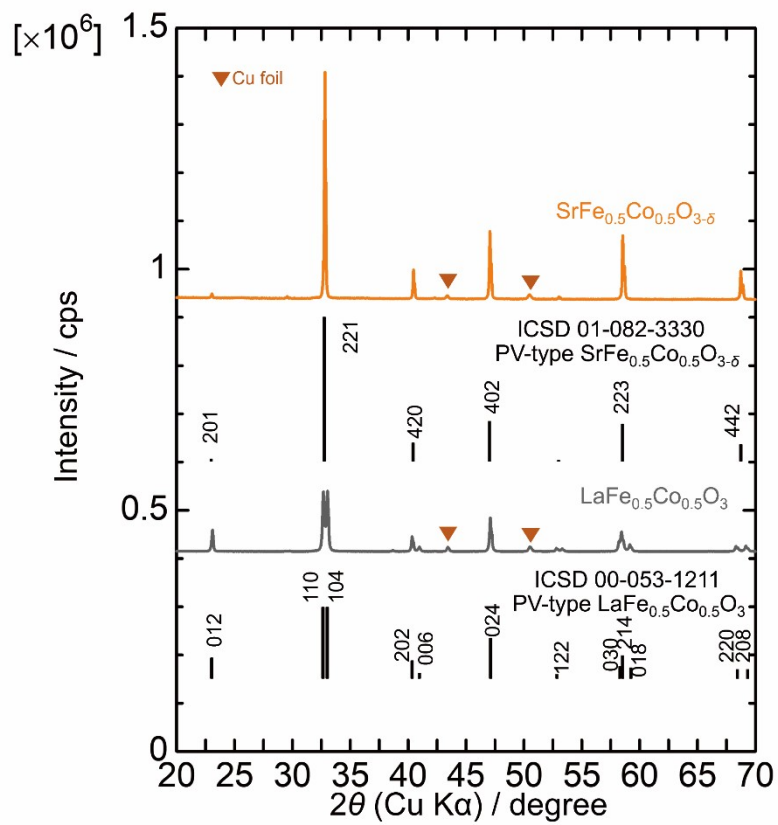
**Figure S3.** (a) Fe 2p, (b) Co 2p, (c) O 1s, (d) Ca 2p, (e) La 3d, (f) Sr 3d XPS spectra of as-calcined CFCO- $x$  and PV-type oxides and fitting curves. The O 1s spectra

shows three peaks at 532.4~532.5 eV and 531.2~531.3 eV, 529.3~529.7 eV. They were attributed to moisture on surface and hydroxyl groups or the adsorbed oxygen, lattice oxygen.<sup>S4-S6</sup> For LaFe<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub>, a peak at 530.2 eV was observed, which was attributed to super oxidative oxygen.

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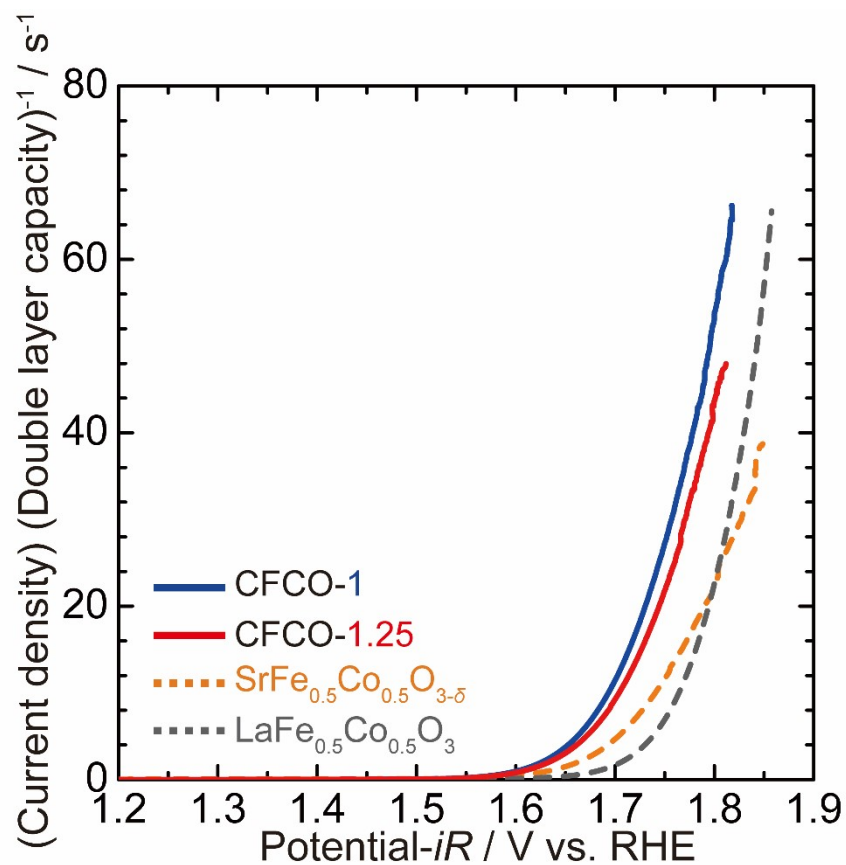


**Figure S4.** (a) Linear sweep voltammograms ( $1 \text{ mV s}^{-1}$ ) of CFCO- $x$  ( $0 \leq x \leq 1.25$ ), PV-type  $\text{LaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$  and  $\text{IrO}_2$  (99.99%, Thermo Scientific™, Ion-exchanged water was used as dispersant because ethanol ignited on contact with  $\text{IrO}_2$ ). (b) Tafel plots of CFCO- $x$  ( $0 \leq x \leq 1.25$ ), PV-type  $\text{LaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$  and  $\text{IrO}_2$ . Tafel plots were obtained by defining the onset potential as the potential showing  $0.05 \text{ mA cm}^{-2}$ . Slope of CFCO- $x$  and  $\text{LaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$  samples is within  $75\text{--}80 \text{ mV/dec}$  and  $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$  is  $101 \text{ mV/dec}$  and  $\text{IrO}_2$  is  $63 \text{ mV/dec}$ .

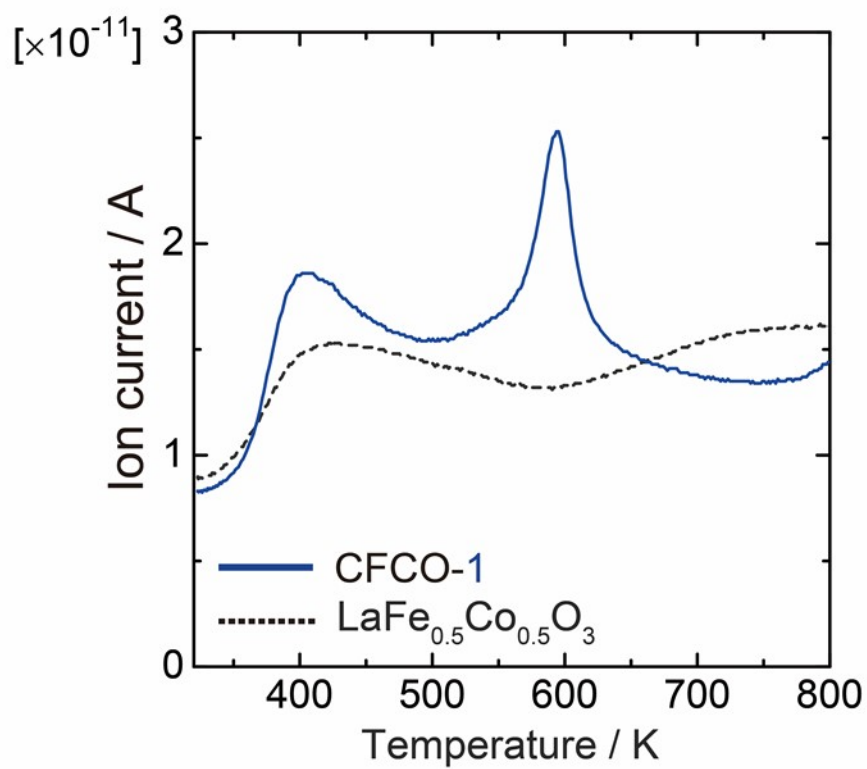


**Figure S5.** X-ray diffraction of PV-type LaFe<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub> and SrFe<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3- $\delta$</sub> .

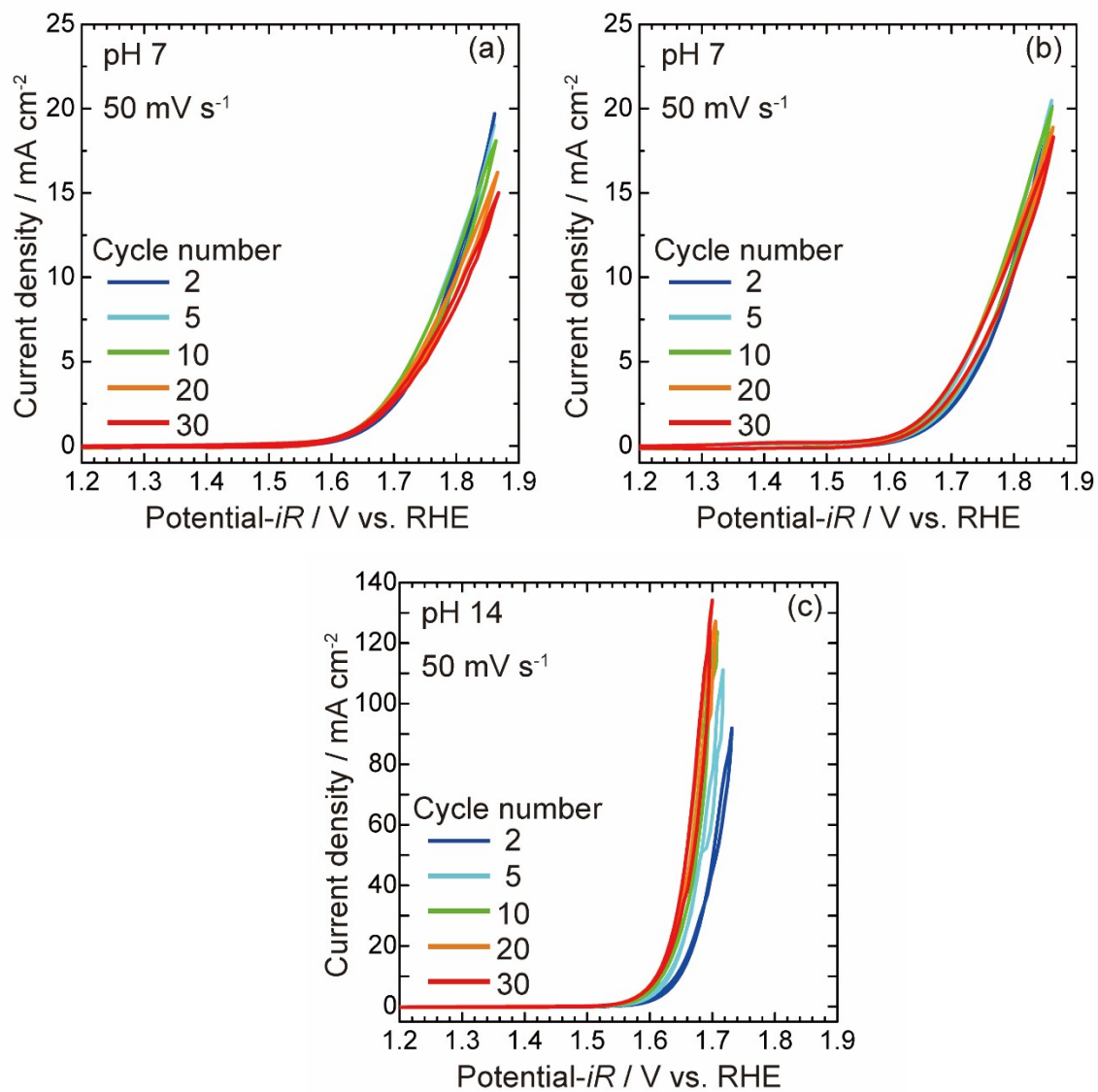




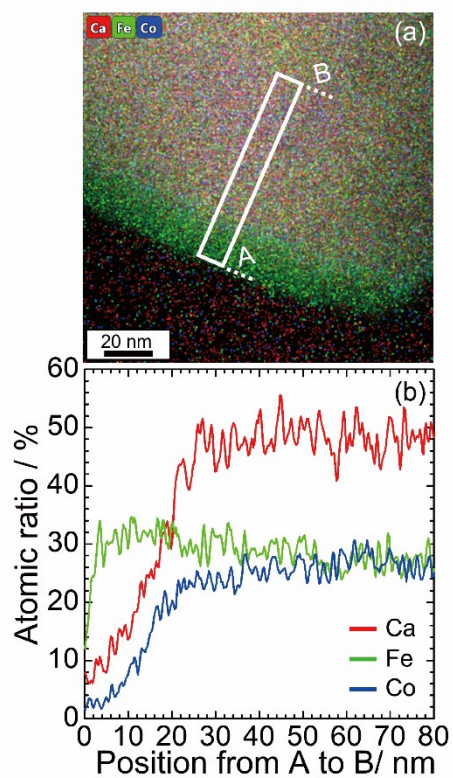
**Figure S6.** Linear sweep voltammograms ( $1 \text{ mV s}^{-1}$ ) of CFCO- $x$  ( $x = 1, 1.25$ ) and PV-type  $\text{LaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$  corrected by double layer capacitance obtained by cyclic voltammogram ( $50 \text{ mV s}^{-1}$ ) at  $\text{pH} = 7$  in a potential range of 1.25~1.35 V vs. RHE.



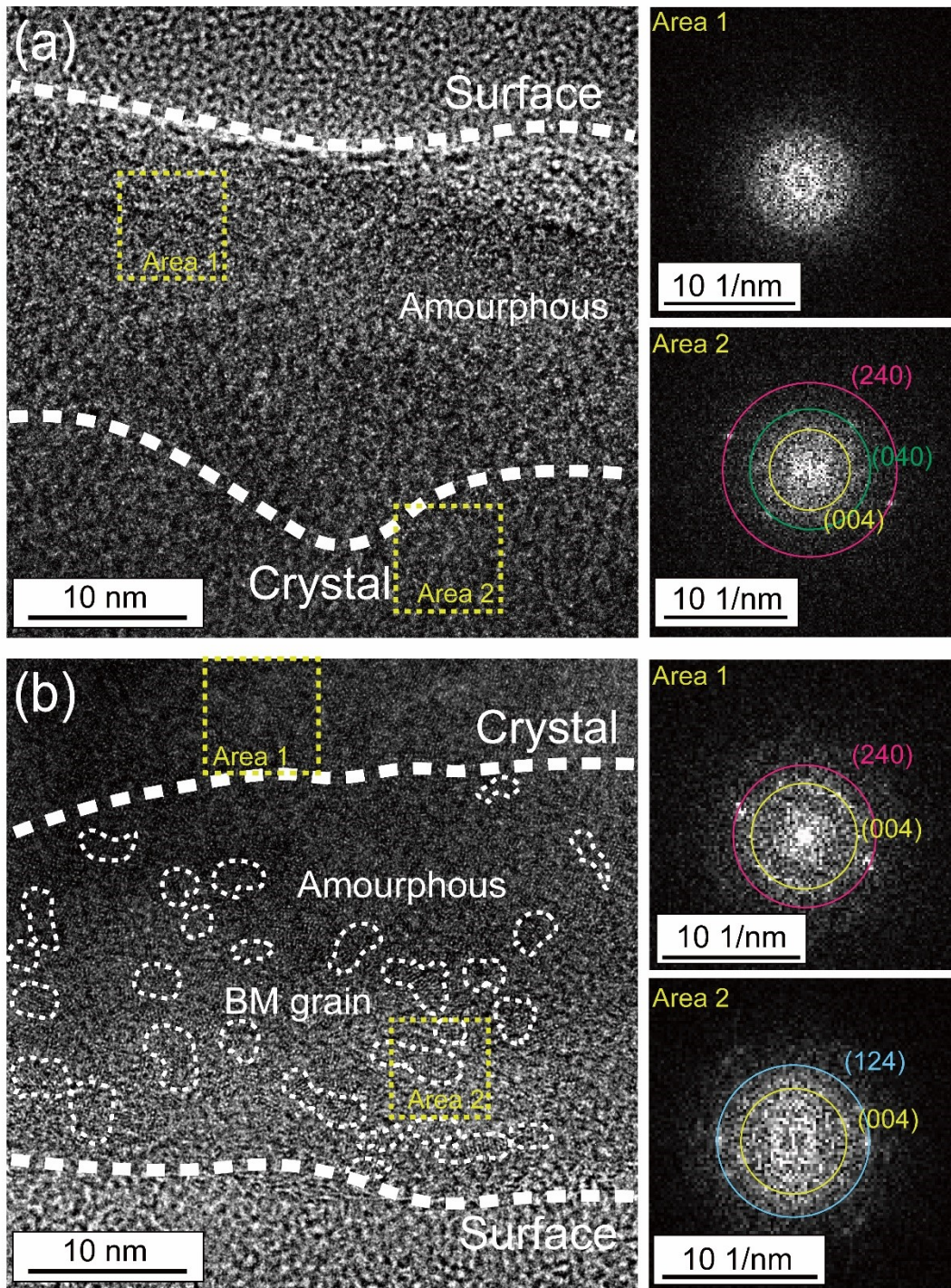
**Figure S7.** Desorption behaviors of adsorbed water on CFCO-1 and PV-type LaFe<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub> measured by MS-TPD.



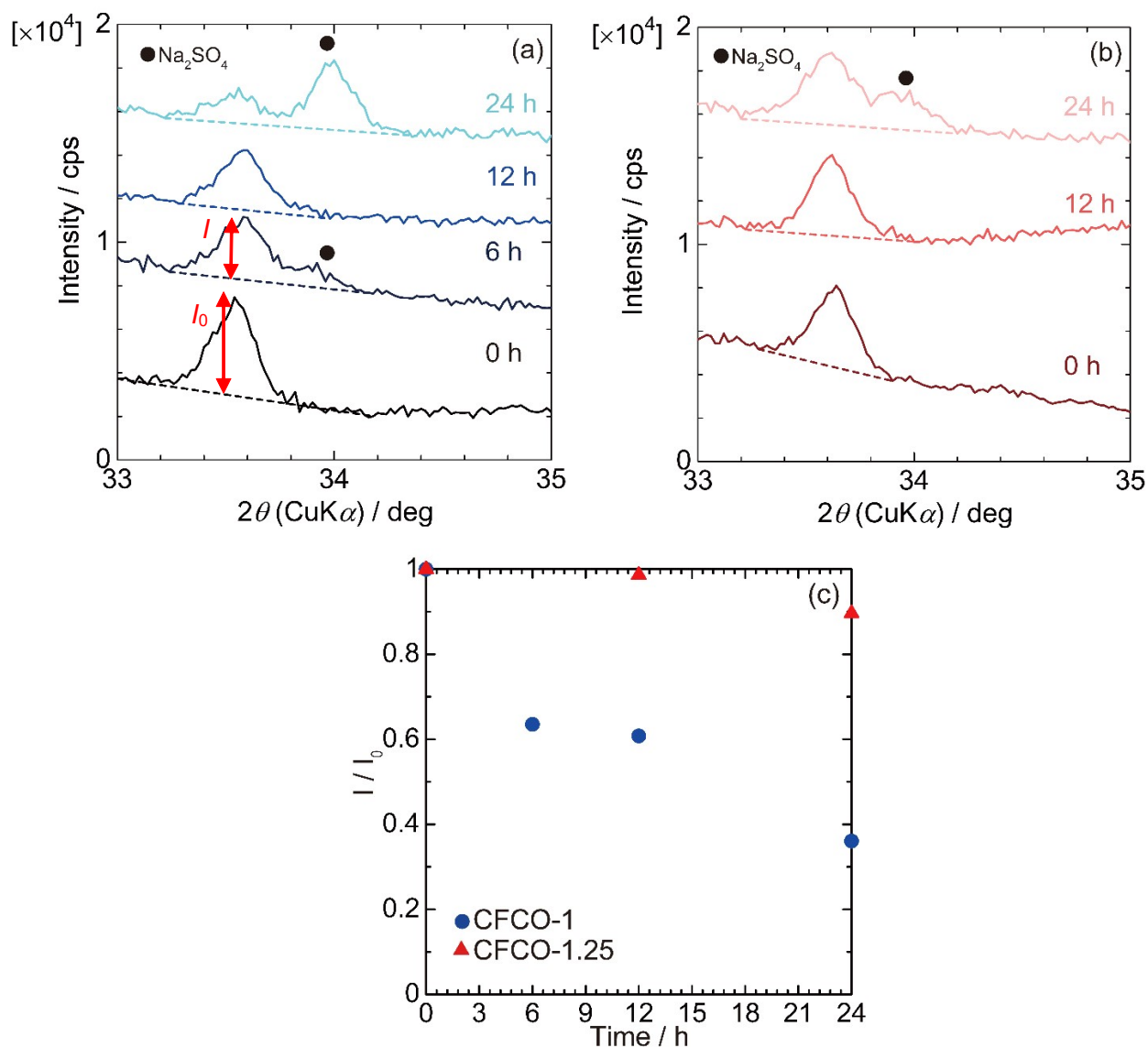
**Figure S8.** Cyclic voltammograms of (a) (c) CFCO-1 and (b) CFCO-1.25 loaded on glassy carbon electrode (BAS Inc., 3 mm in diameter) measured at 50 mV s<sup>-1</sup> for 30 cycles in the (a) (b) neutral and (c) alkaline solution.



**Figure S9.** (a) Energy dispersive spectroscopy mapping and (b) EDS line-scan profile of CFCO-1 after the durability test in the neutral solution at  $4.7 \text{ mA cm}^{-2}$  for 24 h. In the case of CFCO-1, some Fe poor areas were observed except for those seen in Figure 3c.



**Figure S10.** High-resolution transmission electron microscopy images of (a)CFCO-1 and (b)-1.25 after the durability test in the neutral solution at  $4.7 \text{ mA cm}^{-2}$  for 24 h (the same images as Figure 3c-1 and d-1) and fast Fourier transforms (FFT) from area 1 and 2.

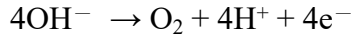


**Figure S11.** X-ray diffraction of (124) for (a)CFCO-1 and (b)CFCO-1.25 on carbon paper (CP) electrodes after applying a constant current of  $4.7 \text{ mA cm}^{-2}$  in the neutral solution ( $\text{N}_2$ -saturated electrolyte containing  $0.4 \text{ mol dm}^{-3} \text{ NaH}_2\text{PO}_4$ ,  $0.6 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$  and  $\text{NaOH}$  whose amount was adjusted to keep pH at 7) for 0, 6, 12, 24 h. (c) Plot of X- ray diffraction intensity ratio versus time. For each measurement, a new electrode was prepared. Before and after applying the constant current, the electrodes were washed by water and dried in air, then, crystallinity of the CFCO/CP substrates were investigated by XRD. The peak derived from  $\text{Na}_2\text{SO}_4$  used in the electrolyte was observed around  $33.6^\circ$ .  $I_0$  and  $I$  are the intensity of CFCO before and after the durability test.

**Table S1.** Amounts of used electrons and generated oxygen, and Faradic efficiency on CFCO-1.25 at 1.7 V vs. RHE for 20 h.

Catalysts	Used electrons / $\mu\text{mol}$	Oxygen production / $\mu\text{mol}$		Faradic efficiency / %
		Theoretical*	Actual	
CFCO-1.25	313.0	78.3	78.2	99.9

\* Theoretical oxygen production was calculated from used electrons using following reaction formula.



**Table S2.** Double layer capacity of CFCO- $x$  ( $0 \leq x \leq 1.25$ ) and PV-type  $\text{LaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$  and  $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$  calculated from cyclic voltammograms at 1.25 – 1.35 V vs. RHE.

Catalysts	Double layer capacity / $\text{mC cm}^{-2}$
CFCO-0	0.163 $\pm$ 0.01
CFCO-0.25	0.240 $\pm$ 0.06
CFCO-0.5	0.332 $\pm$ 0.03
CFCO-0.75	0.306 $\pm$ 0.06
CFCO-1	0.391 $\pm$ 0.04
CFCo-1.25	0.590 $\pm$ 0.09
$\text{LaFe}_{0.5}\text{Co}_{0.5}\text{O}_3$	0.136
$\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$	0.331

**Table S3.** Average valence and surface chemical composition of as-calcined CFCO- $x$  calculated from XPS.

Catalysts	Average valence		Chemical composition (surface) / atom%		
	Fe	Co	Ca	Fe	Co
CFCO-0	3.2	-	55	45	-
CFCO-0.25	-	-	-	-	-
CFCO-0.5	3.2	2.7	51	27	22
CFCO-0.75	-	-	-	-	-
CFCO-1	3.3	2.8	49	17	34
CFCO-1.25	3.2	2.8	45	13	41

## References

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