



Title	Highly Durable Oxygen Evolution Reaction Catalyst: Amorphous Oxyhydroxide Derived from Brownmillerite-Type $\text{Ca}_2\text{FeCoO}_5$
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A Highly Durable OER Catalyst: Amorphous Oxyhydroxide Derived from Brownmillerite-type $\text{Ca}_2\text{FeCoO}_5$

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ABSTRACT

Brownmillerite-type $\text{Ca}_2\text{FeCoO}_5$ (CFCO) is a highly active electrocatalyst for the oxygen evolution reaction (OER). In this study, we identified the actual catalytically active phase of this oxide formed via the long-term OER and, moreover, demonstrated that the active phase can persist during the OER for four weeks without significant loss of electrocatalytic activity. The long-term durability tests were carried out on CFCO via continuous galvanostatic OER in 4 mol dm^{-3} KOH aqueous solution for periods ranging from a few hours to one month, and the specimens submitted to the tests were characterized by means of electrochemical measurements and structural analysis using scanning electron microscopy, X-ray diffraction, transmission electron microscopy, Auger electron spectroscopy, and X-ray absorption fluorescence spectroscopy. CFCO was readily converted to amorphous cobalt oxyhydroxides with 10% of Fe substituents through the OER process, and these compounds had a similar local rearrangement to the layered $\gamma\text{-CoOOH}$ -type structure. This transformation involved large morphological changes of the oxide particles because of the extensive dissolution of Ca and Fe, yielding skeletal grains made of oxyhydroxide nanosheet aggregates. The extended durability studies with total polarization charge density of the order of 10^5 C cm^{-2} revealed that (Co, Fe)OOH like compound is the actual electrocatalytic phase.

Keywords: OER, Brownmillerite, $\text{Ca}_2\text{FeCoO}_5$, Electrocatalyst, Auger electron spectroscopy, Extended X-ray absorption fine structure

1. INTRODUCTION

The oxygen evolution reaction (OER) is one of the most important reactions for renewable energy conversion and storage systems.¹ For instance, this reaction is widely applied for water splitting for hydrogen production,^{2–4} charging metal–air secondary batteries,^{5–10} and artificial photosynthesis.^{11–13} However, the four-electron OER pathway requires a large overpotential.¹⁴ Some precious-metal-oxide-based catalysts such as RuO_2 ¹⁵ and IrO_2 ¹⁶ are widely used as OER electrocatalysts, but the scarcity of these platinum-group metals has resulted in an urgent need to develop transition-metal-based alternatives with high OER activity and long-term stability in strongly alkaline media.^{17–22}

Intense research in this field, particularly over the last decade, has led to the discovery of many types of transition-metal-oxide electrocatalysts,^{17–24} some of which have been practically used in alkaline electrolysis technology. Recently, Tsuji et al.²² reported that Brownmillerite-type $\text{Ca}_2\text{FeCoO}_5$ (CFCO) shows pronounced catalytic activity for the OER in concentrated alkaline media, yielding an OER current of 5.0 mA per oxide-catalyst surface area at 1.6 V vs. the reversible hydrogen electrode (RHE), which is an order of magnitude larger than the corresponding values

for RuO₂.²² More recently, Kowalski et al. reported that CFCO is readily transformed into an electrocatalytically active amorphous phase through OER in highly concentrated alkaline solution with the formation of edge sharing CoO₆ clusters.²³ Extended X-ray absorption spectroscopy measurements have clarified that the amorphous phase is made of Co-based oxyhydroxide having a γ -CoOOH like local arrangement. Although CFCO is a promising OER catalyst for alkaline electrolysis and air batteries because of its very high activity, earlier results have revealed concerns over the long-term stability of CFCO catalysts, i.e., whether the deformation and dissolution of CFCO catalysts can be terminated. Moreover, it is of fundamental and technological importance to identify the actual active phase of CFCO catalysts that form during the long-term OER if the deformation is terminated within a reasonable period. Herein, we demonstrate that Brownmillerite-type CFCO catalysts are transformed to amorphous oxyhydroxide phases comprising exfoliated γ -CoOOH type nanosheets modified with Fe, and this transition is mediated via the dissolution of the Ca and Fe contents. Finally, the spherical grains of Brownmillerite-type CFCO are converted to 100 nm sized skeletal agglomerates after the OER for four weeks.

2. EXPERIMENTAL

Synthesis of $\text{Ca}_2\text{FeCoO}_5$: For the synthesis of $\text{Ca}_2\text{FeCoO}_5$ (CFCO), the following reagents were used as starting materials: $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Kanto Chemical, 99.9%), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Kanto Chemical, 99.9%), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%, Wako Pure Chemical). Appropriate amounts of these reagents were dissolved in Milli-Q water to which an equal molar quantity of citric acid (Wako Pure Chemical, 98%) was subsequently added as a complexing agent. The citrate solution was stirred and heated at 60–70 °C to promote polymerization. The gelatinous product was pre-fired in air at 450 °C for 1 h and, then, fired at 600 °C for 12 h. Details of the preparation procedure have been described elsewhere.²² The X-ray diffraction (XRD) patterns of CFCO and its precursor are shown in Fig. S1. All the peaks of CFCO are assigned to Brownmillerite-type structure so that the single phase CFCO can be obtained at 600°C. In contrast, Brownmillerite-type phase was absent in the precursor, which contains $\text{Ca}(\text{NO}_3)_2$, Fe_2O_3 , Co_2O_3 phases.

Electrochemical measurements: The carbon support (acetylene black (AB), STR Chemicals) (10 mg) and $\text{Ca}_2\text{FeCoO}_5$ (50 mg) were dispersed ultrasonically in a mixture of 0.2 mL of 5 wt% Na^+ -exchanged Nafion solution (Wako) and 4.8 mL of ethanol to obtain a homogenous black suspension. Nafion was added as a binder and was neutralized before dispersion to prevent CFCO from acidic dissolution.²⁴ The AB additive was pretreated by immersing a commercial AB powder

into concentrated nitric acid at 80°C overnight, followed by filtering and drying at 100°C overnight. For electrocatalyst activity evaluation, 20 µL of the suspension was pipetted onto the surface of a 5 mm diameter glassy carbon (GC) electrode with a rotation rate of 600 rpm. For durability tests, 150 µL of the suspension was pipetted onto the surface of a 15 × 10 mm² carbon paper electrode (ElectroChem, Inc., EC-TP1-060T). This area was demarcated using epoxy resin. On the basis of the above treatments, the catalyst loading on the working electrodes was 1.0 mg cm⁻². The electrochemical measurements were carried out in a three-electrode system using a Princeton Applied Research VersaSTAT 3 potentiostat. A pure carbon sheet and Hg/HgO/4 mol dm⁻³ KOH were used as counter and reference electrodes, respectively. All the measurements were carried out at room temperature (approximately 25 °C) in an aqueous 4 mol dm⁻³ KOH solution (pH 14). The potential (*E*) was iR-corrected with a solution resistance measured by AC impedance spectroscopy before each experiment and converted from the Hg/HgO/4 mol dm⁻³ KOH reference scale to the RHE using the following equation.²²

$$E \text{ vs. RHE} = E_{\text{vs. Hg/HgO/4 mol dm}^{-3} \text{ KOH}} + 0.098 + 0.059 \times \text{pH} \quad (1)$$

Characterization: The electrode surface material morphologies were observed by low-voltage field-emission scanning electron microscopy (SEM, Carl Zeiss Microscopy, Sigma-500) at 1.5 kV. The crystallinity of the CFCO electrode was determined using an X-ray diffractometry (XRD,

Rigaku, Ultima IV) using $\text{Cu-K}\alpha$ radiation. High-resolution transmission electron microscopy (HRTEM) was carried out using a Titan-3 G2 60-300 scanning transmission electron microscope equipped with an energy dispersive X-ray spectrometry (EDS). For TEM observation, the sample electrodes were washed with ethanol (99.5%, Kanto chemical) and sonicated, resulting in a dispersion of the supported catalyst from the electrode. This dispersion was dropped onto the carbon-coated copper TEM grid (Ohken shoji, NP-C15) and used as a TEM sample. The chemical composition was evaluated using scanning Auger electron spectroscopy (AES, JEOL, JAMP-9500F) with a field-emission electron gun at an accelerating voltage of 5 kV and a beam current of 10 nA. The chemical ratios of Co and Fe were determined by fitting the obtained spectrum using the “Spectra Investigator” program (JEOL). The molar ratios of Ca and Co were determined by the relative factor method using the “Auger Master” program (JEOL) from the local maximum value of each element peak.

Extended X-ray absorption fine structure (EXAFS) spectra were obtained for Co and Fe *K*-edges at the BL28XU beamline of SPring-8 (Hyogo, Japan). The synchrotron radiation X-ray from the storage ring was monochromated with a Si(111) double-crystal monochromator. The X-ray absorption near edge spectroscopy (XANES) spectra were measured in the transmission mode using two ionization chambers. Data reduction was carried out with the Demeter program package.

3. RESULTS

Figure 1 shows linear sweep voltammetry (LSV) curves of the CFCO electrodes with and without the AB additive, as measured by a rotating disk electrode (RDE) system at of 800 rpm in aqueous 4 mol dm⁻³ KOH electrolyte. The onset potential, which was defined as the potential to achieve the anodic current of 5.0 mA cm⁻²_{disk}, equals 1.54 V vs. RHE without addition of the AB conductive support. CFCO has a relatively low conductivity,²⁵ and therefore the onset potential of the OER shifts to 1.48 V vs. RHE with the addition of AB. Moreover, The CFCO electrode with AB additive exhibits markedly increased current compared with the AB-free CFCO electrode at higher overpotentials, probably because of the reduction of the electrode resistance.

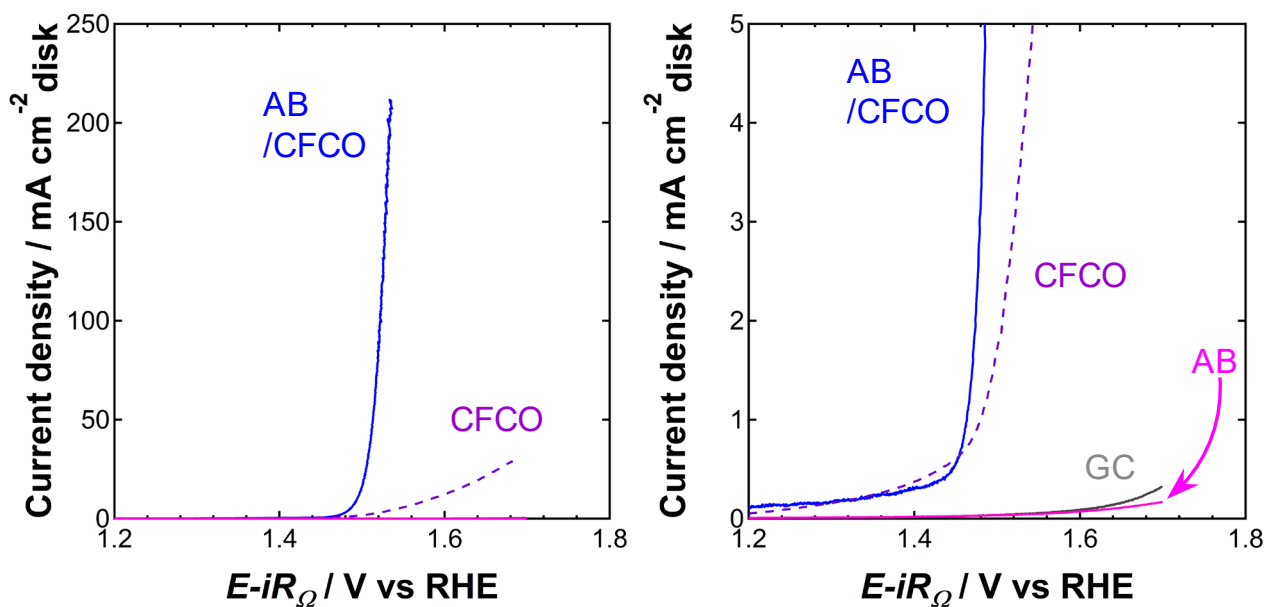


Figure 1. OER LSV curves of CFCO with and without the AB conductive supports measured by a rotating disk electrode (RDE) at 800 RPM in aqueous 4 mol dm⁻³ KOH solution with a potential sweep rate of 1.0 mV s⁻¹. The LSV curves of a bare GC electrodes are shown as a reference.

To evaluate the long-term durability, the OER was continuously carried out for AB/CFCO electrodes for four weeks, in which 2 h cycles of chronopotentiometry at 40 mA cm⁻² and subsequent 15-min rest periods at the open circuit potential (OCP) were repeated for four weeks in 4 mol dm⁻³ KOH solution. During the four weeks of durability test the specimen was polarized with total electric charge of 9x10⁴ C cm⁻². Figure 2a shows the potential–time curve of the OER durability test for four weeks indicating that the overpotentials for the OER increase by about 150 mV in the first 24 h of reaction, whereas the potential is maintained around 1.78 V vs. RHE after 24 h throughout the four weeks test. Figure 2b shows the LSV curves for the OER of the specimens subjected to long-term durability tests. To measure the LSV, the test cycles were suspended temporarily at the beginning of the rest period during different periods of time leading to polarization with a charge density of 0, 4x10², 3x10³, 4.5x10⁴, and 9x10⁴ C cm⁻². These results confirm that the OER activity of the CFCO catalysts persists for four weeks without the need for

carbon fillers at the onset potential region, proving the good durability of the CFCO catalysts for the OER in strongly alkaline conditions.

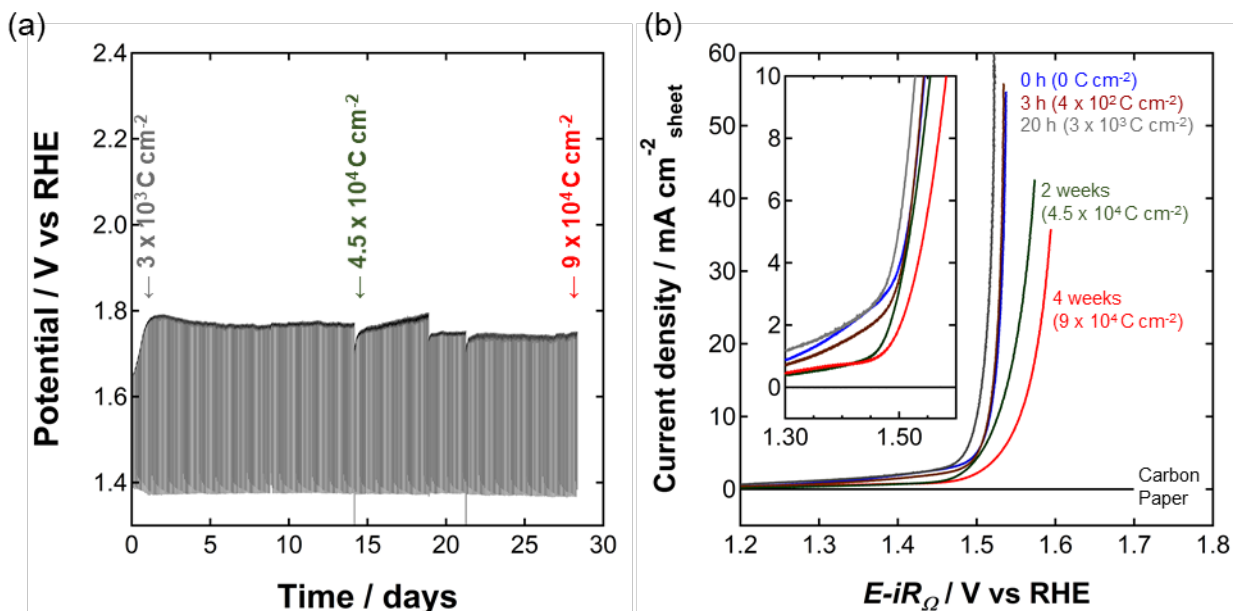


Figure 2. (a) Potential change of the AB/CFCO electrode during OER durability testing in aqueous 4 mol dm⁻³ KOH solution for four weeks leading to total electric charge of $\sim 10^5$ C cm⁻², (b) OER LSV curves obtained at 10 mV s⁻¹ for AB/CFCO polarized with electric charge of 0 - 9×10^4 C cm⁻². The AB/CFCO electrode was prepared by immersion of the carbon paper in the catalyst-ink solution; the LSVs were performed on carbon sheet electrode (0 RPM). Durability tests and OER measurements were carried out in the nitrogen-saturated electrolyte.

Figure 3 shows the XRD patterns of the AB/CFCO electrodes before and after the durability tests. A couple of diffraction peaks of a Brownmillerite-type phase are evident around 32° in the pattern of the electrode before the durability test, but these peaks disappeared after 3 h OER, confirming that the CFCO catalyst is transformed to an amorphous phase by OER.²³ Combining the results of electrochemical and XRD analysis, we determined that the amorphous phase derived from CFCO has well maintained electrocatalytic activity and durability.

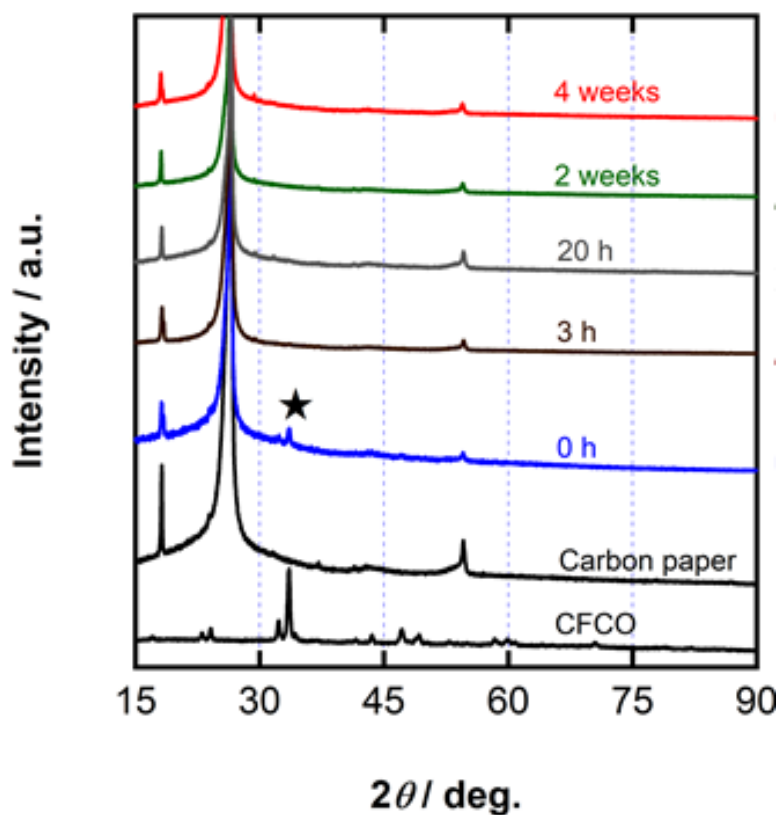


Figure 3. XRD patterns of AB/CFCO electrodes at various periods during OER durability test.

The star symbol indicates the Brownmillerite phase. 0h, 3h, 20h, 2 weeks, and 4 weeks of polarization are corresponding to a charge density of 0, 4×10^2 , 3×10^3 , 4.5×10^4 , and 9×10^4 C cm⁻², respectively.

Figure 4 shows backscattered-electron SEM images of the AB/CFCO electrodes after various periods of OER in the durability tests, in which the dark and bright particles are assigned to AB and CFCO, respectively. The SEM images of the electrodes before the durability test show agglomerates of 100-nm-sized CFCO nanoparticles embedded in the AB conductive filler (Fig. 4a). However, these AB fillers are depleted after 3 h of continuous OER (Fig. 4b), almost disappearing after 20 h (Fig. 4c). In addition, the Nafion binder film is bare at the surface of the specimens after 20 h (Figs. 4c–e). This could be attributed to the oxidative consumption of AB particles under OER potentials because carbon is electrochemically oxidized at potentials above 1.0 V vs. RHE in strongly alkaline media.²⁶⁻²⁹

The morphology of the CFCO particles changed greatly during OER, despite the stable catalytic performances (Fig. 2a). The as-prepared CFCO particles have a spherical shape with an average diameter of about 40 nm (Fig. 4a). These particles are apparently etched, and, thus, the surface was

roughened by the OER for 3 h (Fig. 4b), ultimately resulting in the formation of “skeletal” grains of 100-nm diameter after the OER for 20 h (Fig. 4c). Such skeletal grains tend to be connected to each other with increasing OER duration, coagulating into micrometer-sized agglomerates after four weeks OER (Figs. 4d and 4e).

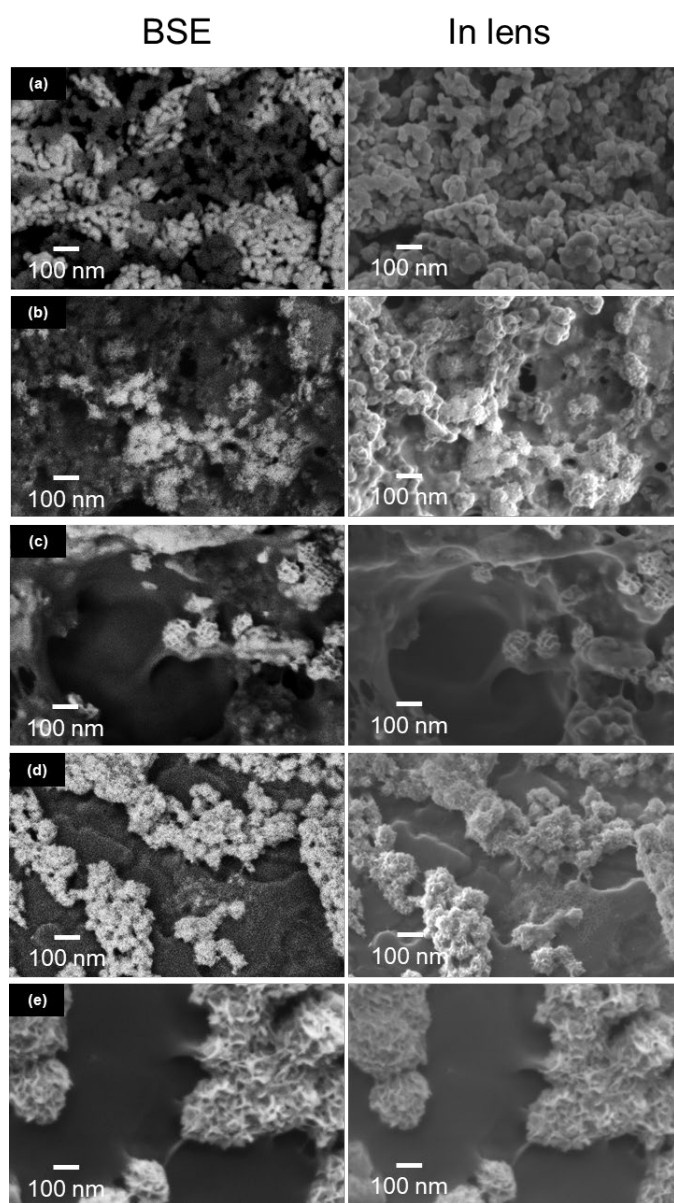


Figure 4. Backscattered-electron SEM images (left column) and In-lens SEM images (right column) of AB/CFCO electrodes at (a) 0 h, (b) 3 h, (c) 20 h, (d) 2 weeks, and (e) 4 weeks of OER durability tests. The SEM images were obtained at acceleration voltage of 1.5 kV.

The corresponding structural and compositional changes were further examined by using high-resolution transmission electron microscopy (HRTEM) and AES. Figure 5 shows the HRTEM images of CFCO before and after the durability tests. The as-prepared CFCO is a well-defined crystalline phase, showing clear lattice fringes identical to the (141) plane of the Brownmillerite structure (Fig. 5a). The crystalline structure is, however, deformed after 3 h of OER, resulting in the formation of an inhomogeneous amorphous phase, in which nanocrystalline domains (0.5–2 nm) of Brownmillerite residues, are dispersed in the amorphous matrices (Fig. 5b). Figure 5b shows the clear contrast of the oxide matrices, which can be attributed to the presence of pores on the particle surface. This feature is in agreement with the SEM observation for the etched surfaces of the catalyst particles (Fig. 4b). The HRTEM images of the CFCO after the OER for 2 weeks and 4 weeks show a mosaic-like pattern of the amorphous phase, as well as sub-nanometer sized crystalline domains with lattice spacings corresponding to the (003) planes (approx. 0.43 nm) of γ -CoOOH (Fig. 5d). EDS-TEM analysis of the 4 weeks OER specimen confirms that the molar ratio of Ca/Fe/Co is equal to 1/1.2/15 (Table 1), which confirms that most of the Ca and Fe cations

are leached out during the OER process. These results unequivocally prove that CFCO is converted to amorphous Co-based oxides (or oxyhydroxides), including a small fraction of the γ -CoOOH type crystalline moiety, by the OER catalytic process.

γ -CoOOH has a layered crystal structure^{30,31}, as shown in Fig. 5f, in which two-dimensional linkages of edge-shared CoO_6 octahedra form $[\text{CoO}_2]_n$ molecular layers, and the $[\text{CoO}_2]_n$ layers are orthogonally stacked via hydrogen bonding. Low-magnification TEM reveals that the skeletal grains of the catalysts are made of crumpled sheet-like materials after 4 weeks of OER (Fig. 5e), which suggests that the skeletal grains are aggregates of exfoliated CoOOH nanosheets.

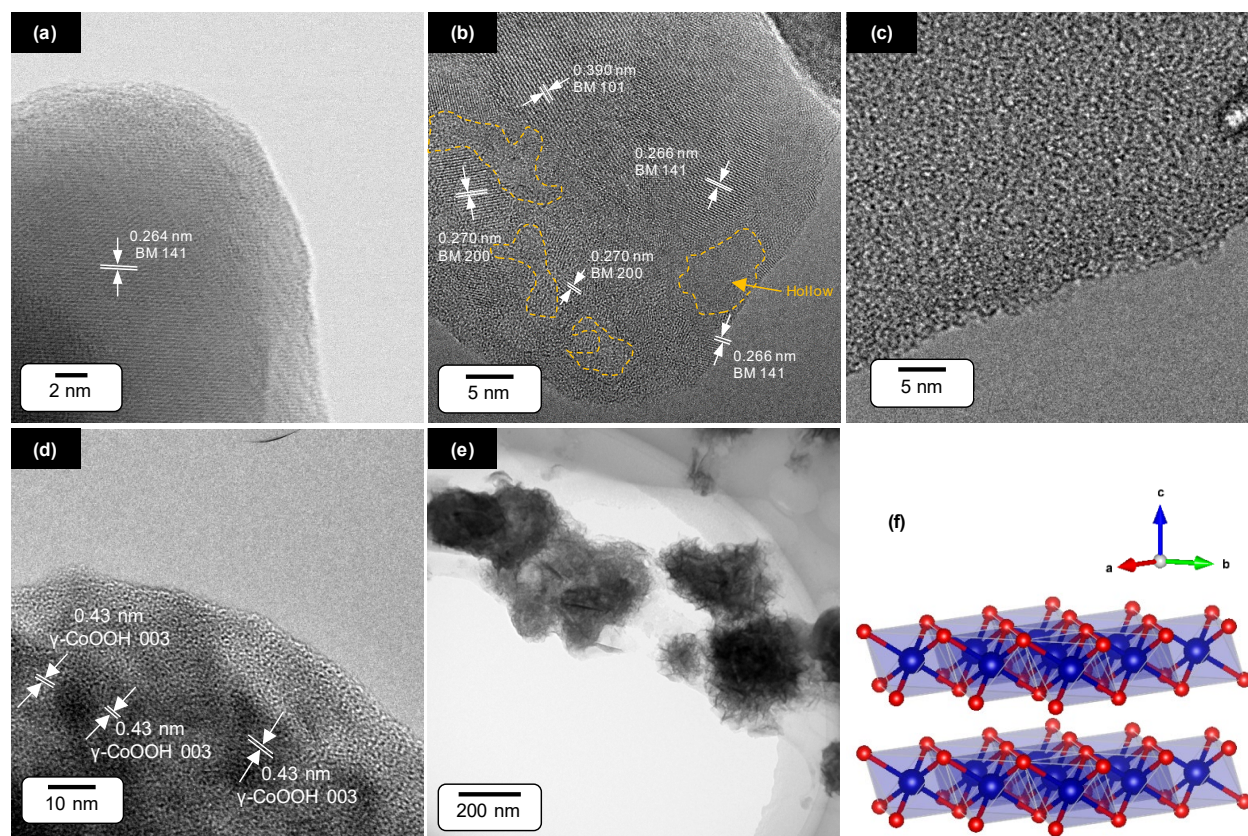


Figure 5. HRTEM images of CFCO at (a) 0 h, (b) 3 h, (c) 2 weeks, and (d) 4 weeks of OER durability test. (e) Low-magnification TEM images of the skeletal grains formed after 4 weeks of OER. (f) Crystal structure of layered γ -CoOOH. The hollow regions of CFCO after 3 h duration (Fig. 5b) were surrounded with the yellow dashed lines.

Table 1. EDS elemental analysis of CFCO after various periods of the OER durability tests.

	Co / at%	Ca / at%	Fe / at%
0 h	24.7	51.7	23.7
3 h	65.5	18.9	15.5
2 weeks	73.5	11.5	15.0
4 weeks	87.0	5.9	7.2

To determine the chemical composition of the amorphous phase more precisely, AES was carried out on a catalyst particle with an electron probe focused on a 10-nm diameter region. Figure 6 shows the differential Auger electron spectra for the AB/CFCO electrodes tested for different OER durations. In these spectra, the KLL transition peaks of C, Ca, O are evident at around 272, 300, and 505 eV, respectively. Fe yields LMM transition peaks at around 598, 651 and 703 eV,

and Co yields those at 656, 716, and 775 eV. Concerning Ca and C in the range of 250 to 300 eV (Fig. 6b), the relatively strong signal of Ca disappears, whereas the C signals remain unchanged after 3 h OER, confirming that most of Ca are leached out from CFCO catalyst during the OER. The very weak Fe signal observed at around 600 eV disappears after 3 h of continuous OER suggesting leaching of iron in the initial stage of durability test. The Fe signals overlapping with Co at 651 and 703 eV are present even after 4 weeks of OER (Fig. 6c) suggesting that a small amount of Fe remains in the catalyst after long term durability test.

Curve fitting analysis was performed for the AES spectra containing Fe and Co peaks from 350 to 800 eV. This curve fitting was used to determine the chemical composition of the catalysts. As shown in Fig. 6c, the Fe and Co signals are overlapped between 650 and 800 eV; thus, the deconvolution of these spectra was assisted by using the data for the standard peak shift database. The Ca/Co/Fe molar ratios are listed in Table 2. The Ca/Co/Fe ratio of the as-prepared CFCO equals 1.5/1/1, which is roughly in agreement with the value of the Brownmillerite phase. The Ca and Fe contents are significantly decreased by 3 h OER, and the Ca/Co/Fe molar ratios of the 4 weeks OER specimen are 0/1/10. In combination with the results of HRTEM measurements, it is unequivocally demonstrated that the catalytically active phase of the CFCO catalysts comprises Fe-modified Co oxides or oxyhydroxides.

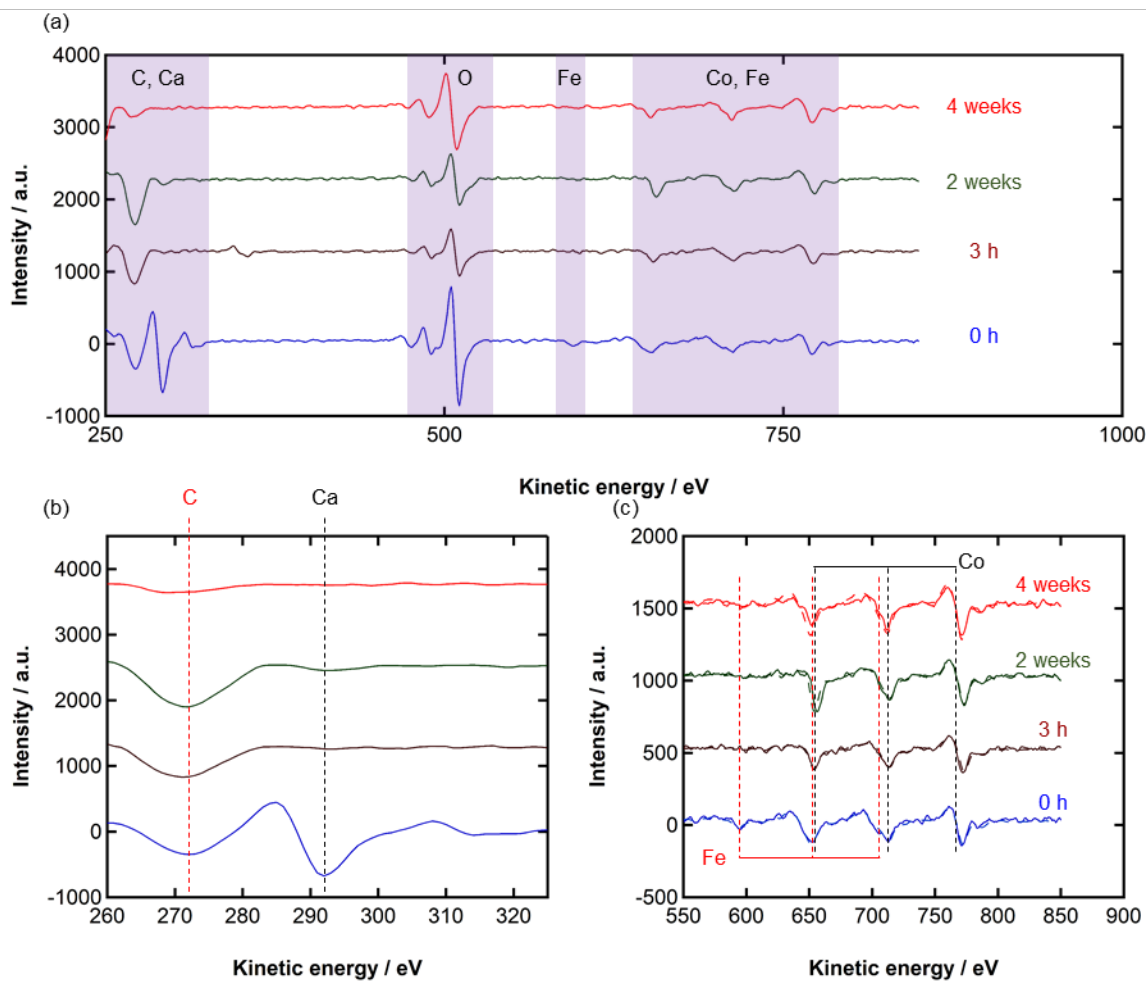


Figure 6. (a) AES spectra of CFCO submitted to OER durability tests for 0 h, 3 h, 2 weeks, and 4 weeks. (b) and (c) are the expansions of (a). In Fig. 6 (c), solid and dashed lines are the experimental and curve-fitted results, respectively.

Table 2. Chemical composition determined by curve fitting of AES spectra

Duration time of durability test	Co / at%	Ca / at%	Fe / at%
0 h	27.9	42.2	29.9
3 h	83.3	6.3	10.5
2 weeks	83.4	7.4	9.2
4 weeks	87.9	0.0	12.1

Finally, we examined the local coordination environment around Co and Fe atoms by EXAFS at the K-edge. Figure 7a shows the normalized adsorption Co K-edge XANES region for CFCO subjected to the OER for various periods. In the spectra, the CFCO samples do not show a systematic chemical shift of the Fe and Co absorption edges over the 4 weeks OER tests (insets of Figs. 7a and 7b), confirming that the oxidation states of both cations are not affected by the OER electrocatalytic process. The structure near the main absorption peak at around 7730 eV was changed significantly by 3 h OER and was not significantly modified by further increasing the OER duration, indicating that the amorphization of CFCO during OER slowed after a few hours, as observed by XRD. The EXAFS measurements provide a clear identification of the

electrocatalytically active phase of the CFCO catalysts, suggesting that the phase comprises Fe-modified cobalt oxyhydroxides with short range ordering in a γ -CoOOH-type arrangement.

The radial distribution functions (RDF) and related k -space oscillation profiles obtained from Fourier transform EXAFS of the Co K -edge are presented in Figs. 7c and 7e, respectively. For the as-prepared CFCO, a strong peak in the first coordination shell at around 1.0–2.0 Å can be attributed to the shortest Co-O bond, and broad features of the second and third coordination shells distributed in the range of 2.0–4.0 Å are assigned to coherence with Ca and Fe neighbors. As expected from the XRD and HRTEM results, the CFCO RDF is drastically changed after the OER. The 3 h OER specimens show a relatively sharp peak corresponding to the second coordination shell in the region of 2.0–3.0 Å compared to that of the as-prepared sample, together with a strong peak for the first Co-O coordination shell in the region of 1.2–2.0 Å. This feature provides clear evidence for the locally ordered structures of the amorphous CFCO catalysts. The Fe- K RDF is similar to the Co- K RDF: the OER results in a strong peak corresponding to the second coordination shell, probably because of the Fe-Co or Fe-Fe separation of 2.7 Å in addition to the first Fe-O coordination shell having a separation of 1.5 Å (Figs. 7d and 7f).

The curve fitting analysis of the first and second coordination shells was carried out for CFCO after 3 h, 2 weeks, and 4 weeks of continuous OER by using the atomic coordinates for the γ -

CoOOH phase.³¹ The fitting was conducted for k -space oscillation profiles weighted by k^3 (k : wave number), and the calculated k -space oscillation replicates the observed profile well; thus, the calculated RDF also fits the observed data well (Figs. 7c–f). The fitting parameters are summarized in Table S1. As for Co, the EXAFS profiles around Fe atoms also replicated the γ -CoOOH structural model very well; however, the spinel-type Fe₃O₄ structure was not adopted, which is a clear suggestion of the formation of Fe and Co mixed oxyhydroxide phase with a γ -CoOOH like local coordination environment. The coordination number (CN) of Co-O is not dependent on the duration of the OER, but the CN of the Co-Co or Co-Fe second coordination shells decreased with increasing OER duration. This result implies that Fe-substitution of Co is increased so that the symmetry of second coordination sphere decreased with increasing OER duration. Notably, in the EXAFS spectra the Co and Fe in the aged materials seem very different. The Debye-Waller factor for Fe case (Table S1) is relatively large after one month of polarization, which means that symmetry of the second shell is very low. Taking the above into the consideration one may consider that the fraction of iron is doped, and other fraction may exist in low symmetric phase, e.g. as precipitate. It is, however, difficult to distinguish both cases from existing EXAFS data.

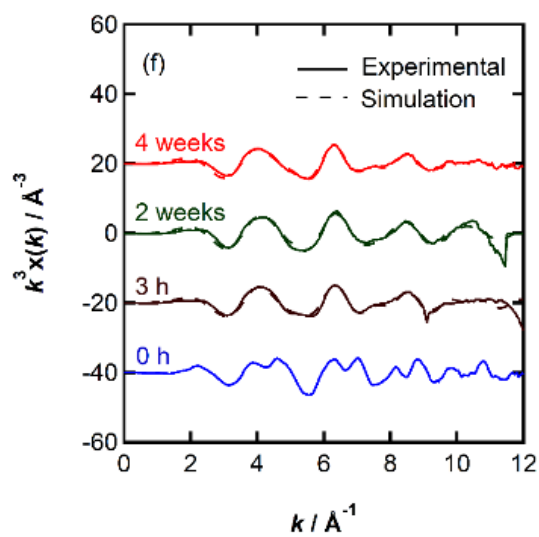
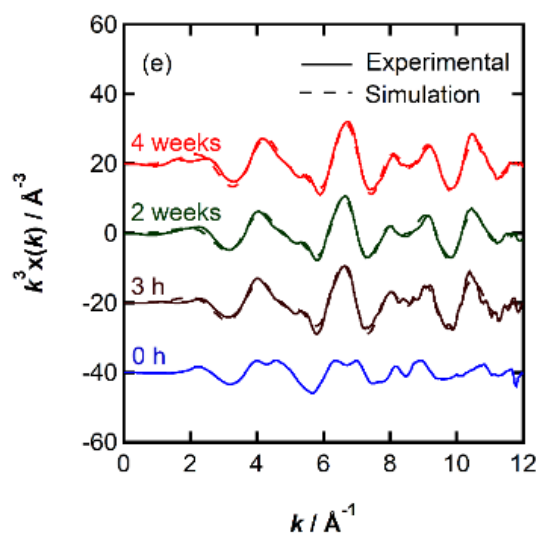
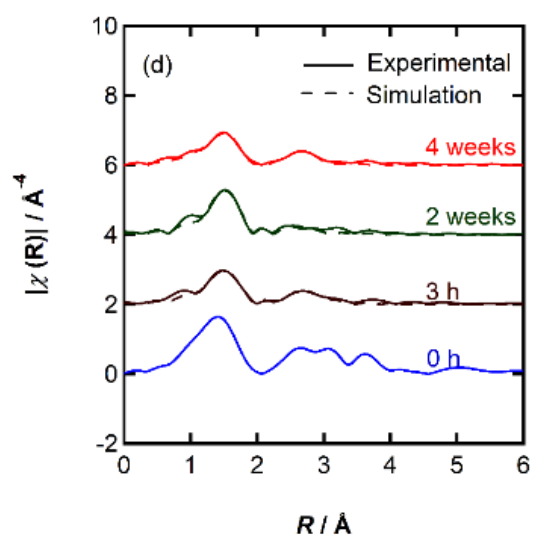
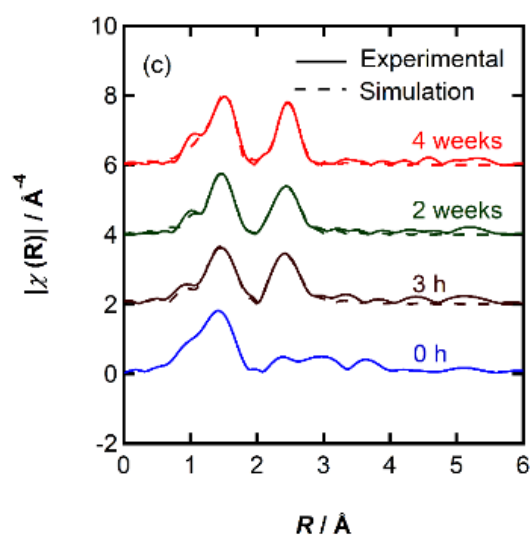
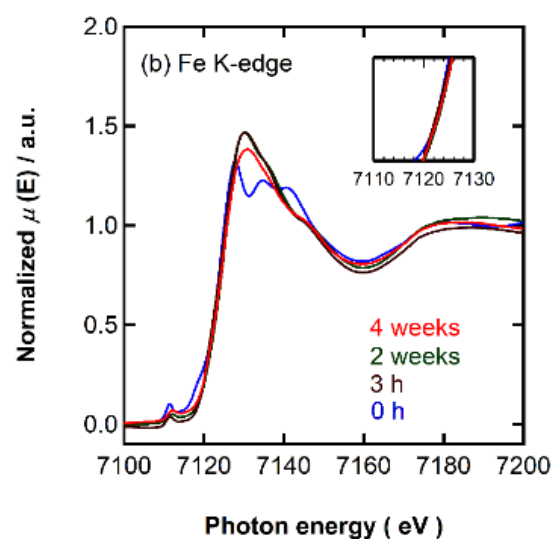
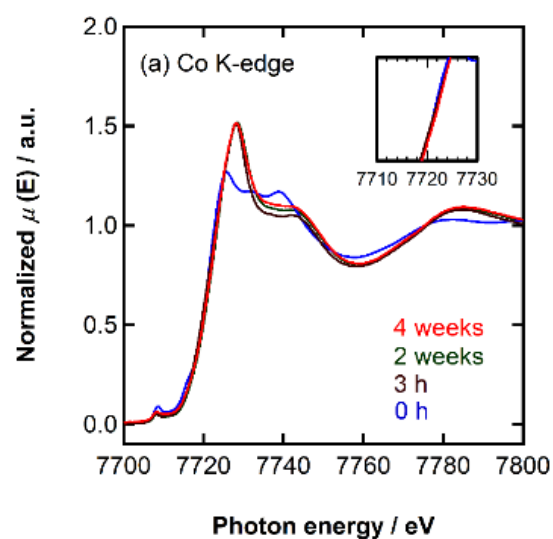


Figure 7. (a) Co and (b) Fe K-edge XANES of CFCO at various periods of the OER durability tests. Radial distribution function around Co (c) and Fe atoms (d) obtained by Fourier transforming the EXAFS profiles and related curve fitting to the first (M-O; M = Co or Fe) and second coordination shells (M-M). *k*-Space oscillation profile around Co (e) and Fe (f) atoms and related optimal fitting curves. (c)–(f) Continuous and dashed lines are the observed and curve-fitted results, respectively.

4. DISCUSSION

Based on our reported results, we concluded that Brownmillerite-type CFCO is modified *in situ* into a catalytically active phase of amorphous Co oxyhydroxides with 10 mol% Fe substitution during the OER process. In the initial stage of the deformation (ca. 3 h), the CFCO particles are etched by extensive dissolution of Ca and Fe cations under OER conditions, thus becoming porous particles (Fig. 4b). Because the leaching of Ca and Fe is accelerated by the porous surface, the amorphization of Brownmillerite-type CFCO proceeds because of the reduced diffusion length; thus, the bulk amorphization and elemental dissolution decay within a few hours, even at room temperature (Fig. 6 and Table 2). As a result of the structural deformation, the morphology of the catalyst particles changes to skeletal grains after 20 h of OER (Fig. 4c) and the grains coagulate to

micrometer-sized agglomerates after further OER (Figs. 4d and 4e), possibly driven by the applied electric field³² or mechanical stress leading to cracking due to the metal cation dissolution³³.

After carrying out the OER for longer than 3 h, the phase becomes X-ray amorphous, and the samples obtained after OER for more than 2 weeks contain mainly amorphous phases, as checked by HRTEM (Figs. 5c and 5d). Meanwhile, EXAFS measurements reveal that local coordination environments around both Fe and Co atoms are similar to those of the γ -CoOOH-type structure, which is based on a two-dimensional network of edge-shared CoO₆ octahedra (Fig. 5f). TEM measurements show the nanosheet like microstructures of the skeletal grains in the 4 weeks OER specimen. These results indicate that the OER active phase of CFCO catalysts comprises aggregates of randomly stacked (Co, Fe)OOH nanosheets. Thus, the amorphous Fe-modified cobalt oxyhydroxides derived from Brownmillerite-type CFCO are promising OER catalysts with good electrocatalytic activity and long-term durability under strongly alkaline conditions.

The *in situ* formation of an OER electrocatalytically active CoOOH phase has been also reported in other systems.³²⁻⁴¹ Zhou et al. reported that catalysts based on the simple Prussian blue analog Na_xCoFe(CN)₆ form a CoOOH active phase with the replacement of oxygen vacancies by the hydroxyl groups driven by an applied electric field.³² Kanan et al. reported that the amorphous cobalt phosphate precipitates formed by the electrolysis in potassium phosphate solution show

pronounced OER activity in neutral media.³⁴ In this case, the active phase has been assigned to γ -CoOOH clusters embedded in phosphate glass matrices by Yoshida et al.³⁵ Enman et al. found that Fe species in CoOOH avoid the oxidation of Co species and proposed the different OER mechanism in CoOOH and Fe-doped CoOOH.³⁶ Most of the above-mentioned studies show that catalyst might undergo modification through clusters formation and/or surface modification under standard OER conditions. Herein, we extended the durability studies to one month leading to polarization of the catalyst with total electric charge of the order of $\sim 10^5$ C cm⁻². Such extended studies lead to structural changes that would not be simply noticeable in classic LSV/CV polarization, and therefore might be helpful to understand the actual phases which are responsible for true catalytic activity of some catalysts, such as Brownmillerite-type and Perovskites.

5. CONCLUSIONS

We have demonstrated the structural and chemical changes of an OER catalyst (Ca₂FeCoO₅) in the OER environment in highly concentrated alkaline solution. The CFCO particles change to skeletal grains of Fe-modified CoOOH nanosheet aggregates through the dissolution of Ca and Fe cations. The resultant oxyhydroxides show enhanced OER activity and long-term stability under strongly alkaline conditions and, thus, retain catalytic performance for continuous OER over one month.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Figure S1 shows the XRD patterns of synthesized CFCO and its precursor; Figure S2 shows the cyclic voltammograms of CFCO during the potential windows; Figure S3 shows the LSV curves before and after the durability test; Figure S4 shows the EDS mapping results of AB/CFCO electrode at fourth week of OER durability tests. ; Table S1 with EXAFS fitting parameters for each samples (PDF).

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REFERENCES

- (1) McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F., Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction, *J. Am. Chem. Soc.*, **2013**, *135*, 16977-16987.
- (2) Ouyang, C.; Wang, X.; Wang, C.; Zhang, X.; Wu, J.; Ma, Z.; Dou, S.; Wang, S., Hierarchically Porous Ni₃S₂ Nanorod Array Foam as Highly Efficient Electrocatalyst for Hydrogen Evolution Reaction and Oxygen Evolution Reaction, *Electrochim. Acta*, **2015**, *174*, 297-301.
- (3) Liu, T.; Liang, Y.; Liu, Q.; Sun, X.; He, Y.; Asiri, A. M., Electrodeposition of cobalt-sulfide nanosheets film as an efficient electrocatalyst for oxygen evolution reaction, *Electrochem. Commun.*, **2015**, *60*, 92-96.
- (4) Man, I. C.; Su, H. Y.; Calle-Vallejo, F.; Hansen, H. A.; Martinez, J. I.; Inoglu, N. G.; Kitchin, J.; Jaramillo, T. F.; Nørskov, J. K.; Rossmeisl, J.; Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces, *ChemCatchem*, **2011**, *3*, 1159-1165.
- (5) Yang, W.; Salim, J.; Ma, C.; Ma, Z.; Sun, C.; Li, J.; Chen, L.; Kim, Y.; Flowerlike Co₃O₄ microspheres loaded with copper nanoparticle as an efficient bifunctional catalyst for lithium–air batteries, *Electrochem. Commun.*, **2013**, *28*, 13-16.

- (6) Li, Y. ; Gong, M.; Liang, Y.; Feng, J.; Kim, J. E.; Wang, H.; Hong, G.; Zhang, B.; Dai, H., Advanced zinc-air batteries based on high-performance hybrid electrocatalysts, *Nature Commun.*, **2013**, 4, 1805 (2013).
- (7) Amiin, I. S.; Liu, X.; Pu, Z.; Li, W.; Zhang, J.; Tang, H.; Zhang, H.; Mu, S., From 3D ZIF Nanocrystals to Co-N_x/C Nanorod Array Electrocatalysts for ORR, OER, and Zn-Air Batteries, *Adv. Funct. Mater.*, **2018**, 28, 1704638.
- (8) Hang, Y.; Zhang, C.; Luo, X.; Xie, Y.; Xin, S.; Li, Y.; Zhang, D.; Goodenough, J. B., α -MnO₂ nanorods supported on porous graphitic carbon nitride as efficient electrocatalysts for lithium-air batteries, *J. Power Sources.*, **2018**, 392, 15-22.
- (9) Zhang, F.; Wei, M.; Sui, J.; Jin, C.; Luo, Y.; Bie, S.; Yang, R., Cobalt phosphide microsphere as an efficient bifunctional oxygen catalyst for Li-air batteries, *J. Alloy. Compd.*, **2018**, 750, 655-658.
- (10) Sun, C.; Li, F.; Ma, C.; Wang, Y.; Ren, Y.; Yang, W.; Ma, Z.; Li, J.; Chan, Y.; Kim, Y.; Chen, L., Graphene-Co₃O₄ nanocomposite as an efficient bifunctional catalyst for lithium-air batteries, *J. Mater. Chem. A*, **2014**, 2, 7188-7196.

- (11) Kim, T. W.; Choi, K. S., Nanoporous BiVO₄ Photoanodes with Dual-Layer Oxygen Evolution Catalysts for Solar Water Splitting, *Science*, **2014**, *14*, 1246913.
- (12) Hisatomi, T.; Kubota, J.; Domen, K.; Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting, *Chem. Soc. Rev.*, **2014**, *43*, 7520-7535.
- (13) Liu, Y.; Wei, C.; Ngaw, K.; Zhou, Y.; Sun, S.; Xi, S.; Du, Y.; Loo, J. S. C.; Ager, J. W. III.; Xu, Z. J., Operando Investigation of Mn₃O_{4+δ} Co-catalyst on Fe₂O₃ Photoanode: Manganese-Valency-Determined Enhancement at Varied Potentials, *ACS Appl. Energy Mater.*, **2018**, *1*, 814-821.
- (14) Tahir, M., Pan. F. Idrees, L.; Zhang, X.; Wang, L.; Zou, J. J.; Wang, Z. L., Electrocatalytic oxygen evolution reaction for energy conversion and storage: A comprehensive review, *Nano Energy*, **2017**, *37*, 136-157.
- (15) Tsuji, E.; Imanishi, A.; Fukui, K. I.; Nakato, Y., Electrocatalytic activity of amorphous RuO₂ electrode for oxygen evolution in an aqueous solution, *Electrochim. Acta*, **2011**, *56*, 2009-2016.
- (16) Yagi, M.; Tomita, E.; Kuwabara, Remarkably high activity of electrodeposited IrO₂ film for electrocatalytic water oxidation, *J. Electroanalytical. Chem.*, **2005**, *579*, 83-88.

- (17) Risch, M.; Stoerzinger, K. A.; Maruyama, S.; Hong, W.T.; Takeuchi, I.; Horn, Y. S.;
La_{0.8}Sr_{0.2}MnO_{3-δ} Decorated with Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}: A Bifunctional Surface for Oxygen
Electrocatalysis with Enhanced Stability and Activity, *J. Am. Chem. Soc.*, **2014**, *136*, 5229-
5232.
- (18) Long, X.; Li, J.; Xiao, S.; Yan, K.; Wang, Z.; Chan, H.; Yang, S., A Strongly Coupled
Graphene and FeNi Double Hydroxide Hybrid as an Excellent Electrocatalyst for the Oxygen
Evolution Reaction, *Angew. Chem. Int. Ed.*, **2014**, *126*, 7714-7718.
- (19) Liu, X.; Jia, H.; Sun, Z.; Chen, H.; Xu, P.; Du, P., Nanostructured copper oxide
electrodeposited from copper(II) complexes as an active catalyst for electrocatalytic oxygen
evolution reaction, *Electrochem. Commun.*, **2014**, *46*, 1-4.
- (20) Sagu, J. S.; Mehta, D.; Wijayantha, K. G. U., Electrocatalytic activity of CoFe₂O₄ thin films
prepared by AACVD towards the oxygen evolution reaction in alkaline media, *Electrochem.*
Commun., **2018**, *87*, 1-4 (2018).
- (21) Guo, M.; Xu, K.; Qu, Y.; Zeng, F.; Yuan, C., Porous Co₃O₄/CoS₂ nanosheet-assembled
hierarchical microspheres as superior electrocatalyst towards oxygen evolution reaction,
Electrochim. Acta, **2018**, *268*, 10-19.

- (22) Tsuji, E.; Motohashi, T.; Noda, H.; Kowalski, D.; Aoki, Y.; Tanida, H.; Nikura, J.; Koyama, Y.; Mori, M.; Arai, H.; Ioroi, T.; Fujiwara, N.; Uchimoto, Y.; Ogumi, Z.; Habazaki, H., Brownmillerite-type $\text{Ca}_2\text{FeCoO}_5$ as a Practicable Oxygen Evolution Reaction Catalyst, *ChemSusChem*, **2017**, *10*, 2864-2868.
- (23) Kowalski, D.; Kiuchi, H.; Motohashi, T.; Aoki, Y.; Habazaki, H., Activation of Catalytically Active Edge-Sharing Domains in $\text{Ca}_2\text{FeCoO}_5$ for Oxygen Evolution Reaction in Highly Alkaline Media, *ACS Appl. Mater. Interfaces*, **2019**, *11*, 28823-28829.
- (24) Grimaud, A.; May, K. J.; Carlton, C. E.; Lee, Y. L.; Risch, M.; Hong, W. T.; Zhou, J.; Horn, Y. S., Double perovskites as a family of highly active catalysts for oxygen evolution in alkaline solution, *Nature Commun.*, **2013**, *4*, 2439.
- (25) Cascos, V.; Martínez-Coronado, R.; Alonso, J. A.; Fernández-Díaz, M. T., Structural and electrical characterization of the Co-doped $\text{Ca}_2\text{Fe}_2\text{O}_5$ brownmillerite: Evaluation as SOFC - cathode materials, *Int. J. Hydrogen Energy*, **2015**, *40*, 5456-5468.
- (26) Sato, Y., Kowalski, D., Aoki, Y.; Habazaki, H., Long-term durability of the platelet type carbon nanofibers for OER and ORR in highly alkaline media, *Applied Catalyst A: General*, **2020**, *597*, 117555

- (27) Ono, K.; Kinumoto, T.; Tsumura, T.; Toyoda, M., Preparation of LaMnO₃-CNF and Its Activity for Oxygen Electrode Reaction in 0.1 mol dm⁻³ KOH Solution, *ECS Trans.*, **2015**, *64*, 29-39.
- (28) Pourbaix, M., Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE, Houston, **1966**.
- (29) Staud, N.; Sokol, H.; Ross, P. N. Jr., “The Corrosion of Carbon Black Anodes in Alkaline Electrolyte IV. Current Efficiencies for Oxygen Evolution from Metal Oxide-Impregnated Graphitized Furnace Blacks”, *J. Electrochem. Soc.*, **1989**, *136*, 3570-3576.
- (30) Momma, K.; Izumi, F., VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, *J. Appl. Crystallogr.*, **2011**, *44*, 1272-1276.
- (31) Delaplane, R. G.; Ibers, J. A.; Ferraro, J. R.; Rush, J. J., Diffraction and Spectroscopic Studies of Cobaltic Acid System HCoO₂-DCoO₂. *J. Chem. Phys.*, **1969**, *50*, 1920-1927.
- (32) Zhou, J.; Wang, Y.; Su, X.; Gu, S.; Liu, R.; Huang, Y.; Yan, S.; Li, J.; Zhang, S.; Electrochemically accessing ultrathin Co (oxy)-hydroxide nanosheets and operando identifying their active phase for the oxygen evolution reaction, *Energy Environ. Sci.*, **2019**, *12*, 739-746.

- (33) Dette, C.; Hurst, M. R.; Deng, J.; Nellist, M. R.; Boettcher, S. W.; Structural Evolution of Metal (Oxy)hydroxide Nanosheets during the Oxygen Evolution Reaction, *ACS Appl. Mater. Interfaces*, **2018**, *11*, 5590-5594.
- (34) Kanan, M. W.; Nocera, D. G., In situ formation of an oxygen-evolving catalyst in neutral water containing phosphate and Co^{2+} , *Science*, **2008**, *22*, 1072-1075.
- (35) Yoshida, M.; Mineo, T.; Mitsutomi, Y.; Yamamoto, F.; Kurosu, H.; Takakusagi, S.; Asakura, K.; Kondoh, H.; Structural Relationship between CoO_6 Cluster and Phosphate Species in a CobaltPhosphate Water Oxidation Catalyst Investigated by Co and P K-edge XAFS, *Chem. Lett*, **2016**, *45*, 277-279.
- (36) Enman, L. J.; Stevens, M. B.; Dahan, M. H.; Nellist, M. R.; Toroker, M. C.; Boettcher, S. W.; Operando X-Ray Absorption Spectroscopy Shows Iron Oxidation Is Concurrent with Oxygen Evolution in Cobalt–Iron (Oxy)hydroxide Electrocatalysts. *Angew. Chem., Int. Ed.*, **2018**, *57* (39), 12840-12844.
- (37) Chang, Z.; Li, H.; Tang, H.; Yuan, X. Z.; Wang, H., Synthesis of $\gamma\text{-CoOOH}$ and its effects on the positive electrodes of nickel batteries, *Int. J. Hydrogen Energy*, **2009**, *34*, 2435-2439.

- (38) Yin, H.; Tang, Z., Ultrathin two-dimensional layered metal hydroxides: an emerging platform for advanced catalysis, energy conversion and storage, *Chem. Soc. Rev.*, **2016**, *45*, 4873.
- (39) Risch, M.; Grimaud, A.; May, K. J.; Stoerzinger, K. A.; Chen, T. J.; Mansour, A. N.; Horn, Y. S., Structural Changes of Cobalt-Based Perovskites upon Water Oxidation Investigated by EXAFS, *J. Phys. Chem. C*, **2013**, *117*, 8628-8635 (2013).
- (40) Ye, S. H.; Shi, Z. X.; Feng, J. X.; Tong, Y. X.; Li, G. R., Activating CoOOH Porous Nanosheet Arrays by Partial Iron Substitution for Efficient Oxygen Evolution Reaction, *Angew. Chem. Int. Ed.*, **2018**, *57*, 2672-2676.
- (41) Huang, J.; Chen, J.; Yao, T.; He, J.; Jiang, S.; Sun, Z.; Liu, Q.; Cheng, W.; Hu, F.; Jiang, Y.; Pan, Z.; Wei, S., CoOOH Nanosheets with High Mass Activity for Water Oxidation, *Angew. Chem. Int. Ed.*, **2015**, *54*, 8722-8727.