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Complete List of Authors:	Okada, Hiroyuki; Tottori University, Center for Research on Green Sustainable Chemistry Tsuji, Etsushi; Tottori University, Center for Research on Green Sustainable Chemistry Hisada, Miho; Tottori University, Center for Research on Green Sustainable Chemistry Kitano, Sho; Hokkaido University, Faculty of Engineering Habazaki, Hiroki; Hokkaido University, Faculty of Engineering Suganuma, Satoshi; Tottori University, Center for Research on Green Sustainable Chemistry Katada, Naonobu; Tottori University, Center for Research on Green Sustainable Chemistry			



# ARTICLE

# Brownmillerite-type Ca<sub>2</sub>Fe<sub>0.75</sub>Co<sub>1.25</sub>O<sub>5</sub> as a Robust Electrocatalyst for Oxygen Evolution Reaction in Neutral Conditions

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Hiroyuki Okada,<sup>a</sup> Etsushi Tsuji,\*<sup>a</sup> Miho Hisada,<sup>a</sup> Sho Kitano,<sup>b</sup> Hiroki Habazaki, <sup>b</sup> Satoshi Suganuma,<sup>a</sup> and Naonobu Katada<sup>a</sup>

Towards development of active and robust electrocatalysts for oxygen evolution reaction (OER) to realize water splitting and CO<sub>2</sub> electroreduction by natural energies in practical conditions, brownmillerite-type composite oxide Ca<sub>2</sub>Fe<sub>2-x</sub>Co<sub>x</sub>O<sub>5</sub> was synthesized by a sol-gel method and examined for OER in neutral conditions. Pure brownmillerite-type Ca<sub>2</sub>Fe<sub>2-x</sub>Co<sub>x</sub>O<sub>5</sub> phase, which was categorized as an oxygen-deficiency-ordered perovskite-type structure, was synthesized in a range of x = 0-1.25. Brownmillerite-type Ca<sub>2</sub>FeCoO<sub>5</sub> showed higher activity and durability for OER in a neutral solution than perovskite-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>3-6</sub>. Furthermore, durability of Ca<sub>2</sub>Fe<sub>2-x</sub>Co<sub>x</sub>O<sub>5</sub> was drastically improved by increasing Co contents from x = 1 to 1.25. Ca<sub>2</sub>Fe<sub>0.75</sub>CO<sub>1.25</sub>O<sub>5</sub> was remarkably durable for about 70 h during OER in the neutral solution where Ca<sub>2</sub>FeCoO<sub>5</sub> lost the activity within 20 h, and perovskite-type oxides lost within a few hours. The detailed analysis of structures and compositions of local regions of Ca<sub>2</sub>Fe<sub>2-x</sub>Co<sub>x</sub>O<sub>5</sub> and their changes by the reaction based on the electron microscopy clarified that important role of brownmillerite structure itself for the catalytic activity in neutral conditions, while, in alkaline conditions, it has been known that amorphous phase derived from the brownmillerite mainly played a role of active species.

#### ARTICLE

# 1. Introduction

The depletion of fossil resources and the progress of global warming have motivated us to accelerate research and development of petroleum alternative energy and clean chemical feed stocks. Both water splitting for  $H_2$  production<sup>1-5</sup> and  $CO_2$  electroreduction for CO, HCOOH and  $CH_3OH^{6-9}$ production using renewable energy are essential reactions for zero-carbon emission. Oxygen evolution reaction (OER) from water is the counter reaction of these reduction reactions in aqueous solutions. OER is generally slow and one of the bottlenecks because it requires multi-electrons transfer,<sup>10-12</sup> leading to large overpotential even at low current density. A number of results have been reported on electrocatalysis for the OER in alkaline conditions, because the OER readily progresses on transition metal oxide catalysts in alkaline electrolytes. However, alkaline water splitting, i.e., water splitting in a basic medium, can be applied to limited fields due to corrosion of equipment and production of environmentallyimpacting waste.<sup>13,14</sup> Thereby potential technology for water splitting in near-neutral pH range is demanded. Use of neutral solutions are also preferable for the CO<sub>2</sub> reduction to avoid from the formation of carbonate in a basic medium.<sup>15</sup> Thus, it is demanded to find active OER catalysts in neutral conditions, even though OER rate in neutral solutions is generally slow due to the low water capacity of the solid surfaces.<sup>16</sup>

Perovskite (PV)-type composite oxides ABO<sub>3</sub>, where A is a rare-earth or alkaline-earth metal, and B is a transition metal, is one of the most deeply investigated electrocatalysts for OER, especially in alkaline conditions. Suntivich et al. have reported that PV-type oxides with  $e_g^1$  electron occupation, for example  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$  and  $La_{0.5}Ca_{0.5}CO_{3-\delta}$ , showed higher catalytic activity for the OER in oxygen-saturated 0.1 mol dm<sup>-3</sup> KOH aqueous solution.<sup>17</sup> They have also reported the OER activity and durability of the PV oxides in neutral conditions.<sup>18</sup> Such a PV-type oxide as  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$  having an  $e_g$  occupancy close to unity or having an O p-band center close to Fermi level showed relatively high activity not only in alkaline conditions but also in neutral conditions. However, leaching of A-site atoms and surface amorphization during OER in the neutral solution resulted in low durability.<sup>18</sup>

Meanwhile, PV-derived composite oxides such as Ruddlesden-Popper,<sup>19,20</sup> doubleperovskite,<sup>21–23</sup> quadrupleperovskite<sup>24–26</sup> and brownmillerite (hereafter BM)-type<sup>27–32</sup> oxides are also known to be active OER catalysts in alkaline conditions. We found that the OER activity of BM-type Ca<sub>2</sub>FeCoO<sub>5</sub>, which has an oxygen-deficiency-ordered PV-type structure containing a layered arrangement of tetrahedral and octahedral sites, was higher than those of PV-type Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3- $\delta$ </sub> and RuO<sub>2</sub>.<sup>27</sup> In this case, the details in structural change have been clarified, and it was not simple;

# Ca<sub>2</sub>FeCoO<sub>5</sub> was amorphized during OER after leaching of Ca in 4 mol dm<sup>-3</sup> KOH aqueous solution, and finally Fe-containing γ-CoOOH as an active species was formed.<sup>32,33</sup> On the other hand, in the case of neutral conditions, we recently revealed that BMtype $Ca_2FeCoO_5$ acted as an active OER co-catalyst, whose activity was comparable to RuO<sub>2</sub>, on anatase-TiO<sub>2</sub> nanoparticles<sup>34</sup> and WO<sub>3</sub> electrode<sup>35</sup> for photo- and photoelectrochemical OER from water, even though the Fecontaining γ-CoOOH was not formed during the photoreactions. Zhou et al. reported higher OER activity of Sr<sub>2</sub>GaCoO<sub>5</sub> with BM structure than those on PV-type LaCoO<sub>3</sub>, and clarified the advantage of BM-type structure for OER in a neutral solution.<sup>15</sup> The octahedral Co<sup>3+</sup> site as the active site in BM-type Sr<sub>2</sub>GaCoO<sub>5</sub> possessed intermediate spin arrangement $(t_{2g}^5 e_g^1)$ , whereas that in PV-type $LaCoO_3$ was low spin ( $t_{2g}^6 e_g^0$ ). This electronic state of Co<sup>3+</sup> enhanced the OER activity in neutral conditions. Furthermore, Sr<sub>2</sub>GaCoO<sub>5</sub> was observed to be durable since it contained gallium at B site, and gallium oxide is durable in the neutral pH region. Therefore, it is expected that brownmillerite $Ca_2Fe_{2-x}Co_xO_5$ shows high performance and durability for the electrochemical OER in neutral conditions.

In this study, the electrocatalytic activity and durability of brownmillerite-type  $Ca_2Fe_{2-x}Co_xO_5$  with  $0 \le x \le 1.25$  for the OER in neutral conditions were investigated. Structure and chemical composition of the catalysts before and after the OER were analysed by high resolution scanning and transmission electron microscopes equipped with energy dispersive spectrometer. We finally found that  $Ca_2Fe_{0.75}Co_{1.25}O_5$  possessed high activity and marked durability for about 70 h during the OER in neutral conditions.

# 2. Experimental

#### 2.1. Synthesis of brownmillerite-type oxide

 $Ca_2Fe_{2-x}Co_xO_5$  ( $0 \le x \le 1.5$ ) was synthesized by a citric acid sol-gel method.<sup>27,35</sup> Ca(NO<sub>3</sub>)<sub>2</sub>•4H<sub>2</sub>O (FUJIFILM Wako Pure Chemical Corp., 98.5%), Fe(NO<sub>3</sub>)<sub>3</sub>•9H<sub>2</sub>O (FUJIFILM Wako Pure Chemical Corp., 99.0%), Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>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 Ca : Fe : Co : citric acid molar ratio = 2: 2-x: x: 4, where x was varied in a range of 0-1.5. The obtained solution was stirred and heated at 363 K to promote polymerization. The products were heated at 0.17 K s<sup>-1</sup> 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, reheated at 0.17 K s<sup>-1</sup> up to 1073 K and calcined at 1073 K for 6 h in air. The calcined products were ground for 30 min in a mortar. The final products were denoted as CFCO-x ( $0 \le x \le 1.5$ ).

For comparisons, PV-type LaFe\_{0.5}Co\_{0.5}O\_3 and SrFe\_{0.5}Co\_{0.5}O\_{3-\delta} were synthesized by a conventional sol-gel method as described in Supplementary Information.

# 2.2. Catalyst ink preparation

A commercial acetylene carbon black (AB) powder (STREM Chemicals, Inc.) was immersed in concentrated nitric acid

<sup>&</sup>lt;sup>a.</sup> Center for Research on Green Sustainable Chemistry, Tottori University, Tottori 680-8552, Japan.

<sup>&</sup>lt;sup>b.</sup> Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan.

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(FUJIFILM Wako Pure Chemical Corp., 69%) at 353 K overnight, then centrifugated and washed until neutralized by ionexchanged water. The Na<sup>+</sup>-exchanged Nafion<sup>®</sup> solution was obtained by mixing a 5 wt% Nafion<sup>®</sup> solution (FUJIFILM Wako Pure Chemical Corp., DE521 CS type) with an appropriate amount of 0.1 mol dm<sup>-3</sup> NaOH aq. A catalyst ink was prepared as follows. 50 mg of the oxide powders, 10 mg of the AB treated by nitric acid as above, and 0.3 mL of 5 wt% Na<sup>+</sup>-exchanged Nafion<sup>®</sup> solution were mixed in 4.7 mL ethanol. The suspension was sonicated for at least 1 h to obtain a homogenous catalyst ink.

### 2.3. Characterization

Crystallinity of all samples were identified by X-ray powder diffraction (XRD; Rigaku, Ultima IV) using Cu Kα radiation with some pieces of small Cu foil for calibration of diffraction angle. The morphology and chemical composition were observed using a scanning electron microscope with energy dispersive spectrometer (SEM-EDS; HITACHI S-4800) operated at 5 kV (SEM mode) or at 15 kV (EDS mode). Crystallinity and chemical composition in near the surface were investigated after dropcasting of catalyst ink (the details of drop-casting are shown in next paragraph) by Cs-corrected scanning and transmission electron microscope with EDS (S/TEM-EDS; Titan3 G2 60-300, FEI Co.) at 300 kV.

#### 2.4. Electrochemical measurements for OER activity test

Working electrode was prepared by drop-casting of the catalyst ink on a glassy carbon (GC) electrode (BAS Inc., disc replaceable electrode GC kit, 4 mm in diameter). The catalyst ink was dropped onto the GC electrode and dried in air for several min. The amount of ink was adjusted to keep 0.2 mgoxide cm<sup>-2</sup> of the oxide loading on the apparent disk surface. The electrochemical measurements were carried out using a normal three-electrode cell with a potentiostat (IVIUM Technologies B. V., CompactStat.h standard). The catalyst-loaded GC electrode, a Pt wire and Ag / AgCl / KCl (satd.) were used as a working, a counter and reference electrodes, respectively. Linear sweep voltammograms (LSV) were measured between 1.10 and 1.88 V vs. RHE with a rotation rate of 1600 rpm at room temperature (ca. 298 K) in a N<sub>2</sub>-saturated electrolyte containing 0.4 mol dm<sup>-3</sup> NaH<sub>2</sub>PO<sub>4</sub>, 0.6 mol dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub> and NaOH whose amount was adjusted to keep pH at 7.0. Scan rates were 1 mV/s for LSV and 10 mV/s for evaluation of overpotential for OER. Using the following equation, the potential U was converted from the Ag / AgCl / KCl (satd.) reference scale to RHE.

#### U vs. RHE = U vs. Ag / AgCl / KCl (satd.) + 0.199 + 0.059 × pH

The current density was corrected on the assumption that *iR* was dropped by a solution resistance ( $R = 18.9 \Omega$ ).

#### 2.5. Electrochemical measurements for durability test

Working electrodes were prepared by drop-casting of the catalyst inks on carbon paper electrodes (Toyo Tanso Co., PERMA-FOIL, 0.25 cm<sup>2</sup>). The amount of ink was adjusted to keep 0.2 mg<sub>oxide</sub>/cm<sup>2</sup> of the oxide loading on the apparent electrode surface. Durability was investigated under a constant current at 4.7 mA cm<sup>-2</sup>. The crystallinity and chemical composition of the

oxide before and after durability test for 24 h were evaluated by the S/TEM-EDS. The catalyst ink containing CFCO-1 or -1.25 was dropped on a carbon-coated copper grid and dried for the observation before the durability test. On the other hand, after the carbon paper-supported electrode was applied to an experimental run at a constant current for 24 h in the same conditions as the durability test, the catalyst layer was scratched and loaded on the grid for the observation after the durability test.

# 3. Results and discussion

#### 3.1. Characterization of CFCO-x



We have reported<sup>27</sup> that CFCO-*x* samples synthesized by the citric acid sol-gel method and calcined at 1073 K kept BM-type crystal phase at least in a range of x = 0-1. The XRD of CFCO-*x* in the range of  $x \le 0.75$  is shown in Figure S1. Here, we focus the crystallinity of CFCO-*x* in  $x \ge 1$ , shown by the XRD in Figure 1a. CFCO-1, -1.25 and -1.3 showed the pattern assigned to BM-type Ca<sub>2</sub>Fe<sub>2-x</sub>Co<sub>x</sub>O<sub>5</sub> with no impurity, whereas CFCO-1.4 and -1.5 had

not only BM-type CFCO but also  $Ca_3Co_2O_6$  as an impurity phase.<sup>36</sup> Figure 1b shows dependence of the interplanar spacing of (124) on the cobalt content (*x*). The interplanar spacing decreased linearly with *x* up to 1.25~1.30, and then, not largely changed in the range of x = 1.3-1.5, suggesting substitution of iron by cobalt in the BM-type CFCO-*x* with  $x = 0^{-1}.3$ .

The SEM tells us that the particle size of CFCO-1.25 was about 200 nm, smaller than CFCO-1, (Figure S2), whereas the particle sizes were similar in the rage of  $0 \le x \le 1$  as already reported.<sup>27</sup> Table 1 shows that the bulk atomic ratio of Co/Fe, determined by SEM-EDS, was well consistent with the starting solutions at least in the range of x = 0-1.25, where the pure BM-type CFCO was formed. In the XPS (Figure S3), Fe<sup>3+</sup>, Fe<sup>4+</sup>, Co<sup>2+</sup> and Co<sup>3+</sup>, whose assignments are according to the literatures,<sup>37–41</sup>, were commonly found on the surfaces of CFCO-x with x < 1.5, in consistent with the bulk valences analysed by XAFS.<sup>27</sup>

	Chemical composition			<i>x</i> in
	/ atom %			Ca <sub>2</sub> Fe <sub>2-x</sub> Co <sub>x</sub> O <sub>5</sub> *
Catalysts	Са	Fe	Co	
CFCO-0	47	53	0	0
CFCO-0.25	46	47	7.4	0.27
CFCO-0.5	46	40	14	0.52
CFCO-0.75	44	35	21	0.75
CFCO-1	45	27	28	1.02
CFCO-1.25	46	20	34	1.26

 Table 1. Chemical compositions of CFCO-x particles analysed by SEM-EDS.

\**x* was calculated by the following equation.

{(Fe / atom%) + (Co / atom%)} : (Co / atom%) = 2 : x

#### 3.2. Electrochemical Activity for OER in Neutral Conditions

LSVs of all CFCO-x in the neutral solution are shown in Figure S4a, and Figure 2 shows LSVs of BM-type CFCO-1 and -1.25, together with those of PV-type LaFe<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub> and  $\text{SrFe}_{0.5}\text{Co}_{0.5}\text{O}_{3\text{-}\delta\text{r}}$  whose synthesis procedures and XRD are shown in Figure S5. All catalysts showed current density for OER at the potential > 1.55 V vs. RHE. Faradic efficiency of CFCO-1.25 for OER, which was calculated from amount of oxygen generated at 1.7 V vs. RHE for 20 h, was 99.9% (Table S1). BMtype CFCO-1 (solid blue line) showed lower onset potential and higher current density than the PV-type oxides with equivalent Fe and Co contents (dash lines). Larger charge capacity was observed on CFCO-1 than those on the PV-type oxides (Table S2), suggesting that one of the reasons for high catalytic activity of BM-type CFCO was high electrochemically active surface area. In addition, the current density on CFCO, even after normalization by the charge capacity, was obviously larger than those on PV-type oxides (Figure S6). The insert of Figure 2 shows the dependence of overpotentials at 0.2 mA cm<sup>-2</sup> of CFCO-x on Co content. The overpotential rapidly decreased with increasing x from 0 to 0.25 in agreement our previous report in alkaline conditions,<sup>27</sup> unlike alkaline conditions, it decreased gradually

even x > 0.5. These results suggest that Co site or combination of Co and Fe sites is active for OER. The overpotential of CFCO-1.25 was higher than that of IrO<sub>2</sub> (Figure S4a) but was comparable to that of cobalt phosphate shown in previous reports (410 mV at 1 mA cm<sup>-2</sup>),<sup>14,42,43</sup> which is one of the most famous catalysts for OER in neutral conditions. The slope of Tafel plot on CFCO-*x* did not change with increasing Co content (Figure S4b) and was almost the same as those on PV-type oxides, suggesting common rate-limiting step over these composite oxides.



**Figure 2.** LSVs at 1 mV s<sup>-1</sup> on CFCO-1 and 1.25, 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>3-6</sub> at pH = 7. Inserted figure is the overpotentials of CFCO-*x* defined to be the potential yielding 0.2 mA cm<sup>-2</sup> measured at 10 mV s<sup>-1</sup> and pH = 7.

As mentioned in Introduction, Sato et al. reported that, by contact with the highly alkaline medium, BM-type CFCO-1 was immediately converted into amorphous cobalt oxyhydroxide with Fe substituents with Fe/(Fe+Co) atomic ratio = 0.1 whose local atomic rearrangement was similar to the layered  $\gamma$ -CoOOH.<sup>33</sup> This (Co, Fe)OOH-like species in the amorphous phase was the actual electrocatalytic phase for OER which brought the high activity of BM-type CFCO-1<sup>27,32</sup> in the cases of alkaline conditions. Details is given later in section 3.3, BM-type CFCO phase also changed to amorphous phase which may not completely be the same as that formed in alkaline conditions but may have something in common. In order to identify whether the active phase in the present neutral solution was common or not, activity of the (Co,Fe)OOH-like species in the amorphous phase formed from CFCO-1 in the alkaline condition was investigated in neutral conditions. CFCO-1 was immersed in 4 mol dm<sup>-3</sup> KOH aq. at room temperature by stirring for 2 h and filtered. Figure 3a shows XRD of CFCO-1 before and after this alkaline treatment. Most CFCO-1 was converted into the amorphous material by the alkaline treatment as previously reported.<sup>32</sup> Figure 3b compares LSVs in the neutral and alkaline solution on the alkaline-untreated and treated CFCO-1 samples. In the neutral solution, the current density for OER of the untreated sample was higher than the alkaline-treated sample, but not in the alkaline solution as previously reported. The untreated sample has been proven to approximately keep the

BM-type structure during OER in neutral conditions (the details of CFCO structures formed during OER in neutral condition is discussed in Figure 5 at section 3.3), and therefore, the observed activity suggests an important role of the BM-type structure for the OER catalysis in neutral conditions. On the other hand, it is speculated that the highly active BM-phase was lost in the alkaline medium, and the formed amorphous material took a role of active phase. In other words, the high OER activity of BM-type CFCO was found in neutral conditions which is suitable for wide application including CO<sub>2</sub> reduction, and unlike in alkaline conditions, the influence of amorphization on the activity was not apparent.



**Figure 3.** (a) X-ray diffraction of before and after alkaline treatment to 4 mol dm–3 KOH aq. for 2 h of CFCO-1, and (b) LSVs of these samples (before: solid lines, after: dashed lines) at pH = 7 (red lines) and 14 (blue lines).

Here origin of the electrocatalytic activity for OER of BMtype CFCO higher than that of PV-type oxides containing Co, as shown in Figure 2, is discussed. A unit cell of PV-type LaCoO<sub>3</sub> has six CoO<sub>6</sub> octahedra, and two of the six octahedra are replaced by two GaO<sub>4</sub> tetrahedra in the BM-type Sr<sub>2</sub>GaCoO<sub>5</sub>, leading to shift of the ground state of Co<sup>3+</sup> from the low spin into intermediate spin ( $t_{2g}^5 e_g^{-1}$ ). It is known that the  $e_g^{-1}$  brings the high electrocatalytic activity.<sup>17</sup> Zhou et al. reported that electrocatalytic activity of BM-type Sr<sub>2</sub>GaCoO<sub>5</sub> for OER in neutral conditions was higher than that of PV-type LaCoO<sub>3</sub>.<sup>15</sup> Therefore, one of the reasons for the high OER activity of BMtype CFCO should be the unique spin state of Co<sup>3+</sup>.<sup>17,18,44</sup> Furthermore, we reported that the valence of Co in BM-type  $Ca_2Fe_{2-x}Co_xO_5$  (0.25  $\le x \le 1$ ) synthesized by the sol-gel method and calcined at 1073 K was +3 as shown by XANES, and octahedral Co<sup>3+</sup> cations were formed at  $x < 0.5.^{27}$  Therefore, it is speculated that spin state of octahedral Co<sup>3+</sup> in BM-type CFCO-1 and -1.25 is the intermediate, leading to unity of e<sub>g</sub> electron and improving the OER activity in neutral conditions.

Another possible reason is the influence of Ca contained by CFCO. Zhang et al. found through their study on RuIrO<sub>x</sub> and RuIrCaO<sub>x</sub><sup>16</sup> that presence of Ca increased the metal-oxygen covalency and electrophilic nature of surface oxygen, leading to enhancing the adsorption of water molecules and acceleration of the reaction through lattice-oxygen. In our present study, amount of adsorbed water molecules on the surface of CFCO containing Ca was found much higher than that on LaFe<sub>0.5</sub>Co<sub>0.5</sub>O<sub>3</sub> (Figure S7). Throughout these observations, the activity was high where Ca was contained in the catalyst. Therefore, the presence of Ca in CFCO may contribute to the OER activity.

On the other hand, cobalt phosphate (Co-Pi) is one of the most famous catalysts for OER in neutral conditions as reported by Kanan et al. in 2008.45 They reported that in-situ electrodeposited Co-Pi showed relatively high activity for OER in a neutral phosphate solution. Possibility of contribution of cobalt phosphate to the OER activity may be pointed out, because the present study uses a neutral solution containing NaH<sub>2</sub>PO<sub>4</sub>. However, in this study, S/TEM-EDS did not detect Co-Pi phase even after durability tests. In addition, only little changes were observed in cyclic voltammograms (CVs) of CFCO-1 and -1.25 during the first several cycles (please see the first ~10 cycles of CVs shown in Figure S8ab). This implies that formation of phosphates possibly caused by the contact of CFCO with electrolyte at the initial stage of measurements did not affect the activity. It is summarized that the activity was mainly owing to BM-type CFCO, even if small amount of cobalt phosphate was formed.

#### 3.3. Electrochemical Durability for OER in Neutral Conditions

Figure 4 shows the time course of potential in the durability test operated at a constant current 4.7 mA cm<sup>-2</sup> in the neutral solution. The potentials 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- $\delta}$  increased with the experimental time in a scale of 15 min – 5 h, indicating quick deactivation (degradation). In contrast, the increase of potential on CFCO-1 with equivalent Fe and Co contents was slow, demonstrating high durability of BM-type CFCO. Furthermore, the most interesting feature is that durability of BM-type CFCO during OER was drastically improved by increasing Co from *x* = 1 to 1.25; the potential of CFCO-1.25 was slightly decreased during about 70 h, while there was no significant difference between the initial OER activities of CFCO-1 and -1.25 as shown in Figure 2.</sub>

Figure 5 shows HR-TEM images, EDS mappings and EDS line profiles of CFCO-1 and -1.25 particles dispersed in the catalyst ink. Before the durability tests (Figure 5a, b), lattice fringes were observed not only in the inner part, but also on the surfaces of both CFCO-1 and -1.25. The spacing of lattice fringes were 0.19,



Figure 4. Time courses of potential in durability tests operated at 4.7 mA cm-2 on CFCO-1 and 1.25, PV-type LaFe0.5Co0.5O3, and SrFe0.5Co0.5O3– $\delta$  at pH = 7. Inserted figure is the enlarged portion at 0 ~ 6 h.

0.37 and 0.38 nm, assigned to (240), (004) and (120) faces of BM-type CFCO, respectively. The x of the inner part of both oxides were about 1 and 1.25 in CFCO-1 and -1.25, respectively (Figure 5a-3, 5b-3), in agreement with SEM-EDS (Table 1). The Ca contents in a surface region (the thickness was ~5 nm) of both oxides were lower than those in the inner parts. It is therefore concluded that the CFCO-1 and -1.25 particles dispersed in the catalyst ink had the BM-type crystal structure with some extent of Ca defects in the near surface region.

The XPS recorded before the dispersion of particles in the catalyst ink indicates the enrichment of Ca on the surfaces of CFCO-1 and -1.25 (Table S3), telling us that some unstable Ca rich phases were formed on the surfaces, and they were removed during the catalyst ink preparation step. The XPS also showed the enrichment of Co on the both surfaces of CFCO-1 and -1.25 (Table S3), although the Co/Fe ratio was almost equivalent on CFCO-1 in the surface and inner regions after the dispersion into ink. It suggests the formation of unstable Co-rich species on the particle, and dissolution of it during the ink preparation step. In other words, the impurity layer was once formed on the surface, but after dispersion in the catalyst ink, the particles possessed the BM-type CFCO structure as stated above.

After the durability tests in the neutral solution at 4.7 mA cm<sup>-2</sup> for 24 h, the CFCO-1 particle showed no lattice fringes ascribable to the BM-type structure near the surface within 20  $\sim$  30 nm thickness in HR-TEM images (Figure 5c-1). Co was significantly removed from the near surface region with  $\sim$ 10 nm thickness, whereas Ca was more significantly removed from the region with  $\sim$ 40 nm thickness (Figure 5c-2, 3). At some places of the inner part ( $\sim$ 20 nm thickness) of CFCO-1 after the durability test, amorphous phase without Ca nor Co was found (show in Figure S9). These results suggest that most CFCO-1 particles were also amorphized during OER in neutral conditions, while Ca and Co in the near surface region were leached in neutral conditions. As mentioned in Introduction and section 3.2, it is

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reported that CFCO-1 were amorphized in highly alkaline conditions, but leached elements were Ca and Fe. Therefore, the amorphous phase formed in the neutral condition may be different from that in the alkaline conditions.

On the other hand, CFCO-1.25 showed a different behaviour. Many BM-type nanocrystals were observed in amorphous matrix near the surface region after the durability test (Figure 5d-1, fast Fourier transform images of these areas were shown in Figure S10). The significant loss of Co in the near surface region was not observed, whereas Ca was removed in the near surface region (Figure 5d-2, 3).

The related intensity  $I/I_0$  ( $I_0$  and I are the intensity of CFCO before and after the durability test) of (124) phase of BM-type CFCO-1 decreased with increasing reaction times, whereas that of CFCO-1.25 was almost constant for 24 h (Figure S11). In addition, the electrochemical activity of CFCO-1 and CFCO-1.25 in the neutral solution, which were evaluated by CVs, became lower and maintained during OER (see in Figure S8ab), whereas the activity in the alkaline solution became higher with increasing amorphous phase with (Co,Fe)OOH like species, which was active species in alkaline conditions (Figure S8c). If amorphous phase formed in neutral conditions is relatively active comparing with BM-type phase, the electrocatalytic activity of CFCO should become active with increasing amorphous area during OER in neutral conditions. Therefore, these results also suggest that the BM-type structure of CFCO played important role for OER in neutral conditions.

The found high durability of BM-type CFCO-x, especially at x = 1.25, was remarkable, but the origin should be the subject of future study. Hereafter potential explanations will be noted based on the information already obtained.

In Figure 4, the durability of BM-type CFCO-1 was much higher than those of PV-type oxides with equivalent Fe and Co contents. It was reported that the position of O20-band center relative to the Fermi level of PV-type composite oxide strongly affected the durability during OER in neutral conditions.<sup>18</sup> PVtype oxides with O<sub>2p</sub>-band close to the Fermi level showed a trend of losing A-site atoms and surface amorphization in wide overpotential range under neutral conditions. On the other hand, PV with O<sub>2p</sub>-band far from Fermi level were relatively durable, even at high current or overpotential where the durability was generally lost. Meanwhile, Han et al. showed from DFT (density functional theory) calculations that oxygen deficiency in PV-type oxides induced widening of energy gaps between their  $O_{2p}$ -band center and Fermi level; the  $\delta$  value from 0 (PV-type structure) to 0.5 (BM-type, which is equivalent to the oxygen-deficiency-ordered PV-type) separated the from Fermi level by more than 0.8 eV in SrFeO<sub>3- $\delta$ </sub> and CaFeO<sub>3- $\delta$ </sub>.<sup>46</sup> Therefore, the energy gap between O<sub>2p</sub>-band center and Fermi level of BMtype CFCO-1 is supposed to be larger than those 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>, leading to suppression of leaching of A-site atoms and enhancement of durability during OER in neutral conditions. The DFT calculation of energy gaps between their O20-band center and Fermi level of CFCO-1 and 1.25 and PV-type oxides will be studied as future work.



Figure 5. (a-1) (b-1) (c-1) (d-1) High-resolution transmission electron microscopy images and (a-2) (b-2) (c-2) (d-2) Energy dispersive spectroscopy mappings and (a-3) (b-3) (c-3) (d-3) line-scan profiles of (a) (c) CFCO-1, (b) (d) CFCO-1.25 before and after the durability test in the neutral condition at 4.7 mA cm<sup>-2</sup> for 24 h.





The durability of BM-type CFCO was drastically improved by increasing Co content form x = 1 to 1.25 shown in Figure 4. Zhou et al. reported that durability of BM-type Sr<sub>2</sub>GaCoO<sub>5</sub>, whose tetrahedral sites were occupied by Ga atoms, for OER at neutral pH was much higher than that of BM-type Sr<sub>2</sub>AlCoO<sub>5</sub>.<sup>15</sup> The difference in durability was ascribed to the thermodynamic stabilities of gallium and aluminium oxides against dissolution during OER, as indicated by the Pourbaix diagrams based on DFT calculations. In our previous study, we revealed that Co preferentially substituted Fe at the tetrahedral site of BM-type  $Ca_2Fe_{2-x}Co_xO_5$  in a range of  $x \ge 0.5$ ,<sup>27</sup> implying that the amount of tetrahedral Co sites in CFCO-1.25 is higher than that in CFCO-1. According to the Pourbaix diagrams of cobalt and iron oxides, the former one is durable<sup>47</sup> at pH = 7, while the latter one is dissolved into solution.48,49 Therefore, it is supposed that the higher durability of CFCO-1.25 than CFCO-1 for OER was ascribable to the high thermodynamic stability of cobalt oxide compared iron oxide at pH = 7.

#### 3.4. Degradation Mechanism during OER in the Neutral Conditions

Comparison of the changes of structure and catalytic activity in the durability tests between CFCO-1 and 1.25 indicates that the high activity was observed where the BM-type structure was maintained (initial stage on CFCO-1 and throughout the test on CFCO-1.25). Here the active phase and mechanism of degradation are proposed as drawn in Figure 6. The Co rich layers were formed on the surface of as-synthesized BM-type CFCO particles, but the layers were easily removed in the step of catalyst ink preparation. Simultaneously, BM-type CFCO phase with slightly low Ca concentration was exposed. Here the OER activity was observed on both CFCO-1 and 1.25, presumably due to the BM-type CFCO phase. During OER in the neutral solution, Ca leaching and amorphization gradually progressed from the surface, especially that of CFCO-1. After Ca leaching and amorphization in the near surface region, the leaching of Co started. With the amorphization, the activity was lost, and thus the activity was strongly related with the presence of BM-phase. On the other hand, the increase of Co from CFCO-1 to 1.25 suppressed the amorphization and degradation.

### 4. Conclusions

Brownmillerite-type  $Ca_2Fe_{2-x}Co_xO_5$  was formed in a range of  $0 \le x \le 1.25$  by the citric acid sol-gel method. Brownmillerite-type  $Ca_2FeCoO_5$  showed high activity and durability for oxygen evolution reaction in a neutral solution compared to perovskite-type  $LaFe_{0.5}Co_{0.5}O_3$  and  $SrFe_{0.5}Co_{0.5}O_{3-\delta}$ . Furthermore, durability of  $Ca_2Fe_{2-x}Co_xO_5$  was remarkably improved by increasing cobalt content from x = 1 to 1.25.

# **Author Contributions**

H. Okada wrote the manuscript and measured and analysed of data. E. Tsuji was a super visor, contributed to the concept of this study, helped to write the manuscript. M. Hisada measured and analysed of data and revised the manuscript. S. Kitano and H. Habazaki helped to acquisition of data and reviewed the manuscript. S. Suganuma and N. Katada were a co-supervisor, discussed data and reviewed the manuscript.

# **Conflicts of interest**

There are no conflicts to declare.

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