Bifunctional Oxygen Reduction and Evolution Activity in Brownmillerites Ca$_2$Fe$_{(1-x)}$Co$_x$O$_5$

Shibin Thundiyil,*§ Sreekumar Kurungoti,*§‡ and R. Nandini Devi*†§

*†Catalysis and Inorganic Chemistry Division and  ‡Physical and Material Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, India
§Academy of Scientific and Innovative Research (AcSIR), Kamla Nehru Nagar, Ghaziabad 201002, India

ABSTRACT: State-of-the-art catalysts for oxygen reduction and evolution reactions (ORR and OER), which form the basis of advanced fuel cell applications, are based on noble metals such as Pt and Ir. However, high cost and scarcity of noble metals have led to an increased demand of earth-abundant metal oxide catalysts, especially for bifunctional activity in ORR and OER. The fact that Pt and Ir or Co, the cost-effective alternatives suggested, do not display satisfactory bifunctional activity has also helped in turning the interest to metal oxides which are stable under both ORR and OER conditions. Brownmillerite A$_2$B$_2$O$_5$ type oxides are promising as bifunctional oxygen electrocatalysts because of intrinsic structural features, viz., oxygen vacancy and catalytic activity of the B-site transition metal. In this study, Co-doped Ca$_2$Fe$_2$O$_5$ compounds are synthesized by the solid state method and structurally analyzed by Rietveld refinement of powder X-ray diffraction data. The compound Ca$_2$Fe$_2$O$_5$ crystallizing in the Pbam space group has alternative Fe$_{O_4}$ tetrahedral and Fe$_{O_6}$ octahedral layers. Its Co-doped analogue, Ca$_2$Fe$_{1.75}$Co$_{0.25}$O$_5$, also crystallizes in the same space group with both tetrahedral and octahedral Fe positions substituted with Co. However, Ca$_2$FeCoO$_5$ in the Pbcn space group shows interlayer ordering with Co-rich octahedra connected to Fe-rich tetrahedra and vice versa. Oxygen bifunctional activities of these catalysts are monitored by rotating disc electrode and rotating ring disc electrode techniques in alkaline media. A close analysis of the ORR and OER was conducted through comparison of various parameters such as onset potential, current density, halfwave potential, and other kinetic parameters, which suggests that the presence of Co in the B site aids in achieving better bifunctional activity and bulk conductivity. In addition, Co(II)/Co(III) redox systems and their comparative concentrations also play a decisive role in enhancing the activity.

INTRODUCTION

Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are the two fundamental electrochemical reactions in fuel cells and energy storage devices, which are gaining renewed attention because of the thrust in sustainable energy production. In ORR, strong double bonds have to be broken for the formation of hydroxyl or peroxide ions from oxygen molecule and vice versa is true for OER, both reactions involving four electrons. Hence, they are often described as sluggish compared to their anodic counterparts, viz., hydrogen evolution and oxidation which are two electron processes.1,2 It is therefore necessary that the catalysts used for ORR and OER are highly active for achieving better performance parameters of the devices. A novel concept which has emerged recently evokes catalysts which are simultaneously active for both ORR and OER in a bifunctional mode. Such bifunctional catalysts can be applied in advanced energy systems such as unitized regenerative fuel cells (URFC), and metal–air batteries.3 A URFC is a combination of an electrolyzer and fuel cell, providing high energy densities, where OER and ORR form the base reactions in the individual components, respectively. In metal–air batteries, OER and ORR occur in the same device, while charging and discharging, respectively. There are severe challenges in using conventional noble metal catalysts, that is, Pt for ORR and IrO$_2$ or RuO$_2$ for OER, in a bifunctional mode in these energy systems as IrO$_2$ and RuO$_2$ are not active for OER and Pt forms a surface oxide layer under OER conditions, which affects its durability. Any combinations or alloys of these noble metals would render the catalyst prohibitively expensive. Other less expensive alternatives suggested are carbon-based materials, which, even though abundant and cheap, corrode in the OER experimental conditions because of rapid oxidation of carbon to CO$_2$. In this scenario, transition-metal oxides from earth-abundant elements present an interesting substitute because of high stability in oxidative environments and cost effectiveness.

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Hence, structured oxides, such as perovskites, spinels, and so forth, synthesized from first-row transition metals, which are structurally conducive for manipulations to enhance various electronic and structural properties such as oxygen vacancies, have garnered attention lately.\(^5\)

Strategies like doping can be adopted in the perovskite structure to induce redox couple formation increasing its bulk conductivity. Another important consequence of doping is creation of defect structures through oxygen vacancies which in turn result in excellent oxygen ion mobility and exchange kinetics.\(^6\) Oxygen vacancies can directly influence the electrochemical oxygen reduction and evolution activities of the catalyst, which has been reported recently by us and other research groups.\(^7-11\) In this respect, brownmillerites, with general formula \(A_xB_2O_5\), are more advantageous because more oxygen vacancies can be accommodated in their crystal lattice. Brownmillerites are structurally similar to perovskites but with ordered oxygen vacancies placed near coordinatively unsaturated \(B\) sites. This ordering occurs in a variety of forms, such as layered or columnar. The oxygen vacancies act as potential oxygen adsorption and transport sites. As they exist within the coordination sphere of a transition-metal ion in \(B\) site, this ion’s catalytic activity plays an important role in further reduction and oxidation reactions of the adsorbed oxygen species.

This is parameterized in terms of filling of the cation as activity descriptors in oxide catalysts for both OER and ORR reactions. Suntivich et al. suggested that the activity can be improved by increasing the covalency between metal 3d and \(\delta^+\) species.\(^\text{16,17}\) The best fit (on occupancy refining) was obtained by higher concentration of Co in the tetrahedral site (\(\sim 12.7\%\)) and decrease in octahedral position occupancy (\(\sim 10.8\%)\) than the nominal input composition of 12.5%. The polyhedral representation of the layers is given in Figure 1c. Mixed octahedral occupancy by both Co and Fe in a single site is represented by green.

The reported structure of \(\text{Ca}_2\text{FeCoO}_5\) (ICSD no. 169345) crystallizing in the \(Pbca\) space group consists of two distinct crystallographic tetrahedral sites and two octahedral sites based on single crystal XRD studies.\(^\text{16,18}\) In addition, such intralayer ordering is also observed in substituted calcium ferrates, \(\text{Ca}_2\text{FeMnO}_5\) and \(\text{Ca}_2\text{Fe}_{1.5}\text{Cr}_0.5\text{O}_5\), where Mn\(^{\text{II+}}\) and Cr\(^{\text{III}}\) show strong site preference for the octahedral site.\(^\text{19}\) However, neutron diffraction, which distinguishes Fe and Co positions, indicates interlayer ordering also in \(\text{Ca}_2\text{FeCoO}_5\); the only brownmillerite which is found to do so. In such an interlayer ordering between tetrahedral and octahedral layers, Fe in tetrahedral coordination is attached to \(\text{Co-rich octahedra from above and below and vice versa.}\(^\text{18}\)

Refinement of the data for CFCO2 in the current study was tried using the \(Pbca\) space group as in the matching PXRD data of intralayer ordered \(\text{Ca}_2\text{FeMnO}_5\) (PDF no. 88-0814), but it was unsuccessful; however, refinement proceeded smoothly by following the abovementioned interlayer ordered model.\(^\text{18}\) On indexing, we observed that the cell parameters are interchanged compared to the parent structure and the relation, \(a' = c, b' = 2a,\) and \(c' = b\) was adopted for further refinement (Figure S2). In contrast to the other two compounds, CFO and CFCO1, this structure consists of six different oxygen atoms because of interlayer ordering and the refinement proceeded smoothly by mixing the occupancy of Fe and Co in both sites. Three metal sites are defined—\(\text{Co}(1)(\text{Fe}1)\) in tetrahedral coordination and \(\text{Co}(2)(\text{Fe}2)\) and \(\text{Co}(3)(\text{Fe}3)\) occupying octahedral sites show variations in metal concentrations. Occupancy at \(4a\) position by Co\(^{\text{II}}\) and Fe\(^{\text{III}}\) is in the ratio of 70:30% which is denoted as site B. 1d position is
Table 1. Rietveld Refinement Data of the Compounds<sup>a,b,c</sup>

|                  | Ca<sub>2</sub>Fe<sub>3</sub>O<sub>5</sub> | Ca<sub>2</sub>Fe<sub>1.75</sub>Co<sub>0.25</sub>O<sub>5</sub> | Ca<sub>2</sub>FeCoO<sub>5</sub> |
|------------------|----------------------------------|---------------------------------|---------------------------------|
| χ²               | 1.29                             | 1.89                            | 2.35                            |
| wR<sub>p</sub> (%)| 3.26                             | 1.79                            | 1.66                            |
| R<sub>p</sub> (%) | 2.42                             | 1.36                            | 1.23                            |
| space group      | Pnma                            | Pnma                            | Pnma                            |
| a                | 5.5953(1)                        | 5.7474(2)                       | 5.5396(1)                       |
| b                | 14.7617(2)                       | 14.7677(2)                      | 11.0840(2)                      |
| c                | 5.4237(1)                        | 5.3999(1)                       | 14.7893(2)                      |
| Ca               |                                  |                                 |                                 |
| x                | 0.023523                         | 0.22960                         | −0.007998, 0.488738             |
| y                | 0.108931                         | 0.108883                        | 0.7558885, 0.511944             |
| z                | 0.481264                         | 0.476070                        | 0.387727, 0.607547              |
| occupancy        | 1                                | 1                               |                                 |
| Fe<sub>1</sub>/Co<sub>1</sub> |                                 |                                 |                                 |
| x                | 0                                | 0                               | −0.045956, 0.429302             |
| y                | 0                                | 0                               | 0.531271, 0.716078              |
| z                | 0                                | 0                               | 0.25000, 0.25000                |
| occupancy        | 0.9833Fe                         | Fe: 0.8446                      | Co: 0.1082                      |
| Fe<sub>2</sub>/Co<sub>2</sub> |                                 |                                 |                                 |
| x                | 0.935308                         | 0.935746                        | −0.499167, −0.511687           |
| y                | 0.250000                         | 0.250000                        | 0.75000, 0.75000                |
| z                | 0.946397                         | 0.94306                        | 0.50000, 0.50000                |
| occupancy        | 1.0097                           | Fe: 0.8844                      | Co: 0.1271                      |
| Fe<sub>3</sub>/Co<sub>3</sub> |                                 |                                 |                                 |
| x                | 0                                | 0                               |                               |
| y                | 0                                | 0                               |                               |
| z                | 0                                | 0                               |                               |
| occupancy        | 0.2819                           |                                 |                               |

O1 X 0.238170 0.240763 0.09148
Y 0.983867 0.983865 0.69356
Z 0.258984 0.266735 0.25
occupancy 0.984480 0.98322 1.022

O2 X 0.073149 0.067866 0.5928
Y 0.142049 0.141957 0.56399
Z 0.021618 0.022841 0.25
occupancy 1.001463 1.026854 1.021

O3 X 0.874449 0.882798 −0.258810
Y 0.250000 0.250000 0.61815
Z 0.601177 0.593653 0.48739
occupancy 1.006836 1.026698 0.972

impurity phases (wt %)
FeO1 ≈ 1.3
FeO2 ≈ 4.8

Co2 octahedra, with O6 bridging the cobalt-rich tetrahedra (Co1O4) and iron-rich octahedra. O3 and O4 are commonly shared with the cobalt-rich octahedra (Co3/Fe3O6) and iron-rich octahedra (Co2/Fe2O3). O5 bridges cobalt-rich octahedra (Co3/Fe3O4) and iron-rich tetrahedra (Fe1O4). Occupancy factors were also refined and found to be changed from the input stoichiometric factor during the refinement process to obtain the chemical formula of Ca2Fe1.05Co0.91O5+, which is corroborated by energy-dispersive system (EDS) analysis (Section S3, Supporting Information).

On comparing the structural details of the three compounds, CFO, CFCO1, and CFCO2, it is revealed that progressive substitution of Co in the octahedral and tetrahedral sites leads to small polyhedral distortions. For example, Oh−O−Td angle is more or less the same for CFO and CFCO1 (139.98 and 140.61°, respectively) but increases to 143.82° in CFCO2, whereas a more gradual decrease in Oh−O−Oh (intralayer) angle occurs from 165.28 to 163.61° across the series.

Once the structural details were understood, we proceeded further with electrochemical studies by cyclic voltammetry (CV), rotating disc electrode (RDE) and rotating ring disc electrode (RRDE) techniques. Linear sweep voltammograms of the catalysts under oxygen saturation with 10 mV/s scan rate with 1600 rpm rotation are shown in Figure 2a. Cyclic voltammograms at 50 mV/s scan rate and 900 rpm rotation are given in the inset. In nitrogen saturation, they are nearly rectangular and the reduction peak in the oxygen saturation in each pattern represents the ORR activity of the compound. Both CFCO1 and CFO are found to be displaying the same onset potential value of 0.811 V with respect to the reversible hydrogen electrode (RHE) in the linear sweep voltammetry (LSV) profiles. Also, both of these compositions exhibit an onset potential, which is ~10 mV higher than that of CFCO2. Even though the onset potentials are almost in the same range, we observe an enhancement in the profile quality on cobalt incorporation. CFO and CFCO1 display profiles, which are gradually increasing current density, whereas CFCO2 displays a limiting current plateau from ~0.6 to ~0.3 V versus RHE. This can be because of the improved mechanism with Co doping. In the plateau region, the reaction may be occurring through a desired four-electron mechanism, thereafter, shifting to two-electron mechanism or mixed mechanism as exhibited by CFO and CFCO1, which is later confirmed by Koutechy–Levich (K–L) plots analysis and RRDE experiments.

Further, geometric limiting current density was also found to increase with increase in Co concentration, which is a direct implication of the availability of active sites in the catalyst.

Another parameter which is of importance in understanding catalytic activity is halfwave potential. Determination of the halfwave potential is not trivial in case of oxides because the profile does not reach the limiting current as in the case of metals. Hence, the method adopted for comparing the halfwave potential is to select a common potential and to analyze the current density, and the potential at which half that current density is acquired is noted as the halfwave potential. Determination of the half-wave potential of these compounds at a common potential of 0.4 V revealed that CFCO2 exhibited better halfwave potential of 0.7 V versus RHE, which was 10 and 50 mV higher than that of CFCO1 and CFO, respectively. This is a clear indication of enhancement of ORR kinetics on cobalt doping in calcium ferrate.

The K–L plots (equation and details in Supporting Information) of the compounds are represented in Figure 33.

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2b. CFO exhibited two distinctly different slopes indicating a multiple electron-transfer mechanism with an overall slope value of 0.555 mA cm$^{-2}$ S$^{1/2}$. CFCO1 also behaved similarly with overall slope of 0.5572 mA cm$^{-2}$ S$^{1/2}$. However, a straight line was obtained in the K–L plot of CFCO2 with the slope value of 0.5264 mA cm$^{-2}$ S$^{1/2}$. Hence, it is clear that the reaction adopts a four-electron pathway as the Co concentration increases. The compounds CFO and CFCO1 also displayed Tafel slopes of $-142.1$ and $-124.5$ mV/decade (Figure 2c; equation and details in Supporting Information), indicating nearly similar mechanisms in these compounds with first electron reduction as the rate-determining step (rds). However, for CFCO2, the value was $-59.2$ mV/decade, pointing to a pseudo two-electron reduction and migration of the superoxide ion for further reduction as the rds.$^{20}$

Figure 3 shows the dependence of potential on the electron transfer number. The compound CFO has reasonable stability in the electron transfer number in the given potential window for the reaction. The CFO and the two compositions, viz. CFCO1 and CFCO2, approach the electron count of 4 at lower potentials comparable with that of a standard 40 wt % Pt/C (Figure S6, Supporting Information). Close analysis of the e–n plot suggests that at higher cathodic potential, the electron transfer mechanism is similar in all compounds. There is a distinct change in the mechanism in CFCO2 after ~0.3 V. Peroxide yield, which is also an important parameter in judging the stability and mechanistic aspects of ORR, is usually higher...
when the reaction proceeds through 2-electron mechanism. The catalyst which undergoes 2-e pathway is useful in the electrochemical synthesis of H₂O₂, but in fuel cell applications, H₂O₂ production is harmful and the 4-e mechanism is preferred to get maximum power output with only pure water as the exhaust.21−23 The peroxide yield is more in CFO compared to the Co-doped varieties. This implies that as the cobalt concentration increases the mechanism shifts from the 2-e to 4-e route as evidenced from the e⁻n plot. It is noteworthy here that the trend in electron count and peroxide yield is favorably different in the Co-doped catalysts than the parent Fe-based brownmillerite at higher potentials. CFCO₂ shows a steady electron count of 3.5 till 0.4 V, after which it starts an upward trend to reach 3.9 at 0.7 V. A similar trend is seen in the peroxide yield also with a decrease from 25% at 0.4 V to 10% at 0.7 V. CFCO₁ also shows a similar inflection point at 0.5 V. Very interestingly, the behavior of this compound mirrors that of the parent compound CFO at lower potentials, as evident from the decrease in electron count and increase in peroxide yield till 0.5 V.

Here, we hypothesize that such an inflection point observed in CFCO₁ and CFCO₂ may be due to the occurrence of some redox processes at potentials above 0.4 V. To get more insights into this, X-ray photoelectron spectroscopy (XPS) analysis was carried out on fresh catalysts as well after applying potential in the range of 0.4−0.7 V where such behavior was observed. In both compounds, relative percentage of Co(II) species increased after potential treatment. Percentage of Co(II) increased from 25 to 39 and 37 to 41% in CFCO₂ and CFCO₁, respectively. Hence, we can infer that Co in +2 oxidation state is more conducive for ORR, and CFCO₂ not only has higher concentrations of Co but has more Co(II) content also.

Accelerated durability test was conducted for 5000 cycles in Co-doped compounds, and they were found to be stable. XRD analysis of the samples after 3000 segments in CV did not show any change of phase indicating structural stability (Supporting Information Section S6.5).

OER was conducted in 0.1 M alkaline solution in a potential range of 0.87−1.97 V with respect to RHE. Figure 5a shows the comparison of the OER activity of the catalysts and that of Vulcan carbon. The scan rate in all cycles was 10 mV/s with nitrogen saturation. Here also we observed a substantial increase in activity on progressive Co doping (Figure 5a). The onset potential for the most active composition CFCO₂ was 1.53 V, whereas the onset potential for CFCO₁ was slightly higher at ~1.64 V (vs RHE). CFO shows the highest overpotential at ~1.73 V, which is comparable to Vulcan carbon.

![Figure 4](image1.png)

**Figure 4.** (a) Co 2p XPS of CFCO₁ (red) and CFCO₂ (black) (b) Co 2p XPS of used catalyst CFCO₁ (red) and CFCO₂ (black).

![Figure 5](image2.png)

**Figure 5.** (a) Cyclic voltammogram for OER at 1600 rpm with a scan rate of 10 mV/s (b) OER current density at 1600 rpm at 1.8 V vs RHE (c) Tafel plots for OER reaction of the catalysts, where empty symbols represent raw data and the solid line represents the linear fit of the raw data.
carbon at \( \sim 1.82 \) V. The electrochemical performance parameters of these catalysts are comparable with those of state-of-the-art noble metal-based catalysts. Onset potential of the Co-doped compounds range from 1.53 to 1.64 V, whereas that of IrO\(_2\) is 1.5 V. In addition, the potential required to reach current density of 10 mA cm\(^{-2}\) is only \( \sim 0.2 \) V higher than that of IrO\(_2\). Current densities of the compounds were monitored at 1.8 V and plotted in Figure 5b. As expected, when Co concentration increases, oxygen evolution activity also increases.

The kinetics of OER was studied by calculating the Tafel slope values (Figure 5c). The compound CFO exhibited higher value of Tafel slope at 139 mV/decades, whereas it reduced advantageously for both Co-doped compounds (CFCO1: 50.32 mV/decades and CFCO2: 58.05 mV/decades). These values are comparable to the highly active quadrupole perovskites reported recently, and the intrinsic activity was much higher than that reported for the perovskites CaMnO\(_3\) and LaMnO\(_3\) (Tafel slope: \( \sim 155 \) mV/decades). To explain this, OER can also be considered to follow a mechanism similar to that of ORR, as suggested by De Faria et al. The CFCO2 carries out the mechanism similar to that of ORR, as suggested by De Faria et al.34

\[
\begin{align*}
S + H_2O & \rightarrow OH^* + H^+ + e^- \\
S-OH^* & \rightarrow S-OH \\
S-OH + S-OH & \rightarrow S-O + H_2O \\
S-O + S-O & \rightarrow 2S + O_2
\end{align*}
\]

where S is the surface active site; the intermediate species distinguished with an asterisk sign are in different energy levels. Similar to ORR, when the rds is the first step, involving one electron transfer, the Tafel slope value is 120 mV/decades.

If the rds is the second step, involving the migration of the surface intermediate species, the Tafel slope value will be 60 mV/decades. In the present study, the undoped CFO exhibits the Tafel slope value of 139 mV/decade, indicating the first electron transfer step to be the rds. On doping with Co, the Tafel slope value is reduced considerably, indicating an enhancement in intrinsic activity with the rds understood to be surface migration.

Further, effect of doping on the bulk conductivity of the material was studied by plotting the \( \log \) – \( \log \) curve over a potential window of \(-0.1\) to \(+0.1\) V. Samples were made into pellets of 13 mm diameter and current–potential relation was analyzed to obtain conductivity data (Figure S1, Supporting Information). Conductivity of CFCO1 and CFCO2 increased about six- and tenfold, respectively, when compared to that of CFO, indicating that Co doping of Ca\(_2\)Fe\(_2\)O\(_5\) definitely improved its bulk conductivity.

Various catalysts ranging from noble metal mixture to cost effective modified carbon-based structures are studied for their bifunctional oxygen electrocatalytic studies. The brownmillerite oxide is advantageous in terms of abundance of raw materials and catalytic activity. The CFCO2 carries out the ORR in a near 4-electron pathway and the lowest Tafel slope value of \( \sim 59 \) mV/decade compared to the best catalysts. OER Tafel slope values of cobalt-doped analogues are still lesser than the recently reported bifunctional catalysts such as sulfided LDH\(^+\) and N-doped graphene/single-walled carbon nanotube hybrids. From these studies, it is clear that all electrochemical performance parameters for the Co-doped compounds are superior to that of the parent Fe compound and such doping strategies can be used further for developing potential alternatives to noble metal-based electrocatalysts.

### CONCLUSIONS

Brownmillerite Ca\(_2\)Fe\(_2\)O\(_5\) and two of its Co-doped analogues (Ca\(_2\)FeCo\(_2\)O\(_5\) and Ca\(_2\)Fe\(_{1.75}\)Co\(_{0.25}\)O\(_5\)) were synthesized by solid state reaction and detailed structural studies conducted by Rietveld refinement of the PXRD patterns. No specific crystallographic site preference could be identified for Co doping, and partial occupancy of both octahedral and tetrahedral coordinations with small polyhedral distortions was observed. The catalysts are tested for simultaneous activity in two important electrochemical reactions viz., ORR and OER. The dopant Co was expected to have a role in the enhancement of activity as per the earlier reports on the activity descriptors. The intrinsic conductivity of the material is found to be enhanced with increase of dopant concentration. The ORR activity in terms of onset potential and half-wave potential alternatives to noble metal-based electrocatalysts. Such doping strategies can be used further for developing potential alternatives to noble metal-based electrocatalysts.

### EXPERIMENTAL SECTION

The compounds were synthesized by the solid state method using CaCO\(_3\) (Sigma-Aldrich, \( \geq 99.0\)%), Fe\(_2\)O\(_3\) (Sigma-Aldrich, 99.98%), and Co\(_2\)O\(_3\)·xH\(_2\)O (Sigma-Aldrich, \( Co = 43\)–47%) as the starting materials. The precursors in stoichiometric proportions were weighed and ball milled at 150 rpm for 2 h and calcined at 1100 °C for 12 h with intermittent grinding. Bulk composition was confirmed by plasma atomic emission spectrometer (MP-AES, Agilent, wavelength range 190–770 nm) with a charge-coupled device detector. Surface area measurement was carried out in QUADRASORB SI automated surface area and pore size analyzer (Quantachrome Instruments). Morphology and surface composition were analyzed by scanning electron microscope (Leica Stereoscan 440) with an EDS attachment (Bruker, D451-10c energy dispersive X-ray spectrometer). Phase formation was confirmed with PXRD in PANalytical Xpert Pro dual goniometer.
differactometer with Ni as the filter and Cu Kα source operating at 40 kV and 30 mA. Room temperature diffraction patterns were recorded with X’Celerator solid state detector with step size 0.008° and time per step 96.52 s. The obtained patterns were refined using the GSAS-EXPGUI suite of programs to calculate unit cell parameters and structure parameters. Electrochemical properties were analyzed by Biologic SP-300 electrochemical workstation, equipped with pine electrode speed control. Catalyst ink applied on the surface of the glassy carbon electrode connected to a rotating shaft acted as the working electrode. Graphite rod was taken as the auxiliary electrode, and Hg/HgO was the reference electrode. The techniques used were CV and LSV. First, Vulcan XC 72 carbon electrode connected to a rotating shaft acted as the speed control. Catalyst ink applied on the surface of the glassy electrochemical workstation, equipped with pine electrode. Electrochemical properties were analyzed by Biologic SP-300 with the same catalyst ink separately in N2 saturation at 1600 rpm rotation with 10 mV/s scan rate, where the potential obtained for the Co and Fe were...

The C 1s was standardized to 284.8 eV, and the curves background subtraction method using XPS PEAK41 software. XPS data of all three compounds were...

This mixture and dispersing in 40 μL IPA... The obtained patterns were recorded in 10 mV/s scan rate in 400, 900, 1200, 1600, 2000, and 2500 rpm rotations using RDE. The RRDE technique was used to determine the electron transfer number associated with the reaction. Pt/C ink (40 wt %) prepared in water mixture. Catalyst ink (10 μL) was applied to the glassy carbon surface for electrochemical analysis. ORR study was conducted both with N2 and O2 saturation. CV experiments were conducted with 50 mV/s scan rate from 0.2 to −0.9 V with respect to Hg/HgO. LSV profiles were recorded in 10 mV/s scan rate in 400, 900, 1200, 1600, 2000, and 2500 rpm rotations using RDE. The RRDE technique was used to determine the electron transfer number associated with the reaction. Pt/C ink (40 wt %) prepared in the same manner was used as a standard for the reaction; the sample was scanned in the same potential window at 10 mV/s at 1600 rpm in O2 saturation. OER studies were conducted with the same catalyst ink separately in N2 saturation at 1600 rpm rotation with 10 mV/s scan rate, where the potential window applied was maintained from 0 to 1 V with respect to Hg/HgO. All the above electrochemical analysis was performed in alkaline medium of 0.1 M KOH (Sigma-Aldrich) in demineralized water. XPS studies were done by K-Alpha+ model (Thermo Fischer Scientific, UK) with Al Kα source. XPS data of all three compounds were fitted with Shirley-type background subtraction method using XPS PEAK41 software. The C 1s was standardized to 284.8 eV, and the curves obtained for the Co and Fe were fitted by applying charge correction factor.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02468.

XRD pattern of the compounds, unit cell polyhedral representation, EDAX and ICP−MS data, EDAX elemental composition of Ca2Fe2−xCo1−yO5.5, SEM images, surface area data, XPS, and electrochemical data (PDF)

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: k.sreekumar@ncl.res.in (S.K.).
*E-mail: nr.devi@ncl.res.in (R.N.D.).

Sreekumar Kurungot: 0000-0001-5446-7923
R. Nandini Devi: 0000-0002-6219-8089

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
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