

Dual-site catalysis of Fe-incorporated oxychlorides as oxygen evolution electrocatalysts

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ABSTRACT: Electrocatalysts with high activity for the oxygen evolution reaction (OER) play a pivotal role in various electrochemical devices such as water electrolyzers and metal-air batteries. Electronic interactions between these catalysts and chemical reactants control the activity and efficiency, and hence need to be optimized, but only the cation components have been of interest. Here, through the optimization of both cation and anion components, we demonstrate that a Ruddlesden-Popper-type oxychloride $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ successfully outperforms $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, which is a well-known highly active OER catalyst. Moreover, $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ also catalyzes the oxygen reduction reaction (ORR) and minimizes the overpotentials of both the ORR and OER, compared with previously reported conventional perovskite-type catalysts. We discuss possible descriptors of the catalytic activity of $\text{Sr}_2\text{Co}_{1-x}\text{Fe}_x\text{O}_3\text{Cl}$ to clarify the origin of its activity, and highlight a new reaction pathway for OER that involves catalysis by both Co and Fe.

Introduction

There has been growing interest in energy-storage devices such as water-splitting devices,¹ regenerative fuel cells,²⁻⁴ and rechargeable metal-air batteries.⁵⁻⁷ Since one of the biggest challenges with these devices is the sluggish kinetics of the oxygen evolution reaction (OER), much effort has been devoted to the development of OER catalysts. Although some precious metal oxides (*e.g.*, IrO_2 and RuO_2) show good OER activities,⁸ their high cost and scarcity have hindered their large-scale implementation. Therefore, many studies have sought to identify cost-effective transition-metal catalysts with high OER activity.⁹ Among various crystal structures, a family of perovskite compounds such as ABO_3 single perovskites,^{10,11} $\text{A}_2\text{BB}'\text{O}_6$ or $\text{AA}'\text{B}_2\text{O}_6$ double perovskites,¹²⁻¹⁵ $\text{AB}'_3\text{B}_4\text{O}_{12}$ quadruple perovskites,^{16,17} $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ Ruddlesden-Popper-type layered perovskites¹⁸⁻²⁰, and others with unique structure/hybrids^{21,22} ($\text{A}, \text{A}' =$ lanthanides or alkaline earth metals, $\text{B}, \text{B}' =$ transition metals) is considered to be an attractive choice in terms of its structural and compositional flexibility.²³ Several studies on perovskites as OER catalysts have clarified that the choice of the *B*-site cation plays an important role, and their OER performance is maximal when *d*-electrons in the e_g orbital of the *B*-site cation is near unity.^{24,25} Partial substitution of their *A*- or *B*-site cations is also an important strategy because the electronic configuration in the e_g orbital of their *B*-site or O *p*-band center can be modified indirectly.^{12,25,26}

Recently, in contrast, some studies have clarified that, for transition metal oxides, partial or total substitution of their oxygen anion by other anions is another effective strategy for enhancing OER activities.²⁷⁻³⁰ We have also demonstrated that Ruddlesden-Popper-type Co-based layered

perovskite oxychlorides $\text{Sr}_2\text{CoO}_3\text{Cl}$ and $\text{Sr}_3\text{Co}_2\text{O}_5\text{Cl}_2$, which can be synthesized by a simple solid-state method in ambient air, function as highly active OER catalysts, and clarified that their enhanced OER activities can be attributed to their upshifted O *p*-band centers.³¹ From the viewpoint of cation selection, on the other hand, there is room for improvement in the composition of their transition metal sites: oxychlorides still have the potential to achieve better OER performance. As has been widely reported,³²⁻³⁶ Fe doping in Co-based transition metal catalysts is one of the most familiar and effective strategy for OER enhancement, which motivated us to investigate the OER activity of Co-Fe-based perovskite oxychlorides. On the other hand, the role of Fe in enhanced OER activities is not universal for the above-mentioned OER catalysts: $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (stabilization of its perovskite structure),³² $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ (lower theoretical overpotential at Fe site),¹³ $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and $\text{PrBaCo}_{2(1-x)}\text{Fe}_{2x}\text{O}_{6-\delta}$ (altered intrinsic properties such as charge stabilization of Co and thermodynamic metastability),^{33,34} LiCoO_2 (synergistic interplay of Co and Fe),³⁵ CoFe layered double hydroxides (LDHs, formation of γ -phase and O-bridged Fe-Co reaction centers),³⁶ Therefore, it is also important to identify the role of Fe in OER activity for the present perovskite oxychlorides.

In the present work, we selected $\text{Sr}_2\text{CoO}_3\text{Cl}$ for the incorporation of Fe, since the synthetic route and magnetic properties of $\text{Sr}_2\text{Co}_{1-x}\text{Fe}_x\text{O}_3\text{Cl}$, which is essential for theoretical calculation, has been reported previously.³⁷ We first investigated OER activities of Co-Fe-based layered perovskite oxychlorides $\text{Sr}_2\text{Co}_{1-x}\text{Fe}_x\text{O}_3\text{Cl}$, and discuss the effect of the incorporation of Fe on their OER properties. The incorporation of Fe dramatically enhances their OER activity, and the OER activity of $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ outperforms that of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF). Moreover, $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$

can serve as a highly active bifunctional catalyst for both the OER and oxygen reduction reaction (ORR). OER free-energy diagrams of the oxychlorides clarified that the incorporation of Fe into $\text{Sr}_2\text{CoO}_3\text{Cl}$ dramatically lowers their theoretical OER overpotentials by providing a new synergistic dual-site mechanism where Co and Fe have different roles in catalyzing the OER.

EXPERIMENTAL SECTION

Preparation and Characterization of Catalysts

$\text{Sr}_2\text{Co}_{1-x}\text{Fe}_x\text{O}_3\text{Cl}$ were prepared by a solid-state method.^{37,38} $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ compounds were firstly synthesized by heating a stoichiometric mixture of SrCO_3 (99.99%, Wako Pure Chemical), Co_3O_4 (99.5%, Sigma-Aldrich), and Fe_2O_3 (99%, Sigma-Aldrich) at 1333 K for 1 day in air. Then, $\text{Sr}_2\text{Co}_{2(1-x)}\text{Fe}_{2x}\text{O}_5$ precursors were prepared by heating the $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ at 1123 K for 1 day in flowing Ar gas.³⁹ Finally, $\text{Sr}_2\text{Co}_{2(1-x)}\text{Fe}_{2x}\text{O}_5$, SrCO_3 , and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (99%, Nacalai Tesque) by 1 : 1 : 1 molar ratio were mixed, and heated at 1123 K for 1 day in air. More details including methods for the preparation of LaCoO_3 (LCO), LaSrCoO_4 (LSC214), BSCF, and IrO_2 which were used as OER-benchmarking catalysts are provided in the Supporting Information.

X-ray diffraction (XRD) measurements were conducted using a RINT-2200 (Rigaku) with $\text{CuK}\alpha$ radiation. Scanning electron microscopy (SEM) observations were performed with an S3000-H (Hitachi). Energy-dispersive X-ray spectroscopy (EDX) was carried out with an EX-220 (Horiba) attached to the chamber of the SEM apparatus. Specific surface area measurements by the Brunauer-Emmett-Teller (BET) analysis were performed with a BELSORP-max (BEL Japan). X-ray photoelectron spectroscopy (XPS) was carried out using a 5500MT (ULVAC-PHI) with $\text{MgK}\alpha$ radiation. The energy scale was calibrated by using a C 1s peak equal to 284.8 eV. Room-temperature Mössbauer spectra with a transmission setup using a $^{57}\text{Co}/\text{Rh}$ source were obtained at the Research Institute for Production Development (Kyoto, Japan).

Density Functional Theory (DFT) Calculations

DFT calculations with a Hubbard U correction for Co 3d ($U_{\text{eff}} = 3.3$ eV) and Fe 3d ($U_{\text{eff}} = 4.0$ eV) electrons were performed with the Vienna Ab initio Simulation Package (VASP).⁴⁰ The energy was calculated using the generalized gradient approximation (GGA) of DFT proposed by the Perdew-Wang functional (PW91).⁴¹ The electronic states were expanded using a plane wave basis set with a cutoff of 500 eV. The Monkhorst-Pack k-point mesh was set with a separation of *ca.* $0.07 \text{ \AA}^{-1}$. As has been suggested previously, all calculations were performed by considering spin states of Co and Fe as both high spins.³⁷ We chose the (001)- CoO_2 termination with SrO subsurface for theoretical calculation (see details in the Supporting Information).

Electrochemical Measurements

A three-electrode cell with a rotating disk electrode (RDE) setup was used for measurements of ORR and OER polarization curves and chronopotentiograms. Pt wire and in-house reversible hydrogen electrode (RHE), which was fabricated by supplying ultrapure H_2 gas to a double-walled glass tube, where a piece of Pt mesh was placed, with glass

filter at its bottom, were used as the counter and the reference electrodes, respectively. Catalyst films with a composition of $250 \mu\text{g cm}^{-2}$ (oxides or oxychlorides), $50 \mu\text{g cm}^{-2}$ (Vulcan XC-72, Cabot), and $50 \mu\text{g cm}^{-2}$ (AS-4, Tokuyama) were formed on a glassy-carbon RDE (disk area: 0.2826 cm^2) by drop-casting a catalyst ink dispersed in 1-hexanol and used as the working electrode. ORR and OER polarization curves were obtained in oxygen-saturated 1.0 mol dm^{-3} KOH at a scan rate of 10 mV s^{-1} . Rotation rates were set at 400, 600, 900, 1200, and 1600 rpm for ORR, and 1600 rpm for OER. For OER Tafel plots, average currents of positive and negative scans were normalized by the BET surface area of the catalysts. Four-step chronopotentiometry was conducted continuously at BET-normalized current densities of 0.1, 0.2, 0.5 and $1.0 \text{ mA cm}^{-2}_{\text{BET}}$ each for 15 min. (Pseudo)capacitances and $\text{Co}^{3+}/\text{Co}^{2+}$ redox behaviors were investigated by cyclic voltammetry in Ar-saturated 1.0 mol dm^{-3} KOH at a rotation rate of 0 rpm. Diffusion coefficients accompanied by redox reactions of Co was also measured in the same setup with chronoamperometry based on a diffusion model proposed by Van Buren *et al.* (see details in the Supporting Information).⁴² Detection of evolved oxygen was performed with a rotating ring disk electrode (RRDE: Pt ring and GC disk). Catalyst films were formed on the GC disk electrode in the same manner as RDEs and were used as the oxygen-evolving electrode. The evolved oxygen was re-reduced at the Pt ring electrode held at 0.4 V (vs. RHE). Calibration of collection efficiency was conducted in $2.0 \text{ mmol K}_3[\text{Fe}(\text{CN})_6]$ in 1.0 mol dm^{-3} KOH.

A two-electrode home-made cell with electrode areas of 3.14 cm^2 was assembled for performance comparison of the catalysts as rechargeable zinc-air batteries. Working electrodes were prepared by spray-coating a catalyst layer (1.35 mg cm^{-2} oxide or oxychloride, 1.35 mg cm^{-2} Vulcan XC-72 and 0.30 mg cm^{-2} polytetrafluoroethylene) on a carbon paper (EC-TP1-120T, Toray). A solution of 6.0 mol dm^{-3} KOH containing 0.20 mol dm^{-3} ZnO, Zn foil (99.5%, Nilaco) and ultrapure oxygen gas were used for the electrolyte, counter electrode, and gas source, respectively. A current density of 5.0 mA cm^{-2} was applied and its direction was switched every 10 min.

RESULTS and DISCUSSION

Characterization Results of $\text{Sr}_2\text{Co}_{1-x}\text{Fe}_x\text{O}_3\text{Cl}$

Based on an analysis by SEM-EDX, all oxychlorides had the desired elemental compositions with average particle sizes of several micrometers (Figure S1 and Table S1). Mössbauer spectra measured at room temperature (Figure S2) revealed that the isomer shifts of all fitted components were *ca.* 0.3 mm s^{-1} , indicating that the valence state of Fe in oxychlorides was +3. In addition, the theoretical energy for the formation of an oxygen vacancy (Figure S3) showed that it is much more difficult to form an oxygen vacancy on oxychlorides than on BSCF,^{25,43} and hence the present oxychlorides would be oxygen stoichiometric compounds. Based on the above results, the detailed chemical formulae of the present oxychlorides are considered to be $\text{Sr}_2\text{Co}^{\text{III}}_{1-x}\text{Fe}^{\text{III}}_x\text{O}_3\text{Cl}$. Wide-range XRD patterns (Figure 1a) revealed that, while a trace amount of $\text{Sr}_6\text{Co}_5\text{O}_{15}$ was observed as an impurity for oxychlorides with $x = 0.0$ and 0.1, this

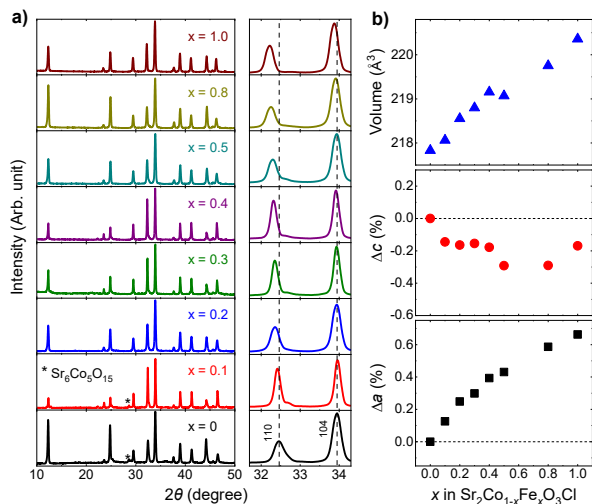


Figure 1. Structural properties of $\text{Sr}_2\text{Co}_{1-x}\text{Fe}_x\text{O}_3\text{Cl}$. (a) (left) Wide-range and (right) narrow-range XRD patterns of $\text{Sr}_2\text{Co}_{1-x}\text{Fe}_x\text{O}_3\text{Cl}$. (b) Lattice parameters of $\text{Sr}_2\text{Co}_{1-x}\text{Fe}_x\text{O}_3\text{Cl}$.

impurity was not observed for $x \geq 0.2$, suggesting that more than 20% substitution of Fe in $\text{Sr}_2\text{CoO}_3\text{Cl}$ enhanced the phase stability of oxychlorides. A similar trend has been observed for a family of Sr-Co-Fe-based perovskite oxides, which argues that the incorporation of Fe improved their stability of perovskite structure.^{32,44} All of the other peaks were assigned to the Ruddlesden-Popper-type structure, and the peak shifts associated with their Fe contents were dependent upon their Miller indices (Figure 1a, right). Accordingly, the changes in the a - and c -axis lattice constants (obtained using “CellCalc” software⁴⁵) had different trends (Figure 1b). As for c -axis lattice constants, a similar trend that mixed-Co/Fe compounds had smaller c -axis lattice constants than pure Co and Fe compounds was reported.³⁷ This contraction behavior might be originated from shortened Co/Fe—Cl length caused by increased disorder in their B site.³⁷ On the other hand, a linear relationship following Vegard’s law was observed for the a -axis lattice constant, which suggested that more homogeneous solid solutions were formed along the ab plane. The difference of a -axis lattice constants for $\text{Sr}_2\text{CoO}_3\text{Cl}$ and $\text{Sr}_2\text{FeO}_3\text{Cl}$ was 0.26 Å, which was better agreement with the differences in effective ionic radii⁴⁶ for high spin Co^{3+} (0.61 Å) and Fe^{3+} (0.645 Å) than those for low spin Co^{3+} (0.545 Å) and Fe^{3+} (0.55 Å). In comparison to the previous literature,³⁷ we observed clear linearity for the a -axis lattice constant in the present study. While a mixture of Fe_2O_3 and $\text{Sr}_2\text{Co}_2\text{O}_5$ was used in the previous study,³⁷ we used a $\text{Sr}_2\text{Co}_{2(1-x)}\text{Fe}_{2x}\text{O}_5$ precursor to synthesize oxychlorides: a more homogeneous mixture of Co and Fe. Based on the above results and the almost linear relationship of their lattice volumes, we confirmed that solid solutions of Co-Fe-based layered perovskite oxychlorides were successfully prepared using $\text{Sr}_2\text{Co}_{2(1-x)}\text{Fe}_{2x}\text{O}_5$ precursors.

OER Activity

Figure 2a shows OER polarization curves of $\text{Sr}_2\text{Co}_{1-x}\text{Fe}_x\text{O}_3\text{Cl}$ with $x = 0.0, 0.2, 0.5, 0.8$ and 1.0 , and benchmark catalysts (LCO, LSC214, BSCF, and IrO_2) in oxygen-

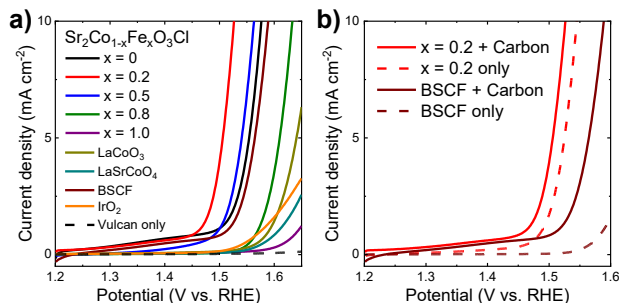


Figure 2. Catalytic activities of oxychlorides and other oxides. (a) OER polarization curves of $\text{Sr}_2\text{Co}_{1-x}\text{Fe}_x\text{O}_3\text{Cl}$ ($x = 0.0, 0.2, 0.5, 0.8$ and 1.0), LaCoO_3 , LaSrCoO_4 , $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and Vulcan composite electrodes. (b) OER polarization curves of (black) $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ and (brown) BSCF. Solid lines represent results from a catalyst layer consisting of perovskites and AS-4, and dashed lines represent those from a layer consisting of perovskites, Vulcan and AS-4. Polarization curves were obtained in oxygen-saturated 1.0 mol dm^{-3} KOH at 1600 rpm.

saturated 1.0 mol dm^{-3} KOH at a rotation rate of 1600 rpm. Their OER activities were maintained for at least 10 cycles, except for $x = 1.0$ (Figure S4). Interestingly, even the incorporation of only 10% Fe dramatically enhanced its OER activity (Figure S5), and the oxychloride with $x = 0.2$ showed the highest OER activity. This enhancement was very interesting because $\text{Sr}_2\text{FeO}_3\text{Cl}$ ($x = 1.0$) showed quite low activities. Normally, $\text{Co}^{\text{III}}\text{-Fe}^{\text{III}}$ mixed perovskite oxides show a gradual change in activity as a function of their composition; for example, $\text{LaCo}_{1-x}\text{Fe}_x\text{O}_3$ in the literature⁴⁴ and our results (Figure S6). The detailed mechanism of this activity-enhancement will be discussed later. We should note that verification of the measured oxidation current has been carried out by a technique using an RRDE (Pt ring/GC disk). In the technique, evolved oxygen at the catalyst layer on the GC disk electrode were re-reduced at Pt-ring electrode held at 0.4 V (vs. RHE).^{25,47} The resultant collection efficiency of the $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ composite catalyst at the ring electrode were *ca.* 0.35 (Figure S7), which was in good agreement with the calibrated value ($N \approx 0.36$, Figure S8), indicating that the resultant oxidation current was almost fully from OER.

The OER overpotential of $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ at 10 mA cm^{-2} decreased by *ca.* 50 mV compared with $\text{Sr}_2\text{CoO}_3\text{Cl}$, and by *ca.* 60 mV compared with BSCF, which indicates that $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ was comparable in catalytic activity to state-of-the-art perovskite catalysts such as $\text{CaCu}_3\text{Fe}_4\text{O}_{12}$,¹⁶ a hybrid of $\text{LaSr}_3\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_{10-\delta}$ / $\text{La}_{0.25}\text{Sr}_{0.75}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$,²² and $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$.¹³ The superior OER activity of $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ was not limited to 1.0 mol dm^{-3} KOH ($\text{pH} = 14$), but was also seen with 0.1 mol dm^{-3} KOH ($\text{pH} = 13$) (Figure S9). Another interesting feature of $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ is that carbon was not necessary for the OER (Figure 2b). In general, carbon activates oxide catalysts such as BSCF, and therefore, carbon is essential to build catalyst electrodes.⁴⁸ Furthermore, the OER activity of $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ without carbon was still higher than that of a BSCF electrode with carbon, meaning that only $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ had a high OER activity. These results clearly indicate that $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ is attractive as a practical OER anode, where the oxidative

decomposition of carbon is inevitable from a thermodynamic viewpoint.⁴⁹

Figure 3a and Table S2 show BET-normalized Tafel plots

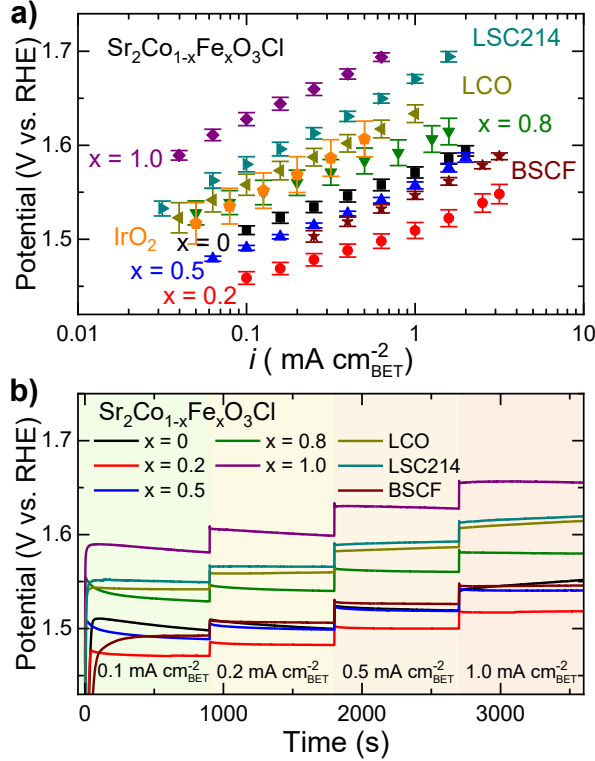


Figure 3. Electrode performance of oxychlorides and oxides. (a) Tafel plots of the catalysts. Error bars represent standard deviation obtained from at least three independent measurements. (b) Four-step (0.1, 0.2, 0.5 and 1.0 mA cm⁻²_{BET}) chronopotentiograms of the catalysts.

(see Figure S10 and Table S3 for their BET data) and Tafel slopes of the representative oxychlorides and benchmark catalysts. Clearly, Sr₂Co_{0.8}Fe_{0.2}O₃Cl had better OER performance than BSCF in terms of their Tafel plots and Tafel slopes. Moreover, much better specific activity of Sr₂Co_{0.8}Fe_{0.2}O₃Cl than IrO₂ exhibits its superiority as an OER catalyst. The smaller value of the Tafel slope for Sr₂Co_{0.8}Fe_{0.2}O₃Cl implies that it had faster OER kinetics than Sr₂CoO₃Cl, which can be associated with the electronic interaction between Co and Fe, as we discuss later. Chronopotentiometry was performed to evaluate the short-term stability of the oxychlorides (Figure 3b). As with other methods used in the present study, Sr₂Co_{0.8}Fe_{0.2}O₃Cl showed the highest OER activity with almost no decrease in activity. The stable OER current of Sr₂Co_{0.8}Fe_{0.2}O₃Cl was further confirmed in a prolonged chronopotentiometry for 12 h at 10 mA cm⁻²_{GC} (Figure S11). Further post-OER characterization associated with surface reconstruction is an ongoing work. The total number of moles of electrons during chronopotentiometry calculated from the OER current from Figure 3b was roughly 100 times larger than that of catalysts loaded on RDE. Therefore, it was clearly proved that the measured oxidation current was not due to oxidative decomposition of the oxychlorides, but rather from electrocatalytic oxygen evolution (see Supporting Information for detailed calculation).

In addition to its high OER activity, Sr₂Co_{0.8}Fe_{0.2}O₃Cl also showed fairly good ORR activity (Figure 4a,b). As a result,

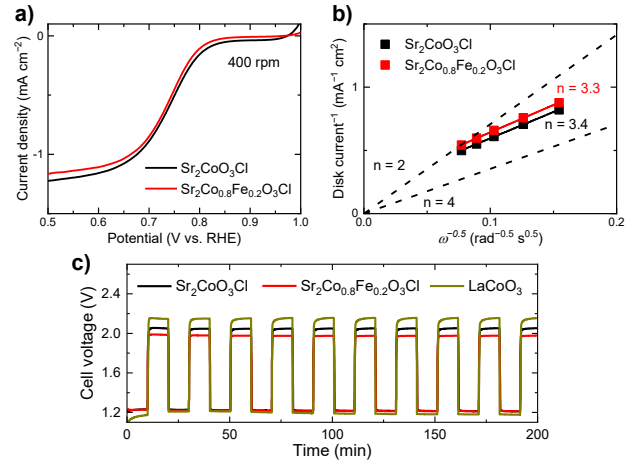


Figure 4. ORR and battery performance of oxychlorides. (a) ORR polarization curves of (black) Sr₂CoO₃Cl and (red) Sr₂Co_{0.8}Fe_{0.2}O₃Cl in oxygen-saturated 1.0 mol dm⁻³ KOH at 400 rpm. (b) Koutecký-Levich plots of the corresponding oxychlorides. (c) Charge-discharge voltages of prototype rechargeable zinc-air batteries using (black) Sr₂CoO₃Cl, (red) Sr₂Co_{0.8}Fe_{0.2}O₃Cl and (yellow) LaCoO₃ catalysts at a current density of 5.0 mA cm⁻².

the sum of its ORR and OER overpotentials (defined by -50 μ A cm⁻²_{BET} for ORR overpotential and 100 μ A cm⁻²_{BET} for OER overpotential) was as low as Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} ||La_{0.8}Sr_{0.2}MnO_{3- δ} ||Nb-doped SrTiO₃ thin film, which is known as a bifunctional catalyst with high specific activities (Table S4).⁵⁰ Moreover, as can be seen in the results with a prototype rechargeable zinc-air battery (Figure 4c), not only the OER overpotential but also the sum of the ORR and OER overpotentials of Sr₂Co_{0.8}Fe_{0.2}O₃Cl were considerably lower than those of LCO, which is a conventional bifunctional catalyst. It should be emphasized that the lower OER overpotential of Sr₂Co_{0.8}Fe_{0.2}O₃Cl consequently contributes to the higher ORR potential because oxidative decomposition of carbon, which is considered to play an electrocatalytic role to reduce O₂ to HO₂⁻ during the ORR,^{51,52} was suppressed during the OER. In addition to catalytic activity, Sr₂Co_{0.8}Fe_{0.2}O₃Cl showed the most stable ORR/OER voltages during cycles, proving another advantageous feature of the oxychloride as an oxygen electrode catalyst.

OER Descriptors of Sr₂Co_{1-x}Fe_xO₃Cl

The key factors that underlie the present enhanced OER activity are different than those for well-known BSCF for the following reasons. While BSCF is a highly oxygen-deficient compound,^{25,43} which can promote OER kinetics via a mechanism involving lattice-oxygen sites,^{53,54} Sr₂Co_{0.8}Fe_{0.2}O₃Cl is an oxygen-stoichiometric compound. Furthermore, from the viewpoint of its e_g filling of Co, while Co for BSCF is in an intermediate spin state (Co^{2.8+}, $t_{2g}^5e_g^{1.2}$), which is known to be a key factor for its high OER activity,²⁵ Sr₂Co_{0.8}Fe_{0.2}O₃Cl has a high spin state (Co³⁺, $t_{2g}^4e_g^2$).^{37,38,55} To explain the highest OER activity of Sr₂Co_{0.8}Fe_{0.2}O₃Cl, we have to explore other possible mechanisms. We first conducted first-principles calculations for O p -band centers, which have been suggested to be a descriptor for OER activities of oxide

catalysts.¹² Despite the fact that OER activity order of $\text{Sr}_2\text{CoO}_3\text{Cl}$ and LaSrCoO_4 can be explained by their O p -band centers,³¹ those of $\text{Sr}_2\text{CoO}_3\text{Cl}$, $\text{Sr}_2\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_3\text{Cl}$, $\text{Sr}_2\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_3\text{Cl}$ and $\text{Sr}_2\text{FeO}_3\text{Cl}$ (Table S5) did not follow their OER activity order, suggesting that the O p -band center of Co-Fe-based oxychlorides is not applicable to their OER descriptor. This might be due to the fact that charge-transfer energies, which is indirectly associated with the rate-determining step of OER among perovskites with different B-site cations, depend not only on their O p -band centers, but also their unoccupied B $3d$ -band centers.²⁶ Also, XPS Co $2p$, Fe $2p$ and O $1s$ spectra of oxychlorides (Figure S12) were almost invariant, except for O $1s$ of $x = 1.0$, suggesting that the valence states of the B-site elements and relative contents of $\text{O}_2^{2-}/\text{O}^-$ were not a dominating factor for their OER activities.

Next, we calculated the free energies of OER intermediates by assuming a four-step mechanism at a Co or Fe site (Table S6). Figure 5a shows computed OER free-energy diagrams of $\text{Sr}_2\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_3\text{Cl}$ at a single Co or Fe site. Theoretical overpotentials of $\text{Sr}_2\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_3\text{Cl}$ were calculated to be 1.63 V at Fe site and 1.64 V at Co site. Compared with Co-Fe system, theoretical overpotential of $\text{Sr}_2\text{CoO}_3\text{Cl}$ were also almost the same (1.64 V) although their rate-limiting steps were different. Different from $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ system,¹³ these calculations indicated that Fe in $\text{Sr}_2\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_3\text{Cl}$ does not have higher intrinsic OER activity, and that a simple one-site mechanism does not explain the experimental finding of enhanced OER activities. On the other hand, the free energies of their OOH^* intermediates were quite different. While the free energies of relaxed Co-OOH (Figure 5b, left) and Co-OH followed a scaling relation of $\Delta G_{\text{OOH}} - \Delta G_{\text{OH}} \approx 3.1$ eV,⁵⁶ those of relaxed Fe-OOH (Figure 5b, right) and Fe-OH did not follow the scaling relationship, due to stabilization of the proton in Fe-OOH by neighboring O (*i.e.*, $-\text{Co}-(\text{OH})-\text{Fe}(\text{OO})-$). Similar behavior has been observed for some hybrid or multi-transition metal catalysts: MnO_x/Au ,⁵⁷ Co oxides/ Au ,^{58,59} NiO/NiFe LDH,⁶⁰ and $\gamma\text{-FeOOH}/\gamma\text{-NiOOH}$ ⁶¹ in alkaline media,

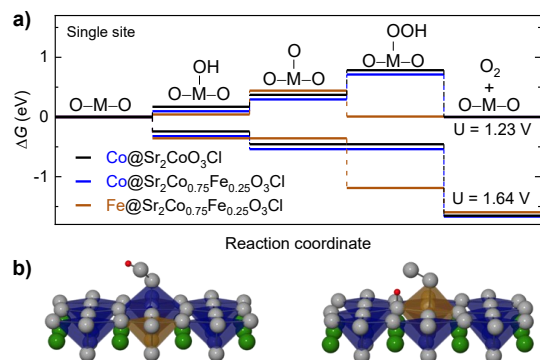


Figure 5. Energy diagram of OER on single-site oxychlorides. (a) Free-energy diagrams of $\text{Sr}_2\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_3\text{Cl}$ involving a conventional four-step mechanism on a Fe or Co site. (b) Snapshots of (left) relaxed Co-OOH and (right) Fe-OOH intermediates. Grey, green, and red spheres represent O, Sr, and H atoms, respectively. Blue and brown polyhedrons represent those of cobalt and iron, respectively.

and Co- or Ni-doped RuO_2 ⁶² in acidic media. In these systems, the theoretical OER overpotential can be decreased beyond the so-called “volcano limitation”⁶³ because of the stabilization of OOH^* intermediates. In the present oxychlorides, therefore, we propose a dual-site mechanism with hydroxide diffusion in the reaction step 4 in alkaline media (Figure 6a), which corresponds to proton diffusion in acidic media (Figure S13). It should be noted that the resultant intermediate after hydroxide diffusion at step 4 was shown as $-(\text{OH})-\text{Fe}(\text{OO})-$, which is a relaxed structure of Fe-OOH (as displayed in Figure 6b). In this mechanism, Co and Fe sites act as in a relay race: the intermediate formed on Co is passed to Fe. The difference in free energy in reaction step 4 was *ca.* 0.055 eV uphill (Figure 6b), which is sufficiently small that it is likely to occur at some rate at room temperature. In alkaline media, once hydroxide diffuses from Co to Fe sites, the next OER step on an Fe site is sufficiently downhill at any OER potential region, which probably accelerates

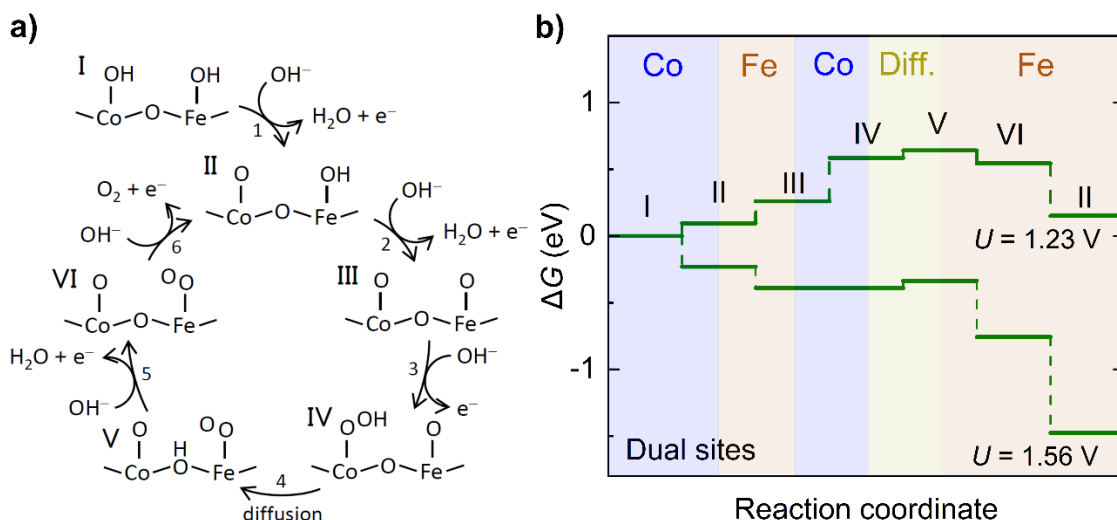


Figure 6. (a) A proposed dual-site mechanism for $\text{Sr}_2\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_3\text{Cl}$ in alkaline media. (b) Free-energy diagram of $\text{Sr}_2\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_3\text{Cl}$ involving a new dual-site mechanism.

the further diffusion of hydroxide from Co to Fe sites. The high diffusion coefficient accompanied by redox reactions of Co especially at high Co content (Table S7) further supports that the step 4 proceeds at a certain kinetic rate. The calculated theoretical overpotential of $\text{Sr}_2\text{Co}_{0.75}\text{Fe}_{0.25}\text{O}_3\text{Cl}$ using the above-mentioned dual-site mechanism was 0.33 V, which is smaller than that of $\text{Sr}_2\text{CoO}_3\text{Cl}$ (0.41 V). The difference of calculated OER overpotentials (80 mV) was in good agreement with that of the BET-normalized experimental values (*ca.* 60 mV at 1 mA cm⁻²_{BET}), indicating that OER enhancement of $\text{Sr}_2\text{CoO}_3\text{Cl}$ was successfully achieved by the incorporation of Fe.

Finally, we conducted cyclic voltammetry for oxychlorides in a potential range where OER did not occur (Figure 7). Clear redox peaks were observed for $x = 0 \sim 0.3$ at *ca.* 1.0

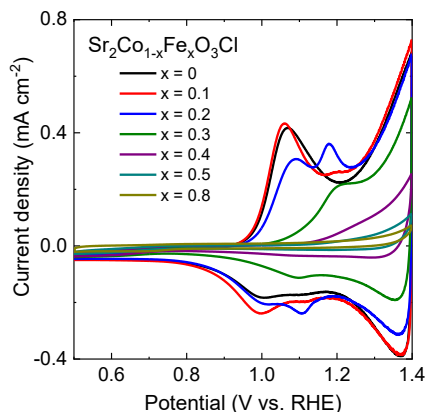


Figure 7. Cyclic voltammograms of $\text{Sr}_2\text{Co}_{1-x}\text{Fe}_x\text{O}_3\text{Cl}$ in an Ar-saturated 1.0 M KOH solution.

~ 1.2 V vs. RHE, which were also present even at the first cycle of the negative sweep (Figure S14). Given that the valence state of Co in the pristine oxychlorides was mainly +3 (Figure S12a), the observed redox peaks can be attributed to $\text{Co}^{3+}/\text{Co}^{2+}$. A trend that the $\text{Co}^{3+}/\text{Co}^{2+}$ redox potentials were shifted to higher potentials with an increase in their Fe contents could be ascribed to an electronic interaction between Co and Fe, leading to a modification of cobalt *d* electronic configuration.^{64,65} Both the peak areas of $\text{Co}^{3+}/\text{Co}^{2+}$ and the (pseudo)capacitances of oxychlorides, which are associated with their electrochemically active sites and electrochemical surface areas (ECSAs), respectively, decreased with an increase in their Fe contents. Therefore, the increase in their Fe contents had a negative impact on their OER activities from the viewpoint of their Co active sites and ECSAs. In addition, the electronic resistivities of oxychlorides (Table S8) also monotonously increased with an increase in their Fe contents, which also has a negative impact on their OER activities. Taken together, these results suggest that the incorporation of Fe is a double-edged sword: it had both positive and negative impacts on OER activities, and the Fe content was optimized at *ca.* $x = 0.2$ in terms of reaction pathways, electronic conductivities, active sites, and ECSAs.

CONCLUSION

We investigated the OER activities of $\text{Sr}_2\text{Co}_{1-x}\text{Fe}_x\text{O}_3\text{Cl}$ in alkaline media and demonstrated that the OER activity of $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ was remarkably higher than that of BSCF.

Moreover, the finding that OER activity was almost completely independent of the existence of conductive additives and the moderate ORR activity of $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ strongly suggested that $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ is a promising candidate not only for use in OER anodes in water-splitting devices, but also for bifunctional electrodes in metal-air batteries. The calculated free energies of OER intermediates revealed that Co and Fe sites worked synergistically. The high OER activity of $\text{Sr}_2\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3\text{Cl}$ could be attributed to its optimized OER descriptors (*i.e.*, active sites, ECSAs, electronic resistivities, and reaction pathways) for the present oxychlorides. These results demonstrate that tailoring both the cation and anion compositions can be a powerful tool for enhancing oxygen electrocatalytic activities of transition metal catalysts.

ASSOCIATED CONTENT

Supporting Information

Details of oxide catalyst preparation, DFT calculations, calculation of total electron mole, Koutecký-Levich plots, and measurement of diffusion coefficients; SEM-EDX; Mössbauer spectra; oxygen vacancy formation energy; polarization curves; BET plots; XPS spectra; dual-site mechanism in acidic media; Tafel slopes; BET surface areas; sum overpotentials of ORR and OER; O *p*-band centers; DFT-calculated energies; diffusion coefficients; resistivities. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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