Electronic Supplementary Information (ESI) for

Strontium Cobalt Oxychloride: Enhanced Electrocatalysts for Oxygen Reduction and Evolution Reactions

Yuto Miyahara, Kohei Miyazaki*, Tomokazu Fukutsuka, Takeshi Abe
1. Experimental Methods

Preparation of catalysts

**Sr$_2$CoO$_3$Cl and Sr$_3$Co$_2$O$_5$Cl$_2$:** Sr$_2$CoO$_3$Cl and Sr$_3$Co$_2$O$_5$Cl$_2$ were prepared by a solid state reaction.$^{S1}$ Prior to the synthesis of the oxychlorides, Sr$_2$Co$_2$O$_5$ was firstly prepared by heating a mixture of SrCO$_3$ (Wako, 99.99%) and Co$_3$O$_4$ (Aldrich, 99.5%) (3 : 1 by molar ratio) at 1273 K for 24 h in air, and followed by quenching by liquid N$_2$. Sr$_2$Co$_2$O$_5$, SrCO$_3$, and SrCl$_2$ (Nacalai Tesque, 99%) (1 : 1 : 1 by molar ratio), or Sr$_2$Co$_2$O$_5$ and SrCl$_2$ (1 : 1 by molar ratio) were mixed, and heated at 1123 K for 24 h in air and cooled at a rate of ca. 5 K min$^{-1}$ to obtain Sr$_2$CoO$_3$Cl or Sr$_3$Co$_2$O$_5$Cl$_2$, respectively.

**LaSrCoO$_4$:** LaSrCoO$_4$ was prepared by a solid state reaction. La$_2$O$_3$ (Nacalai Tesque, 99.99%), SrCO$_3$ (Wako, 99.99%), and Co$_3$O$_4$ (Wako, 99.5%) (3 : 6 : 2 by molar ratio) were mixed, and heated at 1373 K for 8 h in air and cooled at a rate of ca. 5 K min$^{-1}$.

**LaCoO$_3$:** LaCoO$_3$ was prepared by a sol-gel method.$^{S2}$ La(NO$_3$)$_3$·6H$_2$O (Nacalai Tesque, 99.9%), Co(NO$_3$)$_2$·6H$_2$O (Wako, 99.5%), and C$_6$H$_8$O$_7$ (citric acid; Nacalai Tesque, 99%) (1 : 1 : 1 by molar ratio) were dissolved in deionized water (18.2 MΩ). The solution was heated at ca. 80 °C until a viscous gel was obtained. The gel was then calcined at 1023 K for 5 h in air and cooled at a rate of ca. 5 K min$^{-1}$.

**Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_3$-d (BSCF):** BSCF was prepared by a sol-gel method.$^{S3}$ Ba(NO$_3$)$_2$ (Wako, 99.9%), Sr(NO$_3$)$_2$ (Wako, 98%), Co(NO$_3$)$_2$·6H$_2$O (Wako, 99.5%), Fe(NO$_3$)$_3$·9H$_2$O (Wako, 99.9%), and C$_6$H$_8$O$_7$ (citric acid) (Nacalai Tesque, 99%) (5 : 5 : 8 : 2 : 40 by molar ratio) were dissolved in deionized water (18.2 MΩ). Aqueous ammonia (28%, Nacalai Tesque) was added until the pH of the solution became ca. 7. The solution was heated at ca. 80 °C until a viscous gel was obtained. The gel was then calcined at 1023 K for 5 h in air and cooled at a rate of ca. 5 K min$^{-1}$.

**La$_{1-x}$Sr$_x$FeO$_{3-d}$F$_x$ (LSFO/F, x = 0.5, 1):** LSFO/F were prepared by a solid state reaction.$^{S4,5}$ La$_2$O$_3$ (Nacalai Tesque, 99.99%), SrCO$_3$ (Wako, 99.99%), and Fe$_2$O$_3$ (Aldrich, 99%) were mixed, and heated twice at 1523 K for 30 h in air with intermediate grinding at a rotation rate of 300 rpm in ethanol and cooled at a rate of ca. 1 K min$^{-1}$ to obtain La$_{1-x}$Sr$_x$FeO$_3$ (LSFO). Fluorination of LSFO was performed

S1
by using poly(vinylidenefluoride) (PVDF; Aldrich). LSFO and PVDF (LSFO : monomer unit = 1 : 0.75 by molar ratio) were mixed, and heated at 623 K for 24 h in air and cooled at a rate of \( \text{ca.} \ 1 \ \text{K min}^{-1} \). 

**Characterization of catalysts**

X-ray diffraction (XRD) measurements were conducted by RINT-2200 (Rigaku) with Cu Kα radiation operated at 40 kV and 40 mA. Scanning electron microscopy (SEM) observation of the prepared catalysts were performed with S3000-H (Hitachi). Energy-dispersible X-ray spectroscopy (EDX) was carried out by EX-220 (Horiba) attached to the chamber of SEM apparatus. Specific surface area measurements by the Brunauer-Emmet-Teller (BET) analysis were performed by BELSORP-max (BEL Japan). X-ray photoelectron spectroscopy (XPS) was carried out by ULVAC-PHI 5500MT with Mg Kα operated at 15 kV and 400 W.

**DFT studies**

DFT calculations with Hubbard U (\( U_{\text{eff}} = 3.3 \ \text{eV} \)) correction for the Co 3d electrons were performed with the CASTEP in the Materials Studio package. The energy was calculated using the generalized gradient approximation (GGA) of DFT proposed by Perdew, Burke, and Ernzerhof (PBE). The electronic states were expanded using a plane wave basis set with a cutoff of 340 eV. Geometry optimization calculation was performed before electronic structure calculation using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm. The Monkhorst-Pack k-point mesh was set with a separation of \( \text{ca.} \ 0.07 \ \text{Å}^{-1} \). All calculations were performed in the high-spin state (+4) of Co 3d electrons.

**Electrochemical measurements**

All electrochemical measurements were performed in a three-electrode cell with a rotating disk electrode (RDE) using ALS 600A electrochemical analyzer (CH Instruments) or HZ-7000 (HOKUTO DENKO). The electrolyte of 1 mol dm\(^{-3}\) (M) KOH was prepared using KOH pellets (Nacalai Tesque, 85%) and
deionized water (18.2 MΩ). Pt wire and reversible hydrogen electrode (RHE) were used as the counter and reference electrodes, respectively. Perovskite composite electrodes were prepared by drop-casting a catalyst ink and were used as the working electrode. The catalyst ink was prepared by dispersing perovskite powders, carbon black (Vulcan XC-72, Cabot) in 1-hexanol (Nacalai Tesque, 98%) using an ultrasonic bath. After dropping and drying the catalyst layer, an anion-exchange ionomer solution (AS-4, Tokuyama) was dropped onto the catalyst layer, and then dried. Final composition of the composite electrodes was 250 µg cm⁻² (perovskites), 50 µg cm⁻² (Vulcan), and 50 µg cm⁻² (AS-4). During the electrochemical measurements, the electrolyte was continuously bubbled with ultra-pure oxygen or argon gas. Polarization curves were obtained from negative scan for oxygen reduction reaction (ORR) and positive scan for oxygen evolution reaction (OER) at a scan rate of 10 mV s⁻¹.

**Koutecky-Levich plots**

The ORR electron transfer numbers \((n)\) of the composite electrodes were calculated by the Koutecky-Levich equation:

\[
\frac{1}{I} = \frac{1}{I_k} + \frac{1}{0.62nFAC_o_2D_{O_2}^{2/3}v^{-1/6}\omega^{1/2}}
\]

where \(I\) is the measured current, \(I_k\) is the kinetic current, \(n\) is the ORR electron transfer number, \(F\) is the Faraday constant (96485 C mol⁻¹), \(A\) is the geometric surface area (0.2826 cm²), \(C_{O_2}\) is the oxygen concentration in the electrolyte \((8.7\times10^{-7} \text{ mol cm}^{-3})\), \(D_{O_2}\) is the oxygen diffusion coefficient \((1.53\times10^{-5} \text{ cm}^2 \text{ s}^{-1})\), \(v\) is the kinematic viscosity \((8.7\times10^{-3} \text{ cm}^2 \text{ s}^{-1})\), and \(\omega\) is the rotation rate. An ideal \(n\) value of 4.0 was obtained for Pt(40wt%)/Vulcan (E-TEK) (Fig. S4) from the linear relationship between \(I^{-1}\) and \(\omega^{-1/2}\).
2. Supplementary Tables and Figures

Fig. S1 ORR polarization curves of (a) \( \text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3 - \text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{2.5} \cdot \text{F}_{0.5} \) and (b) \( \text{SrFeO}_3 - \text{d} - \text{SrFeO}_2 \cdot \text{F} \) composite electrodes in oxygen-saturated 1 M KOH at a scan rate of 10 mV s\(^{-1}\) and rotation rates of 400, 900, and 1600 rpm. OER polarization curves of (c) \( \text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3 - \text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{2.5} \cdot \text{F}_{0.5} \) and (d) \( \text{SrFeO}_3 - \text{d} - \text{SrFeO}_2 \cdot \text{F} \) composite electrodes in oxygen-saturated 1 M KOH at a scan rate of 10 mV s\(^{-1}\) and a rotation rate of 1600 rpm.
Fig. S2 XRD patterns of (a) Sr$_2$CoO$_3$Cl, (b) Sr$_3$Co$_2$O$_5$Cl$_2$, (c) LaSrCoO$_4$, (d) LaCoO$_3$, and (e) Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-d}$.
Fig. S3 SEM images of (left) Sr$_2$CoO$_3$Cl and (right) Sr$_3$Co$_2$O$_5$Cl$_2$.

Table S1 Atomic compositions of prepared oxychlorides determined by EDX analysis

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>Experimental composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_2$CoO$_3$Cl</td>
<td>Sr$_{1.98}$CoO$<em>x$Cl$</em>{0.93}$</td>
</tr>
<tr>
<td>Sr$_3$Co$_2$O$_5$Cl$_2$</td>
<td>Sr$_{3.07}$Co$_2$O$<em>x$Cl$</em>{1.96}$</td>
</tr>
</tbody>
</table>

Experimental compositions were normalized with nominal B site composition of 1 for Sr$_2$CoO$_3$Cl and 2 for Sr$_3$Co$_2$O$_5$Cl$_2$. 
Table S2 BET surface areas of the prepared samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr₂CoO₃Cl</td>
<td>2.6</td>
</tr>
<tr>
<td>Sr₃Co₂O₅Cl₂</td>
<td>2.6</td>
</tr>
<tr>
<td>LaSrCoO₄</td>
<td>1.4</td>
</tr>
<tr>
<td>LaCoO₃</td>
<td>2.0</td>
</tr>
<tr>
<td>Ba₀.₅Sr₀.₅Co₀.₅Fe₀.₂O₃·d</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Fig. S4 XPS Co2p spectra of (black) Sr₂CoO₃Cl, (red) Sr₃Co₂O₅Cl₂, (blue) LaCoO₃, and (green) LaSrCoO₄.
Fig. S5 Cyclic voltammograms of (a) Sr$_2$CoO$_3$Cl and (b) Sr$_3$Co$_2$O$_5$Cl$_2$ in argon-saturated 1 M KOH at a scan rate of 10 mV s$^{-1}$ and a rotation rate of 0 rpm.
Fig. S6 ORR polarization curves of (a) LaCoO$_3$, (b) Pt(40wt%)/Vulcan, (c) LaSrCoO$_4$, and (d) Vulcan composite electrodes in oxygen-saturated 1 M KOH at a scan rate of 10 mV s$^{-1}$ and rotation rates of 400, 600, 900, 1200, and 1600 rpm.
Fig. S7 OER polarization curves of (a) Sr$_2$CoO$_3$Cl, (b) Sr$_3$Co$_2$O$_5$Cl$_2$, (c) Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$, (d) LaSrCoO$_4$, and (e) LaCoO$_3$ composite electrodes in oxygen-saturated 1 M KOH at a scan rate of 10 mV s$^{-1}$ and a rotation rate of 1600 rpm.
Fig. S8 (a) Comparison of OER polarization and (b) corresponding pseudocapacitive region prior to OER in oxygen-saturated 0.1 M KOH at a scan rate of 10 mV s$^{-1}$ and a rotation rate of 1600 rpm.

Fig. S9 Total density of states and partial density of states of (a) LaCoO$_3$ and (b) LaSrCoO$_4$. 
References


