Electronic Supplementary Information

Hydrated strontium cobalt oxyhydroxide Ruddlesden–Popper phase as an oxygen electrocatalyst for aqueous lithium–oxygen rechargeable batteries

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Supplementary methods

Sample preparation.

$Sr_3Co_2O_5(OH)_2 \cdot 2H_2O$ was synthesized by solid-state reaction. Appropriate amounts of $SrCO_3$ (99.9%, Sigma-Aldrich) and Co_3O_4 (99.9%, Kojundo Chemical Laboratory) were mixed in an agate mortar and pestle. The powder was pelletized and calcined at 1000 °C for 12 h in air. The pellet was reground, pelletized, sintered at 1000 °C for 48 h in an oxygen atmosphere, and then annealed at 200 °C for 9 h. The obtained sample reacted spontaneously with moisture in the air to form the hydrated oxyhydroxide.

$LaCoO_3$ and $LaSrCoO_4$ were synthesized by solid-state reaction. Stoichiometric amounts of La_2O_3 (99.9%, Rare Metallic), $SrCO_3$ (99.9%, Sigma-Aldrich), and Co_3O_4 (99.9%, Kojundo Chemical Laboratory) were mixed in an agate mortar and pestle. The molar ratios of La_2O_3 to $SrCO_3$ to Co_3O_4 were 3:0:2 and 3:6:2 for $LaCoO_3$ and $LaSrCoO_4$ compositions, respectively. The powder was pelletized and calcined at 1000 °C for 12 h in air. The pellet was then ground, pelletized again, and sintered at 1350 °C for $LaCoO_3$ and at 1150 °C for $LaSrCoO_4$ for 12 h in air.

$La_4Co_3O_{10}$ was synthesized by a sol–gel-based Pechini method. Required amounts of $La(NO_3)_3 \cdot 6H_2O$ (99.9%, Nacalai Tesque) and $Co(CH_3COO)_2 \cdot 4H_2O$ (99.0%, Nacalai Tesque) in a molar ratio of 4:3 were dissolved in $C_6H_8O_7$ (citric acid; 99.0%, Nacalai Tesque) solution. The clear pink solution was placed on a hot plate stirrer and heated at 80 °C. The solution was subsequently heated at 200 °C to obtain a viscous gel and then burned at 450 °C for 12 h. The resultant powder was pelletized and sintered at 1100 °C for 12 h in a nitrogen atmosphere.

$LaSr_3Fe_3O_{10}$ was synthesized by solid-state reaction. Stoichiometric amounts of La_2O_3 (99.9%, Rare Metallic), $SrCO_3$ (99.9%, Sigma-Aldrich), and Fe_2O_3 (99%, Sigma-

Aldrich) were mixed in an agate mortar and pestle. The powder was pelletized and calcined at 1400 °C for 3 h in air.

Sample characterization.

Powder X-ray diffraction (XRD; D8 Advance, Bruker) measurements were performed to characterize the synthesized compounds using Cu *Kα* radiation. The elemental composition of $Sr_3Co_2O_5(OH)_2{\cdot}2H_2O$ was analyzed using an inductively coupled plasma–optical emission spectrometer (720 ICP-OES, Agilent Technologies). The sample morphology and elemental composition were characterized using a scanning electron microscope (SEM; S-4800, Hitachi) with an energy dispersive X-ray spectrometer (EX-350, Horiba). Particle size distributions were measured with a particle size analyzer (MT3300EXII, Microtrac). The Brunauer–Emmett–Teller (BET) specific surface areas were measured using a surface area and porosity analyzer (TriStar 3000, Micromeritics).

Preparation of gas-diffusion electrode (GDE).

Carbon-based GDEs with $Sr_3Co_2O_5(OH)_2{\cdot}2H_2O$ and $LaCoO_3$, and without any catalysts were prepared with weight ratios of catalyst–Ketjenblack (EC600JD, Lion)–polytetrafluoroethylene (F-104, Daikin) of 4:5:1, 4.6:5:1, and 0:5:1, respectively, where the surface area of $LaCoO_3$ was adjusted to that of the oxyhydroxide. The powder was mixed in an agate mortar and pestle with a small amount of ethanol. The mixture was rolled out to form a 0.4 mm thick sheet and dried under vacuum at 80 °C.

Electrolyte preparation.

An aqueous solution of 10.0 mol L^{-1} LiCl + 2.0 mol L^{-1} LiOH was prepared according to the following procedure. LiCl (99.0%, Nacalai Tesque) and $LiOH{\cdot}H_2O$ (99.0%, Nacalai Tesque) were dissolved in distilled water with nitrogen bubbling. The solution was stirred for 24 h to obtain the desired electrolyte solution.

Electrochemical measurements.

All electrochemical measurements were conducted using a bipotentiostat (DY2325, ALS) or a multi-channel potentiostat/galvanostat (VMP3, Bio-Logic). Rotating disk electrode (RDE) measurements were performed with an RDE apparatus (RRDE-3A, ALS). The discharge/charge behavior of the GDE was also tested in a conventional three-electrode system with a Pt/Pt black counter electrode and a Ag/AgCl reference electrode. The reference electrode is unstable in alkaline environment; therefore, it was separated with a salt bridge. The cell was placed in an oxygen-filled chamber. One side of the GDE was in contact with the electrolyte solution, while the other side was in contact with the gas phase.

Dissolved oxygen titration.

The concentration of oxygen in the prepared solution was determined using the Winkler titration method, which is based on the following equations:

$$Mn^{2+} + 2OH^{-} \rightarrow Mn(OH)_2\downarrow \tag{1}$$

$$Mn(OH)_2 + 1/2O_2 \rightarrow MnO(OH)_2\downarrow \tag{2}$$

$$MnO(OH)_2 + 2I^{-} + 4H^{+} \rightarrow Mn^{2+} + 3H_2O + I_2 \tag{3}$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^{-} + S_4O_6^{2-} \tag{4}$$

The solution was bubbled with oxygen prior to titration. The solution was filled into a glass bottle making sure that no bubbles were present. A 2.0 mol L^{-1} $MnSO_4$ solution and 12.5 mol L^{-1} NaOH + 0.9 mol L^{-1} KI solution were added to the analyte and the bottle was capped (Equations 1 and 2). The solution was shaken for a minute and moved into a nitrogen filled glove bag to avoid contact with oxygen. The contents of the bottle were then poured into a flask, and H_2SO_4 was added dropwise (Equation 3). The solution was titrated with 2.50×10^{-3} mol L^{-1} $Na_2S_2O_3$ solution (Equation 4), and the oxygen concentration C_{O2}, was calculated to be 3.77×10^{-5} mol L^{-1}.

Diffusion coefficient of oxygen.

The diffusion coefficient of oxygen in the electrolyte solution D_{O2}, was obtained using a potential step technique. The potential of a platinum disk electrode was stepped from 1.23 V to 0.4 V *vs.* reversible hydrogen electrode (RHE) and kept for 1 s in the oxygen-saturated electrolyte solution. The working electrode was then rotated at 3600 rpm to remove the reaction products and the measurement was repeated after a 5 min rest. The observed current can be described as follows:[S1]

$$I = n_{\mathrm{ORR}} F A C_{\mathrm{O2}} (D_{\mathrm{O2}}/\pi t)^{1/2} + (\Delta E/R)\exp(-t/RC_{\mathrm{dl}}), \qquad (5)$$

where I is the current intensity, n_{ORR} is the oxygen reduction reaction (ORR) electron transfer number (3.94), F is the Faraday constant (96485 C mol^{-1}), A is the geometric surface area of the electrode (0.0707 cm^2), C_{O2} is the bulk concentration of oxygen (3.77×10^{-8} mol cm^{-3}), D_{O2} is the diffusion coefficient of oxygen, t is the time, ΔE is the applied potential, R is the solution resistance (36.0 Ω), and C_{dl} is the differential capacitance of the double layer (1.18×10^{-5} F). The first and second terms represent the diffusion-controlled ORR current and double layer current respectively. At the beginning of the potential step, an extremely large double layer current was observed. However, this current decayed within a few milliseconds (the time constant, $RC_{\mathrm{dl}} = 4.25 \times 10^{-4}$ s); therefore, the second term of Equation 5 can be negligible at 1 s. As a result, D_{O2} was calculated to be $(1.00 \pm 0.27) \times 10^{-5}$ cm^2 s^{-1} by the first term of Equation 5. The values represent the mean ± standard deviation of eight repeated measurements.

Koutecký–Levich analysis.

The ORR electron transfer number n_{ORR}, and kinetic current I_{K}, were calculated from the following Koutecký–Levich equation:[S1]

$$I^{-1} = I_{\mathrm{K}}^{-1} + (0.62 n_{\mathrm{ORR}} F A C_{\mathrm{O2}} D_{\mathrm{O2}}^{2/3} v^{-1/6})^{-1} \omega^{-1/2}, \qquad (6)$$

where D_{O2} is the diffusion coefficient of oxygen (1.00×10^{-5} cm^2 s^{-1}), v is the kinematic viscosity of the electrolyte (8.88×10^{-2} cm^2 s^{-1}), and ω is the rotation rate. Koutecký–Levich plots (Fig. 3c) were obtained from the voltammograms shown in Fig. 3b and Fig. S5. The plots show linear relationships between the reciprocal of the current intensity at 0.4 V *vs.* RHE and the reciprocal of the square root of the rotation rate. Accordingly, n_{ORR} and I_{K} can be estimated from the slope and y-intercept of the I^{-1} *vs.* $\omega^{-1/2}$ plot, respectively.

Supplementary figures and tables

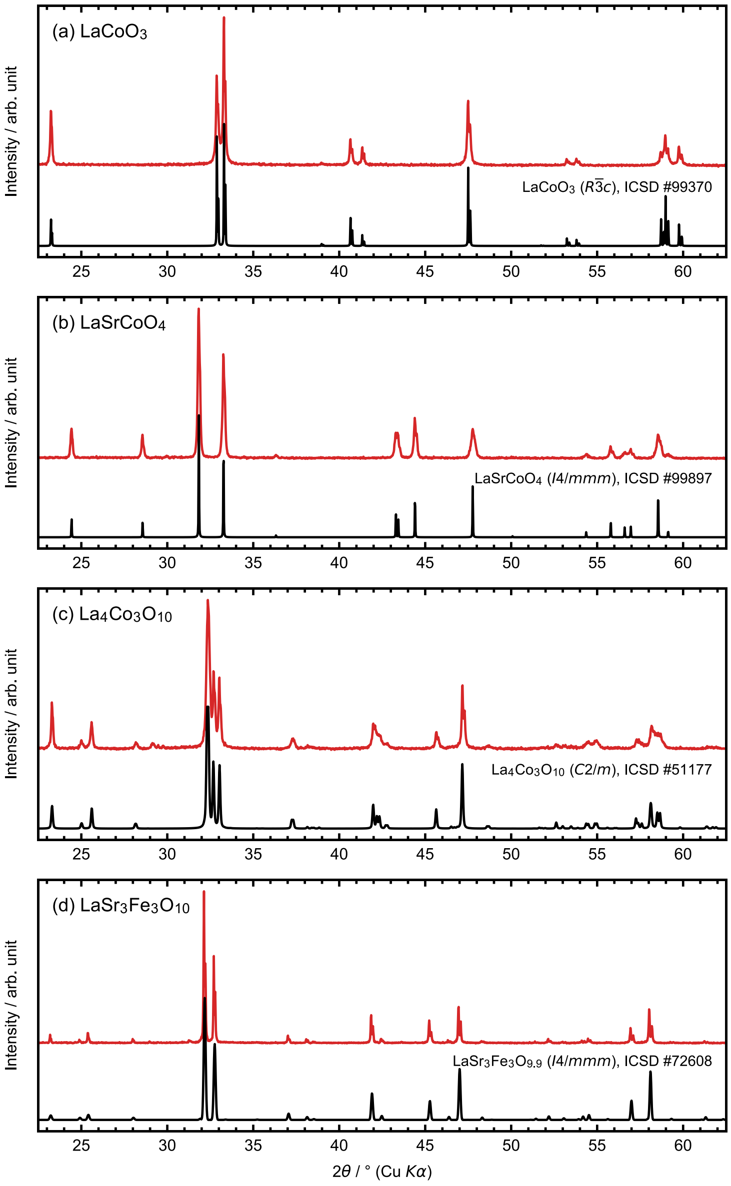

Fig. S1 XRD patterns of (a) $LaCoO_3$, (b) $LaSrCoO_4$, (c) $La_4Co_3O_{10}$, and (d) $LaSr_3Fe_3O_{10}$.

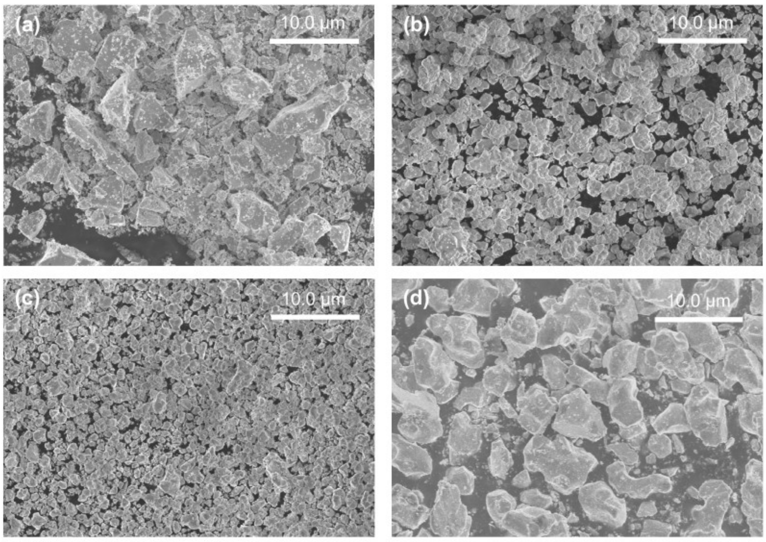

Fig. S2 SEM images of (a) $LaCoO_3$, (b) $LaSrCoO_4$, (c) $La_4Co_3O_{10}$, and (d) $LaSr_3Fe_3O_{10}$.

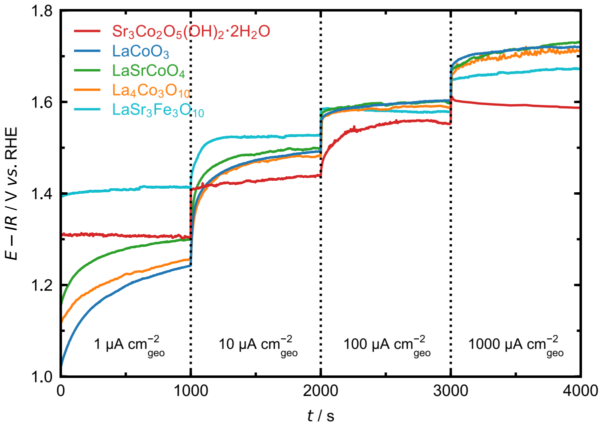

Fig. S3 Representative chronopotentiograms for $Sr_3Co_2O_5(OH)_2{\cdot}2H_2O$ (red), $LaCoO_3$ (blue), $LaSrCoO_4$ (green), $La_4Co_3O_{10}$ (orange), and $LaSr_3Fe_3O_{10}$ (cyan) at current densities of 1, 10, 100, and 1000 μA cm_{geo}^{-2}.

Table S1 BET specific surface areas of the synthesized compounds

Catalyst	BET specific surface area / $m^2\ g^{-1}$
$Sr_3Co_2O_5(OH)_2{\cdot}2H_2O$	1.09
$LaCoO_3$	0.95
$LaSrCoO_4$	1.09
$La_4Co_3O_{10}$	1.88
$LaSr_3Fe_3O_{10}$	1.00

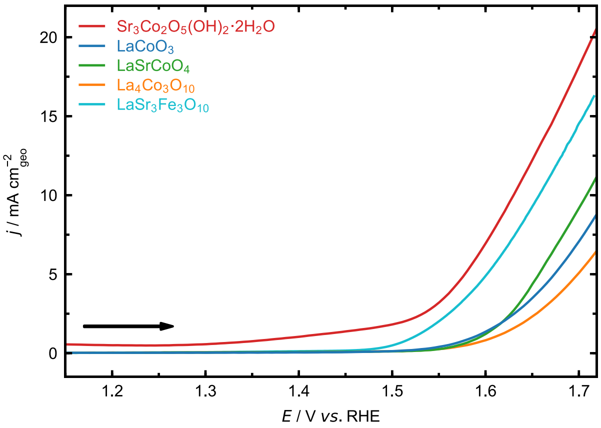

Fig. S4 OER polarization curves for $Sr_3Co_2O_5(OH)_2{\cdot}2H_2O$ (red), $LaCoO_3$ (blue), $LaSrCoO_4$ (green), $La_4Co_3O_{10}$ (orange), and $LaSr_3Fe_3O_{10}$ (cyan) measured at a rotation rate of 1600 rpm and at a scan rate of 1 mV s^{-1} in an oxygen-saturated aqueous solution with 0.1 mol L^{-1} KOH.

Table S2 ORR onset potentials E_{onset}, and half-wave potentials $E_{1/2}$, estimated from hydrodynamic voltammograms measured at 3600 rpm at 1 mV s^{-1}

Material	E_{onset} / V *vs.* RHE	$E_{1/2}$ / V *vs.* RHE
$Sr_3Co_2O_5(OH)_2{\cdot}2H_2O$	1.011	0.760
$LaCoO_3$	0.873	0.727
$LaSrCoO_4$	0.824	0.759
$La_4Co_3O_{10}$	0.821	0.772

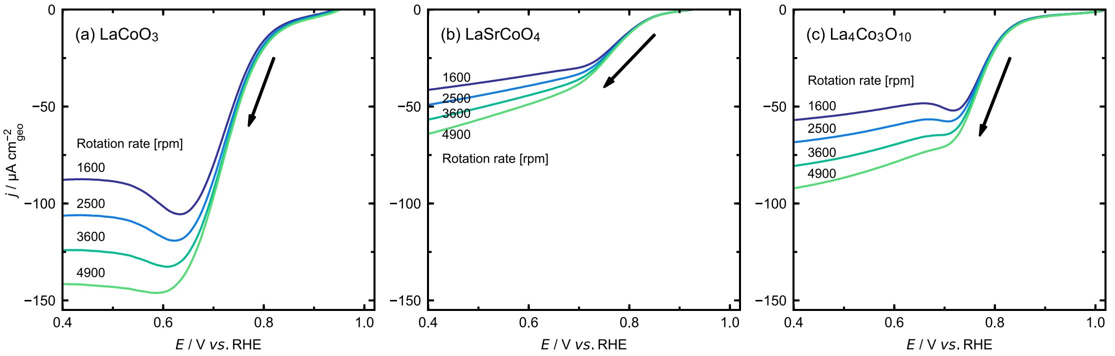

Fig. S5 Hydrodynamic voltammograms for (a) $LaCoO_3$, (b) $LaSrCoO_4$, and (c) $La_4Co_3O_{10}$ at rotation rates of 1600, 2500, 3600, and 4900 rpm and at a scan rate of 1 mV s^{-1}.

Table S3 Kinetic current I_K, given by the y-intercepts of extrapolated Koutecký–Levich plots

Material	I_K / μA
$Sr_3Co_2O_5(OH)_2 \cdot 2H_2O$	−32.0
$LaCoO_3$	−197
$LaSrCoO_4$	−29.5
$La_4Co_3O_{10}$	−49.2

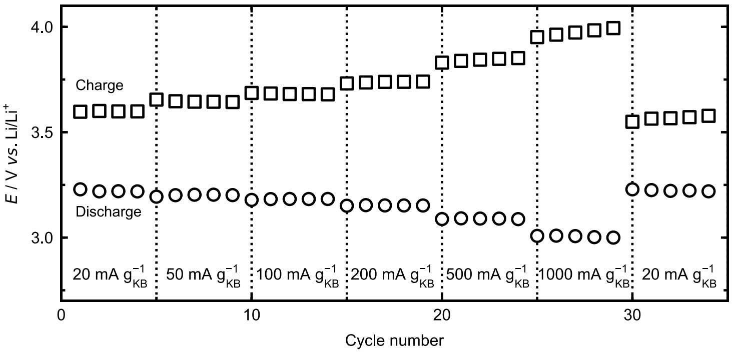

Fig. S6 Cycling performance of the GDE with $Sr_3Co_2O_5(OH)_2 \cdot 2H_2O$. The plots represent the potentials at the end of each cycle. The current was sequentially changed during the galvanostatic discharge/charge test.

Supplementary Reference

S1 A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York, NY, 2nd edn., 2000.