Science Advances

Supplementary Materials for

Exceptional oxygen evolution reactivities on CaCoO$_3$ and SrCoO$_3$

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This PDF file includes:

Fig. S1. SEM images and particle size distribution of CaCoO₃ and SrCoO₃. The particle

size distribution was conducted with the software ImageJ.
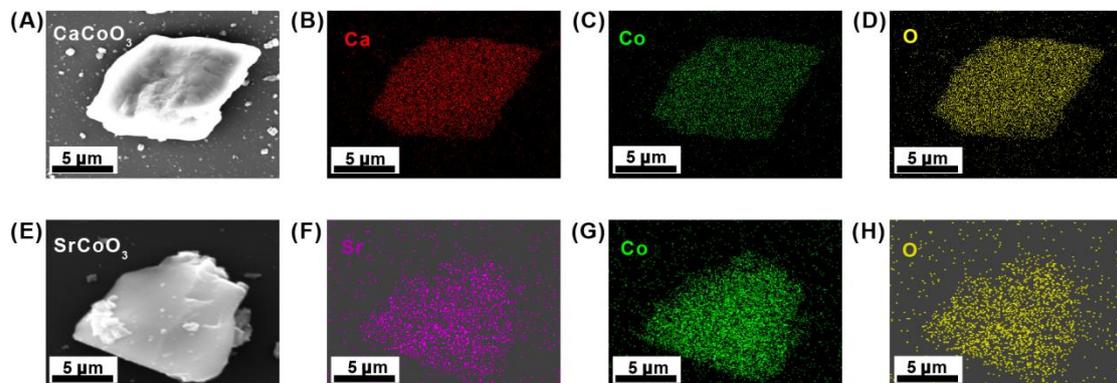
Fig. S2. Elemental distribution of CaCoO₃ and SrCoO₃. EDS mapping of (A to D) CaCoO₃

and (E to H) SrCoO₃.
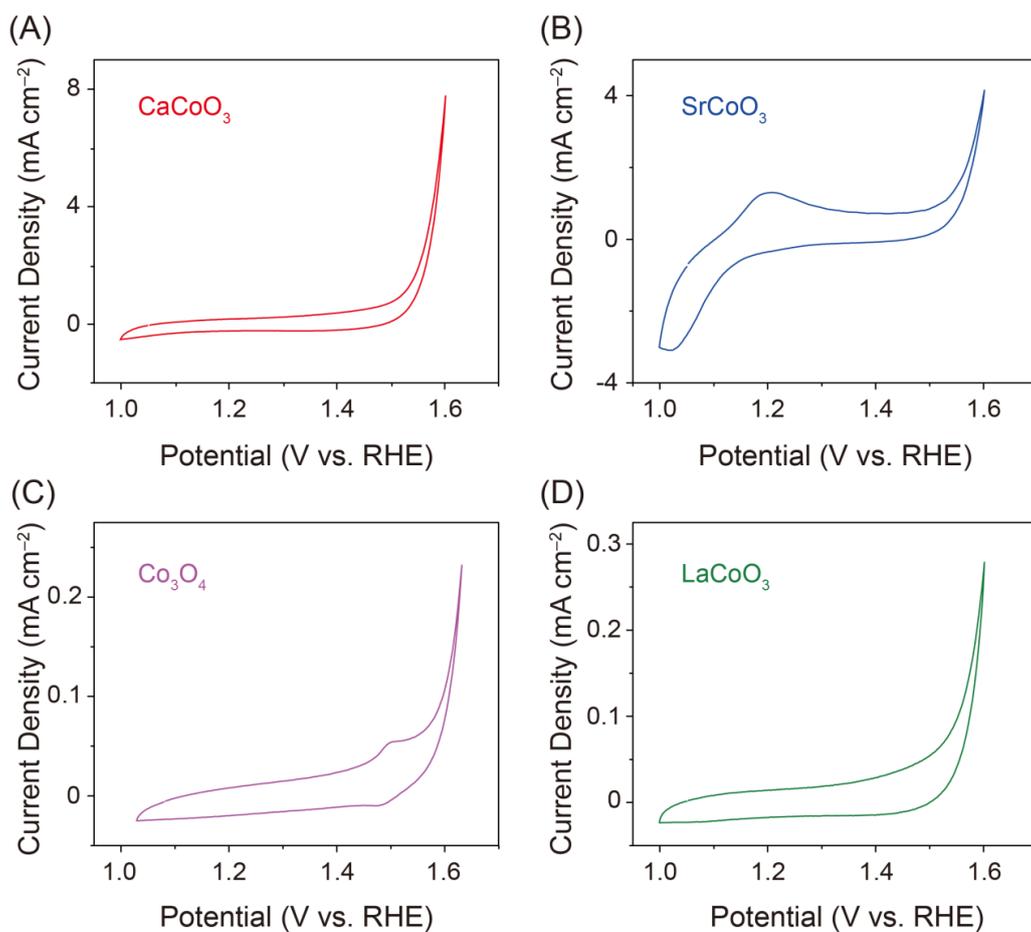
Fig. S3. CV curves of Co-based catalysts. (A) $CaCoO_3$, (B) $SrCoO_3$, (C) Co_3O_4, (D) $LaCoO_3$ at the potential range of 1.0 V to 1.65 V.
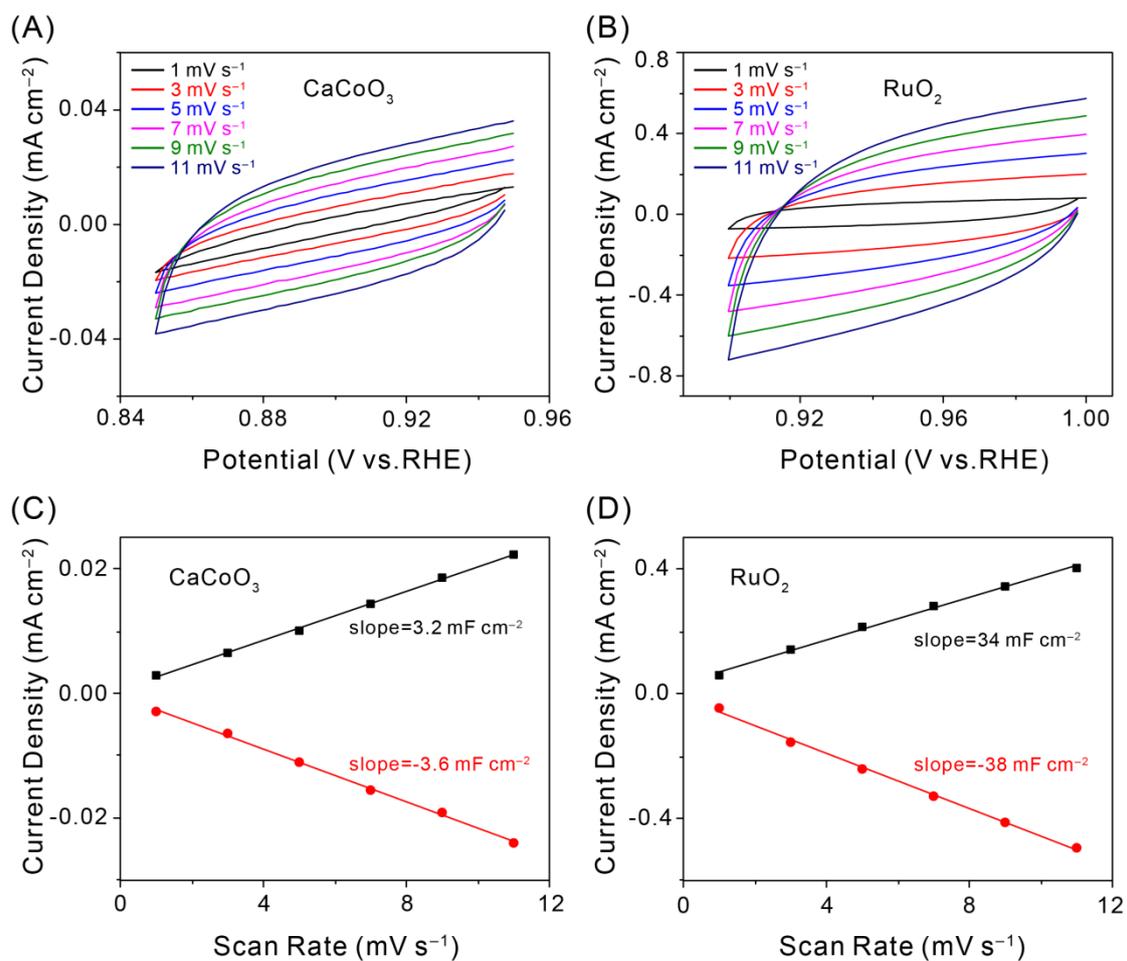
Fig. S4. Double-layer capacitance measurement to determine the electrochemically active surface area of CaCoO₃ and RuO₂. CV curves of (A) CaCoO$_3$ and (B) RuO$_2$ were measured in a non-Faradaic region at scan rates from 1 to 11 mV s^{-1}; Current density as a function of the scan rate for (C) CaCoO$_3$ at 0.9 V and (D) RuO$_2$ at 0.95 V.
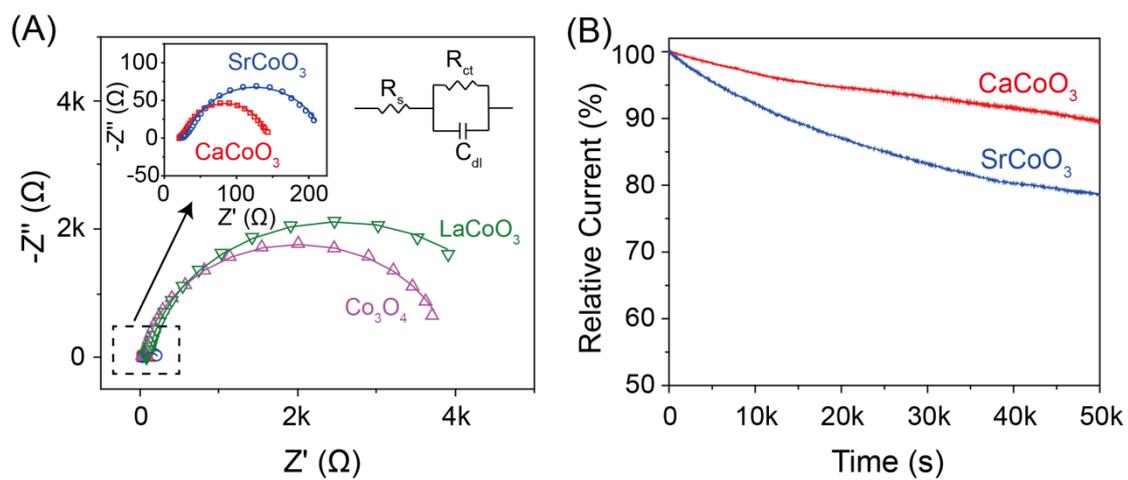
Fig. S5. The impedance plots and cycling stability of the catalysts studied in this work.

(A) Nyquist plots and fitting result of the catalysts studied in this work. Inserted is the Electrical equivalent circuit; (B) The chronoamperometric curves of $CaCoO_3$ and $SrCoO_3$ during 50000 s in an O_2–saturated 0.1 M KOH electrolyte at 1.6 V vs. RHE.
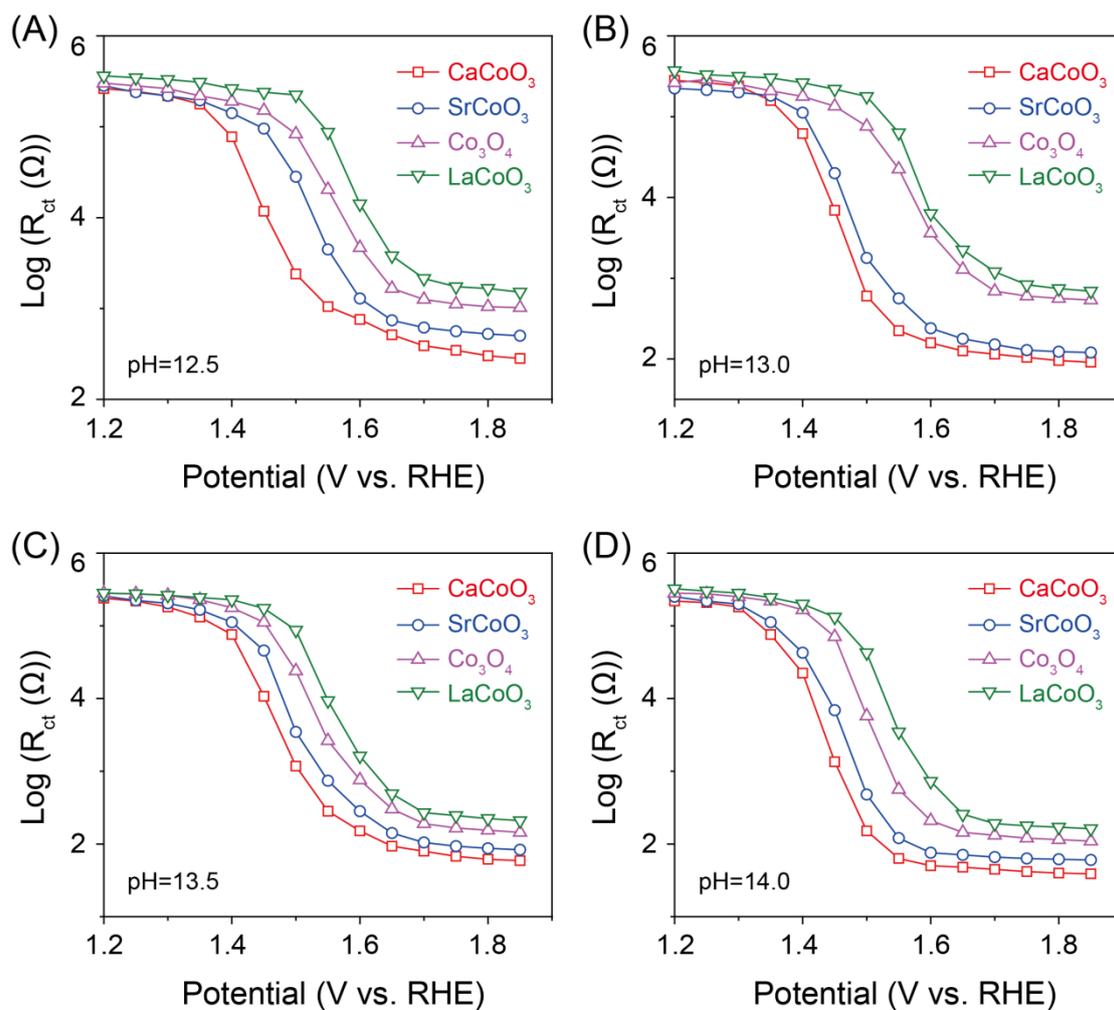
Fig. S6. Response of charge transfer resistance (R_{ct}) to applied potential of the catalysts studied in this work to applied potential in the solution of pH = 12.5, 13, 13.5 and 14.
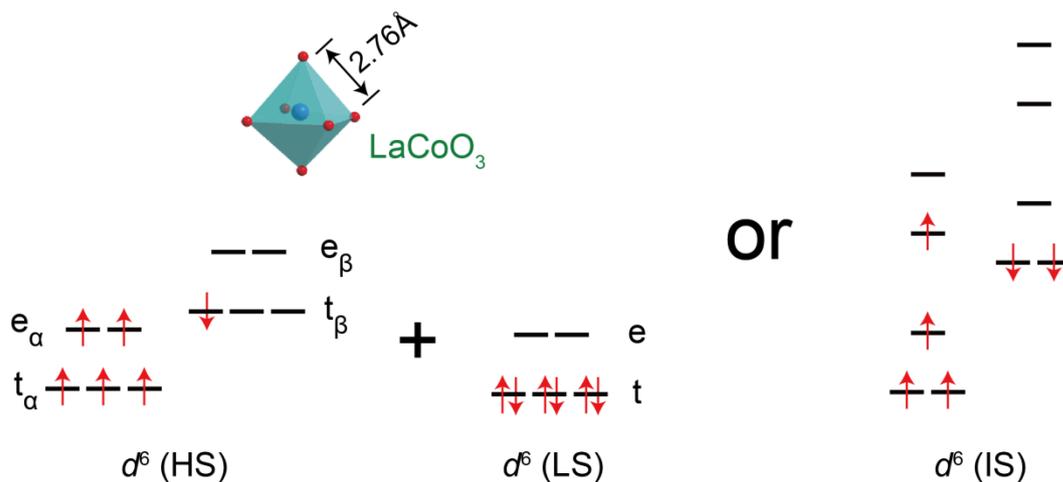
Fig. S7. The intermediate spin state (IS) of Co^{III} in LaCoO$_3$ (t^4e^1, $S = 1$) at 25 °C. There are two possible scenarios to explain the IS mechanism .
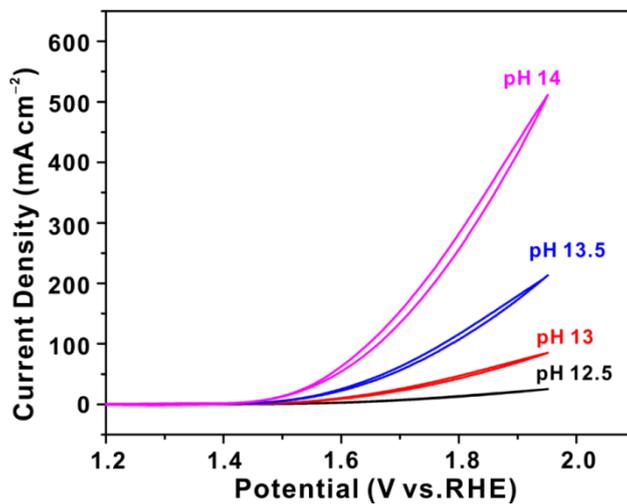
Fig. S8. pH-dependent OER activity of RuO$_2$ in an O$_2$-saturated KOH with pH 12.5–14.

Table S1. Structural refinements of CaCoO₃ and SrCoO₃ obtained at room temperature.

	$CaCoO_3$	$SrCoO_3$	Co_3O_4	$LaCoO_3$
Space group	*Pm-3m*	*Pm-3m*	*Fd-3m*	*R-3c h*
Lattice parameter (Å)	a=b=c=3.734	a=b=c=3.829	a=b=c=0.781	a=b=0.5445, c=1.3093
Atomic positions	Ca (0.5, 0.5, 0.5) Co (0, 0, 0) O (0.5, 0, 0)	Sr (0.5, 0.5, 0.5) Co (0, 0, 0) O (0.5, 0, 0)	Co1 (0, 0, 0) Co2 (0.675, 0.675, 0.675) O (0.388, 0.388, 0.388)	La (0, 0, 0.25) Co (0, 0, 0) O (0.454, 0, 0.25)
Nearest bond length Co-O (Å)	1.867	1.915	1.926	1.930
R$_{wp}$ (%)	3.62	3.72		
R$_p$ (%)	2.84	2.92		
χ^2	1.43	1.53		

Electrochemical double layer capacitance (C_{DL}) was determined with cyclic voltammetry measurements. The potential range was determined at a 0.1 V window centered at open-circuit potential (OCP), where there is non-Faradaic current response. CV measurements were conducted in quiescent solution at different scan rates from 1 to 11 mV s^{-1}. The C_{DL} can be calculated by Eq S1

$$j = \upsilon C_{DL} \quad (S1)$$

j is the current at the central of CV potential range and υ is the scan rate. Plotting *j* as a function of υ yields a straight line with slope equal to C_{DL}. The electrochemically active surface area (ECSA) of the catalyst can be calculated by dividing C_{DL} by the specific capacitance (C_S) of the sample as shown in Eq S2

$$ECSA = \frac{C_{DL}}{C_S} \quad (S2)$$

Here we use a general specific capacitance (C_S) of 0.040 mF cm^{-2} for all examples in 0.1 M KOH. The value of C_{DL} and ECSA of the catalysts were shown in Table S2.

Table S2. OER activity and ECSA of all studied catalysts.

Catalyst	Onset potential (V)	Overpotential (V) at 10 mA cm^{-2}	Tafel slope (mV dec^{-1})	C_{DL} (mF)	ECSA (cm^2)
CaCoO$_3$	1.48	0.26	42	3.4	85
SrCoO$_3$	1.51	0.29	49	5.2	130
RuO$_2$	1.50	0.28	58	36.0	900
Co$_3$O$_4$	1.60	0.43	66	25.2	630
LaCoO$_3$	1.65	0.49	71	17.8	445