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# Short O–O separation in layered oxide Na<sub>0.67</sub>CoO<sub>2</sub> enables an ultrafast oxygen evolution reaction

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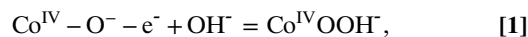
The layered oxide Na<sub>0.67</sub>CoO<sub>2</sub> with Na<sup>+</sup> occupying trigonal prismatic sites between CoO<sub>2</sub> layers exhibits a remarkably high room temperature oxygen evolution reaction (OER) activity in alkaline solution. The high activity is attributed to an unusually short O–O separation that favors formation of peroxide ions by O<sup>–</sup>–O<sup>–</sup> interactions followed by O<sub>2</sub> evolution in preference to the conventional route through surface O–OH<sup>–</sup> species. The dependence of the onset potential on the pH of the alkaline solution was found to be consistent with the loss of H<sup>+</sup> ions from the surface oxygen to provide surface O<sup>–</sup> that may either be attacked by solution OH<sup>–</sup> or react with another O<sup>–</sup>; a short O–O separation favors the latter route. The role of a strong hybridization of the O–2p and low-spin Co<sup>III</sup>/Co<sup>IV</sup> π-bonding d states is also important; the OER on other Co<sup>III</sup>/Co<sup>IV</sup> oxides is compared with that on Na<sub>0.67</sub>CoO<sub>2</sub> as well as that on IrO<sub>2</sub>.

air electrodes | water electrolysis | catalytic mechanisms | structure–property relationship

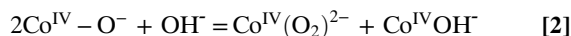
Highly active oxygen evolution reaction (OER) catalysts with a long-term stability are required to reduce the energy loss, increase the rate performance, and improve the cycling stability of different energy conversion and storage systems, particularly in electrochemical water electrolysis and rechargeable metal–air aqueous electrolyte batteries (1–4). The most active OER catalyst, IrO<sub>2</sub>, is expensive and shows a high overpotential of 0.3 V at 10 mA·cm<sup>–2</sup>; moreover, it is unstable at the applied potential in an alkaline electrolyte, which degrades its activity and limits its application (5–7).

Low-cost transition metal (TM) oxides are promising candidates for OER catalysts (8–17). AMO<sub>3</sub> perovskites with controllable chemical compositions and electronic structures by substituting the cations on A and M sites have been extensively investigated as OER catalysts (18–22). Some perovskite oxides (e.g., Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3–8</sub>, Hg<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub>, and CaCu<sub>3</sub>Fe<sub>4</sub>O<sub>12</sub>) exhibit comparable or even better OER catalytic activity than that of IrO<sub>2</sub> (3, 5, 23). However, the obtained OER descriptor of  $e_g \approx 1$  on the d-orbital manifold of M<sup>n+</sup> ions in AMO<sub>3</sub> perovskites for their excellent OER activity is challenged by the good OER on 4d/5d TM oxide catalysts with zero antibonding  $e_g$  electrons such as IrO<sub>2</sub> and Hg<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> (24–27). In addition to the OER activity, the stability and the preparation condition of the catalysts are 2 other critical parameters for their large-scale application. For example, the crystalline Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3–8</sub> phase becomes amorphous after OER testing in an alkaline electrolyte, and the stable Hg<sub>2</sub>Ru<sub>2</sub>O<sub>7</sub> and CaCu<sub>3</sub>Fe<sub>4</sub>O<sub>12</sub> catalysts with high valence Ru<sup>4+</sup> and Fe<sup>4+</sup> ions can only be prepared at an extremely high pressure of 6 and 15 GPa, respectively (23). The instability of TM oxides originates from cations that can dissolve into the alkaline solution and from lattice oxygen loss during the OER (28). Increasing the M<sup>n+</sup>–O<sup>2–</sup> bond strength of oxides helps to improve their stability. Therefore, developing an easily prepared, efficient, and durable OER catalyst based on Earth-abundant elements is still a challenge.

We have recently studied the onset potentials and OER activities of 2 cubic perovskites, CaCoO<sub>3</sub> and SrCoO<sub>3</sub>, prepared under high pressure (29); both have Co<sup>IV</sup> ions having similar intermediate spin states  $t^4e^*$ , but CaCoO<sub>3</sub> had a significantly shorter Co<sup>IV</sup>–O bond (1.87 Å) and showed a higher OER activity than SrCoO<sub>3</sub> as a result of its reduced lattice parameter. After surface deprotonation at a charging potential  $V_{\text{ch}} = V_{\text{on}}$ , where  $V_{\text{on}}$  was the onset potential, the surface Co<sup>IV</sup>–O<sup>–</sup> were attacked by solution OH<sup>–</sup>,



but the competitive reaction



followed by



was much stronger on CaCoO<sub>3</sub> because of its much smaller lattice parameter, which reduced the surface O–O separation. The O<sup>–</sup> + O<sup>–</sup> = (O<sub>2</sub>)<sup>2–</sup> reaction is faster the shorter the O–O separation of the catalyst. In the conventional reaction route, the O<sup>–</sup> ion is attacked by a solution OH<sup>–</sup> to form OOH<sup>–</sup>, and the OOH<sup>–</sup> + OH<sup>–</sup> = (O<sub>2</sub>)<sup>2–</sup> + H<sub>2</sub>O; this mechanism is independent of the O–O separation.

These findings recommended to us a search for stable oxides with a shorter surface oxygen separation that can be prepared at

## Significance

The development of a low-cost, stable, and more active electrocatalyst for the oxygen evolution reaction (OER) is critical for the practical storage of electric power in hydrogen gas produced by the electrolysis of water. We demonstrate a stable OER of higher rate at a lower voltage with a low-cost oxide that provides, as an alternative to the conventional reaction route, a faster route that is greatly enhanced by an unusually short O–O separation.

Author contributions: Y.L. and J.B.G. conceived the idea and designed research; H.W., A.D., Y.L., X.L., N.W., M.L., and W.Y. performed research; H.W., J.W., A.D., Y.L., K.P., and S.X. analyzed data; Y.L. and J.B.G. wrote the paper; J.W. and W.Y. performed the sXAS and mRIXS characterization; A.D. performed the time-of-flight secondary ion mass spectrometry (TOF-SIMS); and X.L. did the synchrotron experiment.

Reviewers: P.B., University of St. Andrews; and J.-M.T., Collège de France.

The authors declare no competing interest.

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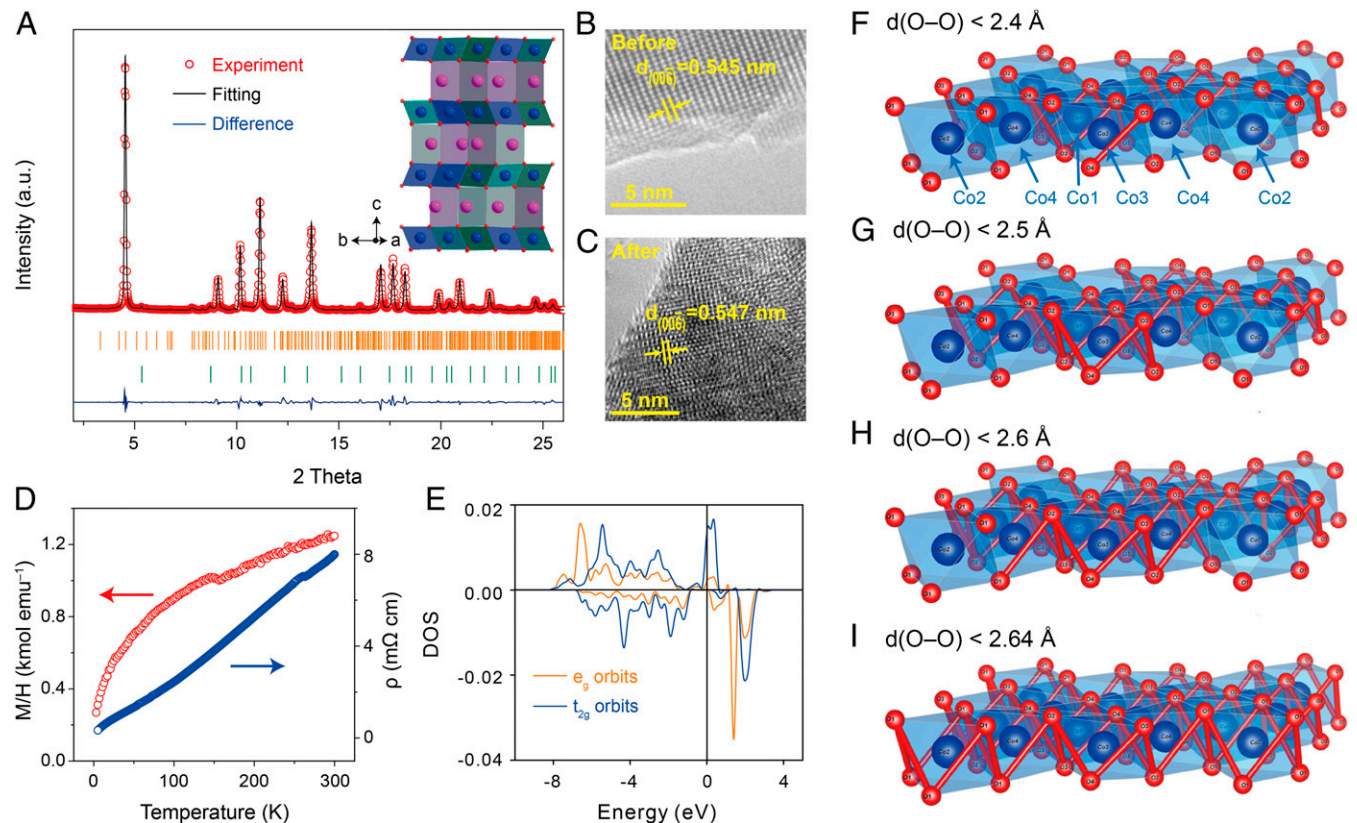
ambient pressure. Therefore, we prepared a metallic layered oxide  $\text{Na}_{0.67}\text{CoO}_2$  with low-spin  $\text{Co}^{\text{III/IV}}$  ions ( $\text{Co}^{\text{III}}$ :  $\pi^*6\sigma^*0$ ;  $\text{Co}^{\text{IV}}$ :  $\pi^*5\sigma^*0$ ) and a much shorter O–O separation than on  $\text{CaCoO}_3$  to study further the influence of zeta potential, surface oxygen separation, and the pH of the aqueous medium on the onset potential and OER activity. Metallic, low-spin  $\text{Na}_{0.67}\text{CoO}_2$  has a strong  $\text{Co}^{\text{III/IV}}\text{--O}$  interaction as a result of empty  $\sigma$ -antibond  $e_g$  orbitals and itinerant  $\pi$ -bonding electrons, which reduces the charge transfer resistance during the OER;  $\text{Na}_{0.67}\text{CoO}_2$  has a zero zeta potential at pH = 4 and shows a pH-dependent onset potential for the OER consistent with the potential for the  $\text{CoOH}^- - e^- + \text{OH}^- = \text{CoO}^- + \text{H}_2\text{O}$  reaction.

## Results

**The Crystal and Electronic Structure of  $\text{Na}_{0.67}\text{CoO}_2$ .** Synchrotron powder X-ray diffraction (XRD) and powder X-ray diffraction patterns of as-prepared  $\text{Na}_{0.67}\text{CoO}_2$  (Fig. 1 and *SI Appendix, Fig. S1*) confirm the layered structure of  $\text{Na}_{0.67}\text{CoO}_2$ . Two-dimensional  $\text{CoO}_2$  layers with edge-sharing  $\text{CoO}_6$  octahedra in trigonal  $\text{Na}_{0.67}\text{CoO}_2$  (space group: R-3c) are separated by sodium layers. The  $\text{Na}^+$  occupy 3 different trigonal prismatic sites, Na1 and Na2 (Na2a and Na2b) in *SI Appendix, Table S1*; each shares 6 edges and 2 triangular faces along the  $c$  axis with the  $\text{CoO}_6$  octahedra vertically above and below. The Na1 ions are energetically less favorable because of the coulombic repulsions from 2 Co ions in face-sharing octahedra. The Co ions of  $\text{Na}_{0.67}\text{CoO}_2$  have 4 different positions; the distorted  $\text{CoO}_6$  octahedra have a similar average Co–O bond distance, but one shortest O–O separation (2.30 Å; Fig. 1F) than that of cubic  $\text{CaCoO}_3$  (O–O: 2.64 Å) in which the  $\text{Co}^{\text{IV}}$  have an intermediate spin state ( $t^4\sigma^*1$ ). About 0.3 wt%  $\text{Co}_3\text{O}_4$  impurity was found to exist in the sample by refining the synchrotron data. The  $\text{Na}_{0.67}\text{CoO}_2$  sample had an average particle size of 15  $\mu\text{m}$  (*SI Appendix, Fig. S3*), and the energy dispersive spectroscopy (EDS) mapping revealed a uniform distribution of Na, Co, and O elements.

The electronic conductivity and magnetic properties of  $\text{Na}_{0.67}\text{CoO}_2$  were investigated to determine the  $d$ -electron configuration of the  $\text{Co}^{\text{III/IV}}$  ions (Fig. 1D). The temperature dependence of resistivity of  $\text{Na}_{0.67}\text{CoO}_2$  shows a metallic behavior down to 2 K, with a large residual resistance ratio; a nonlinear magnetic susceptibility curve from 2 to 300 K is also consistent with itinerant  $d$  electrons. A spin-polarized first-principle calculation was performed, and the density of states of Co ions from  $\text{Na}_{0.67}\text{CoO}_2$  is shown in Fig. 1E. The conduction band of  $\text{Na}_{0.67}\text{CoO}_2$ , which contains one spin component of  $t_{2g}$  orbitals, is not full, indicating a metallic conductivity of  $\text{Na}_{0.67}\text{CoO}_2$ . The higher electronic conductivity of  $\text{Na}_{0.67}\text{CoO}_2$  reduces the charge transfer resistance ( $R_{\text{ct}}$ ) and the ohmic potential drop of the OER; the  $R_{\text{ct}}$  of  $\text{Na}_{0.67}\text{CoO}_2$  is one order of magnitude smaller than that of the electronic insulator  $\text{Co}_3\text{O}_4$ , which is above 1.6 V (*SI Appendix, Fig. S4*).

Soft X-ray absorption spectroscopy (sXAS), which is quite sensitive to the TM  $3d$  states because of the strong dipole-allowed  $2p\text{--}3d$  ( $L$  edge) excitations (30–33), was performed to explore the valence and spin states of the Co ions of  $\text{Na}_{0.67}\text{CoO}_2$  (Fig. 2). With a probe depth of 10 nm, the total electron yield (TEY) mode of sXAS is quite an effective surface-sensitive probe, as shown in Fig. 2A and B. Due to the core-hole spin-orbit coupling, the Co  $L$  edge in Fig. 2A is well separated into 2 branches, that is,  $L_3$  (between 774 and 787 eV) and  $L_2$  (between 788 and 799 eV). The branching ratio of the  $L_3$  and  $L_2$  edges, which is greatly affected by



**Fig. 1.** Crystal structure and magnetic and transport properties of  $\text{Na}_{0.67}\text{CoO}_2$ . (A) Observed, calculated patterns, and their difference for the Rietveld refinement of the synchrotron XRD of  $\text{Na}_{0.67}\text{CoO}_2$ ; (Inset) its crystal structure (pink, Na; blue, Co; red, O). (B and C) TEM images of  $\text{Na}_{0.67}\text{CoO}_2$  before and after OER measurements. (D) Temperature dependence of resistivity and magnetization. (E) Electronic spin states of  $\text{Co}^{\text{IV}}$  ions and schematic band diagrams of  $\text{Na}_{0.67}\text{CoO}_2$ . (F–I) The O–O bonds shorter than (2.4 to 2.64) Å are highlighted with thick red lines.

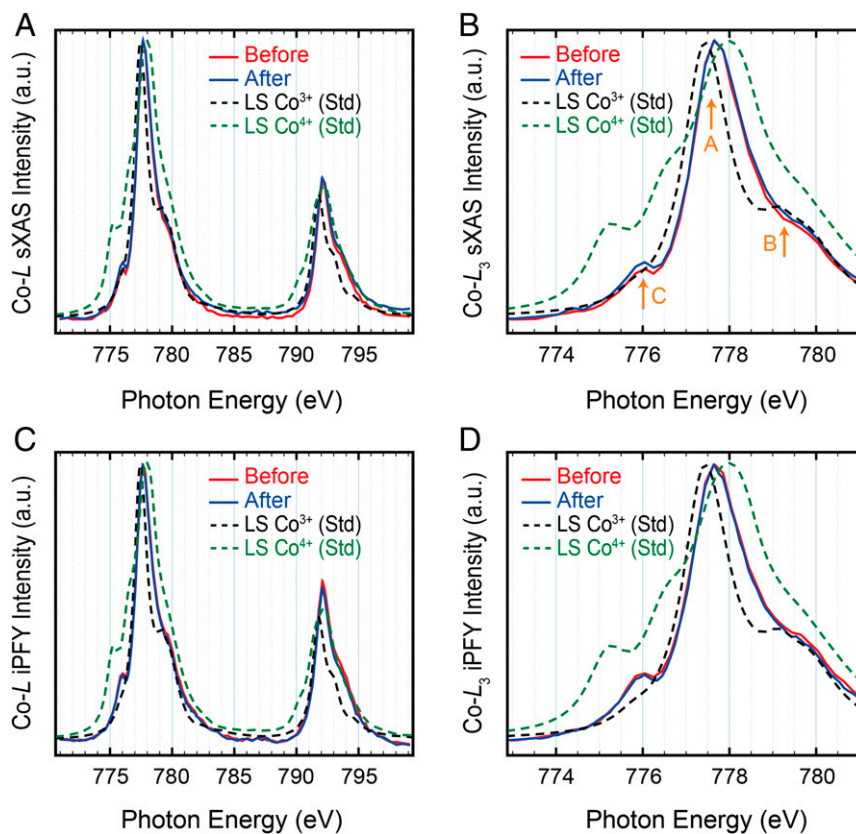


Fig. 2. The absorption profiles of  $\text{Co}^{\text{III}}$  and  $\text{Co}^{\text{IV}}$  in  $\text{Na}_{0.67}\text{CoO}_2$  probed by sXAS and mRIXS. (A and B) The sXAS TEY of (A) Co  $L$  edge and (B) magnified  $L_3$  edge obtained with a surface probe having a probe depth of 10 nm. (C and D) The mRIXS iPFY of (C) Co  $L$  edge and (D) magnified  $L_3$  edge by a bulk probe with a probe depth of 100 nm.

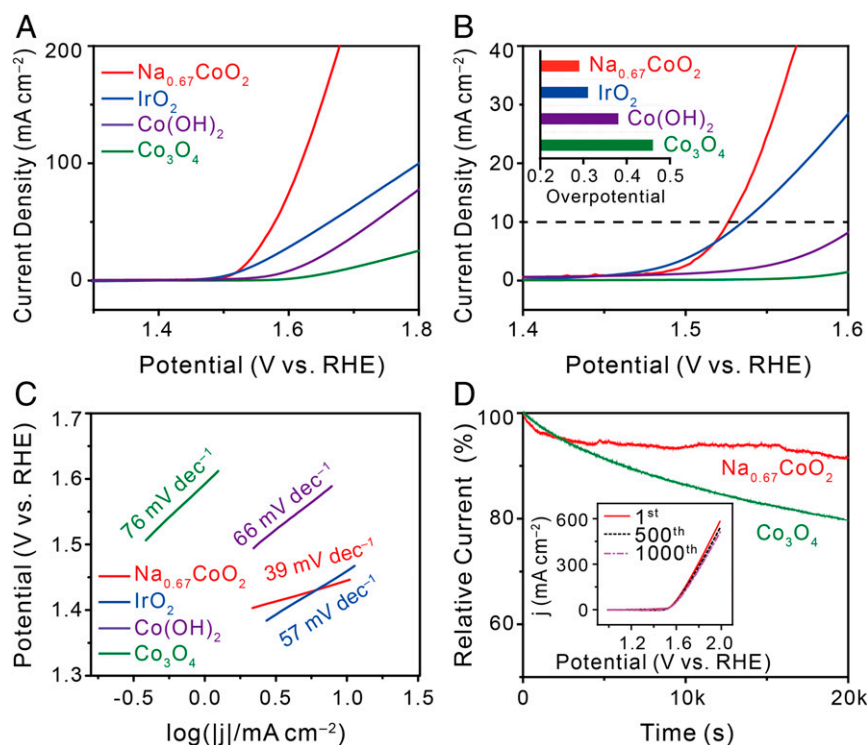
the spin-orbit coupling and especially by the  $2p-3d$  multiplet effects, can be utilized to deduce the spin state of Co (34, 35). Quantitatively, for the statistical ratio of the integrated intensity of 2 edges, namely  $I_{L_3}/(I_{L_3} + I_{L_2})$ , the high-spin state has a higher one than the low-spin state. Respectively for the samples before and after catalysis reaction, the statistical branching ratio of the Co  $L$  inverse partial fluorescence yield (iPFY) is  $0.689 \pm 0.005$  and  $0.686 \pm 0.005$ . Based on the atomic multiplet calculations (36, 37), the standard spectra of LS Co within the octahedral ( $\text{CoO}_6$ ) structure is achieved as shown by dashed lines in Fig. 2 A and B, and that of HS is done as shown in *SI Appendix, Fig. S6*. While the calculated spectrum of LS Co (either  $\text{Co}^{3+}$  or  $\text{Co}^{4+}$ ) has a branching ratio of  $0.698 \pm 0.005$ , very close to the experimental Co  $L$  iPFY, that of HS has a much higher one of  $0.780 \pm 0.005$ , suggesting that  $\text{Na}_{0.67}\text{CoO}_2$  has a low-spin state ( $\text{Co}^{\text{III}}$ :  $t^6e^0$ ,  $\text{Co}^{\text{IV}}$ :  $t^5e^0$ ). The density of states of Co ions from  $\text{Na}_{0.67}\text{CoO}_2$ , which is shown in Fig. 1E, also indicates low-spin  $\text{Co}^{\text{III/IV}}$  ions. The valence state of the Co ions can be inferred by the Co  $L_3$  peak position. As shown in Fig. 2B, the peak A located at 777.6 eV, which is 0.2 eV from the standard  $\text{Co}^{3+}$  (777.4 eV) and 0.4 eV from the standard  $\text{Co}^{4+}$  (778.0 eV). This position indicates that the valence of the Co ions is about 3.3+, consistent with the expected stoichiometry as prepared.

In addition, we demonstrate the bulk information as a supplement. Resulting from the self-absorption and saturation effects (38, 39), the bulk probe of sXAS, that is, total fluorescence yield mode with a probe depth of 100 nm (40), provided a noisy lineshape and an unreliable  $L_2/L_3$  intensity ratio as shown in *SI Appendix, Fig. S5*. The iPFY is theoretically an undistorted absorption profile that can be extracted from the map of resonant inelastic X-ray scattering (mRIXS). In this work, we performed the Co  $L$  mRIXS measurement on  $\text{Na}_{0.67}\text{CoO}_2$ , and achieved the iPFY for characterizing the bulk Co status. (For the convenience

of the reader, we introduce how to extract the Co  $L$  iPFY from the mRIXS in *SI Appendix, Fig. S5*.) As shown in Fig. 2 C and D, the Co  $L$  iPFY spectra demonstrate a consistent lineshape with the TEY spectra, indicating that Co ions in the bulk of  $\text{Na}_{0.67}\text{CoO}_2$  present the same low-spin electronic and 3.3+ valence state as those on the surface.

**The OER Activity of  $\text{Na}_{0.67}\text{CoO}_2$ .** The OER performance of  $\text{Na}_{0.67}\text{CoO}_2$  was compared with that of rutile  $\text{IrO}_2$ , spinel  $\text{Co}_3\text{O}_4$ , and layered  $\text{Co}(\text{OH})_2$  (Fig. 3). The current densities of all of the samples were normalized to the electrochemically active surface area to exclude geometric effects (*SI Appendix, Fig. S7 and Table S2*). The catalysts with different particle size have similar OER activities when the current density is normalized to the electrochemical surface area or the surface area confirmed by Brunauer-Emmett-Teller measurement (41).  $\text{Na}_{0.67}\text{CoO}_2$  with an onset potential of 1.5 V vs. a reversible hydrogen electrode (RHE) had the smallest overpotential (0.29 V) at 10  $\text{mA cm}^{-2}$  and the highest current density at voltages above 1.6 V; the layered  $\text{Co}(\text{OH})_2$  and spinel  $\text{Co}_3\text{O}_4$  exhibited a negligible catalytic current density compared with  $\text{Na}_{0.67}\text{CoO}_2$ . The smallest Tafel slope of 39  $\text{mV} \cdot \text{dec}^{-1}$  (Fig. 3C) for  $\text{Na}_{0.67}\text{CoO}_2$  also indicates its excellent OER kinetics. The layered  $\text{Li}_{1-x}\text{CoO}_2$  has a structure and  $\text{Co}^{\text{III/IV}}-\text{O}$  bond similar to that in  $\text{Na}_{0.67}\text{CoO}_2$ , but the  $\text{Li}^+$  are in octahedral sites and no O-O separation is reduced; it has a much higher onset potential and a smaller OER current density than  $\text{Na}_{0.67}\text{CoO}_2$  (6).

**The Surface Charge Density of  $\text{Na}_{0.67}\text{CoO}_2$ .** The mean surface charge density of  $\text{Na}_{0.67}\text{CoO}_2$  (Fig. 4A) was evaluated by its zeta potential in water with different pH.  $\text{Na}_{0.67}\text{CoO}_2$  has a zero zeta potential at pH = 4; the strong covalence of the  $\text{Co}^{\text{III/IV}}-\text{O}$  bond of  $\text{Na}_{0.67}\text{CoO}_2$  makes it more acidic than the spinel  $\text{Co}_3\text{O}_4$ , which



**Fig. 3.** OER performance of  $\text{Na}_{0.67}\text{CoO}_2$ ,  $\text{IrO}_2$ ,  $\text{Co}(\text{OH})_2$ , and  $\text{Co}_3\text{O}_4$ . (A) Linear sweep voltammograms at 1,600 revolutions per minute. in 0.1 M KOH. (B) The overpotential at  $10 \text{ mA cm}^{-2}$  (dashed line). (C) Tafel plots. (D) The chronoamperometric curves in an  $\text{O}_2$ -saturated 0.1 M KOH electrolyte at 1.6 V vs. RHE and the CV curves of first, 500th, and 1,000th cycles (Inset).

has a weaker  $\text{Co}^{\text{III/IV}}\text{-O}$  bond and a high zero-zeta potential at  $\text{pH} = 7.5$ .  $\text{IrO}_2$  with a strong  $\text{Ir}^{\text{IV}}\text{-O}$  bond has a similar zeta potential curve to that of  $\text{Na}_{0.67}\text{CoO}_2$ , indicating analogous acidity of the surface states and pH influence on their OER.

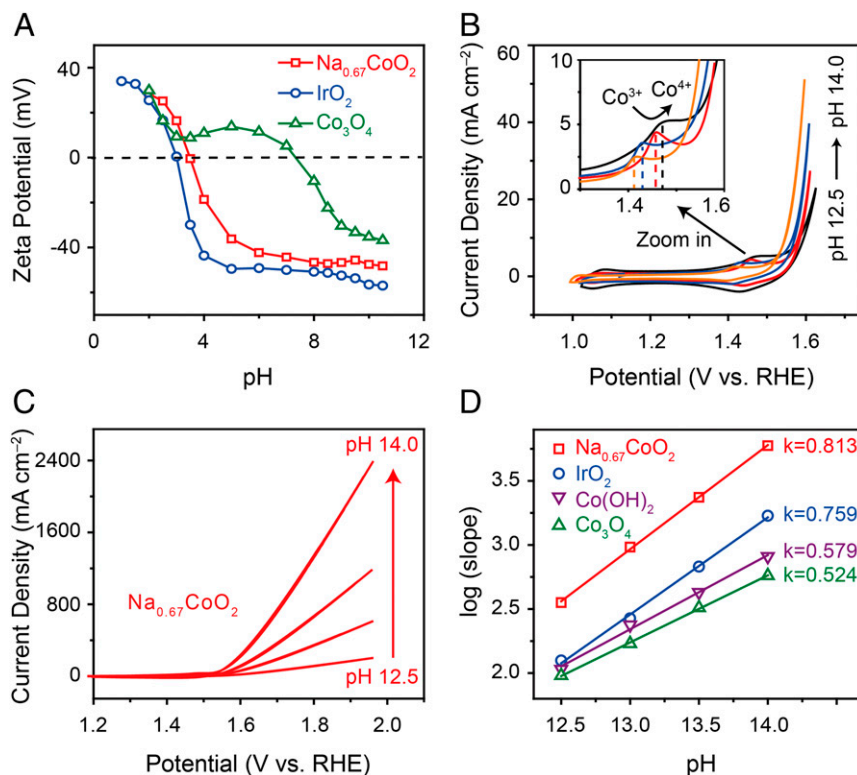
The onset potential and activity of  $\text{Na}_{0.67}\text{CoO}_2$  at different pH are compared with those of  $\text{Co}_3\text{O}_4$ ,  $\text{Co}(\text{OH})_2$  and  $\text{IrO}_2$  in Fig. 4 and *SI Appendix, Fig. S8*. The oxidation voltage of surface  $\text{Co}^{\text{III}}$  to  $\text{Co}^{\text{IV}}$  and the onset potential of  $\text{Na}_{0.67}\text{CoO}_2$  were reduced with increasing pH (Fig. 4B) because of the easier deprotonation process at higher pH; the activities of  $\text{Na}_{0.67}\text{CoO}_2$  and  $\text{IrO}_2$  show a similar pH-dependent behavior on the RHE scale, and their OER currents increase significantly at high pH; however, both  $\text{Co}_3\text{O}_4$  and  $\text{Co}(\text{OH})_2$  have no significant OER current increase. The slope of all CV curves of these catalysts at voltages above 1.6 V increases exponentially with pH (Fig. 4D), and the most active  $\text{Na}_{0.67}\text{CoO}_2$  has the biggest slope of all of the catalysts at different pH. Both  $\text{Na}_{0.67}\text{CoO}_2$  and  $\text{IrO}_2$  have a much larger slope change than  $\text{Co}_3\text{O}_4$  and  $\text{Co}(\text{OH})_2$ , indicating different OER mechanisms in these catalysts.

**The OER Stability of  $\text{Na}_{0.67}\text{CoO}_2$ .**  $\text{Na}_{0.67}\text{CoO}_2$  shows an excellent OER stability in an  $\text{O}_2$ -saturated electrolyte with  $\text{pH} = 13$  (Fig. 3D). More than 90% of its initial current density after 20,000 s was retained; and, after 1,000 cyclic voltammetry (CV) cycles,  $\text{Na}_{0.67}\text{CoO}_2$  showed almost the same OER activity. The transmission electron microscopy (TEM) image (Fig. 1C) and XRD (*SI Appendix, Fig. S1*) results confirmed the same crystalline structure of bulk and surface  $\text{Na}_{0.67}\text{CoO}_2$  before and after OER testing. The X-ray photoelectron spectroscopy (XPS) spectra of fresh  $\text{Na}_{0.67}\text{CoO}_2$ ,  $\text{Na}_{0.67}\text{CoO}_2$  soaked in KOH for a week, and  $\text{Na}_{0.67}\text{CoO}_2$  after 1,000 CV cycles are shown in *SI Appendix, Fig. S9*; the Na, Co, and O peaks of  $\text{Na}_{0.67}\text{CoO}_2$  after cycling are much weaker because of the covering Nafion binder on the particle surface; all of these XPS peaks retain the same positions, verifying the good stability of  $\text{Na}_{0.67}\text{CoO}_2$  during OER.  $\text{Na}_{0.67}\text{CoO}_2$  shows a stable peak position in sXAS, and the valence state of Co sXAS remains unchanged in the  $\text{Na}_{0.67}\text{CoO}_2$  powder before

and after OER (Fig. 2). The strong Co–O bonds of  $\text{Na}_{0.67}\text{CoO}_2$  increase its stability in alkaline solution.

**The Surface of  $\text{Na}_{0.67}\text{CoO}_2$  after OER.** Because surface oxygens of  $\text{Na}_{0.67}\text{CoO}_2$  participate in the OER, bulk lattice oxygen can diffuse to the surface oxygen vacancies after  $\text{O}_2$  gas release and capture a proton from solution before the solution  $\text{OH}^-$  enters, and then the vacancies will be generated on these oxygens. The Co and O ions of a minimum 14-nm-thick surface of perovskite  $\text{SrCoO}_{3-x}$  have been reported to participate in the OER (42).

Time-of-flight secondary ion mass spectrometry (TOF-SIMS), which is an ultrahigh elemental and surface sensitive technique, was employed to study whether any chemical composition change occurs on the surface of  $\text{Na}_{0.67}\text{CoO}_2$  before and after OER testing. Given the destructive nature of TOF-SIMS, all ionized fragments detected imply chemical bonding between the fragment elements prior to sputtering (43). TOF-SIMS depth profiling and high-resolution mapping were used to show the presence of  $\text{CoOH}$  and  $\text{CoO}_2\text{H}$  on the surface of the  $\text{Na}_{0.67}\text{CoO}_2$  particles following OER (Fig. 5 and *SI Appendix, Fig. S10*). Due to the naturally high surface corrugation of  $\text{Na}_{0.67}\text{CoO}_2$ , both  $\text{CoOH}^-$  and  $\text{CoO}_2\text{H}^-$  secondary ion depth profiles were normalized by the corresponding  $\text{Co}^-$  profile in each sample to account for the topography changes between the  $\text{Na}_{0.67}\text{CoO}_2$  surfaces before and after OER. As a proxy for bulk  $\text{Na}_{0.67}\text{CoO}_2$ , the  $\text{Co}^-$  signal was selected for normalization. Finally, we used the ratio between the  $\text{Co}^-$ -normalized  $\text{CoOH}^-$  and  $\text{CoO}_2\text{H}^-$  profiles before and after OER to demonstrate their surface localization after the OER in a  $\sim 70$ -nm layer; the peak position of this ratio in Fig. 5A and B provided the localization. In comparison, the  $\text{CoO}^-/\text{Co}^-$  profile appears less enhanced at the surface, which suggests the OER produces only a limited amount of CoO at the  $\text{Na}_{0.67}\text{CoO}_2$  surface (Fig. 5C). However, given the natural fragmentation of  $\text{Na}_{0.67}\text{CoO}_2$  upon sputtering, the  $\text{CoO}^-$  signal could also be used as a marker for the bulk  $\text{Na}_{0.67}\text{CoO}_2$ . As such, TOF-SIMS high-resolution mapping of

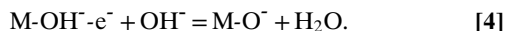


**Fig. 4.** The pH-dependent OER behavior of  $\text{Na}_{0.67}\text{CoO}_2$ . (A) Zeta potential of the catalysts. (B and C) CV measurements of  $\text{Na}_{0.67}\text{CoO}_2$  in  $\text{O}_2$ -saturated KOH with pH 12.5 to 14. Inset shows the enlarged CV part from 1.3 to 1.6 V. (D) The slope change of the linear CV curves at voltages above 1.7 V in B and C and *SI Appendix, Fig. S8* with different pH.

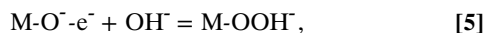
$\text{CoO}^-$  and  $\text{CoOH}^-$  secondary ion fragments was performed to show directly the formation of  $\text{CoOH}$  at the surface of  $\text{Na}_{0.67}\text{CoO}_2$  (Fig. 5D). Indeed, deep sputtering of the  $\text{Na}_{0.67}\text{CoO}_2$  particles confirms the continuous presence of  $\text{CoOH}$  at their surface, as presented in Fig. 5D in the dual color overlay as a function of depth, that is, of  $\text{Cs}^+$  sputtering time. The Na/Co ratio of  $\text{Na}_{0.67}\text{CoO}_2$  was confirmed, by inductively coupled plasma mass spectrometry, not to change from before to after OER testing (*SI Appendix, Table S3*).

## Discussion

In air, an exposed surface cation M of an oxide, especially one with a strong octahedral site preference energy, attracts water to complete its oxygen coordination; the hydrogen atoms of the adsorbed water  $\text{H}_2\text{O}$  are dispersed over the surface oxygen to create surface  $\text{M-OH}^-$ . In alkaline solution, an exposed surface cation attracts solution  $\text{OH}^-$  when it is oxidized during charge. Continuing removal of electrons from the oxide during charge in KOH solution induces the reaction (Fig. 6A)



This reaction occurs at a critical potential  $V_c \leq V_{\text{on}}$ , where  $V_{\text{on}}$  is the onset potential for the OER to occur with continuing charge; the resulting  $\text{MO}^-$  may be attacked by the solution  $\text{OH}^-$ ,

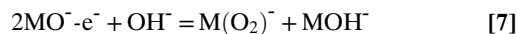


and the subsequent OER activity then depends on the relative rates of removal of the  $\text{H}^+$ ,



and displacement of the  $\text{O}_2\text{H}^-$  by a solution  $\text{OH}^-$ . An  $\text{O}_2\text{H}^-$  can be an unwanted by-product of reaction 5.

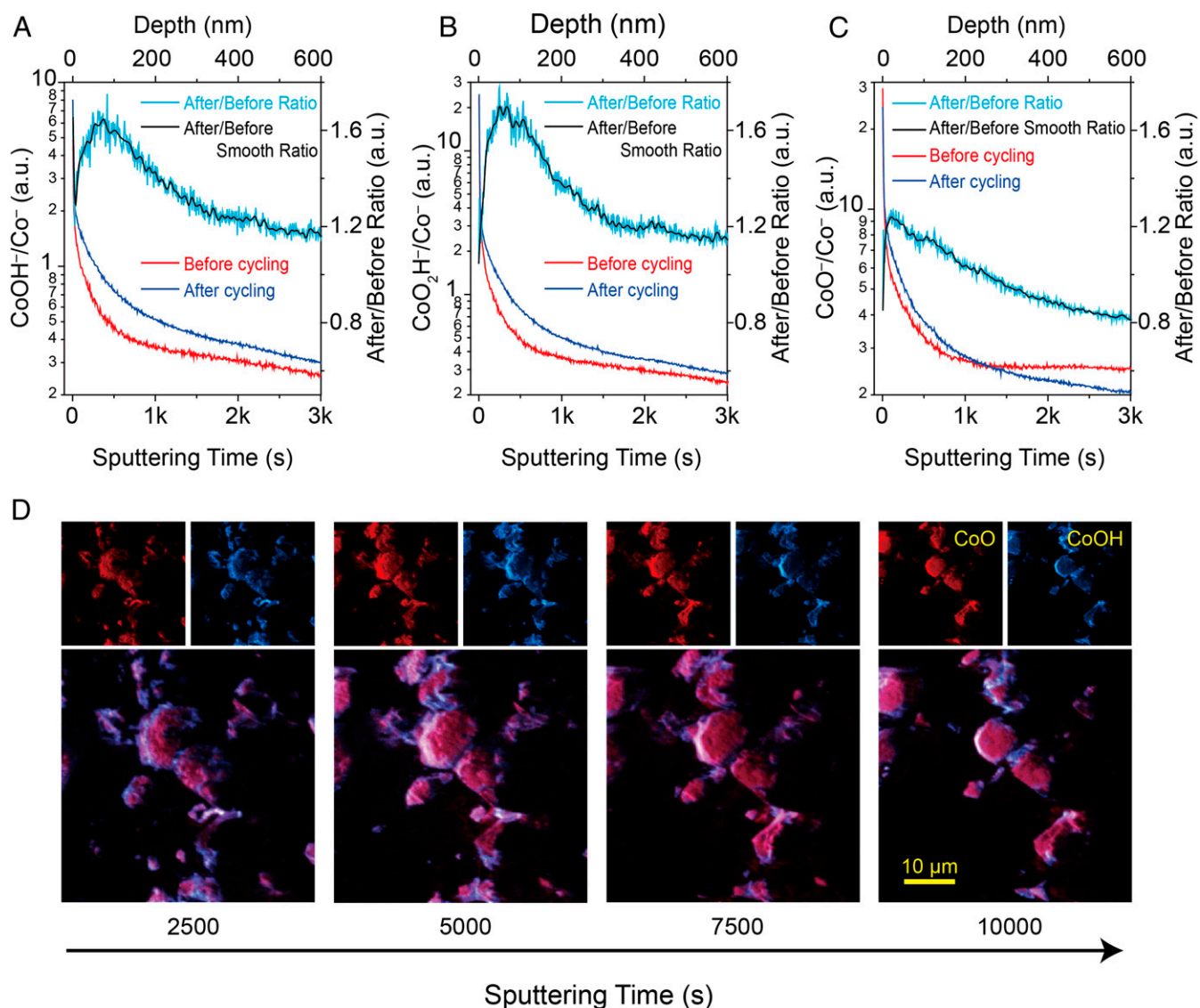
Alternatively, 2 neighboring surface  $\text{O}^-$  may react with one another (Fig. 6B),



followed by



The rate of reaction 7 competes with that of reaction 5; it increases strongly with decreasing surface O–O separation. Therefore, the activity of the OER above the onset potential depends strongly on the surface O–O separation. The observation of an ultrafast OER in  $\text{Na}_{0.67}\text{CoO}_2$  with an unusually short O–O separation demonstrates this dependence. A layer oxide  $\text{Na}_x\text{CoO}_2$  with  $x = 0.52, 0.65, \text{ and } 0.75$  has a different crystal structure (space group: P63/mmc) with our  $\text{Na}_{0.67}\text{CoO}_2$  (R-3c); all of these 3 materials show almost the same OER activity after cycling. Our  $\text{Na}_{0.67}\text{CoO}_2$  shows a much higher OER activity than the reported  $\text{Na}_x\text{CoO}_2$ ; the overpotential at  $10 \text{ mA}\cdot\text{cm}^{-2}$  of our  $\text{Na}_{0.67}\text{CoO}_2$  is 0.29 V, which is much smaller than their  $\text{Na}_x\text{CoO}_2$  (0.45 to 0.47 V) (44). In  $\text{Na}_x\text{CoO}_2$  with space group P63/mmc, for example,  $\text{Na}_{0.65}\text{CoO}_2$ , Na and Co ions occupy 2 and 1 different positions, respectively; however, there are 3 Na and 4 Co positions in  $\text{Na}_{0.67}\text{CoO}_2$  with space group R-3c. The O–O separation in  $\text{Na}_{0.65}\text{CoO}_2$  is 2.57 Å, while the O–O separation of our  $\text{Na}_{0.67}\text{CoO}_2$  is much smaller (the shortest O–O is 2.30 Å); the large O–O separation difference is caused by the different crystal structure and Na ordering. Their results also well support our conclusion that short O–O separation determines the OER activity. The relationship between the catalytic performance and the O–O bond length in  $\text{Na}_x\text{CoO}_2$  and  $\text{Li}_x\text{CoO}_2$  with different  $\text{Na}^+$  and  $\text{Li}^+$  proportion according to the previous report is shown



**Fig. 5.** TOF-SIMS depth profiling and high-resolution mapping of  $\text{Na}_{0.67}\text{CoO}_2$  particles before and after OER. (A–C) TOF-SIMS depth profiling of  $\text{Na}_{0.67}\text{CoO}_2$  before and after cycling. The intermediates  $\text{CoOH}^-$ ,  $\text{CoO}_2\text{H}^-$ , and  $\text{CoO}^-$  increase after cycling. (D) Dual color overlays of high-resolution maps of the  $\text{CoO}^-$  and  $\text{CoOH}^-$  secondary ion signals demonstrating that  $\text{CoOH}^-$  mainly exists on the surface of the catalyst particles.

in *SI Appendix, Fig. S2*. The shorter the O–O bond length in these oxides, the smaller the overpotentials at  $5 \text{ mA}\cdot\text{cm}^{-2}$ , which confirms the key role of the short O–O separation in the OER performance of the  $\text{Na}_{0.67}\text{CoO}_2$ .

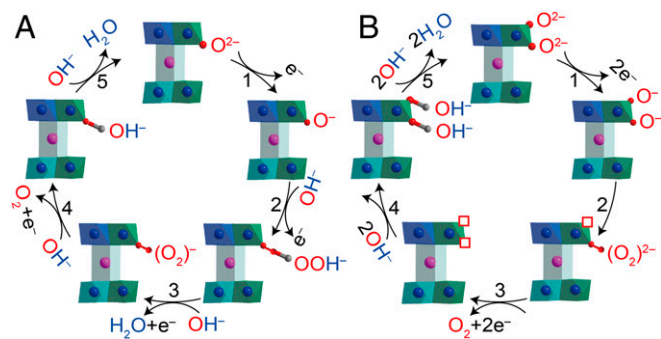
Reaction 4, which sets the onset potential, depends on the zeta potential of the oxide and the pH of the solution. Reaction 4 is favored the higher the pH of the solution and the greater the acidity of the oxide. The stronger the M–O bond, the more acidic is the oxide. The existence of itinerant electrons in  $\pi$ -bonding orbitals of  $d$ -wave symmetry not only lowers the resistance to the OER, but also testifies to a strong O-2p hybridization in the  $\pi$ -bonding as well as  $\sigma$ -bonding orbitals of  $d$ -wave symmetry.

### Summary

The excellent OER activity of  $\text{Na}_{0.67}\text{CoO}_2$  is the result of a short O–O separation that increases the rate of reaction 7 relative to reaction 5 and demonstrates the superior rate capability of reaction 7. The stability of the catalyst is the result of strong Co–O  $\sigma$ -bonding with the  $\text{Co}^{\text{IV}}$  configuration on  $\pi^*5\sigma^*0$ .

### Materials and Methods

$\text{Na}_{0.67}\text{CoO}_2$  was prepared by a typical solid-state reaction with analytical grade  $\text{Na}_2\text{CO}_3$  and  $\text{Co}_3\text{O}_4$  as raw materials. First of all, the mixture of  $\text{Na}_2\text{CO}_3$



**Fig. 6.** Competing OER mechanisms on  $\text{Na}_{0.67}\text{CoO}_2$ . OER mechanism with surface lattice oxygen activated for OER to form peroxide either (A) in a  $\text{CoO}_2$  layer or (B) between 2 neighboring  $\text{CoO}_2$  layers.

and  $\text{Co}_3\text{O}_4$  in a stoichiometric ratio with an excess of 5 mol%  $\text{Na}_2\text{CO}_3$  was thoroughly ground in agate bowls, pressed into pellets, and sintered at 700 °C for 2 d, 900 °C for 15 h, and 950 °C for 10 h at a heating rate of 3 °C·min<sup>-1</sup> with intermediate grinding. These pellets, after sintering, were crushed and powdered to obtain a fine particle size. For comparison, commercial  $\text{IrO}_2$ ,  $\text{Co}(\text{OH})_2$ , and  $\text{Co}_3\text{O}_4$  were purchased from Alfa Aesar and used without further purification.

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