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### Short O-O Separation in Layered Oxide $\text{Na}_{0.67}\text{CoO}_2$ Enable an Ultrafast Oxygen Evolution Reaction

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**Keywords:** Air electrodes, water electrolysis, catalytic mechanisms, structure-property relationship

## **Abstract**

The layered oxide  $\text{Na}_{0.67}\text{CoO}_2$  with  $\text{Na}^+$  occupying trigonal-prismatic sites between  $\text{CoO}_2$  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  $\text{O}^-$ - $\text{O}^-$  interactions followed by  $\text{O}_2$  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  $\text{H}^+$  ions from the surface oxygen to provide surface  $\text{O}^-$  that may either be attacked by solution  $\text{OH}^-$  or react with one another; a short O-O separation favors the latter route. The role of a strong hybridization of the O-2*p* and low-spin  $\text{Co}^{\text{III}}/\text{Co}^{\text{IV}}$   $\pi$ -bonding *d* states is also important; the OER on other  $\text{Co}^{\text{III}}/\text{Co}^{\text{IV}}$  oxides is compared with that on  $\text{Na}_{0.67}\text{CoO}_2$  as well as that on  $\text{IrO}_2$ .

**Significance Statement**

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.

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).

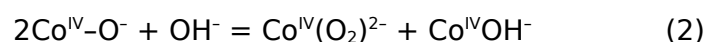
Low-cost transition-metal oxides are promising candidates for OER catalysts (8-17). AMO<sub>3</sub> perovskites with controllable chemical compositions and electronic structures by substituting the cations on A and M sites have been extensively investigated as OER catalysts (18-22). Some perovskite oxides (e.g., Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-6</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 4*d*/5*d*-transition-metal-oxide catalysts with zero antibonding *e<sub>g</sub>* 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 two 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>3-6</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>5+</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 transition-metal 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 two 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  $t^4\sigma^{*1}$ , 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  $V_{ch} = V_{on}$ , where  $V_{on}$  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.

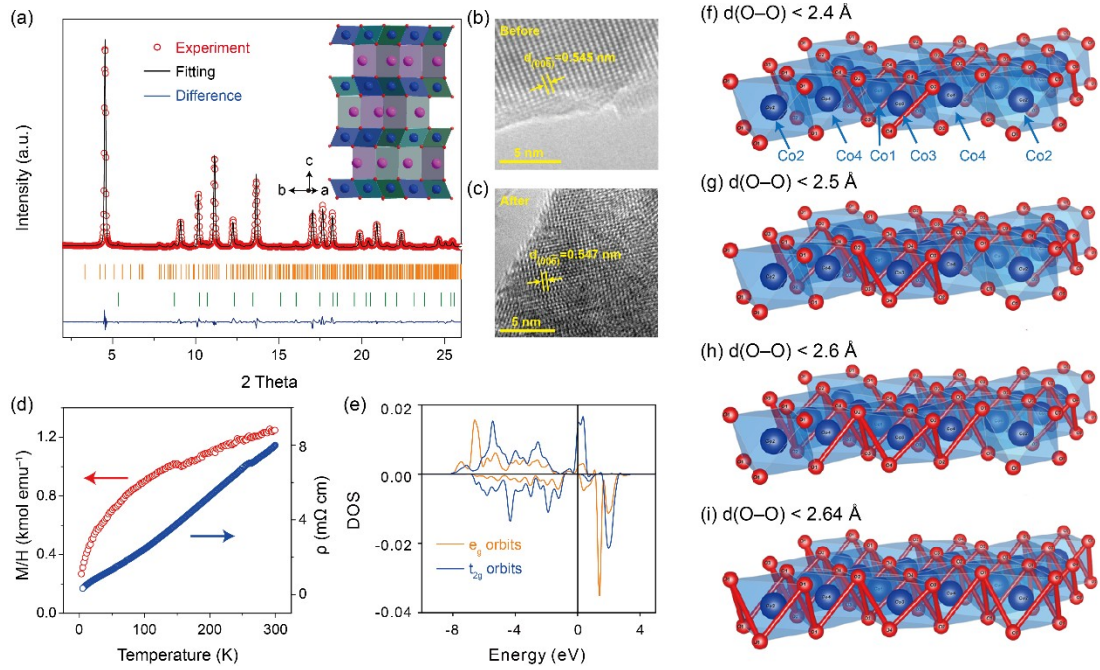
These findings recommend to us a search for stable oxides with a shorter surface oxygen separation that can be prepared at ambient pressure. Therefore, we prepared a metallic layered-oxide Na<sub>0.67</sub>CoO<sub>2</sub> with low-spin Co<sup>III/IV</sup> ions (Co<sup>III</sup>: π\*<sup>6</sup>σ\*<sup>0</sup>; Co<sup>IV</sup>: π\*<sup>5</sup>σ\*<sup>0</sup>) and a much shorter O-O separation than on CaCoO<sub>3</sub> 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 Na<sub>0.67</sub>CoO<sub>2</sub> has a strong Co<sup>III/IV</sup>-O interaction as a result of empty σ-antibond e<sub>g</sub> orbitals and itinerant π-bonding electrons, which reduces the charge transfer resistance during the OER; Na<sub>0.67</sub>CoO<sub>2</sub> has a zero zeta potential at pH =4 and shows a pH-dependent onset potential for the OER consistent with the potential for the CoOH<sup>-</sup> - e<sup>-</sup> + OH<sup>-</sup> = CoO<sup>-</sup> + H<sub>2</sub>O reaction.

## Results

**The crystal and electronic structure of Na<sub>0.67</sub>CoO<sub>2</sub>.** Synchrotron powder X-ray diffraction and powder X-ray diffraction patterns of as-prepared Na<sub>0.67</sub>CoO<sub>2</sub> (Fig. 1 and SI Appendix Fig. S1) confirm the layered structure of Na<sub>0.67</sub>CoO<sub>2</sub>. Two-dimensional CoO<sub>2</sub> layers with edge-sharing CoO<sub>6</sub> octahedra in trigonal Na<sub>0.67</sub>CoO<sub>2</sub> (space group: R-3c) are separated by sodium layers. The

Na<sup>+</sup> occupy three different trigonal prismatic sites, Na1 and Na2 (Na2a and Na2b) in SI Appendix Table S1; each shares six edges and two triangular faces along the c axis with the CoO<sub>6</sub> octahedra vertically above and below. The Na1 ions are energetically less favorable because of the coulombic repulsions from two Co ions in face-sharing octahedra. The Co ions of Na<sub>0.67</sub>CoO<sub>2</sub> have four different positions; the distorted Co–O octahedra have a similar average Co–O bond distance, but one shortest O–O separation (2.30 Å, Fig 1f) than that of cubic CaCoO<sub>3</sub> (O–O: 2.64 Å) in which the Co<sup>IV</sup> have an intermediate spin state (t<sup>4</sup>σ\*<sup>1</sup>). About 0.3 wt% Co<sub>3</sub>O<sub>4</sub> impurity was found to exist in the sample by refining the synchrotron data. The Na<sub>0.67</sub>CoO<sub>2</sub> sample had an average particle size of 15 μm (SI Appendix Fig. S3), and the EDS mapping revealed a uniform distribution of Na, Co, and O elements.

The electronic conductivity and magnetic properties of Na<sub>0.67</sub>CoO<sub>2</sub> were investigated to determine the *d*-electron configuration of the Co<sup>III/IV</sup> ions (Fig. 1d). The temperature dependence of resistivity of Na<sub>0.67</sub>CoO<sub>2</sub> 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. Spin-polarized first-principle calculation was performed and the density of states of Co ions from Na<sub>0.67</sub>CoO<sub>2</sub> was shown in Fig. 1e. The conducting band of Na<sub>0.67</sub>CoO<sub>2</sub>, which is contributed by one spin component of t<sub>2g</sub> orbitals, are not full-filled, indicating that metallic property of Na<sub>0.67</sub>CoO<sub>2</sub>. The higher electronic conductivity of Na<sub>0.67</sub>CoO<sub>2</sub> reduces the charge transfer resistance (R<sub>ct</sub>) and the ohmic potential drop of the OER; the R<sub>ct</sub> of Na<sub>0.67</sub>CoO<sub>2</sub> is one order of magnitude smaller than that of the electronic insulator Co<sub>3</sub>O<sub>4</sub> which is above 1.6 V (SI Appendix Fig. S4).



**Fig. 1. Crystal structure, 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  $\text{Na}_{0.67}\text{CoO}_2$ ; the inset shows its crystal structure (pink, Na; blue, Co; red, O). (b-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) The O-O bonds shorter than 2.4 Å are highlighted with thick red lines. All side edges of Co1 and 1/3 side edges of Co3 octahedra are shorter than 2.4 Å. (g) The O-O bonds shorter than 2.5 Å are highlighted. All side edges of Co1 and Co3 octahedra are shorter than 2.5 Å. (h) The O-O bonds shorter than 2.6 Å are highlighted. All side edges of Co1, Co3, and Co4 octahedra are shorter than 2.6 Å. (i) The O-O bonds shorter than 2.64 Å are highlighted. All side edges of Co octahedra are shorter than 2.64 Å that is the O-O bond length of cubic  $\text{CaCoO}_3$ .

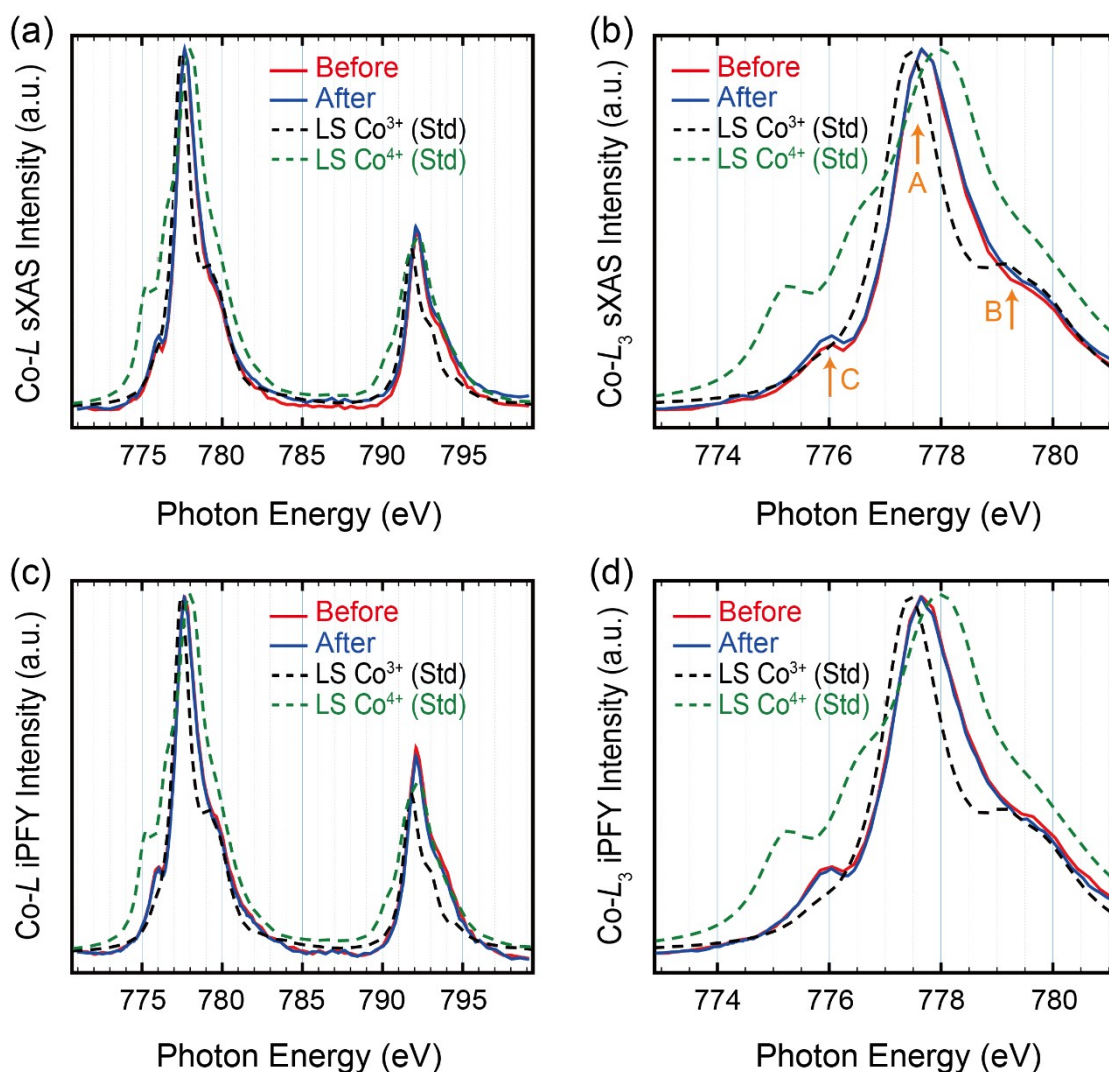
Soft X-ray absorption spectroscopy (sXAS), which is quite sensitive to the transition-metal (TM) 3d states because of the strong dipole-allowed 2p-3d (L-edge) excitations(30-33), was performed to explore the valence and spin states of the Co ions of  $\text{Na}_{0.67}\text{CoO}_2$  (Fig. 2). With a probe depth of 10 nm, the total electron yield mode of sXAS is quite an effective surface-sensitive probe, as shown in Figs. 2a, b. Due to the core-hole spin-orbit coupling, the Co L-



edge in Fig. 2a is well-separated into two branches, i.e.,  $L_3$  (between 774 and 787 eV) and  $L_2$  (between 788 and 799 eV). The branching ratio of the  $L_3$  and  $L_2$  edges is greatly affected by the spin-orbit coupling and especially by the  $2p$ - $3d$  multiplet effects, thus can be utilized to deduce the spin-state nature of Co (34, 35). Quantitatively, for the statistical ratio of the integrated intensity of two edges, namely  $I_{L3}/(I_{L3}+I_{L2})$ , 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 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. 2a-b, and that of HS is done as shown in 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  $\text{Na}_{0.67}\text{CoO}_2$  have a low-spin state ( $\text{Co}^{\text{III}}$ :  $t^6e^0$ ,  $\text{Co}^{\text{IV}}$ :  $t^5e^0$ ). The the density of states of Co ions from  $\text{Na}_{0.67}\text{CoO}_2$  shown in Fig. 1e can also indicate the 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, i.e. total fluorescence yield (TFY) 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. Inverse partial fluorescence yield (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 Figs. 2c,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.

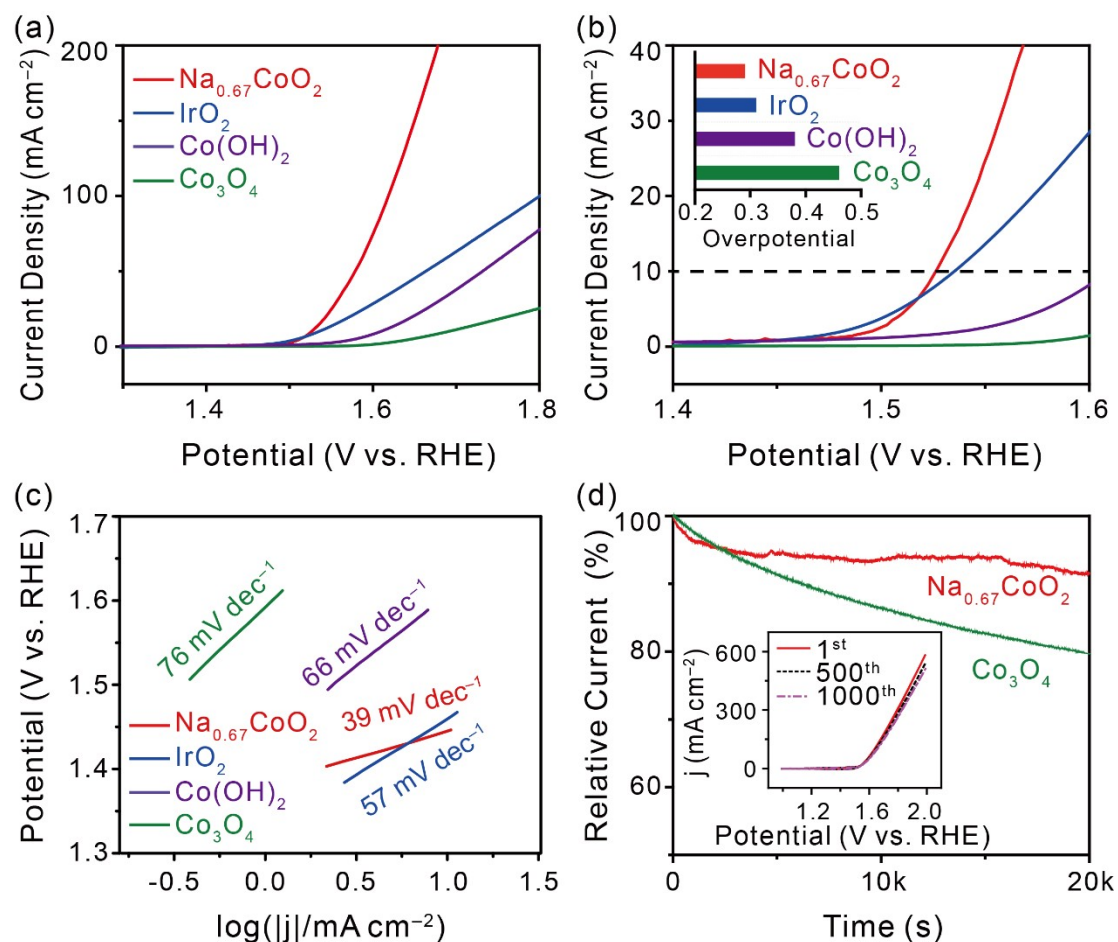


**Fig. 2. The unoccupied electronic states of  $\text{Co}^{\text{III}}$  and  $\text{Co}^{\text{IV}}$  in  $\text{Na}_{0.67}\text{CoO}_2$ .**

**(a-b)** TEY of Co L-edge. **(c-d)** iPFY of Co L-edge.

**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 the samples were normalized to the electrochemically active surface area (ECSA) to exclude geometric effects (SI Appendix Fig. S7 and SI Appendix 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 (BET) 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 mA cm<sup>-2</sup> and the highest current density at voltages above 1.6 V; the layered Co(OH)<sub>2</sub> and spinel Co<sub>3</sub>O<sub>4</sub> exhibited a negligible catalytic current density compared with Na<sub>0.67</sub>CoO<sub>2</sub>. The smallest Tafel slope of 39 mV dec<sup>-1</sup> (Fig. 3c) for Na<sub>0.67</sub>CoO<sub>2</sub> also indicates its excellent OER kinetics. The layered Li<sub>1-x</sub>CoO<sub>2</sub> has a structure and Co<sup>III/IV</sup>-O bond similar to that in Na<sub>0.67</sub>CoO<sub>2</sub>, but the Li<sup>+</sup> 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 Na<sub>0.67</sub>CoO<sub>2</sub> (6).

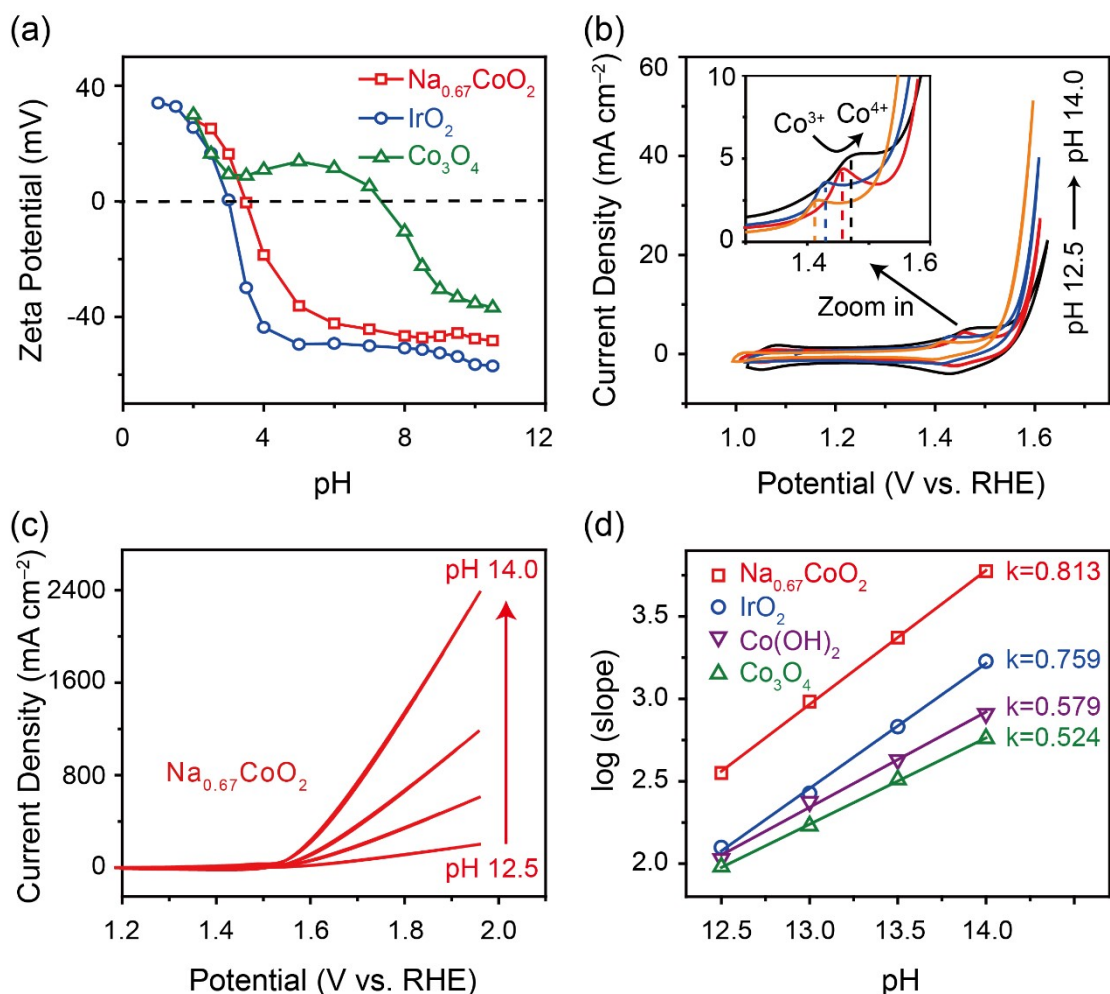


**Fig. 3. OER performance of Na<sub>0.67</sub>CoO<sub>2</sub>, IrO<sub>2</sub>, Co(OH)<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>.** (a) Linear sweep voltammograms at 1600 r.p.m. in 0.1M KOH. (b) The overpotential at 10 mA cm<sup>-2</sup>. (c) Tafel plots. (d) The chronoamperometric curves in an O<sub>2</sub>-saturated 0.1 M KOH electrolyte at 1.6 V vs. RHE and the CV curves of 1<sup>st</sup>, 500<sup>th</sup>, and 1000<sup>th</sup> cycles.

**The surface charge density of Na<sub>0.67</sub>CoO<sub>2</sub>.** The mean surface charge density of Na<sub>0.67</sub>CoO<sub>2</sub> (Fig. 4a) was evaluated by its zeta potential in water with different pH. Na<sub>0.67</sub>CoO<sub>2</sub> has a zero zeta potential at pH = 4; the strong

covalence of the Co<sup>III/IV</sup>-O bond of Na<sub>0.67</sub>CoO<sub>2</sub> makes it more acidic than the spinel Co<sub>3</sub>O<sub>4</sub>, which has a weaker Co<sup>III</sup>-O bond and a high zero-zeta potential at pH = 7.5. IrO<sub>2</sub> with a strong Ir<sup>IV</sup>-O bond has a similar zeta-potential curve to that of Na<sub>0.67</sub>CoO<sub>2</sub>, indicating analogous acidity of the surface states and pH influence on their OER.

The onset potential and activity of Na<sub>0.67</sub>CoO<sub>2</sub> at different pH are compared with those of Co<sub>3</sub>O<sub>4</sub>, Co(OH)<sub>2</sub> and IrO<sub>2</sub> in Fig. 4 and SI Appendix Fig. S8. The oxidation voltage of surface Co<sup>III</sup> to Co<sup>IV</sup> and the onset potential of Na<sub>0.67</sub>CoO<sub>2</sub> were reduced with increasing pH (Fig. 4b) because of the easier deprotonation process at higher pH; the activities of Na<sub>0.67</sub>CoO<sub>2</sub> and IrO<sub>2</sub> show a similar pH-dependent behavior on the RHE scale, and their OER currents increase significantly at high pH; however, both Co<sub>3</sub>O<sub>4</sub> and Co(OH)<sub>2</sub> 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 Na<sub>0.67</sub>CoO<sub>2</sub> has the biggest slope of all the catalysts at different pH. Both Na<sub>0.67</sub>CoO<sub>2</sub> and IrO<sub>2</sub> have a much larger slope change than Co<sub>3</sub>O<sub>4</sub> and Co(OH)<sub>2</sub>, indicating different OER mechanisms in these catalysts.



**Fig. 4. pH-dependent OER behavior of  $\text{Na}_{0.67}\text{CoO}_2$ .** (a) Zeta potential of the catalysts. (b-c) CV measurements of  $\text{Na}_{0.67}\text{CoO}_2$  and  $\text{Co}_3\text{O}_4$  in  $\text{O}_2$ -saturated KOH with pH 12.5-14. (d) The slope change of the linear CV curves at voltages above 1.7 V in (b,c) and SI Appendix Fig. S8 with different pH.

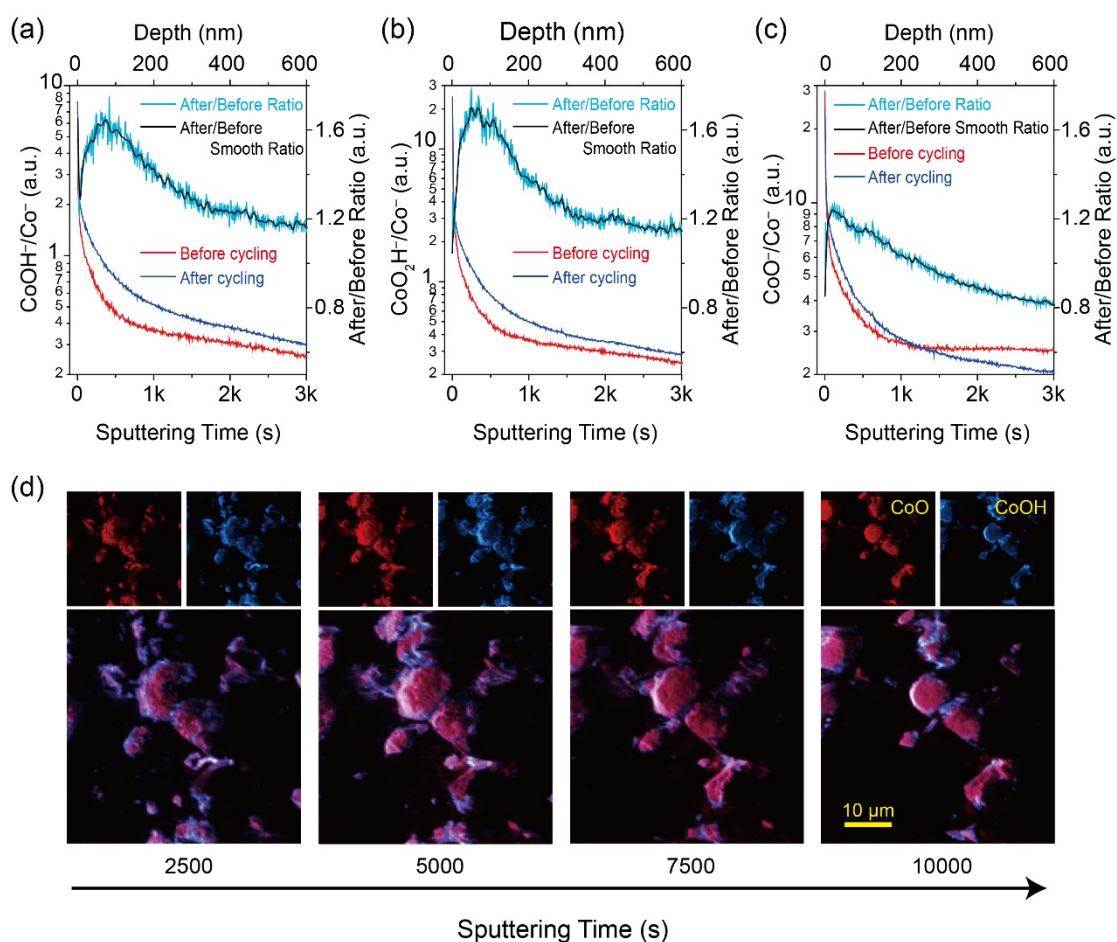
**The OER stability of  $\text{Na}_{0.67}\text{CoO}_2$ .**  $\text{Na}_{0.67}\text{CoO}_2$  shows an excellent OER stability in an  $\text{O}_2$ -saturated electrolyte with pH = 13 (Fig. 3d). More than 90 % of its initial current density after 20,000 s was retained; and after 1000 CV cycles  $\text{Na}_{0.67}\text{CoO}_2$  showed almost the same OER activity. The TEM (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 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 1000 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 these XPS peaks retains 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 ultra-high 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 Figs. 5a,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  $\text{CoO}$  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  $\text{CoO}^-$  and  $\text{CoOH}^-$

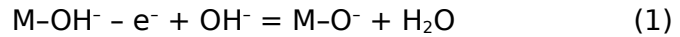
secondary ion fragments was performed to show directly the formation of CoOH at the surface of  $\text{Na}_{0.67}\text{CoO}_2$  (Fig. 5d). Indeed, deep sputtering of the  $\text{Na}_{0.67}\text{CoO}_2$  particles confirms the continuous presence of CoOH at their surface, as presented in Fig. 5d in the dual color overlay as a function of depth, i.e., 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 (ICP-MS) not to change from before to after OER testing (SI Appendix Table S3).



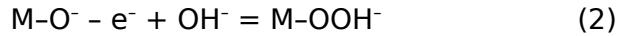
**Fig. 5. TOF-SIMS depth profiling and high-resolution mapping of  $\text{Na}_{0.67}\text{CoO}_2$  particles before and after OER. (a-c)** TOF-SIMS depth profiling of  $\text{Na}_{0.67}\text{CoO}_2$  before and after cycling. The intermediates  $\text{CoOH}^-$ ,  $\text{CoO}_2\text{H}^-$  and  $\text{CoO}^-$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

## Discussion

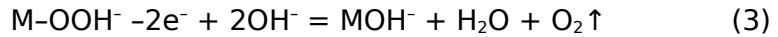
In air, an exposed surface cation M of an oxide, especially one with a strong octahedral-site preference energy, attracts water to complete its oxygen coordination; the hydrogen atom of the adsorbed water H<sub>2</sub>O are dispersed over the surface oxygen to create surface M-OH<sup>-</sup>. In alkaline solution, an exposed surface cation attracts solution OH<sup>-</sup> 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  $V_c \leq V_{on}$ , where  $V_{on}$  is the onset potential for the OER to occur with continuing charge; the resulting MO<sup>-</sup> may be attacked by the solution OH<sup>-</sup>:

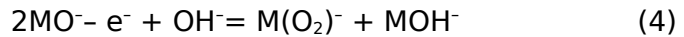


and the subsequent OER activity then depends on the relative rates of removal of the H<sup>+</sup>:

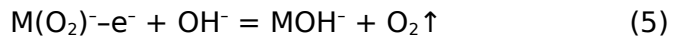


and displacement of the O<sub>2</sub>H<sup>-</sup> by a solution OH<sup>-</sup>. An O<sub>2</sub>H<sup>-</sup> can be an unwanted by-product of reaction (2).

Alternatively, two neighboring surface O<sup>-</sup> may react with one another (Fig. 6b):



followed by

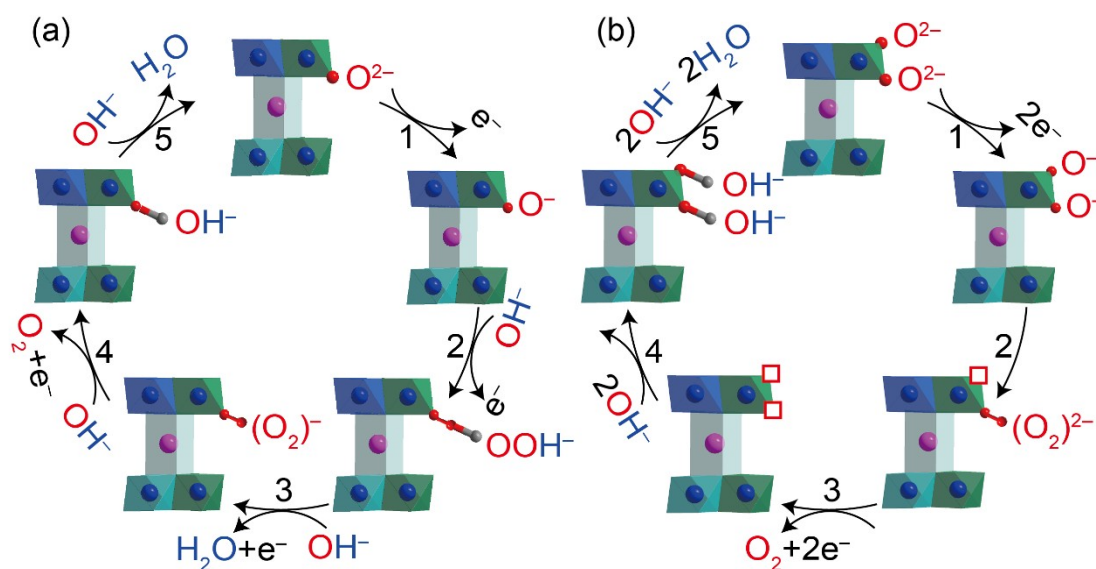


The rate of reaction (4) competes with that of reaction (2); it increases strongly with decreasing surface O-O separation. Therefore, the activity of the OER above the onset potential depends strongly on the surface O-O separation. The observation of an ultrafast OER in Na<sub>0.67</sub>CoO<sub>2</sub> with an unusually short O-O separation demonstrates this dependence. A layer-oxide Na<sub>x</sub>CoO<sub>2</sub> with x = 0.52, 0.65 and 0.75 has a different crystal structure (space group: P63/mmc) with our Na<sub>0.67</sub>CoO<sub>2</sub> (R-3c); all these three materials show almost the same OER activity after cycling. Our Na<sub>0.67</sub>CoO<sub>2</sub> shows a much higher OER activity than the reported Na<sub>x</sub>CoO<sub>2</sub>; the overpotential at 10 mA cm<sup>-2</sup>



<sup>2</sup> of Our  $\text{Na}_{0.67}\text{CoO}_2$  is 0.29 V, which is much smaller than their  $\text{Na}_x\text{CoO}_2$  (0.45-0.47 V) (44). In  $\text{Na}_x\text{CoO}_2$  with space group P63/mmc, e.g.,  $\text{Na}_{0.65}\text{CoO}_2$ , Na and Co ions occupy two and one different positions, respectively; however, there are three Na and four 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 was shown in SI Appendix Fig. S2. The shorter the O-O bond length in these oxides, the smaller overpotentials at 5 mA  $\text{cm}^{-2}$  are becoming smaller which can support perfectly the idea that the short O-O separation is the key role for the outstanding OER performance of the  $\text{Na}_{0.67}\text{CoO}_2$ .**

Reaction (1), which sets the onset potential, depends on the zeta potential of the oxide and the pH of the solution. Reaction (1) 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-2*p* hybridization in the  $\pi$ -bonding as well as  $\sigma$ -bonding orbitals of *d*-wave symmetry.



**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 two neighboring  $\text{CoO}_2$  layers.

## 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 (4) relative to reaction (2) and demonstrates the superior rate capability of reaction (4). 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  $\text{Na}_2\text{CO}_3$  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 days, 900 °C for 15 h and 950 °C for 10 h at a heating rate of 3 °C  $\text{min}^{-1}$  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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## Figure Legends

**Fig. 1. Crystal structure, 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  $\text{Na}_{0.67}\text{CoO}_2$ ; the inset shows its crystal structure (pink, Na; blue, Co; red, O). (b-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) The O-O bonds shorter than 2.4 Å are highlighted with thick red lines. All side edges of Co1 and 1/3 side edges of Co3 octahedra are shorter than 2.4 Å. (g) The O-O bonds shorter than 2.5 Å are highlighted. All side edges of Co1 and Co3 octahedra are shorter than 2.5 Å. (h) The O-O bonds shorter than 2.6 Å are highlighted. All side edges of Co1, Co3, and Co4 octahedra are shorter than 2.6 Å. (i) The O-O bonds shorter than 2.64 Å are highlighted. All side edges of Co octahedra are shorter than 2.64 Å that is the O-O bond length of cubic  $\text{CaCoO}_3$ .

**Fig. 2. The electronic states of  $\text{Co}^{\text{III}}$  and  $\text{Co}^{\text{IV}}$  in  $\text{Na}_{0.67}\text{CoO}_2$ .** (a-b) TEY of Co L-edge. (c-d) iPFY of Co L-edge.

**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 1600 r.p.m. in 0.1M KOH. (b) The overpotential at 10  $\text{mA cm}^{-2}$ . (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 1<sup>st</sup>, 500<sup>th</sup>, and 1000<sup>th</sup> cycles.

**Fig. 4. pH-dependent OER behavior of  $\text{Na}_{0.67}\text{CoO}_2$ .** (a) Zeta potential of the catalysts. (b-c) CV measurements of  $\text{Na}_{0.67}\text{CoO}_2$  and  $\text{Co}_3\text{O}_4$  in  $\text{O}_2$ -saturated KOH with pH 12.5-14. (d) The slope change of the linear CV curves at voltages above 1.7 V in (b,c) and SI Appendix Fig. S8 with different pH.

**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 (SI) signals demonstrating that  $\text{CoOH}^-$

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**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 two neighboring  $\text{CoO}_2$  layers.