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Water electrolysis on La$_{1-x}$Sr$_x$CoO$_3$$_{-\delta}$ perovskite electrocatalysts

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Perovskite oxides are attractive candidates as catalysts for the electrolysis of water in alkaline energy storage and conversion systems. However, the rational design of active catalysts has been hampered by the lack of understanding of the mechanism of water electrolysis on perovskite surfaces. Key parameters that have been overlooked include the role of oxygen vacancies, B–O bond covalency, and redox activity of lattice oxygen species. Here we present a series of cobaltite perovskites where the covalency of the Co–O bond and the concentration of oxygen vacancies are controlled through Sr$^{2+}$ substitution into La$_{1-x}$Sr$_x$CoO$_3$$_{-\delta}$. We attempt to rationalize the high activities of La$_{1-x}$Sr$_x$CoO$_3$$_{-\delta}$ through the electronic structure and participation of lattice oxygen in the mechanism of water electrolysis as revealed through ab initio modelling. Using this approach, we report a material, SrCoO$_{2.7}$, with a high, room temperature-specific activity and mass activity towards alkaline water electrolysis.
The scarcity of fossil fuels and the increasing awareness of the environmental and geopolitical problems associated with their use have encouraged significant efforts towards the development of advanced energy storage and conversion systems using materials that are cheap, abundant and environmentally benign. A major thrust in the field of renewable energy has been to develop higher power and more energy-dense storage devices, including low-temperature regenerative fuel cells and rechargeable metal-air batteries that function through the electrocatalysis of oxygen. Inherent to these systems are the electrolysis of water \( 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \) at early stages (OER) and the reduction of molecular oxygen \( \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \) at late stages (ORR), both of which require the use of an electrocatalyst due to their slow reaction kinetics. The most active catalysts for the ORR are Pt-alloys and other precious metals, Ir, Ru and Pd. However, while the Pt group metals perform well for the ORR, the formation of an oxide surface film at high potentials, especially in the case of Pt, decreases their ability to catalyse the OER. This problem, coupled with the Pt group metal scarcity especially in the case of Pt, decreases their ability to catalyse the OER. Inherent to these systems are the oxygen vacancy defects and the oxidation state of cobalt can be tuned through the relation:

\[
\text{LaCo}_{x+y}^3+ + x\text{Sr}_{x+y}^{2+} \rightarrow \text{La}_{1-x}\text{Sr}_{x}\text{Co}_{1-y}^3+\text{Co}_{1+y}^{1+}\text{O}_{1-y}^{0-x} + \frac{\delta}{2}\text{O}_2
\]

where, \( \delta \) is the oxygen non-stoichiometry parameter, \( x \) is the amount of \( \text{Sr}^{2+} \), and \( y \) is the amount of \( \text{Co}^{3+} \) in \( \text{La}_{1-x}\text{Sr}_{x}\text{Co}_{1-y}^3+\text{Co}_{1+y}^{1+}\text{O}_{1-y}^{0-x} \), hereafter referred to as LSCO(1-x)x (that is, LSCO28 for La0.2Sr0.8CoO3-

In order to improve the performance of these systems, the underlying electronic structure of these materials has been studied reactions, predating even the fields of catalysis and electrochemistry of water to oxygen. Inherent to these systems are the oxygen vacancy defects and the oxidation state of cobalt can be tuned through the relation:

\[
\text{LaCo}_{x+y}^3+ + x\text{Sr}_{x+y}^{2+} \rightarrow \text{La}_{1-x}\text{Sr}_{x}\text{Co}_{1-y}^3+\text{Co}_{1+y}^{1+}\text{O}_{1-y}^{0-x} + \frac{\delta}{2}\text{O}_2
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Herein, we describe the intrinsic activities of LSCO(1-x)x for the OER across the full series from \( 0 \leq x \leq 1 \), including the previously unreported perovskite phase \( \text{SrCoO}_{2.7} \) with the layered ordering of oxygen vacancies. The controlled substitution of \( \text{Sr}^{2+} \) for \( \text{La}^{3+} \) across the full phase space of the LSCO system while maintaining the perovskite structure allows us to probe the effects of covalency, vacancy defects and oxygen exchange on the electrocatalysis of the OER. The high activities for materials with \( x > 0.4 \) are rationalized through the high oxygen ion diffusivity and the covalency of the Co 3d and O 2p bonding in these materials allowing access to a newly hypothesized lattice oxygen-based mechanism as predicted through DFT modelling.

**Results**

Crystallographic characterization. LCO, LSCO and SCO samples were synthesized using our previously developed reverse-phase hydrolysis scheme, using a 950 °C calcination temperature.
instead of 700 °C to ensure that the correct phase was synthesized\textsuperscript{16,17,27}. Figure 2a shows the powder X-ray diffraction patterns for the system, demonstrating the successful synthesis of the perovskite phases across the whole-composition range. The only minor admixture found in the LCO and LSCO samples was Co\textsubscript{3}O\textsubscript{4}. The crystal structures of all compositions have been verified using a combination of powder X-ray diffraction and transmission electron microscopy. The unit cell parameters and space groups of the respective materials are given in Supplementary Table 1. The powder X-ray diffraction and selected area electron diffraction (SAED) patterns of the (x = 0–0.4 compositions are characteristic of the perovskite R3c structure with the \(a\), \(a\), \(a\)\(\bar{a}\) tilting distortion of the octahedral framework (Fig. 2b,c). The monoclinic distortion due to orbital ordering reported for this compositional range was not detected being beyond resolution of our powder X-ray diffraction experiment\textsuperscript{29–31}. The LSCO\textsubscript{46} composition crystallizes in a cubic Pm\textsubscript{3}m perovskite structure. In the crystal structures of LSCO\textsubscript{28} and SCO perovskite ordering of oxygen vacancies becomes obvious from both SAED patterns and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Fig. 2c,d,f,g). Oxygen vacancies reside in the (CoO\textsubscript{2}) anion-deficient perovskite layers alternating with the complete (CoO\textsubscript{2}) layers that results in a tetragonal \(a_p \times a_p \times 2a_p\) (\(a_p\) indicates the parameter of the perovskite subcell) supercell in LSCO\textsubscript{28}. The anion-deficient layers manifest themselves as faintly darker stripes in the HAADF-STEM images (marked with arrowheads in Fig. 2f,g), which according to Kim et al.\textsuperscript{32} is related to the structural relaxation in these planes. The anion-deficient layers form nanoscale-twinned patterns in both the LSCO\textsubscript{28} and SCO samples (Fig. 2f,g). In general, the crystallographic observations on the LCO and LSCO samples are in agreement with the La\textsubscript{1}–\textsubscript{x}Sm\textsubscript{x}CoO\textsubscript{3–\(\delta\)} phase diagram\textsuperscript{33}. However, in contrast to the earlier reported Sr\textsubscript{2}Co\textsubscript{2}O\textsubscript{5} brownmillerite or hexagonal Sr\textsubscript{r}Co\textsubscript{r}O\textsubscript{r}1\textsubscript{r} phases\textsuperscript{34,35}, the SCO sample demonstrates another type of oxygen vacancy ordering. The \([010]_p\) SAED pattern of SCO (Fig. 2d, top) is strongly reminiscent to that of the Ln\textsubscript{1}–\textsubscript{x}Sr\textsubscript{x}CoO\textsubscript{3–\(\delta\)} (Ln = Sm-Yb, Y) perovskites with the I\(\bar{4}\)/m\textsubscript{mmm} 2\(a_p\) \(\times\) \(2a_p\) \(\times\) \(4a_p\) supercell\textsuperscript{33,36,37}. A detailed deconvolution of this SAED pattern into contributions from the twinned domains is presented in Supplementary Fig. 1. This supercell also allows complete indexing of the powder X-ray diffraction pattern of SCO (Supplementary Fig. 2). The layered ordering of the oxygen vacancies in the LSCO\textsubscript{28} and SCO samples was directly visualized using annular bright-field STEM (ABF-STEM) imaging (Fig. 3a,b). In both structures the anion-complete (CoO\textsubscript{2}) and anion-deficient (CoO\textsubscript{2}–\(\delta\)) layers can be clearly distinguished, alternating along the c-axis of the tetragonal supercells. However,

Figure 2 | Structural characterization of La\textsubscript{1–\(x\)}Sr\textsubscript{x}CoO\textsubscript{3–\(\delta\)} (a) Powder X-ray diffraction patterns for La\textsubscript{1–\(x\)}Sr\textsubscript{x}CoO\textsubscript{3–\(\delta\)} (0 \(\leq\) x \(\leq\) 1). The reflection from Co\textsubscript{3}O\textsubscript{4} is marked with an asterisk. (b-d) SAED patterns of LSCO\textsubscript{28} (b), LSCO\textsubscript{28} (c) and SCO (d). The reflections of the basic perovskite structure are indexed. The \([010]_p\) SAED pattern of LSCO\textsubscript{28} shows weak \(G_p \pm 1/2 <111>_p\)\(\bar{p}\) type reflections (\(G_p\)—reciprocal lattice vector of the perovskite structure) characteristic of the \(a\), \(a\), \(\bar{a}\) octahedral tilting distortion of the perovskite structure. The \([010]_p\) SAED pattern of LSCO\textsubscript{28} demonstrates the orientationally twinned \(G_p \pm 1/2 <001>_p\)\(\bar{p}\) superlattice reflections resulting in the P4\text/m\text{mmm} \(2a_p\) \(\times\) \(2a_p\) \(\times\) \(4a_p\) supercell. The superstructure in the \([010]_p\) SAED pattern of SCO can be described with the \(G_p \pm n/4 <201>_p\)\(\bar{p}\) \((n\)—integer) and \(G_p \pm 1/2 <110>_p\)\(\bar{p}\) superstructure vectors corresponding to the orientationally twinned I\(\bar{4}\)/m\text{mmm} \(2a_p\) \(\times\) \(2a_p\) \(\times\) \(4a_p\) supercell (see details in Supplementary Fig. 1). Note that the \(G_p \pm 1/2 <110>_p\)\(\bar{p}\) superlattice reflections are barely visible in the \([110]_p\) SAED patterns of SCO, but the intensity profile (shown as insert in d) along the area marked with the white rectangle demonstrates their presence undoubtedly. (e-g) \([010]_p\) HAADF-STEM images of LSCO\textsubscript{28} (e), LSCO\textsubscript{28} (f) and SCO (g). The image of LSCO\textsubscript{28} shows uniform perovskite structure, whereas the images of LSCO\textsubscript{28} and SCO show faint darker stripes spaced by \(2a_p\) (marked by arrowheads) indicating nanoscale-twinned arrangement of the alternating (CoO\textsubscript{2}) perovskite layers and (CoO\textsubscript{2}–\(\delta\)) anion-deficient layers. Scale bars are 5 nm.
establishing the exact ordering patterns of the oxygen atoms and vacancies in these \((\text{CoO}_2)\) layers requires more detailed neutron powder diffraction investigation.

In order to understand the effects of \(\text{Sr}^{2+}\) substitution on oxygen vacancy concentrations in \(\text{La}_{1-x}\text{Sr}_x\text{CoO}_3\) \((x=0.8, 1.0)\), isometric titrations were performed. It should be noted that processing conditions affect the oxygen content and oxidation state of cobalt significantly through equation 1. The results of the isometric titrations are presented in Table 1. As can be seen, there is both an increase in the bulk oxidation state of \(\text{Co}\) as well as an increase in the concentration of oxygen vacancies as lower valence \(\text{Sr}^{2+}\) is substituted for \(\text{La}^{3+}\). The high concentration of oxygen vacancies in \(\text{SrCoO}_2.7\) corroborates their pronounced layered ordering.

**Microstructural characterization.** The overall morphology of the LSCO series was investigated with bright-field TEM images, presented in Supplementary Fig. 3. The samples consist of highly agglomerated and partially sintered nanoparticles with size ranging from 20–50 nm to few hundred nanometres. The LCO and SCO materials demonstrate somewhat larger and more sintered crystallites compared with those of the mixed LSCO samples. HAADF-STEM and ABF-STEM images of the surface structure of LCO and SCO are shown in Supplementary Fig. 4, where the particles remain crystalline at the surface and for SCO the anion-deficient layers, evident through the nanoscale-twinned domain columns, extend to the surface. Brunauer–Emmett–Teller surface areas measured through \(\text{N}_2\) adsorption showed similar surface areas for all samples of \(3.1–4.5 \text{ m}^2\text{ g}^{-1}\) (Supplementary Table 2). This surface area is approximately half the surface area of the materials reported in our previous studies, which results from the higher calcination temperatures used for the LSCO series than the previously investigated \(\text{LaCoO}_3\), \(\text{LaNiO}_3\), \(\text{LaMnO}_3\) and \(\text{LaNi}_{0.75}\text{Fe}_{0.25}\text{O}_3\).

**Electrochemical characterization.** In order to better understand the role of oxygen vacancies in \(\text{La}_{1-x}\text{Sr}_x\text{CoO}_3\) \((x=0.8, 1.0)\) during electrochemical applications, the intercalation of oxygen in LSCO was studied using cyclic voltammetry in \(\text{Ar}\) saturated 1 M KOH solutions. The insertion and removal of oxygen ions appear as redox peaks in Fig. 4a. It is apparent that an increase in the oxygen vacancy concentration as \(\text{Sr}^{2+}\) is substituted for \(\text{La}^{3+}\) in LSCO increases the tendency for oxygen intercalation as indicated through the high current densities measured in the intercalation region. In addition, it is interesting to note that the position of the intercalation redox peaks shifts to higher potentials with increased oxygen vacancies which can be described through the common pseudocapacitive Nernst Equation:

$$E = E^0 + \frac{RT}{nF} \ln \frac{\sigma}{1 - \sigma}$$

where, \(E\) represents the measured potential for oxygen intercalation, \(E^0\) represents the standard potential for oxygen intercalation, \(R\) is the universal gas constant \((8.3145 \text{ J K}^{-1} \text{ mol}^{-1})\), \(T\) is the temperature during the measurement, \(F\) is
and a diffusion rate of $D = \frac{B}{C_0}$; $\sigma$ is the occupancy fraction of accessible lattice vacancy sites for the reaction:

$$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3 - \delta + 2\sigma\text{OH}^- \rightarrow \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 - \delta + \sigma\text{H}_2\text{O} + 2\sigma^-$$

(3)

This type of Nernst Equation is commonly associated with pseudocapacitive-type intercalation mechanisms, indicative of facile oxygen ion diffusion.

The diffusion rates of oxygen ions in LSCO were measured chronoamperometrically based on a bounded 3D solid-state diffusion model with a rotating disk electrode (RRDE) rotating at 1,600 r.p.m. in Ar saturated 1 M KOH. These results are presented in Fig. 4b, and a more detailed description of the theory behind the model is included as Supplementary Fig. 5. It was found that SCO, with a vacancy concentration of $\delta = 0.30 \pm 0.03$, had a diffusion rate of $D = 1.2 \pm 0.1 \times 10^{-12} \text{cm}^2\text{s}^{-1}$ at room temperature, which is $\sim 40 \times$ faster than for LCO, with a complete oxygen sublattice and a diffusion rate of $D = 3 \pm 1 \times 10^{-14} \text{cm}^2\text{s}^{-1}$. As a general comment, diffusion coefficients in the range of $10^{-9}$ to $10^{-14} \text{cm}^2\text{s}^{-1}$ have been found as usual values for the short circuit diffusion of oxygen along high-diffusivity pathways, including grain boundaries. Although it is unclear whether the measured diffusion rates are from bulk diffusion or along grain boundaries, isotopic tracer studies have shown that diffusion rates trend in the order of surface oxygen $>$ oxygen at grain boundaries $>$ bulk oxygen in perovskite systems, and thus the fast diffusion rates found in this study represent the lower boundary on the mobility of oxygen at the surface. Further, the crystallite size and density of grain boundaries is relatively consistent across the LSCO series due to the similar synthetic conditions, indicating that the diffusion rates can at least be compared against each other. The results indicate that the diffusion rates scale with Sr concentration because of the correlation with vacancies and Sr content. The results highlight the benefit of substitution of a lower valence ion into the A-site as an effective means of increasing the mobility of oxygen in perovskite oxide electrodes.

**The electrolysis of water.** The OER activities for LSCO and for a commercial IrO$_2$ sample were quantified through cyclic voltammetry in O$_2$ saturated 0.1 M KOH at 1,600 r.p.m., as shown in Fig. 5a. Each material was mixed at a mass loading of 30 wt% perovskite on a mesoporous nitrogen-doped carbon (NC) or onto Vulcan Carbon XC-72 (VC) for stability measurements. An evaluation of the carbon loading and total mass loading is presented in Supplementary Fig. 6, Supplementary Table 5 and the Supplementary Discussion. There is a shift towards more active Tafel slopes with increasing Sr content, with LCO and IrO$_2$ having similar Tafel slopes of $\partial V/\partial \ln i = 58 \text{mV dec}^{-1}$ ($\approx 2RT/F$) which decreases towards SCO with a Tafel slope of $\partial V/\partial \ln i = 31 \text{mV dec}^{-1}$ ($\approx 2RT/F$). This shift of Tafel slope for the OER may be indicative of the facile surface kinetics for oxygen exchange with increasing vacancy content, whereby OER kinetics that are limited by high-coverage Langmuir-like behaviour where surface oxygen is not exchanged rapidly ($\theta \rightarrow 1$) show Tafel slopes of $2RT/F$. In contrast, those materials showing more rapid surface oxygen exchange in the intermediate coverage Temkin condition regime ($0.2 < \theta < 0.8$) have slopes of $RT/F$. The specific activities at an overpotential of 400 mV, based on perovskite surface area from BET, are presented in Fig. 5b. It is clear that substitution of Sr$^{2+}$ for La$^{3+}$ in LSCO, and thereby the creation of oxygen vacancies, is beneficial to the OER, with the fully substituted SrCoO$_{2.7}$ at 28.4 mA cm$^{-2}$ which is $\sim 6 \times$ more active than LaCoO$_{3.005}$ (4.3 mA cm$^{-2}$), $\sim 23 \times$ more active than the commercial IrO$_2$ sample (1.2 mA cm$^{-2}$), and $\sim 1.5 \times$ more active than previously reported high-vacancy concentration cobaltite perovskites (Ba$_0$.Sr$_0$.Co$_0$.Fe$_0$.O$_{2.6}$: $\sim 20$ mA cm$^{-2}$; Pr$_0$.Ba$_0$.Co$_0$.O$_{2.5}$: $\sim 20$ mA cm$^{-2}$) (refs 14,43). In addition, due to the small particle size from the reverse-phase hydrolysis synthesis, SrCoO$_{2.7}$ (3.6 m$^2$g$^{-1}$) had a mass activity of $1.020 \pm 20$ mA mg$^{-1}$ at $+1.63$ V versus the reversible hydrogen electrode (RHE), which is $\sim 2 \times$ more active than BSCF with a similar surface area ($\sim 500$ mA mg$^{-1}$) (ref. 14). To verify that the measured current was due only to the OER, and not to side-reactions or corrosion of the electrode material, rotating-ring-disk (RRDE) cyclic voltammetry was performed with a Pt ring poised at $+0.4$ V versus RHE, whereby O$_2$ generated at the disk from the OER is collected and reduced at the ring. The results for SrCoO$_{2.7}$/NC and IrO$_2$/NC are shown in Fig. 5c. The collection efficiency for both SrCoO$_{2.7}$/NC and IrO$_2$/NC was 37%, which was equal to the collection efficiency measured during calibration of the RRDE for the oxidation of 0.3 mM ferrocene-methanol in 0.1 M KCl. Therefore, we can confirm that the current is exclusively due to the generation of oxygen on the SCO or the IrO$_2$ surface within the precision of the RRDE measurements.

The stability of SrCoO$_{2.7}$ and of the carbon supports under OER conditions were tested galvanostatically at 10 A g$^{-1}$ ox and 1,600 r.p.m., shown in Fig. 5d. As is readily apparent, both the
NC and VC are not stable carbon supports for the OER, and we hypothesize that this dominates the mechanism of failure for the composite electrodes at potentials $> +1.65\, \text{V versus RHE}$. However, other variables may be responsible for the failure of the electrodes, including the degradation of the Nafion binder at the anodic potentials of the OER, forming the soluble complex $\text{IrO}_2$ and $\text{IrO}_2$ supported on two different carbons, 2 at % nitrogen-doped NC and non-nitrogen doped VC. It is evident that both carbons are unstable at the anodic potentials of the OER, with rapid degradation occurring for all samples once the potential is $> +1.65\, \text{V versus RHE}$. The high activity and stability of $\text{SrCoO}_2.7$ on NC allows the electrode to generate $10\, \text{A g}^{-1}$ without reaching the potential where rapid carbon corrosion occurs. Further studies are needed in order to better understand the variables that influence catalyst stability, however, it is clear that carbon may not be the optimal catalyst support under the OER conditions. In addition, it should be noted that $\text{IrO}_2$ which has become the benchmark comparison for OER catalysts is not stable under the anodic conditions of the OER, forming the soluble complex $\text{IrO}_2$ in alkaline environments.$^{44}$ This is demonstrated in the stability plot in Fig. 5d, where even the unsupported $\text{IrO}_2$ electrode failed after $\sim 14\, \text{h}$.

The catalytic activity towards the OER was found to strongly correlate with the oxygen diffusion rate and the vacancy concentration, $\delta$, presented in Fig. 6c,d. On the basis of these correlations, we hypothesize a new OER mechanism in Fig. 6a based on the exchange of lattice oxygen species that takes into account the role of surface oxygen vacancies and B–O bond covalency (lattice oxygen-mediated OER, LOM). In contrast to the general adsorbate evolution mechanism (AEM) which considers only the redox activity of the transition metal B-site, we find a better electronic explanation arises when the covalency of the M–O bond is considered, indicative of the overlap of the Co 3d and O 2p bands in the crystal, as first proposed by Matsumoto et al.$^{44,45}$ As the oxidation state of Co is increased, the $d$ orbitals of the Co ion have a greater overlap with the $s$, $p$ orbitals of the $O^{2-}$ ion, leading to the formation of $\pi^*$ and $\sigma^*$ bands, as described through Fig. 1 and in the partial density of states (PDOS) diagrams in Fig. 6a and refs 11,13,22,43. When the overlap is great enough, ligand holes (oxygen vacancies) are formed and the metal 3d $\pi^*$ band can no longer be treated as isolated in energy from the oxygen O 2p $\pi^*$ band. At this point, the surface of the crystal and bound intermediates can be treated as a single energy surface, where the Fermi energy can be modulated through the hybridized Co 3d–O 2p $\pi^*$ band with applied electrical potential, opening up the possibility for lattice oxygen redox activity.$^{46}$ A recent in situ ambient pressure XPS study has confirmed the validity of this model in perovskites and other oxides.$^{47,48}$ In addition, oxygen redox activity has been observed in LSCO with high $\text{Sr}^{3+}$ content in the regime of oxygen intercalation, which occurs approximately at the onset potentials of the OER in these materials.$^{49–51}$

To test the validity of this lattice oxygen-mediated mechanism (LOM) and identify the rate-determining step, we modelled the reaction pathway using density functional theory.$^{52}$ Supplementary Fig. 7a shows that $\text{OH}^{-}$(aq) tends to electrochemically fill the surface O vacancies of LSCO under the operational electrode potential of OER, as described through
reaction 3 and LOM 1 in Fig. 6a, leading to an in situ surface–layer stoichiometry close to that of stoichiometric bulk ABO₃. Consequently, we begin by constructing the [001] BO₂ terminated surfaces (Supplementary Fig. 8a) with ½ ML OER intermediate adsorbates⁵² based on the 2×2×2 cubic stoichiometric bulk LSCO for the initial identification of the reactivity trend and reaction mechanism⁵³. We subsequently investigated more realistic bulk phases with oxygen vacancies and various surface structures, which we find do not alter the preference of LOM over AEM; further details of these computations are provided in the Supplementary Methods.

Our results show that Step 1 differentiates the LOM, involving the intermediate with adsorbed −OO and lattice O vacancies (I₁ in Figs 6a and 7a), from the AEM, involving the generally proposed adsorbed −O (I₀ in Figs 6a and 7a). Therefore, the relative stabilities (free energy difference, ΔG) between these two isomeric intermediates are key to identifying if OER proceeds via the LOM or AEM for a given LSCO composition. This identification approach has been successfully used to demonstrate the preference of LOM on LaNiO₃ (ref. 52). The computed values of ΔG are shown as a function of LSCO composition in Fig. 7b, which illustrates two key points. First, increasing x in La₁₋ₓSrₓCoO₃−δ reduces the O vacancy formation energy and therefore bulk stability. Second, ΔG decreases with the decreased bulk stability, becoming negative between 0.25<x<0.5. Therefore, OER on perovskites with low stability such as La₀.₅Sr₀.₅CoO₃−δ, La₀.₇₅Sr₀.₂₅CoO₃−δ and SrCoO₃−δ is predicted to occur via the LOM, whereas LaCoO₃ and La₀.₇₅Sr₀.₂₅CoO₃−δ are expected to follow the AEM. The transition from the AEM to the LOM is related to the ineffectiveness of the surface Co as electron donors. The double bond of the adsorbed O formed in reaction 1 of the AEM...
significantly increases the oxidation state of surface Co to $3^+$. In the LOM step 1, the transfer of a surface O to form a surface O vacancy and the single-bonded –OO adsorbate decreases the nominal valence charge on the Co to $3^+$. Thus, the LOM pathway has higher stability than the AEM pathway, particularly for those LSCO with large $x$. The relative stability of $I_1$ to $I_0$ is also apparent in the projected density of states of the d-band for the active surface Co and the overall p-band for its ligand O (Fig. 7c). The overlap of the peaks in these two bands indicates the orbital hybridization and Co–O binding. For the AEM intermediate on LaCoO$_3$ ($I_0$), the strong overlap of peaks in the spin-up (down) bands centred around $-1$ eV (0.5 eV) indicates the strong Co–O covalent bonding state. These overlaps, however, are significantly weakened for $I_1$, consistent with the stability. The reverse is true for the LSCO with low stability. Compared with $I_0$ for SrCoO$_3$, $I_1$ preserves a significant overlap of spin-up state around $-1$ eV, but has negligible overlap of the unoccupied spin-down states, which are anti-bonding in character, indicating the greater stability of $I_1$.

To understand the phase and stoichiometry effects on the relative stability of $I_1$ to $I_0$, we perform the analogous calculations on the rhombohedral LaCoO$_3$ and the nonstoichiometric SrCoO$_{2.7}$ phases. The rhombohedral LaCoO$_3$ phase is modelled by optimizing an initial $2 \times 2 \times 2$ orthorhombic cell with octahedral rotation; the optimized structure exhibits a Co–O–Co angle of $162^\circ$ and a Co–O distance of 1.96 Å, consistent with experimental measurements. The SrCoO$_{2.7}$ phase is approximated as SrCoO$_{2.75}$, which can be modelled by relaxing the cubic $2 \times 2 \times 2$ SrCoO$_3$ structure with two oxygen vacancies. By comprehensively searching the vacancy ordering, we identify the most stable configuration as the presence of the two vacancies surrounding one Co, which therefore leads to the formation of a...
tetrahedral CoO₄ linked to two tetragonal pyramidal CoO₃ units (Supplementary Fig. 8b). The lattice constant of this optimized SrCoO₂₋₇₅ is within 1.1% difference from that of the derived pseudocubic SrCoO₂₋₇ (Supplementary Table 1). This configuration is further validated by introducing two more vacancies to form SrCoO₂₋₅ in the same way, so as to maximize the number of tetrahedral CoO₄. The relaxed SrCoO₂₋₅ shows alternating octahedral (CoO₂) and tetrahedral zigzag-like (CoO) layers with respect to the (001) direction of the reference cubic phase (Supplementary Fig. 8b), in full agreement with experimental observations. The SrCoO₂₋₇₅ slab is subsequently constructed by exposing the (CoO₂−₅) layer (Supplementary Fig. 8c), but with added oxygen anions to attain the correct stoichiometry (Supplementary Fig. 8d) to simulate the intercalation phenomenon as described by Supplementary Fig. 7a and LOM Step 3. As Fig. 7b shows, the octahedral rotation stabilizes the rhombohedral LaCoO₃, leading to a slight increase in the oxygen vacancy formation energy and ΔG. In the case of SrCoO₂₋₇₅, the existing oxygen deficiency increases the oxygen vacancy formation energy by 0.33 eV, while slightly stabilizing I₁ relative to I₀, compared with SrCoO₂. The lattice constant of the predicted SrCoO₂₋₇₅ is 0.7% larger than that of SrCoO₂, leading to the slightly weaker adsorption strength and lower stability of I₀ (ref. 54). However, the small magnitude of this change indicates the similar reactivity of SrCoO₂ to that of the intercalated SrCoO₂₋₅ surface under OER conditions. From the above analysis, we conclude that neither the phase nor the non-stoichiometry alters the qualitative stability of I₁ to I₀, although it leads to a horizontal shift in the overall trend of bulk vacancy formation to higher energetic cost.

We also compute the free energy of electrochemical OER on SrCoO₂ to demonstrate the switch in the reaction mechanism due to the relative change in I₁ to I₀, stability on SrCoO₂₋₇₅. In accordance with the procedure in ref. 53 the free energy of each reaction step is determined by ΔGₙ = E + ΔZPE − TΔS − eUₓ/RHₓ at Uₓ/RHₓ = +1.23 V, where ΔE is the DFT-computed enthalpy change for ½ ML of intermediates relative to H₂O and H₂ molecules (Supplementary Table 3) and ΔZPE−TΔS gives the corrections for zero-point energy and entropy of both adsorbates and H₂(g) and H₂O (l) under OER conditions (Supplementary Table 4) (refs 53,54). The largest free energy is the estimated overpotential, η. As ΔGₑ is independent of the initial OER intermediate considered, we—in practice—start from the stoichiometric hydroxylated surface (the surface before LOM 1). Figure 7d shows that the first step (−OH to I₀) of AEM is the potential-determining step, with η = 0.4 V. However, it becomes remarkably energetically favourable to follow LOM 1, forming the superoxide-like −OO (V₀) adsorbates (I₁) with an O-to-O bond length of 1.28 Å. Therefore, LOM is the relevant mechanism for SrCoO₂₋₇. Once I₁ forms, it requires small energetically uphill and downhill reactions, respectively, to evolve back to −OH (V₀) and electrochemically fill the vacancy by OH⁻ (aq) in Step 2 and 3 of the LOM. This electrochemical surface hydroxylation during Step 3 occurs concomitantly with an electron transfer to leave the surface in a neutral state. The subsequent step of electrochemical deporation is identified as the potential-determining step, similar to the results for LaNiO₃ (ref. 52). Further, the computed overpotential of 0.22 V is fully consistent with experiments.

We note that consideration of modified surface configurations, which may occur under operating conditions, could lead to different values of ΔG. For example, full surface hydroxylation can further decrease the value of ΔG due to the oxidation of the surface Co, making the LOM more favourable, while moderate protonation of surface oxygen can increase ΔG by donating electrons to the surface. In addition, the O-to-O overbinding effects in the superoxide formation (I₁) by RPBE can increase ΔG by <0.3 eV (ref. 55), while the use of GGA + U₀.4 can lead to the weaker adsorption strength of I₀, decreasing ΔG by >0.3 eV (ref. 56). Nevertheless, the behaviour of the model surfaces expected to be qualitatively correct for these systems, and also independent of exchange correlation functional, as demonstrated for LaNiO₃.

Interestingly, significant oxygen deficiencies of the LSCO series begin to appear at x = 0.4, matching well with the predicted transition from the AEM to LOM at 0.25 < x < 0.50. These oxygen deficiencies reveal the saturated charge states of Co, which become unable to donate enough electrons to attain oxygen stoichiometry as described through Fig. 1. The bulk oxygen deficiency is consequently indicative of the LOM, since the double bonded −O (AEM) induces a higher oxidation state of the surface Co than that in the bulk. The transition is further demonstrated by the experimental observation that the current density at Uₓ/RHₓ = +1.63 V increases on a very different scale with increasing δ when x > 0.4 from that when x < 0.4. Our work thus provides a strong theoretical framework, consistent with experiments, to describe the transition of the OER mechanism as a function of bulk stability. Further discussion about the applicability of this mechanism to other metal oxide catalysts is included in Supplementary Fig. 9 and in the Supplementary Discussion.

Discussion

We have demonstrated that oxygen vacancy defects are a crucial parameter in improving the electrocatalysis of oxygen at metal oxide surfaces, whereby they may control the physical parameters of ionic diffusion rates and reflect the underlying electronic structure of the catalyst. The vacancy-mediated mechanism proposed offers insight into the design of highly active OER catalysts, and allows for the rationalization of the electrolysis of water using surface chemistry parameters, as described through the modulation of the Fermi energy through transition metal 3d and oxygen 2p partial density of states at the surface. As such, the role of oxygen vacancy defects cannot be ignored, and should be a critical component in the benchmarking of metal oxide oxygen electrocatalysts and the advancement of the mechanistic theory behind the OER.

Methods

General. All chemicals were used as received. Anhydrous ethanol and 5 wt% Nafion solution in lower alcohols were purchased from Sigma-Aldrich. Lanthanum (III) nitrate hexahydrate (99.99%), strontium (II) nitrate hexahydrate (99.9%), cobalt (II) nitrate hexahydrate (99.9%), tetrapropylammonium bromide (98%), tetrathymethyloxonium hydroxide (TMAB) pentahydrate (99%), 2-propanol, potassium hydroxide, potassium iodide (≥ 99%), sodium thiosulfate (0.1 N), potassium iodate (0.1 N) and hydrochloric acid were obtained from Fisher Scientific. Absolute ethanol (200 proof) was obtained from Aaper alcohol. The commercial IrO₃ sample was obtained from Sterm Chemicals. Oxygen (99.9999%) and argon (99.999%) gases were obtained from Praxair. VC was obtained from Cabot Corporation and the NC was prepared as reported elsewhere.

Synthesis of La₁₋ₓSrCoO₃₋₄. La₁₋ₓSrCoO₃₋₄ was synthesized following our previously reported reverse-phase hydrolysis approach. Mixed metal hydroxides were prepared by reverse-phase hydrolysis of La, Sr and Co nitrates in the presence of an equimolar amount of tetrapropylammonium bromide (TPAB) dissolved in 1 wt% TMAB. An ~10 mL solution of mixed metal nitrates of the appropriate stoichiometry was added dropwise at ~1–2 mL min⁻¹ to 200 mL of the 1 wt% TMAB solution containing TPAB. The resulting precipitated mixed metal hydroxide nanopowders were collected by centrifugation and washed with deionized water, followed by re-suspension in deionized water through probe sonication. The solution was frozen as a thin film on a rotating steel tube at cryogenic temperatures (~79 °C), and then lyophilized at ~10⁻⁴ Pa at a fixed pressure of ~50 mTorr for 20 h. The lyophilized powder was calcined in a tube furnace under dehumidified air at a flow rate of 150 ml min⁻¹ for 5 h at 950 °C. The resulting perovskites are then washed with ethanol followed by water and allowed to dry in an oven at 80 °C overnight.

Synthesis of SrCoO₂₋₅. Synthesis of SrCoO₂₋₅ followed a similar procedure to the one used above, but used a slower addition rate of metal nitrate solution to TMAB/TPAB of <0.5 ml min⁻¹. In addition, the hydrolysis reaction was allowed to

NATURE COMMUNICATIONS | DOI: 10.1038/ncomms11053

9
proceed for 5 days before collection by centrifugation. Finally, the flow rate of dehumidified air during calcination was adjusted to 20 ml min⁻¹.

**Materials characterization.** Bulk crystal structures were determined through wide-angle X-ray diffraction (Rigaku Spider, Cu Kα radiation, λ = 1.5418 Å) and analysed with JANA2006 software⁴⁹. The TEM samples were prepared by crushing the crystals in a mortar in ethanol and depositing drops of suspension onto holey carbon grid. Electron diffraction patterns, TEM images, HAADF-STEM images, ABF-STEM images and energy dispersive X-ray spectra were obtained with an aberration-corrected Titan TEM electron microscope operated at 200 kV using a convergence semi-angle of 21.6 mrad. The HAADF and ABF inner collection semi-angles were 70 mrad and 10 mrad, respectively. Isodometric titrations were performed according to the referenced procedure⁵⁰. In short, 3 ml of de-oxygenated 2 M KCl solution was added to a flask containing 15–20 mg of perovskite under Ar atmosphere. This solution was stirred and allowed to disperse for three minutes. After a further minute of 1 M HCl is added and the perovskite is allowed to dissolve. This solution is then titrated to a faint golden colour with a solution of ~40 μM solution of Na₂S₂O₄ that has been pre-standardized with 0.1 N KIO₃. Starch indicator is then added and the solution is titrated until clear, marking the end point. BET surface area measurements were performed through nitrogen sorption on a Quantachrome Instruments NOVA 2000 high-speed surface area BET analyser at a temperature of 77 K, using 7 points from the linear region of the adsorption isotherm to determine the surface area.

**Electrode preparation.** All La₉₋ₓSrₓCoO₃₋ₓ nanoparticles and the commercial IrO₂ sample were loaded onto carbon through ball milling with a Wig-L-Bug ball mill. For the rotating disk (RDE) and for the RRDE measurement and for the LDSCO nanopowders were loaded at a mass loading of ~30 wt% on NC. For the galvanostatic stability tests, LDSCO nanopowders and IrO₂ were also loaded onto VC (XC-72, Cabot Corporation) at a mass loading of ~30 wt%. The LDSCO/carbon mixtures were dispersed in ethanol containing 0.05 wt% Na-substituted Nafion at a ratio of 1:10. The solution was spun-cast onto a glassy carbon RDE (0.196 cm²/pin, Pine Instruments) and for the RRDE (Glassy Carbon Disk: 0.2472 cm²/pin, Pt ring: 0.1859 cm²/pin, Pine Instruments) at a total mass loading of 31.0 μg cm⁻²/pin disk (LDSCO loading: 15.3 μg cm⁻²/pin). The synthesis of the NC is described elsewhere⁵¹. For the oxygen intercalation cyclic voltammetry studies the LDSCO nanopowders were loaded at a mass loading of 85 wt% on VC (Cabot Corporation). The LDSCO/carbon mixtures were dispersed in ethanol containing 0.1 wt% Na-substituted Nafion at a ratio of 2 mg ml⁻¹ and sonicated for 45 min. This solution was spun cast onto the glassy carbon RDE at a total mass loading of 102.0 μg cm⁻²/pin disk (LDSCO loading 86.7 μg cm⁻²/pin). The electrodes were cleaned before spin casting by sonication in a 1:1 deionized water-ethanol solution. The electrodes were then polished using 50 nm alumina powder, sonicated in a fresh deionized water:ethanol solution and dried under a nitrogen stream as described above. The electrodes were stationary during testing and cycled twice. The current was plotted versus time for 4 h. The current was plotted versus t⁻¹/₂ and the linear section of the curve was fit to find the intercept with the t⁻¹/₂ axis. Using a bounded 3-dimensional solid-state diffusion model, this intersect is indicative of the diffusion rate of oxygen according to the relation λ = Dp/n, where, λ is a shape factor for the particles (in this case λ = 2 for rounded parallelepipeds), a is the radius of the particle (in this case 150 nm was used for all LDSCO samples), t⁻¹/₂ is determined from the intersection with the t⁻¹/₂ axis, and D is the diffusion rate of oxygen ions in the crystal measured at room temperature.

**Density function theory calculations and surface models.** DFT calculations⁵²,⁵³,⁵⁴ are performed using VASP with PAW pseudopotentials and the RPBE-GGA functional. More details are provided in the Supplementary Methods.

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Author contributions

J.T.M. and W.G.H. performed the synthesis. J.T.M. performed the X-ray diffraction, and electrochemical characterization. X.R. and A.M.K. performed the DFT modelling. A.M.A. performed the SAED, HAAFD-STEM, AFM-STEM, energy dispersive X-ray measurements and crystallographic analysis. S.D. contributed the carbon support. J.T.M., K.P.J., and E.J.S. planned the experiment and analysed the data. All authors contributed to the writing of the paper.

Additional information

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