Factors controlling surface oxygen exchange in oxides

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Reducing the working temperature of solid oxide fuel cells is critical to their increased commercialization but is inhibited by the slow oxygen exchange kinetics at the cathode, which limits the overall rate of the oxygen reduction reaction. We use ab initio methods to develop a quantitative elementary reaction model of oxygen exchange in a representative cathode material, La\textsubscript{0.5}Sr\textsubscript{0.5}CoO\textsubscript{3-δ}, and predict that under operating conditions the rate-limiting step for oxygen incorporation from O\textsubscript{2} gas on the stable, (001)-SrO surface is lateral (surface) diffusion of O-adatoms and oxygen surface vacancies. We predict that a high vacancy concentration on the metastable CoO\textsubscript{2} termination enables a vacancy-assisted O\textsubscript{2} dissociation that is $10^2$–$10^3$ times faster than the rate limiting step on the Sr-rich (La,Sr)O termination. This result implies that dramatically enhanced oxygen exchange performance could potentially be obtained by suppressing the (La,Sr)O termination and stabilizing highly active CoO\textsubscript{2} termination.

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n solid oxide fuel cell (SOFC) cathodes, which are the primary process for this oxygen exchange study, the forward process of oxygen exchange is oxygen reduction reaction (ORR) that takes gas phase $O_2$ and transforms it to solid phase $O_2^{-}$ in the cathode. The exchange is comprised of $O_2$ adsorption, dissociation, and incorporation at the surface, followed by $O_2^{-}$ diffusion in the bulk$^{1,2}$. SOFC cathode materials that perform these operations efficiently are almost all mixed electronic and ionic conducting complex oxides, and typically have the perovskite structure (Fig. 1) with stoichiometry ABO$_{3-δ}$, where (A and B are generally metal and transition metal elements, respectively). In spite of many experimental$^{3-9}$ and modeling$^{10-15}$ efforts, a quantitative molecular understanding of oxygen exchange at the surface of mixed conducting oxides remains elusive. This limited understanding means one cannot presently predict which materials or surfaces will be most active for exchange and inhibits rational design of optimal materials.

Previous ab initio studies$^{14-20}$ have investigated the nature of stable surfaces and adsorbates on SOFC cathodes, but typically without developing quantitative models for oxygen exchange and usually with a limited focus on the (001) BO$_2$ terminated surface (Fig. 1b). However, recent work strongly suggests that Sr-doped perovskites such as La$_{1-x}$Sr$_x$MnO$_3$ (LSM)$^{21}$, La$_{1-x}$Sr$_x$CoO$_{2-δ}$ (LSC)$^{22-26}$ and La$_{1-x}$Sr$_x$Co$_1$Fe$_2$O$_{6-δ}$ (LSCF)$^{27}$ all have Sr enrichment in the surface, which indicate Sr segregation and/or precipitation of the second phase. Furthermore, experiments$^{23,25,27,28}$ and ab initio studies$^{29}$ show some specific evidence for stabilized Sr-rich (La, Sr) O (or AO) terminations, demonstrating the need to understand the exchange process on the AO surface. Recent work on (La, Sr)CoO$_2$ cathodes in particular has also shown significant oxygen exchange rate degradation within hours of operation$^{24,30}$, strong Sr segregation$^{22,23,26,31,32}$, reversal of degradation after chemical etching$^{33}$ in Sr-doped cathode materials, and a major role for a small number of highly active Co sites in the oxygen exchange rate of the AO surface$^{34}$. The coupling of these chemical and performance changes cannot be understood without a detailed model for the oxygen exchange. A recent semi-quantitative work by Mastrivet et al.$^{15}$ predicts an approximate 5 orders of magnitude difference of exchange rate between Mn$_2$O$_3$ termination and (La, Sr)O termination in LSM, although without a comprehensive kinetic model. There is therefore a strong need to develop better understanding of the atomic scale mechanisms controlling the oxygen exchange.

Here we combine ab initio (Density Functional Theory) reaction energetics, defect chemistry and microkinetic modeling to calculate and compare absolute rates for 53 different mechanisms of oxygen exchange (see “Results” section) on both AO (Fig. 1a) and BO$_2$ (Fig. 1b) surfaces of La$_{0.5}$Sr$_{0.5}$CoO$_{3-δ}$ (LSC-50), a representative transition metal perovskite cathode for SOFCs. We note that this is a simplified model that leaves out many possible complexities, including other active surface orientations, possible roles for steps/corners and other undercoordinated surface sites, and the impact of possible additional phases at the surface (e.g., SrO$_2$ and Ruddlesden–Popper phases$^{35}$). In particular, we cannot be sure that the assumption for SrO$_2$ termination will be satisfied by the materials used in the experiments$^{35,7-9}$ to which we compare (see “Results” section). However, there are many experiments$^{23,25,27,28}$ and ab initio studies$^{29}$ that strongly support our assumption, so we think it is a reasonable one. While the present model provides valuable insights and good agreement with available experiments, we do not mean to suggest that this model provides the definitive mechanistic understanding for all possible conditions for LSC oxygen exchange.

**Results**

**Thermodynamic and kinetic model.** To quantify the activity of a surface towards oxygen exchange we will follow common practice and use the surface exchange coefficient, $K_{O_2}$, which is defined as the proportionality between the rate of oxygen incorporation, $r$, and deviation of surface oxygen concentration $\left [ O_{O,S}^{eq} \right ]$, from equilibrium $\left [ \left [ O_{O,S}^{eq} \right ] \right ]$, through the relationship, $r = -K_{O_2} \left [ \left [ O_{O,S}^{eq} \right ] - \left [ O_{O,S}^{eq} \right ] \right ]$. We will also make use of a more fundamental parameter, the equilibrium surface exchange rate, $R_0$, which gives the amount of oxygen per unit area and time that is exchanged between the material and gas at equilibrium and is easily related to $K_{O_2}$ (see the Rate expressions section in the “Methods” section and ref. 11).

In this work, kinetic rate expressions for individual ORR mechanisms are formulated assuming a particular step of the mechanism being rate-limiting, implying that the overall driving force (which equals the total free energy change for the reaction of $O_2$ getting incorporated into bulk of the cathode $O_2 + 2V_{O} + 4e^- \rightarrow 2O_{O_S}$) equals the free-energy change in the specific rate-limiting elementary step$^{11}$. To describe the thermodynamics of various elementary steps of ORR we use a neutral building-unit representation of reactants and products, which facilitates the formulation of chemical potentials and description of mechanisms. These are defined in Supplementary Table 1 (SrO surface) and Supplementary Table 4 (CoO$_2$ surface). For example, neutral building units $'s$ , $'O_S$' , 'CoO' denote surface oxygen vacancy, $O_2$ inserted into surface vacancy, and O-adatom on surface Co, respectively. We use Kröger–Vink notations for defects. For more details of the thermo-kinetic framework used in this work please refer to Adler et al.$^{11}$.

As a specific example, we describe one of the mechanisms on CoO$_2$ termination and then formulate the rate expressions (refer to “Methods” section for the rate expression). The same framework has been used for all the other mechanisms. The following describes Mechanism B3 of Supplementary Table 6, which involves adsorption at an oxygen vacancy.

**Step 1.** $O_2$ adsorption on a vacancy and dissociation by insertion into the vacancy, $(2s + O_2 \rightarrow 2O_{ads} + 2(s))$ or,

$$2V_{O_S}^{q0} + O_2^{q0} + q_{ads}e^- + q_{diss}e^- \rightarrow \left ( O_{O_S}^{q0} - O_{O_S}^{q0} \right )$$

(1a)

Here, $q_{ads}$ denotes charge transferred to oxygen from the LSC surface during adsorption, $q_{diss}$ denotes charge transferred to oxygen from the LSC surface during insertion into nearby vacancy, regular brackets on product side indicate $O$–O configuration inserted into a vacancy on the CoO$_2$ surface (denoted $sO_2$ in neutral building unit notation).

**Step 2.** Diffusion of $^*$O towards surface vacancy $(sO_2 + s(far) \rightarrow CoO + s(near))$ or,

$$O_{O_S}^{q0} + V_{O_S}^{q0} + q_{diffusion}e^- \rightarrow O_{Co}^{q0} + V_{O_S}^{q0}$$

(1b)

**Step 3.** Incorporation into the surface, $(CoO + s(near) \rightarrow null)$ or,

$$O_{Co}^{q0} + V_{O_S}^{q0} + q_{surface-incorp}e^- \rightarrow O_{O_S}^{q0}$$

(1c)

**Step 4.** Incorporation into the bulk LSC-50: $(v \rightarrow s) \times 2$ or,

$$O_{O_S}^{q0} + V_{O_S}^{q0} + q_{bulk-incorp}e^- \rightarrow O_{O_S}^{q0} + V_{O_S}^{q0}$$

(1d)

Where $q_{diffusion}$, $q_{surface-incorp}$, $q_{bulk-incorp}$ are charge transfer
involved in diffusion, surface incorporation and bulk incorporation of oxygen respectively. The “Methods” section details the calculations of exchange rates based on DFT energetics. DFT-predicted molecular configurations of various ORR intermediates (products of oxygen adsorption dissociation, incorporation) are depicted in Fig. 2a (SrO termination) and in Fig. 2b (CoO2 termination). Based on the DFT-predicted Gibb’s free energy relative to O2 gas, the concentrations of these species is also indicated at relevant SOFC conditions (oxygen partial pressure pO2 = 0.2 atm, temperature T = 650 °C) in these figures as well as Supplementary Table 8. Many distinct (surface site-specific) reaction mechanisms may proceed through these surface intermediates, each potentially contributing to the overall ORR reaction of O2(gas) incorporation into the bulk oxide. For convenience, these mechanisms are classified here by their initial adsorption step and the consequent dissociation step(s).

In this way, 41 distinct mechanisms emerge on the SrO termination (see Supplementary Table 2) and 12 mechanisms on CoO2 termination (see Supplementary Table 5). The ORR is unlikely to proceed through the mechanisms for which the surface intermediate concentrations are predicted to be too low (such as CoO2 + 2s (far) intermediate, see Fig. 2b), whereas more stable surface intermediates (such as s, CoO + s(far) on CoO2 surface, O2- top on SrO surface) would be expected to appear in the most prominent (fastest) mechanisms, since kinetic rates generally scale with concentration of (reactant) surface intermediates. Figure 3 show the DFT-predicted energy landscape of key mechanisms on SrO and CoO2 terminations, respectively. The y-axis of Fig. 3 is DFT corrected enthalpies (relative to O2 molecular and isolated vacancies on the oxide surface), where the corrections are described in the DFT Corrections section of the “Methods” section. The initial step in the energy landscape of all mechanisms is O2(gas) + 2s, whereas the final step is two oxygen ions incorporated in the bulk.

Surface oxygen exchange activity. The predicted exchange rates R0 (given in this work in number of O2 - Co−1s−1), where Co are top or second layer depending on the surface termination) of the fastest oxygen exchange mechanisms are shown in Fig. 4 (SrO surface) and Fig. 5 (CoO2 surface) at relevant SOFC conditions (pO2 = 0.2 atm, T = 650 °C). The calculation details are in the Methods section. Mechanisms A9, A20, A23, A26, and B3 are predicted to be the fastest, and therefore dominant, on the SrO and CoO2 surfaces, respectively. As shown in Fig. 4, mechanisms A9, A20, A23, A26 on the SrO termination have one common rate-limiting step, which involves Oads and vacancy lateral diffusion to find each other, with a rate governed by the expression R0(diffusion) = (8 × Dv × 2Γ × Γoads)/pO2. This process involves dilute species, so can be modeled accurately in terms of each species undergoing long-range diffusion and undergoing collisions at a rate governed by mean-field theory (see Supplementary Note 2). As illustrated in Fig. 5, mechanism B3 on CoO2 termination is limited by the initial O2 adsorption and incorporation step (see “Methods” section below for details on calculation of this rate). The thermodynamic stability of the SrO surface suggests that Mechanism A9, A20, A23, A26 should give the best match for experiments and the result is very close to experimental surface exchange data at pO2 = 0.2 atm, T = 650 °C25.9−9 (blue line of Fig. 4) and over a range of T-pO2 (discussed below and in Fig. 6). It should be noted that the predicted log(R0) vs. log(pO2) is very linear, similar to the experimental trends at 650 °C, but missing an apparent curvature observed at 800 °C in Egger’s data and identified by Adler, et al.11 as illustrating a quadratic dependence of R0 on bulk vacancy concentration with changing pO2. The model trends with pO2 are governed by bulk oxygen vacancy xΓ and surface oxygen concentration ΓO2 which decrease and increase almost linearly with increasing pO2 in our model, respectively. The xΓ behavior is taken directly from experimental measurement46, and therefore we assume it is correct. The ΓO2 behavior is expected from simple thermodynamic arguments if O adatoms are thermodynamically ideal, and they are in our model. However, it is possible that the model has missed some electronic transfer to the O adatom, which would weaken binding as the system is oxidized at higher pO2 and lead to curvature in the log(R0) vs. log(pO2) plot. Such a mechanism might be expected to be suppressed at high Sr content as the oxidized system would have reduced electron transfer to the adatom, which is consistent with what is seen in Egger’s data7.

The different behavior of these surfaces can be understood in terms of their oxidation state. We focus on pO2 = 0.2 atm, T = 650 °C but the qualitative arguments given here are true for a wide range of relevant conditions. The SrO surface is more reduced (less oxidized) than the CoO2 surface17, as the former has balanced nominal charges of [Sr2+O2−] while the latter is oxidized, with nominal charges [Co3+(O2−)]. The different oxidation level leads to more stable oxidizing defects (e.g., O adatoms) and less stable reducing defects (e.g., oxygen vacancies) on the SrO vs. CoO2 surface. This effect can also be understood as due to compensating polarity of the surface.20 The differences in the surfaces lead to a dramatic difference in their surface oxygen vacancy concentrations, Γs(SrOsurf) = 6 × 10−5 and Γs(CoO2surf) = 0.28, which difference leads to the vacancy assisted O2 dissociation mechanism being much more active on the latter. The 102−103 times faster oxygen exchange rate of CoO2 surface vs. SrO surface is due to the high vacancy concentration on CoO2, which assists O2 adsorption on CoO2 through a strong stabilization of O2 adsorbate with nearby vacancies. Also, vacancies assist O2 dissociation to have a much lower barrier on the CoO2 surface than SrO surface.

The importance of surface segregated Sr can now also be understood in terms of surface oxidation state and the active mechanisms. The fastest mechanism (A9, A20, A23, A26) is rate limited by Oads and O2 diffusion, and the rate of this step scales
with the vacancy content on the SrO surface (Fig. 2a). As the oxygen vacancy content is greatly increased by Sr ($I_\Gamma^s$($\text{LaO}_{\text{surf}}$) = $10^{-18}$ is $10^{11}$ times smaller than $I_\Gamma^s$($\text{SrO}_{\text{surf}}$)), it is clear that Sr enrichment within the AO surface enhances activity by stabilizing surface vacancies for oxygen diffusion and incorporation. This result suggests that for the equilibrated LSC material the Sr both in the bulk and segregated to the perovskite surface is critical for good performance. However, precipitation of Sr compounds (such as oxides, hydroxides and/or carbonates) on the surface, perhaps driven in part by Sr segregation, could potentially degrade performance.$^{32}$ Furthermore, overall, AO surface formation is expected to reduce activity vs. the CoO$_2$ surface.

These results suggest that LSC-50, and potentially many other perovskite systems, could be greatly enhanced if a metastable BaO$_2$ termination could be maintained. From a number of recent experiments, the formation of Sr-enhanced phase on the surface is known to be concurrent with ORR performance degradation for various perovskite SOFC cathodes.$^{22,25,30,33,37-39}$ Crystalline LSC-64 thin-films are known to degrade by one to two orders of magnitude$^{24,30,33}$ in their ORR performance within tens of hours$^{24}$ of preparation or annealing, and to regain performance with etching.$^{33}$ Studies of carefully controlled surfaces and Sr and Co deposition have also suggested that Co sites are much more active that Sr.$^{34}$ Based on our results above we propose that these changes can be explained as due to the metastable and highly active CoO$_2$ surface being present in as-received or etched materials and being rapidly replaced by a Sr rich AO surface as the system equilibrates at high temperature. The appearance of degradation at temperatures around 500–600 °C$^{22,30}$ and its time scale of tens of hours$^{24}$ are both consistent with the temperature and time scales associated with the cation mobility required for moving La and Sr to the surface$^{40}$. Many authors have suggested the Sr itself is driving the degradation$^{22,24,30}$, although our model suggests that it is the formation of the AO surface and not Sr itself that leads to the degradation, at least before the formation of Sr-based precipitates on the surface. We note that our proposed mechanism for the degradation is quite speculative and that other mechanisms, e.g., the formation of secondary Sr rich phases and site poisoning, might play a significant or even dominant role. Further work on LSC and related systems is needed to validate these speculations.

Table 1 lists the DFT-predicted reaction kinetic barriers, overall $T$-$po_2$ dependences, and reaction rates ($R_0$) at SOFC conditions. Figure 6a, b show the predicted $T$-$po_2$ dependence of $R_0$ of the key mechanisms of LSC-50. Figure 6c, d show the corresponding plots for $K_{tr}$. The $po_2$ dependence of $R_0$ or $K_{tr}$ is a function of the kinetic symmetry parameter ($\beta$), which is not readily determined from the DFT calculations, and hence value $\beta$ is fit to the experimental $po_2$ dependence. The experimental $R_0$ is derived from the reported $K_{tr}$ data$^{5,7}$, Eq. (4) in the “Methods” section,
and known defect chemistry. Only the fastest mechanisms on both surfaces (BO₂, orange, and AO, blue dashed line) are shown for clarity, along with the initial O₂ adsorption rate (black). The predicted slope of log₁₀(R₀) vs. log₁₀(pO₂) for SrO termination is 0.4–0.6 in Fig. 6, matching well with the range 0.4–0.8 of slope from these experiments in Table 1. The Arrhenius activation energy (describing T-dependence) of experimental Kₐ for LSC-50 is 1.99 eV (and the closely related La₀.9Sr₀.1CoO₃₋δ) ranges from 0.99–1.57 eV for 0.1 atm pO₂ and 0.55–1.67 eV for 10⁻³ atm pO₂. The narrow range of our predicted activation energies for the SrO surface of 1.51 eV (for 0.2 atm pO₂) and 1.31 eV (10⁻³ atm pO₂), respectively (AO surface) agree well with the upper range of these values, although more experimental data is clearly needed for quantitative comparison (see Table 1). Within the uncertainties in the experiments and ab initio energetics, our results on model SrO termination agree very well with the experimental T-pO₂ dependence, providing validation for the model. The agreement between the experiment and the model for Sr-rich AO termination is also fully consistent with the fact that this surface is the thermodynamically stable surface of LSC₂⁻²⁴,2₆,3₁. Figure 6 also shows that the oxygen exchange rates (R₀) and oxygen exchange rate coefficient (Kₐ) at the CO₂ surface can be two to three orders of magnitude larger than SrO surface, for wide range of T-pO₂.

Figure 6 shows the O₂ adsorption step (black). As the first elementary step for all ORR mechanisms, this step sets an ore limiting step.
upper fundamental limitation for ORR on any cathode surface. This limit is set by the kinetic theory of gas absorption (expressed as $R_0$ in Fig. 6a, b and $K_{tr}$ in Fig. 6c, d). Details of these estimates are in the "Methods" section and Fig. 7. At relevant SOFC conditions (0.2 atm $p_{O_2}$, 650 °C), the upper-limit exchange rate set by this step corresponds to $R_0 \sim 3.63 \times 10^5 \text{ O}_2\text{-Co}^{-1}\text{s}^{-1}$, $K_{tr} \sim 1.69 \times 10^{-3} \text{ m}\cdot\text{s}^{-1}$, and an exchange current density of $\sim 170 \text{ A}\cdot\text{cm}^{-2}$ (taking into account the experimental lattice parameters and 4 e$^-$ carried per O$_2$ molecule). Thus at these conditions of T-$p_{O_2}$, we predict that these values are an absolute upper-limit achievable for any active SOFC cathode surface. The $K_{tr}$ for the highly active, but metastable, surface provided by the CoO$_2$ termination of LSC-50 (Fig. 6c, d, orange line) may get close to this upper-limit, which suggests significant opportunity for improving ORR activity for complex oxides. We note that the kinetic model developed here can also be used to predict overpotential as a function of current density. This is done and the results shown
to compare very favorably to experiments in “Methods” section, further supporting the validity of the model.

Discussion

In summary, understanding, controlling, and enhancing oxygen exchange on oxide surfaces is critical to the success of many technologies, especially for lowering the operating temperature of SOFCs. We have developed an ab initio based microkinetic model that provides quantitative predictive ability for oxygen exchange rates vs. temperature and pO2 on La0.5Sr0.5CoO3−δ (LSC-50). The model identifies surface diffusion and adsorption of O2 as the rate-limiting steps on Sr-rich (La,Sr)O-terminated and CoO2-terminated surfaces, respectively, and predicts exchange rates on the stable SrO surface in excellent agreement with experiments. The O2 reduction on the metastable CoO2 surface is predicted to be orders of magnitude faster than on the thermodynamically stable SrO surface, suggesting that the loss of CoO2 termination is most likely the reason for the widely-observed degradation of oxygen exchange rates over tens of hours of annealing. Also, while the (La,Sr)O surface is generally predicted to be less active than the CoO2 surface, the segregation of Sr to form a SrO termination is shown to be critical to good performance on this termination. Finally, this work estimates a fundamental upper-limit of oxygen exchange rate set by the O2 adsorption step. The metastable, pure CoO2 surface of LSC-50 is predicted close to this limit under relevant SOFC conditions, enabling a 2–3 orders of magnitude faster oxygen exchange than Sr rich AO surface. This result demonstrates an inherent potential for enhanced performance in this and related materials if a high concentration of the transition metals can be permanently stabilized on the surface.

Methods

Modeling approach. Calculations were performed with the Vienna Ab initio Simulation Package42-45 (VASP) using Density Functional Theory (DFT) and the Projector-Augmented plane-Wave (PAW)44 method. Exchange-correlation was treated in the Perdew-Wang-91 (PW-9145) Generalized Gradient Approximation (GGA) with electronic configurations of La (5s2 5p6 6s2), Sr (4s2 4p6 5s2) and Co (3d8 4s2). In order to take into account the effect of the strongly correlated electronic systems we applied the U+J formalism46,47 to search the global minimal energy. Bulk calculations were simulated with 80-atom unit cell (2LaO × 2SrO × 2CoO, a$_{pc}$ is the pseudo-cubic lattice constant of LSC). In calculating the bulk oxygen vacancy formation energy matches the experimental data from Mizusaki et al.41. The U+J method with $U$ and $J$ entering as an effective parameter, $U_{eff} = 5.6$ eV, which was fit so our bulk oxygen vacancy formation energy matches the experimental data from Mizusaki et al.41. We used the U+J formalism to search the global minimal energy. Bulk calculations were simulated with 80-atom unit cell (2LaO × 2SrO × 2CoO, a$_{pc}$ is the pseudo-cubic lattice constant of LSC). In calculating the bulk oxygen vacancy formation energy, the oxygen vacancy was placed such that two of its nearest neighbor A-sites are filled with doped Sr and two with La. The surface calculations were done with an eight-layer slab (2Lao × 2Sro × 4aco, with 4 layers of AO, 4 layers of BO2). Slabs were asymmetric (had both AO and BO2 terminations) and dipole corrections were used. In the calculations of the energies of adsorbed oxygen (*O, *O2) on either (001) or (010) surfaces, we embedded a vacancy on the exposed CoO2 termination to represent the significant vacancy concentration expected on this surface. In case of adsorbates on the CoO2 termination itself, the adsorbate and surface vacancy were separated by more than 5 Å in order to reduce the effects of neighbor interactions, except in
Surface structures were calculated by truncating the bulk with insertion of 10 Å vacuum above the surface under periodic conditions.

Surface exchange rates are determined by enumerating possible pathways (mechanisms) and finding the rates of each elementary step, setting the total rate to that slowest elementary step in each mechanism. For the surfaces of LSC-50, we enumerate and organize different mechanistic pathways of ORR in terms of their adsorption and dissociation sites. Supplementary Tables 2 and 3 show the list mechanisms organized according to the adsorption (rows) and dissociation sites. Supplementary Tables 2 and 3 show the list mechanisms organized according to the adsorption (rows) and dissociation sites.

| Table 1 Temperature-dependences and kinetic symmetry parameter |
|---------------------------------------------------------------|
| Kinetic symmetry parameter, β | Rate-limiting step | Slope of log(\(R_0\)) vs. log(\(p_{O_2}\)) | Kinetic barrier for \(K_T\) (eV) | Kinetic barrier for \(k_p\) (TPP) (eV) | log(\(R_0\)) (at \(p_{O_2}=0.2\) atm) |
|--------------------------------|-------------------|----------------------------------|------------------|------------------|-------------------|
| Experiment: van der Haar et al. (LSC(50Sr)) | A2O3 | 0.59 (0.2 atm), 1.67 | 1.42 | 0.99 (0.2 atm), 1.49 |
| Experiment: Egger et al. (LSC(50Sr)) | A2O3 | 0.59 (0.2 atm), 1.67 | 1.42 | 0.99 (0.2 atm), 1.49 |
| Experiment: Egger et al. (LSC(40Sr)) | A2O3 | 0.59 (0.2 atm), 1.67 | 1.42 | 0.99 (0.2 atm), 1.49 |
| Experiment: Lu et al. (LSC(40Sr)) | A2O3 | 0.59 (0.2 atm), 1.67 | 1.42 | 0.99 (0.2 atm), 1.49 |
| CoO2 termination: Mech. B2 | 0.8 | CoO20s = n/n + (dissociation) | 0.5 | 0.9 (0.2 atm), 0.7 (0E) |
| CoO2 termination: Mech. B3 | 0.5 | CoO20s = n/n + (dissociation) | 1.0 | 0.55 (0.2 atm), 0.44 |
| CoO2 termination: Mech. B4 | 0.8 | CoO20s = n/n + (dissociation) | 1.74 (0.2 atm), 1.79 | 0.53 (0.2 atm), 0.52 |
| SrO termination: Mech. A9 | A2O3 | A2O30s = n/n + (dissociation) | 0.4 (650 °C, 0.6 (800 °C) | 0.86 (0.2 atm), 0.66 |

List of \(p_{O_2}\) T-dependences and choice of the kinetic symmetry parameter (β) used in the modeling of ORR mechanisms B2, B3, B4 of CoO2 termination and the mechanism A9 and A20 of the SrO termination. These mechanisms emerge as amongst the fastest in terms of oxygen exchange rates (\(k_{02}-1\)). The unit \(O_2\) is 1 number of adsorbed oxygen molecules at one surface Co area per second. Temperature and \(p_{O_2}\)-dependence of experimental data are calculated using the reported \(K_0\), and converting to \(R_0\) data. All values for various ORR mechanisms are computed for LSC (50% Sr). Experimental data for LSC(40% Sr) is given as a reference. Temperature and \(p_{O_2}\)-dependence of experimental data are calculated using the reported \(K_0\), and converting to \(R_0\) data. All values for various ORR mechanisms are computed for LSC (50% Sr). Experimental data for LSC(40% Sr) is given as a reference.

\[k = \frac{1}{\delta} \left[ \frac{Y_i}{f_i} - \frac{O_2}{O_2} \right] \]  

or \[ \Lambda = \frac{A}{A_0} = \frac{Y_i}{f_i} \frac{O_2}{O_2} \]  

where \(k\) is a temperature-independent pre-exponential factor, \(\Delta G_{i}^{\text{red}}\) is the uncorrected free-energy barrier for the reaction step (evaluated at \(\Delta G = 0\)), \(f_i\) and \(f_i\) are the concentration of reagents \(X\) and \(Y\), and \(\delta\) is a reaction symmetry parameter analogus to that used in electrochemical kinetics, \(\Lambda\) is the total free-energy driving force for the reaction step, \(\lambda\) is the stoichiometric coefficient of the elementary step, and \(\Delta G_{i}^{\text{red}}\) is the energy shift component of the thermodynamic driving force for the \(i\)-th elementary step. Equation (15) gives the net forward rate (\(n\) of a single elementary step) of any reaction mechanism. The driving force for step \(i\), \(\Lambda_i\), is the difference in the free energy of reactants minus products. The driving force for overall oxygen incorporation is the deviation in the chemical potential of O2 due to a deviation in its external pressure from equilibrium. Under the rate-limiting step approximation, the driving force (\(\Lambda\)) for the total reaction is assumed to be contributed in full by the rate-limiting reaction step, i.e., \(|\Lambda_i|\) or \(|\Lambda_j|\).

\[ \Lambda = \Lambda_i \Lambda_j = \frac{k_0 T \lambda_i \lambda_j}{\delta} \frac{1}{p_{O_2}^m} \]  

where \(\delta\) is the stoichiometric ratio between reaction \(i\) and overaall reaction under quasi-equilibrium conditions, \(p_{O_2}^m\) is the partial pressure of oxygen in the gas relative to atmospheric pressure, and \(\delta_{O_2}\) is the oxygen fugacity in the oxide. At no net driving force (\(\Lambda = 0\)), the forward and backward rates will be identical, represented by an equilibrium exchange rate, \(R_e\).
Determining vibrational free energy of solid phase oxygen. In this work we use thermodynamic parameters for bulk oxygen from the work of Mizusaki et al.41. In particular the chemical potential of LSC-50 bulk oxygen in reference to O₂,gas is set using their reported parameters ΔG₀, ΔH₀, and a (Figure 13a of Mizusaki et al.41). However, we need to make use of bulk defect energies from DFT and vibrational models relative to the oxygen gas (obtained from an empirical model from NIST40). To assure that our DFT-based model matches the Mizusaki model here we fit an enthalpy correction and Einstein temperature for our DFT-based model. The fit matches the free energy change of bulk vacancy formation at relevant SPCF conditions between the our calculated and Mizusaki models. This approach is illustrated as follows:

**DFT corrections.** Corrections were applied to DFT energies of surface adsorbates and kinetic barriers, as explained below:

Identifying electron doping contributions: When dealing with formation and adsorption energies, it is useful to separate out the energetics of the process that is associated with electron donation/removal from the Fermi level, as this quantity depends on the overall defect chemistry and therefore T and pO₂. In this work, the DFT simulations of bulk and surfaces of LSC-50 were performed with 2 × 2 × 4 supercells, or with 16 formula units (FUs) of LSC-50, which leads to significant electron donation/removal contributions in the basic DFT energies. For example, when simulating vacancy formation energy, 1 oxygen vacancy is simulated in such a 2 × 2 × 4 supercell, which dopes 2 electrons into the supercell. Following the rigid band formalism for LSC-50 from Lankhorst et al.40, the two electrons will be doped at the Fermi level, and the Fermi level will be incremented by 1.17 eV/Å⁻¹, where n is the density of states at the Fermi level. This density of states has the value g(E_F) = 4/α = 1.71 eV⁻¹-F⁻¹, where α = 2.34 eV is the vacancy interaction parameter from Mizusaki et al.41. Since we calculate oxygen vacancy formation energy as a difference between a two supercell with one vacancy and a perfect (no vacancy) one, an electron donation correction energy (explained above), an energy of ΔEcorr = \(\int_{E_{\text{F}}}^{\infty} v_{\text{gas}}(E) \frac{\partial n}{\partial E} \frac{dn}{E} \) needs to be removed (subtracted) from the vacancy formation energy to remove this energy contribution. Similarly when calculating an adsorption energy of species *O₁₂*, an energy of ΔEcorr = \(\int_{E_{\text{F}}}^{\infty} v_{\text{ads}}(E) \frac{\partial n}{\partial E} \frac{dn}{E} \) needs to be added to the adsorption energy. These corrections are identified by a symbol ΔEcorr in Eqs. (6) and (8) below.

Correction to adsorbate energy that contains O–O bond: As the GGA calculations overestimate the binding energy of oxygen molecule, a standard O₂–overbonding correction (0.33 eV/O2 from the work of Lee et al.) is applied for the DFT-energy of O₂ and surface adsorbates that retain an O–O bond (species of the type *O₂*, *O₃*, *O₅*, *O₇*, *O₉*, where 'n' denotes an adsorbate). Correction to kinetic barrier: The energy component of the driving force shifts the reaction barrier by \(1 - \beta \Delta E\), giving an effective reaction barrier ΔGeff = ΔG₀ – \(1 - \beta \Delta E\), where \(\beta\) is empirical symmetry parameter (usually ranges from 0.5 to 1). For a reaction step involving the breaking of oxygen dimmer bond (O-O dissociation step), applying the above DFT oxygen overbonding correction of \(-0.33\) eV on the initial state of this reaction would result in increasing the driving force for forward reaction, hence decreasing the effective reaction barrier. For example, the corrected effective barrier for oxygen dissociation at bridgacarb (=Mechanism B2) is ΔGeff = ΔG₁ – \(1 - \beta \Delta E\) for \(\beta = 0.33\). Besides these, errors remain in any DFT calculated reaction energies and reaction barriers. These errors are discussed in detail in Supplementary Note 2, where we estimate an error bar of ±1.5 order of magnitude.
terms \( E_{\text{DFT}}^{\text{don}} \) (see section on DFT corrections above) in both \( \Delta G_1 \) and \( \Delta G_2 \) will be equal. Hence, comparing the expressions (6) and (8), difference between \( \Delta G_1 \) and \( \Delta G_2 \) depends on only the difference in the DFT terms:

\[
\Delta G_2 - \Delta G_1 = \left( \frac{1}{2} E_{\text{DFT}}^{\text{don}} - \frac{1}{2} E_{\text{DFT}}^{\text{don}} \right) - \left( \frac{1}{2} E_{\text{DFT}}^{\text{don}} - \frac{1}{2} E_{\text{DFT}}^{\text{don}} \right) = \Delta E_{\text{DFT}}^{\text{don}} - \Delta E_{\text{DFT}}^{\text{don}}
\]

(9)

The site-fraction of surface oxygen vacancies \( (\Gamma_s) \) can be written in terms of \( \Delta G_2 \) as

\[
\Delta G_2 + 2E_i(\Gamma_s) = -k_B T \ln \left( \frac{\Gamma_s}{1 - \Gamma_s} \right)^{1/2}
\]

(10)

Subtracting Eq. (7) from Eq. (10) and rearranging, with the use of Eq. (9) gives:

\[
\frac{E_i}{\Gamma_s} = \frac{n_{\text{bulk}}}{1 - n_{\text{vac}}} \exp \left[ \frac{\left( \Delta G_2 - \Delta G_1 \right)}{k_B T} \right]
\]

(11)

From DFT calculations, we get that vacancy formation on CoO\(_2\) surface of LSC-50 is 0.21 to 0.8 eV/vacancy more favorable than the bulk (the range is due to the wide range of vacancy concentrations on the CoO\(_2\) surface and the strong concentration dependence of the vacancy energetics), while unfavorable by 0.5 eV/vacancy for SrO-terminated LSC-50 (relative to bulk). Based on these values, taking Mizusuki et al.\(^{41}\) experiment data for LSC-50 bulk vacancy concentrations, at typical SOFC conditions (650 °C, 0.2 atm) CoO\(_2\) surface would have 0.28 (per O-site) vacancies, while SrO-termination of LSC-50 would have 5.99 × 10\(^{-3}\) vacancies (per Co-site). Since the high oxygen vacancy concentration will have strong chemisorption interaction, we write \( E_{\text{chem}}(V_{O}) \) as a linear function of oxygen vacancy concentration for BO\(_2\) surface, with a DFT calculated linear dependence on oxygen vacancy concentration of 5.48 eV (per unit concentration) (see Supplementary Table 8). This interaction parameter is estimated by fitting to DFT calculations at surface vacancy concentrations from 0.125 to 0.25 (per O-site), which are close to the final predicted value of 0.28. These calculations therefore should provide a good guide for BO\(_2\) surface oxygen vacancy interactions. Concentrations of surface species such as \( *\text{O}_2 \) and \( *\text{O} \) can be similarly calculated, Supplementary Table 9 lists the assumptions about degrees of freedom used for calculating concentrations of each surface species.

Consider another example for the reaction of bulk vacancy and surface \( ^*\text{O} \):

\[
O^X \rightarrow \text{V}_{\text{O}} + 2e^- + ^*\text{O}
\]

(12)

We use the vibration model in Supplementary Table 9 to calculate the reaction energy. The charge changing for the reaction can be calculated Fig. 2 and Supplementary Table 4.

\[
\Delta G_3 = \left\{ \frac{1}{2} E_{\text{DFT}}^{\text{don}} - \frac{1}{2} E_{\text{DFT}}^{\text{don}} - \frac{1}{2} E_{\text{DFT}}^{\text{don}} - \frac{1}{2} E_{\text{DFT}}^{\text{don}} \right\} + \sum_{i=1}^{N_{\text{chem}}} \theta_i \ln \left( 2 \sinh \left( \frac{\theta_i}{2T} \right) \right)
\]

(13)

\[
\Delta G_3 = \left\{ \frac{1}{2} E_{\text{DFT}}^{\text{don}} - \frac{1}{2} E_{\text{DFT}}^{\text{don}} - \frac{1}{2} E_{\text{DFT}}^{\text{don}} - \frac{1}{2} E_{\text{DFT}}^{\text{don}} \right\} + \sum_{i=1}^{N_{\text{chem}}} \theta_i \ln \left( 2 \sinh \left( \frac{\theta_i}{2T} \right) \right)
\]

(14)

Oxygen adsorption rates from kinetic theory of gases. In the following section, we describe calculations for pre-exponential factors \( k_0 \) of chemisorption of oxygen molecules on the surfaces of a cathode, using transition state theory. Oxygen chemisorption involves a significant change in the degrees of freedom from the initial (gaseous) state to the transition state, and assumptions about the nature of transition state have been made in order to quantify the pre-exponential factors. Below we state the assumptions we make about the nature of chemisorbed transition state, and use them to calculate the pre-exponential factors for immobile (C, I) and mobile (C, M) type chemisorption. These give different pre-exponential factors, \( k_{\text{chem}} \) (immobile) and \( k_{\text{chem}} \) (mobile) as derived below. The surface-site-specific choices of mobile (C, M) or immobile (C, I) transition state for \( O_2 \) adsorption are also listed in column headers of Supplementary Table 2 (mechanisms of SrO termination) and Supplementary Table 5 (mechanisms of CoO\(_2\) termination).

The general framework for treating chemisorption of gas molecules is taken from the books of Chorkendorff et al.\(^{39}\) (chapter 3) and Newman et al.\(^{56}\). Consider a cathode surface with \( M \) sites, total area \( A \) (thus having \( N_{\text{M}} = M \times A \) sites per unit area) in presence of an ideal \( O_2 \) gas at a constant \( T, P_{\text{O}_2} \). Oxygen molecules will adsorb on different surface sites, for example, the surface Co of a CoO\(_2\)-terminated LSC cathode. For a particular type of adsorption site, out of total \( M \) such sites, let us assume \( M' \) sites are free for chemisorption (or having available site fraction, \( \Gamma_r = M'/M \)). According to transition state theory, the forward rate of chemisorption can be expressed assuming a chemical equilibrium between the initial state (\( O_2 \) in gas) and the transition state (denoted by a superscript #) for chemisorption. The forward rate \( (r_f) \) can be expressed as a product of an attempt frequency at the
barrier and concentration of molecules in transition state:
\[ r_I = \frac{iN}{M} \]  
(15)

where, \( i \) is the attempt frequency along the reaction coordinate, \( N \) is the number of \( \text{O}_2 \) in the transition state, \( M \) is the number of available surface sites for physisorption.

It is useful to express \( N \) in terms of the partition functions of the initial \( \{ \rho_{\text{O}_2} \} \) and transition state \( \{ q^s \} \), as it can enable calculation while rigorously including all the relevant physics of the adsorption of \( \text{O}_2 \) molecules. For a given system of \( N \) indistinguishable gas molecules (such as pure \( \text{O}_2 \)) the total partition function of the system is given by \( Q = q^N \) where \( q \) is the total partition function of individual molecule in transition state, expressed as the product of partition functions of constituent degrees of freedom (typically, \( q = \Phi_{\text{trans}} \times \Phi_{\text{rot}} \times \Phi_{\text{elec}} \) where \( \Phi_{\text{trans}} \), \( \Phi_{\text{rot}} \), and \( \Phi_{\text{elec}} \) denote translational, rotational, vibrational and electronic partition functions respectively). The chemical potential of this gas can be expressed in terms of the total individual partition function \( q \).

\[ \mu_{\text{O}_2} = -k_b T \ln \left( \frac{\rho_{\text{O}_2}}{N} \right) \]
\[ = -k_b T \ln \left( \frac{(\text{num}(N))}{\text{den}(N)} \right) \]  
(16)

where, we have used Stirling’s approximation \((\ln(N)) = N - \ln(N) - N\).

The partition function for oxygen molecules in chemisorption transition state can be similarly calculated. If \( N^\prime \) is the number of \( \text{O}_2 \)-chemisorption species transition state, the total partition function (for \( N^\prime \) molecules) and respective chemical potential \( \mu^\prime \) is,

\[ Q^\prime = \frac{N^\prime M^\prime}{N^\prime M} \left( \frac{q^s}{q} \right)^{N^\prime} \Rightarrow \mu^\prime = \frac{\mu_{\text{O}_2}}{N^\prime M^\prime} \]
\[ = \frac{\mu_{\text{O}_2}}{N^\prime M^\prime} \left( M - N^\prime \frac{q^s}{q} \right) \]
\[ = M \left( \frac{\mu_{\text{O}_2}}{N^\prime M^\prime} \right) \]
\[ = MT \frac{q^s}{q} \]  
(18)

Where, \( q^s \) is the coverage of \( \text{O}_2 \) species in transition state, which are likely to be small, compared to the available adsorption sites \((\Gamma = M/M)\) and can be neglected. Substituting Eq. (18) into Eq. (15) (assuming \( O_2 \) as an ideal gas and using \( \rho_{\text{O}_2} V = N_{\text{O}_2} k_b T) \)

\[ r_I = i \frac{N^\prime M^\prime}{M} \frac{\rho_{\text{O}_2} V}{M^\prime} \frac{q^s}{\mu_{\text{O}_2}} = i \frac{\rho_{\text{O}_2} V}{k_b T} \frac{q^s}{\mu_{\text{O}_2}} \]  
(19)

Calculation of the partition function of oxygen gas is straightforward (expressed as \( \rho_{\text{gas}} = \Phi_{\text{trans}} \times \Phi_{\text{rot}} \times \Phi_{\text{elec}} \)), where, \( \Phi_{\text{trans}} \), \( \Phi_{\text{rot}} \), and \( \Phi_{\text{elec}} \) denote 3D translational, rotational and vibrational and electronic partition functions of oxygen gas.

**Immobile transition state for chemisorption.** For the chemisorption transition state of the mobile type, we assume the following about its nature, which allows us to estimate the partition function of transition state.

1. We assume that the transition state of \( \text{O}_2 \) chemisorption is immobile and only retains the vibrational degree of freedom from the 3D-gas phase, but lost all 3-translational modes.
2. We assume the transition state has gained the lattice-vibrational degrees of freedom of the final chemisorbed state, except the ‘reaction coordinate’ degree of freedom. Thus we approximate the partition function of transition state \( q^s \) assuming 4 modes of vibration of lattice oxygen, 1 mode of O–O vibration retained from gas, and the reaction coordinate.

Under these assumptions, \( q^s \) becomes:

\[ q^s = q_{\text{reaction}} \times q_{\text{trans}} \times q_{\text{rot}} \times q_{\text{elec}} \]
\[ = k_b T \frac{\rho_{\text{trans}}}{h} \frac{\rho_{\text{rot}}}{h} \frac{\rho_{\text{elec}}}{h} \frac{\rho_{\text{reaction}}}{h} \]  
(20)

Thus, forward rate of oxygen chemisorption, from combining Eqs. (19) and (20) is,

\[ r_I = \gamma \times \frac{\rho_{\text{trans}} \rho_{\text{rot}} \rho_{\text{elec}}}{h^3} \times \frac{\rho_{\text{reaction}}}{h} \]  
(21)

The ratio of electronic partition functions of the transition and initial state \( \frac{\Phi_{\text{trans}}}{\Phi_{\text{gas}}} \) can be approximated to be \( e^{-\Delta G_{\text{eff}}}/\gamma \) where, \( \Delta G_{\text{eff}} = \Delta G_q^2 - (1 - \beta \Delta E) \) as described above, is the difference between the electronic energy of the transition state and the initial (gas) state, estimated using DFT. For an ideal gas, the forward rate then becomes,

\[ r_I = \frac{MT \rho_{\text{trans}} \rho_{\text{rot}} \rho_{\text{elec}}}{h^3} \times \frac{\gamma}{\gamma} \times \frac{\Phi_{\text{trans}}}{\Phi_{\text{gas}}} \]  
(22)

where, \( N_0, A \) are as defined above, and \( \Phi_{\text{trans}} = A (2\pi m k_b T)^{3/2} \) is the partition function for 2D ideal gas, normalized per adsorption site (hence divided by \( M \)).

The forward rate of chemisorption reaction \( (\text{O}_2 + \rightarrow \text{O}_2\text{ads}) \) via immobile transition state from the thermo-kinetic model is given by,

\[ r_I = k_{\text{ads}} \times \rho_{\text{trans}} \times \Gamma \times e^{-\Delta G_{\text{eff}}}/\gamma \]  
(23)

where, \( k_{\text{ads}} \) is the pre-exponential factor for oxygen chemisorption via immobile transition state. Clearly,

\[ k_{\text{ads}} = \frac{1}{N_0 \sqrt{2\pi m k_b T}} \left( \frac{\rho_{\text{trans}}}{\rho_{\text{gas}}} \right)^4 \frac{\gamma}{\gamma} \]  
(24)

As discussed in "Methods" section (main text), an Einstein temperature of \( T_e = 275 \text{ K} \), gives accurate expression for enthalpy and entropy of lattice oxygen in equilibrium with the gas. Using this Einstein temperature, the vibrational partition function for lattice-O at \( T = 650 \text{ K} \) is approximately 3.34 (unitless). At \( T = 650 \text{ K} \), the value of pre-exponential factor for oxygen chemisorption via immobile transition state, \( k_{\text{ads}} = 0.65 \text{ m s}^{-1} \). Values of various terms of above equation are in Supplementary Table 8.

**Mobile transition state for chemisorption.** For the chemisorption transition state of the mobile type, we assume the following about its nature, which allows us to estimate the partition function of transition state.

1. We assume that the transition state of \( \text{O}_2 \) chemisorption is relatively mobile, and has retained both the rotational and vibrational degrees of freedom from the 3D-gas phase, but lost all 3-translational modes.
2. We assume the transition state has gained 2 lattice-vibrational degrees of freedom of the final chemisorbed state, and a ‘reaction coordinate’ degree of freedom. Thus we approximate the partition function of transition state \( q^s \) assuming 2 modes of vibration of lattice oxygen, 1 mode of O–O vibration and 2 rotational modes retained from gas, and the reaction coordinate.

Under these assumptions, similar to Eq. (22), \( r_I \) becomes:

\[ r_I = \frac{MT \rho_{\text{trans}} \rho_{\text{rot}} \rho_{\text{elec}}}{h^3} \times \frac{\gamma}{\gamma} \times \frac{\Phi_{\text{trans}}}{\Phi_{\text{gas}}} \times \frac{\rho_{\text{reaction}}}{h} \]  
(25)

The forward rate of chemisorption reaction \( (\text{O}_2 + \rightarrow \text{O}_2\text{ads}) \) via immobile transition state from the thermo-kinetic model is given by,

\[ r_I = k_{\text{ads}} \times \rho_{\text{trans}} \times \Gamma \times e^{-\Delta G_{\text{eff}}}/\gamma \]  
(26)

where, \( k_{\text{ads}} \) is the pre-exponential factor for oxygen chemisorption via a mobile transition state. Thus we can write,

\[ k_{\text{ads}} = \frac{1}{N_0 \sqrt{2\pi m k_b T}} \left( \frac{\rho_{\text{trans}}}{\rho_{\text{gas}}} \right)^4 \frac{\gamma}{\gamma} \]  
(27)
At $T = 650 \degree C$, the value of pre-exponential factor for oxygen chemisorption via mobile transition state, $k_{ads}^0 = 17.55 \text{ m}^{-1}\text{s}^{-1}\text{kg}^{-1}$. Values of various terms of the above equation are in Supplementary Table 8.

Adsortion limit on $R_0$, $K_T$, and oxygen exchange. Here we calculate the fundamental upper limits on $K_T$ (m$^{-1}$s$^{-1}$) as well as ORR rate (moles of O$_2$·m$^{-2}$·s$^{-1}$) for any perovskite oxide cathode material. Recent work by De Souza et al.57 shows the $k^*$ limited by arrival from the gas phase using a simplified kinetic model that requires proposing a critical incident kinetic energy needed to incorporate an arriving O$_2$, $E_i$. Their work predicts a $k^*$ maximum about 10$^9$ cm$^{-1}$s$^{-1}$, which occurs when $E_i = 0$. Our more detailed kinetic model does not require positing a value of $E_i$ and matches the approximate $k^*$ upper limit in De Souza et al.57 when their critical energy is $E_i = 0.3$ eV, which seems a physically reasonable value and lends support to both approaches. To represent typical IT-SOFC working conditions, we calculate the limiting ORR rates and upper limits on $K_T$ for a temperature range of 500–750 °C, at a 0.2 atm oxygen partial pressure. In these conditions, typical SOFC cell voltages are in the range of 1–1.5 V. Let us assume that the entire driving force for the fuel cell is represented in the deviation from equilibrium of the ORR reaction, $\frac{1}{2}$O$_2 + V_0 + 2e^- \rightarrow O^{\circ}_ads$ where $V_0$ is oxygen vacancy and $O^{\circ}_ads$ is lattice oxygen in the cathode.

From Eqs. (5) and (7), we have non-configurational Gibbs free energy $\Delta G = -\Delta G_1$, $\Delta G_1$ represents an ideal, non-configurational Gibbs’s free energy change of the formation of oxygen vacancy.

Thus, at the equilibrium state, we can write the cathode reaction total Gibbs free energy $\Delta G_l$ and cathode potential $E_l$ as,

$$
\Delta G_l = -2F_{E_1}
$$
$$
= -\Delta G_1 - 2F_{E_1}(x_{bulk,eq})
$$
$$
+ k_0 T \ln \left( \frac{1-x_{bulk,eq}}{x_{bulk,eq}} \right) = 0
\tag{28}
$$

$F$ is Faraday constant. Similarly, at the non-equilibrium state, we have the fixed oxygen pressure and new bulk vacancy concentration $x_{bulk}$, the cathode reaction total Gibbs free energy $\Delta G_l'$ and cathode potential $E_l$ is calculated as,

$$
\Delta G_l' = -2F_{E_1}
$$
$$
= -\Delta G_1 - 2E_1 (x_{bulk})
$$
$$
+ k_0 T \ln \left( \frac{1-x_{bulk}}{x_{bulk}} \right) = 0
\tag{29}
$$

At the small overpotential $\eta(V)$,

$$
\eta = E - E_{eq} = E_l - E_{eq}
\tag{30}
$$

For LSC-50 cathode, with typical SOFC cathode overpotential of $\eta = -0.2 \text{ V}$, $pO_2 = 0.2$ atm, the term $\left( O^{\circ}_ads - O^{eq}_ads \right)$ is calculated at $T = 500 \degree C$, $650 \degree C$, $750 \degree C$, $800 \degree C$, respectively, to be 1168 moles-O/m$^3$ (0.015 site-fraction), 2231 moles-O/m$^3$ (0.029 site-fraction), 2929 moles-O/m$^3$ (0.038 site-fraction) and 3299 moles-O/m$^3$ (0.042 site-fraction). Values of $x_c$ are fitted using the parameters from Mizusaki et al.44 for LSC-50. Figure 7 below plots the term $\left( O^{\circ}_ads - O^{eq}_ads \right)$, % O site fraction on the x-axis and ORR rates (moles-O$_2$·m$^{-2}$·s$^{-1}$) on the y-axis. Limiting rates are shown as horizontal lines of the type $y = R_0$ (moles-O$_2$·m$^{-2}$·s$^{-1}$), with $R_0$ of the $O_1$ chemistryorption step that sets the fundamental upper limit to ORR. Limiting $K_T$ is represented by the slope (m) of the line of the type $y = mx$; in other words, a line which gives the limiting rate at the typical values of driving force $\left( O^{\circ}_ads - O^{eq}_ads \right)$. Plots at three different temperatures are made for the purpose of illustration.

Overpotential calculations. Based on our surface reaction model we can calculate the cathode overpotential vs. current density, providing another method of comparing our model to experiments. The calculation involves a few steps, which we describe below. First, we obtain $R_0$ for the material under polarization as follows. From Eq. (30), we can calculate the bulk oxygen vacancy concentration $x_c$ under polarization. We can then use the bulk oxygen vacancy concentration under polarization to calculate the concentration of surface oxygen adatom $\Gamma_{ads}$ and surface oxygen vacancy $\Gamma_c$. The equilibrium exchange rate from our rate limiting step can then be updated to include polarization effect from the equation $R_0$ (diss.) = $(8 \times D_{O_2} \times 2F \times \Gamma_{ads} \times \Gamma_c)$. Now we relate $R_0$ to the current density and overpotential through the total reaction rate.

The total reaction rate $r$ can be written in terms of equilibrium exchange rate $R_0$ in Eq. (3a)

$$
A_l = A_l/\beta_l = k_0 T \ln \left( x_{bulk,eq}/x_{bulk} \right)
\tag{32}
$$

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig9.png}
\caption{Overpotential versus log of the current density plot. X-axis is log of current density (A·cm$^{-2}$). Blue line is our calculated overpotential at 650 °C. Magenta circles line refers to experiment data from N. Imanishi et al.62. Black squares and azure triangles refer to M. Sase and Kawada et al.60 for La$_{0.6}$Sr$_{0.4}$CoO$_3$/Yttria-stabilized zirconia (YSZ) (black squares) by +1.1 log units in current density to obtain the La$_{0.6}$Sr$_{0.4}$CoO$_3$/YSZ “with shifting” (purple squares)60 (see text for details on the shifting) at 650 °C and YSZ (black squares) at 800 °C64.}
\end{figure}
where \( \lambda \) is the stoichiometric ratio between reaction \( i \) and overall reaction under quasi-equilibrium conditions, detail see Adler et al.\(^{11} \). \( \Lambda \) is the driving force for overall reaction.

We can write the current density as \( j = 4e \cdot r/S \). The unit of \( r \) is \( \text{O}_2 \cdot \text{cm}^{-1} \cdot \text{s}^{-1} \). \( S \) is the area of one Co site. \( e \) is the charge of one electron.

Based on the Eqs. (3a), (30) and (32), we can calculate the activation potential of the overpotential curve. The total overpotential consists of activation polarization, ohmic polarization and concentration polarization.\(^{58,59} \) For a dense thin film, the concentration polarization is assumed to be negligible, and for the comparisons in this work we use experimental data from which the ohmic polarization has been subtracted.

The predicted activation polarization values are given in Fig. 9 (overpotential vs. \( \log(I) \) for cathodic polarization). Fig. 10 (overpotential vs. \( I \) for cathodic polarization) and Fig. 11 (\( \log(I) \) vs. overpotential for both anodic and cathodic polarization). In these figures we include a number of experimental data sets on similar materials under similar conditions. However, we were not able to find any studies under the exact conditions of our modeling. Due to the sensitivity of overpotential to exact composition and temperature, a direct quantitative comparison between our model and these studies is difficult. As our best attempt at such a comparison, we shift the \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}/\text{YSZ} \) data from Sase and Kawada\(^{60} \) (black) by +1.1 log units in current density to obtain the \( \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3/\text{YSZ} \) “with shifting” curves (purple data). This shift is based on the \( k^* \) temperature dependence and \( k^* \) difference between \( \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3 \) and \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co} \) from Egger et al.\(^{7} \). Specifically, this data suggests we should expect a shift of +1.1 log units in going from \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Co} \) at 600 °C to \( \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3 \) at 650 °C (which are our modeling conditions), which should lead to an equivalent shift in current density since these measurements on are surface exchange limited films. In comparing our result to that of the shifted curve from Sase and Kawada we see the similar exponential relationship of \( \log(I) \) and overpotential in Fig. 9 and the same decreasing slope in Fig. 10. Given the uncertainties in the experiments and modeling, and the difference of condition, the agreement is very satisfactory. The slope of our prediction in Fig. 9 is slightly smaller than the experiment at high current density. According to the Eq. (30), the overpotential consists of one linear and one log function of a term that changes approximately proportional to oxygen vacancy concentration. At high oxygen vacancy concentration, the linear term will dominate the overpotential. The faster increase of the model as compared to experimental overpotential suggests that the linear term is changing too fast in our model, i.e., too much overpotential is required to create enough vacancies to enable the observed current density. This could be because it is too hard to create oxygen vacancies in our model, particularly at higher oxygen vacancy content. Our model follows that of Mizusaki, et al.\(^{41} \) in having oxygen vacancy formation energies increase with increasing oxygen vacancy concentration through filling of electronic states at the Fermi level, which creates a significant coupling between oxygen vacancy formation and the density of states at the Fermi level. Our density of states is from the fitting from Mizusaki et al.\(^{41} \), and represented by the bulk vacancy interaction parameter “\( a \)” in Table I of Mizusaki et al.\(^{41} \). However, our vacancy concentration at high current density is beyond any values explored in the experimental data that was fit by Mizusaki et al.\(^{41} \). It is therefore possible the bulk vacancy interaction parameter will decrease at high vacancy concentration. That would lead to the decrease of overpotential at high current density, which would match the experiment data in Fig. 9. Further study of the behavior of the vacancy
energetics at high vacancy concentration therefore might be of use, but it beyond the scope of this work.

Data availability

The authors declare that the main data supporting the findings of this study are available within the article and its Supplementary Information files. Extra data that support the findings of this study are available from the authors on reasonable request.

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Author contributions

All authors provided feedback and input to the research, analysis, and manuscript. Y.C., M.J.G., and A.T.N. have equal contributions to this work. M.J.G., A.T.N., D.M., and S.B.A. conceived this project and constructed the basic kinetic theory. M.J.G. and A.T.N. performed initial ab initio calculations and theoretical analyses, with assistance from D.M. and S.B.A. Y.C. performed the final sets of ab initio calculations and theoretical analyses, with assistance from D.M. and S.B.A. All authors contributed to scientific discussions and read and commented on the manuscript. This project was supervised by D.M.

Additional information

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