Role of Adsorbate Coverage on the Oxygen Dissociation Rate on Sr-Doped LaMnO$_3$ Surfaces in the Presence of H$_2$O and CO$_2$

Jing Yang, Jonathan M. Polfus, Zuoan Li, Harry L. Tuller, and Bilge Yildiz

ABSTRACT: Sr-doped LaMnO$_3$ (LSM) is a promising oxygen reduction reaction electrocatalyst in solid oxide fuel cells and other electrochemical devices. The presence of CO$_2$ and H$_2$O has been reported to promote the oxygen dissociation reaction on LSM surfaces. Here, we investigate the coadsorption mechanism of O$_2$ with H$_2$O or CO$_2$ by combining first-principles calculations of the (0 0 1) surface containing 25–100% Sr with thermodynamic adsorption models. The molecules were found to chemisorb by formation of charged oxygen, hydroxide, and carbonate species, and the adsorption energies were exothermic up to monolayer coverage. Low concentrations of H$_2$O or CO$_2$ do not compete with O$_2$ for adsorption sites under relevant conditions. However, their presence contributes to the total amount of oxygen-containing species. The increased coverage of oxygen species provides a quantitative explanation for the reported enhancement in oxygen dissociation kinetics in the presence of H$_2$O/CO$_2$. This study thereby provides insights into oxygen exchange mechanisms on LSM surfaces.

1. INTRODUCTION

Sr-doped LaMnO$_3$ (LSM) is one of the most studied perovskite materials for solid oxide fuel cell (SOFC) cathodes because of its high electronic conductivity, good oxygen reduction kinetics, and thermal and chemical stability with yttria-stabilized zirconia. LSM has also been used in composite electrodes in solid oxide electrolyser cells and catalytic layers and/or electronically conducting phases for mixed conducting membranes and catalytic membrane reactors. At intermediate temperatures (600–800 °C), the main limiting factor for the performance of SOFCs has been ascribed to the oxygen reduction reaction (ORR) at the cathode. Oxygen surface exchange and surface diffusion of oxygen ions have been identified as two key processes that control the ORR. Surface exchange kinetics remains an elusive property because it involves several steps including adsorption and dissociation of molecular oxygen, reduction (charge transfer), and incorporation of oxygen species into the cathode or electrolyte. Depending on the specific application and electrode characteristics, there are multiple possible reaction pathways, and it is inherently challenging to separate individual reaction steps.

LSM has been found to catalyze oxygen exchange mainly through the homoexchange mechanism where LSM provides surface sites for the adsorbates to dissociate, diffuse, and reassociate. Oxygen is subsequently incorporated into the electrolyte at the triple-phase boundaries, which may be the limiting step of the ORR. On the other hand, the heteroexchange mechanism involves lattice oxygen and thereby requires oxygen vacancies at the surface. Although LSM exhibits low bulk oxygen vacancy concentration, heteroexchange may be facilitated by fast diffusion along grain boundaries. In the case of typical mixed conducting cathode materials such as La$_2$NiO$_4$ and Ba$_5$Sr$_3$Co$_9$Fe$_{12}$O$_{33−δ}$, dissociative adsorption of oxygen—rather than incorporation—has been reported to limit the oxygen surface exchange.

In situ isotope-labeled gas-phase exchange experiments have been used to investigate the oxygen exchange reaction. By flowing gas mixtures of $^{18}$O$_2$ and $^{16}$O$_2$ over a catalyst bed, the oxygen dissociation rate can be measured directly as the steady-state concentration of the dissociation product, $^{16}$O$^{18}$O. In such experiments, the oxygen exchange rate can be directly related to the oxygen adsorbate concentration in the case of the homoexchange mechanism. With this approach, Huang et al. recently showed that the presence of H$_2$O and CO$_2$ could enhance the oxygen dissociation rate on LSM surfaces. By adding 2500–3000 ppm of CO$_2$ or H$_2$O to pure 0.05 bar...
oxygen, the oxygen dissociation rate increased by a factor of 1.5–2 and the results showed that both CO$_2$ and H$_2$O participated in the exchange reaction. The detailed understanding of this improvement is still unclear; possible explanations could be the presence of additional oxygen-containing surface species such as hydroxide or carbonate or changes in the reaction mechanisms and/or barriers as suggested for La$_{0.6}$Sr$_{0.4}$CoO$_{2-\delta}$ and SrTiO$_3$.\(^\text{18}\)

In the case of other materials systems, few studies have been performed on the effect of steam on oxygen surface exchange: isotope exchange followed by SIMS measurements has revealed enhanced oxygen surface exchange for mixed conductors such as La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ and PrBaCo$_2$O$_{5+\delta}$ in the presence of steam, which was ascribed to faster water dissociation and dissociation at surface oxygen vacancies, that is, heteroreaction. On the other hand, the presence of CO$_2$ impurities usually has an adverse effect on oxygen surface exchange kinetics because of undesirable reactions and/or degraded performance of the cell.\(^\text{21,22}\)

In this work, we predict the equilibrium adsorbate concentrations on LSM surfaces by combining first-principles calculations and thermodynamic models for gas adsorption. The (La, Sr)O-terminated (0 0 1) surface is selected as the model system as it is shown to be the favored termination in theoretical and experimental studies.\(^\text{5-24}\) We consider the cases of O$_2$/CO$_2$ and O$_2$/H$_2$O coadsorption as a function of partial pressures and temperature. The role of coadsorption can thereby be evaluated in comparison with measured oxygen dissociation rates under given environmental conditions.\(^\text{16}\)

The surface adsorption reactions were described by considering chemisorption and dissociative adsorption. Adsorption of CO$_2$ by formation of a carbonate species can be described by bonding with an LSM surface oxide ion

\[
\text{CO}_2(g) + ^*\text{O}^{2-} = \text{CO}_{3\text{ad}}^{2-}
\]  

(1)

where ^*O denotes a surface O-site. Chemisorption of carbonate species has been reported for LaMnO$_3$ and similar perovskites such as SrTiO$_3$, BaZrO$_3$, and K$_{1-y}$Na$_y$Ta$_2$O$_6$.\(^\text{25,26}\) Second, the dissociative adsorption of water can be described according to

\[
\text{H}_2\text{O}(g) + ^*\text{La}/\text{Sr} = \text{OH}_{\text{ad}}^- + \text{H}_{\text{ad}}^+
\]  

(2)

where ^*La/Sr denotes a surface La or Sr-site and H$_{\text{ad}}^+$ is associated with a surface oxide ion, that is, OH$_2^-$ in Kröger–Vink notation.\(^\text{27}\) Third, the dissociative adsorption of oxygen can be described by the formation of peroxy surface species or oxide ion adsorbates on La/Sr sites

\[
\frac{1}{2}\text{O}_2(g) + ^*\text{O} = \text{O}_{\text{ad}}^{-}
\]  

(3)

\[
\frac{1}{2}\text{O}_2(g) + ^*\text{La}/\text{Sr} = \text{O}_{\text{ad}}^{2-}
\]  

(4)

For O$_2$/H$_2$O coadsorption, the proton may associate with O$_{\text{ad}}^{2-}$ to form 2OH$_{\text{ad}}^-$ (resulting in a different site occupancy than the combination of eqs 2 and 4)

\[
\text{H}_2\text{O}(g) + \text{O}_{\text{ad}}^{2-} + ^*\text{La}/\text{Sr} = 2\text{OH}_{\text{ad}}^-
\]  

(5)

By also considering the coverage dependence of the adsorption energetics, the temperature and pressure ranges, where the surface becomes saturated and coadsorption becomes competitive, can be evaluated. Thereby, we present a quantitative comparison of the changes in overall oxygen coverages and the enhancement in the oxygen dissociation rate by addition of H$_2$O and CO$_2$ reported by Huang et al.\(^\text{16}\)

2. COMPUTATIONAL METHODS

2.1. First-Principles Calculations. Spin-polarized density functional theory (DFT) calculations were carried out using VASP\(^\text{30}\) and the projector-augmented wave method.\(^\text{31}\) PBE-generalized gradient approximation (GGA)\(^\text{32}\) was used with the DFT + U approach by Dudarev et al.\(^\text{33}\) and the on-site Coulomb interaction parameter for Mn was set to 4.0 eV based on previous studies.\(^\text{34-37}\) The energy cutoff for the plane wave basis set was 400 eV. The included valence electrons were La 5s$^2$p$^6$6s$^2$, Sr 4s$^2$5p$^6$, Mn 3p$^6$4s$^2$, and O 2s$^2$p$^4$.

The surface of Sr-doped LaMnO$_3$ was modelled as a symmetric (La, Sr)O-terminated (0 0 1) slab with a thickness of 11 atomic layers and 2 × 2 × 2 cell expansion in the lateral directions (108 atoms). The periodic images of the slab were separated by a vacuum region of about 25 Å. The calculations were performed with a 4 × 4 × 1 k-point grid, and the atomic positions were optimized until the residual forces were within 0.03 eV Å$^{-1}$. In order to avoid spurious structural distortion upon gas adsorption, the orthorhombic structure was used, and the lateral lattice parameters 7.78 and 7.99 Å were obtained from a 2 × 2 × 2 cell with a Sr-dopant concentration of 12.5%. The octahedral tilting in the slab was $a\overline{b}c^-$ in Glazer notation.

By use of symmetric slabs, the surface dipole between the terminating (LaO)$^+$ and (MnO$_2$)$^-_\text{ads}$ layers in stoichiometric (0 0 1) slabs was avoided.\(^\text{23}\) The excess positive charge of the additional (LaO)$^+$ layer in the 2 × 2 slab was compensated by four Sr-dopants. Slabs terminated with three different Sr concentrations were considered: 4(La$_{0.75}$Sr$_{0.25}$O)$^+_{0.75}$, 4(La$_{0.5}$Sr$_{0.5}$O)$^+_{0.5}$, and 4(SrO)$^-$; that is, 25, 50, and 100% Sr, respectively. The tendency for segregation of Sr to the surface of LSM was thereby taken into account.\(^\text{25}\) In the case of the slab with 25% Sr on the surface, the remaining two Sr-dopants were introduced in the subsurface layer to obtain a charge neutral cell. The overall Sr concentration was thereby 16.7% for the slabs terminated with 25–50% Sr and 33.3% for the fully SrO-terminated slab.

Because of the inherent challenge of representing the high-temperature paramagnetic state of LSM, ferromagnetic (half-metallic) ordering was imposed,\(^\text{38}\) and the magnetic moment of Mn was 3.8–4.0 $\mu_B$. Selected calculations were pursued with G-type antiferromagnetic ordering as it has been suggested as more appropriate to represent paramagnetic systems.\(^\text{39}\) Although the antiferromagnetic ordering could not be retained upon adsorption, it has previously been shown not to be important for adsorption calculations in LaMnO$_3$.\(^\text{39}\)

The adsorption energies, $\Delta E_{\text{ads}}$, were calculated as the total energy difference of the adsorption reactions for coverages of 0.25, 0.5, and 1 monolayer. The adsorbates were generally introduced on both sides of the slab, while for some configurations, complete coverage was only achieved with the adsorbate on one side of the slab. The difference in adsorption energy for these two approaches was relatively small (typically ±0.1–0.17 eV). For calculations with higher coverages, the adsorbates were arranged in several symmetrically inequivalent configurations in order to obtain the lowest energy structure. Interactions between different adsorbates were investigated in the case of H$_2$O and O$_2$ according to reaction 5 (Supporting Information), but otherwise not considered. The calculated coverages may therefore be overestimated close to saturation, while the relative coverages of the different adsorbates can be expected to be less affected.

The adsorption thermodynamics were evaluated based on the adsorption energy and configurational and vibrational entropy of the adsorbates. The vibrational frequencies were obtained according to the finite displacement method implemented in VASP with four 0.015 Å displacements of the vibrating species along the crystallographic axes. The vibrational entropy of the adsorbates, $S_{\text{vib}}$, was thereby calculated from the normal mode frequencies, $\nu$, according to
say, each adsorbed CO2 molecule occupies one oxygen site and one cation site can be occupied by OHad with the oxygen and cation sites on the surface. The surface oxygen and is separated into contributions from the adsorbates associated in chemical potential of the gas species with varying partial pressure.

minimizing the total free energy of the system. Here, we list the equilibrium coverage for each adsorbate species by computing equilibrium coverage for each adsorbate species by tables41 and therefore include the loss of translational entropy upon adsorption. Because of the challenges with the O2 molecule within GGA, the chemical potential of O2 was corrected based on the approach by Wang et al.42 by normalizing the calculated enthalpies of formation of a range of binary nontransition metal oxides to the experimental values. The correction amounted to 1.14 eV for the total energy of the O2 molecule (Figure S1).

2.2. Thermodynamic Model. The thermodynamic model computes equilibrium coverage for each adsorbate species by minimizing the total free energy of the system. Here, we list the energetic terms included in the model. For each adsorption species i, the total adsorption Gibbs energy associated with it is a function of its coverage Θi.

\[
\begin{align*}
S^\text{ad}_{\text{config}} &= -k \sum_i \left( \frac{\beta_i}{\exp(\beta_i)} - 1 - \ln(1 - \exp(-\beta_i)) \right) \\
S^\text{ad}_{\text{config}} &= -k \sum_i \left( \frac{\beta_i}{\exp(\beta_i)} - 1 - \ln(1 - \exp(-\beta_i)) \right)
\end{align*}
\] (6)

where \( \beta_i = h\nu/kT \).

Changes in the vibrational frequencies of the LSM surface oxide ion were also included in the cases of 1/2O2 (peroxo), CO2, H2O adsorption. The change in zero-point energy upon adsorption, ΔZPE, was calculated using the same frequencies according to \( \Delta \sum_i(h\nu/2) \). The adsorption entropies, \( \Delta S^\text{ad}_{\text{config}} \), were obtained with the gaseous reference states taken from thermochemical tables41 and therefore include the loss of translational entropy upon adsorption. Because of the challenges with the O2 molecule within GGA, the chemical potential of O2 was corrected based on the approach by Wang et al.42 by normalizing the calculated enthalpies of formation of a range of binary nontransition metal oxides to the experimental values. The correction amounted to −1.14 eV for the total energy of the O2 molecule (Figure S1).

2.2. Thermodynamic Model. The thermodynamic model computes equilibrium coverage for each adsorbate species by minimizing the total free energy of the system. Here, we list the energetic terms included in the model. For each adsorption species i, the total adsorption Gibbs energy associated with it is a function of its coverage Θi.

\[
G^\text{ad}_{\text{config}} = \sum_i G^\text{ad}_{\text{config}} = -k \sum_i \left( \frac{\beta_i}{\exp(\beta_i)} - 1 - \ln(1 - \exp(-\beta_i)) \right)
\] (7)

Here, \( \Delta H^\text{ad}_{\text{config}} = \Delta E^\text{ad}_{\text{config}}(\Theta) + \Delta ZPE \) is the adsorption enthalpy for oxygen atoms, water molecules, and carbon dioxide molecules as obtained from DFT calculations and \( \Delta H = kT \ln(p/p^0) \) is the change in chemical potential of the gas species with varying pressure. The configurational entropy is given by the coverages of all adsorbates and is separated into contributions from the adsorbates associated with the oxygen and cation sites on the surface. The surface oxygen sites can be occupied by Oad, Had+, and carbon in CO3ad2−, while the cation sites can be occupied by OHad−, Oad2+, and oxygen in CO3ad2−. Although each cation site can accommodate only one OHad− or Oad2+, both oxygen atoms of CO3ad2− can be accommodated because of the specific adsorbate configuration upon carbonate formation. That is to say, each adsorbed CO2 molecule occupies one oxygen site and one cation site on the surface. The total configurational entropy can thereby be written as

\[
S^\text{ad}_{\text{config}} = -k \sum_i \left( \frac{\beta_i}{\exp(\beta_i)} - 1 - \ln(1 - \exp(-\beta_i)) \right)
\] (6)

where either Oad2− or Oad− was included.

The total Gibbs energy of the system can thereby be described as

\[
G^\text{ad}_{\text{config}} = \sum_i G^\text{ad}_{\text{config}} - T S^\text{ad}_{\text{config}}
\] (9)

where the sum over i covers all possible adsorbate species. The equilibrium coverages under given conditions were solved by varying the coverages of the coadsorbates and determining the combination of the lowest energy.

For the convenience of further analysis, we also define three additional coverage terms. First, the number of vacant cation adsorption sites, \( \Theta^\text{vac} \), because these are limiting, allows for analyzing whether the surface is saturated by competitive adsorption

\[
\Theta^\text{vac} = 1 - \Theta^\text{O} - \Theta^\text{H2O} - \Theta^\text{CO2}
\] (10)

Second, the total number of adsorbed oxygen species on the surface, \( \Theta^\text{O} \),

\[
\Theta^\text{O} = \Theta^\text{O} + \Theta^\text{H2O} + 2\Theta^\text{CO2}
\] (11)

Third, the total number of adsorbed species on the surface, that is, counting only one of the oxygen atoms of CO2

\[
\Theta^\text{O+H2O+CO2} = \Theta^\text{O} + \Theta^\text{H2O} + \Theta^\text{CO2}
\] (12)

3. RESULTS

3.1. Adsorbate Configurations and Energies. Adsorption of CO2 on LSM (0 0 1) was determined to be energetically most favorable by chemisorption of carbonate species as shown in Figure 1 for coverages of 0.25−1. The carbonate adsorbates were formed by bonding to an LSM surface oxide ion. For coverages of 0.25 and 0.5, the surface oxide ion(s) relaxed out of the LSM surface, leaving...
undercoordinated manganese in the subsurface layer (Figure 1a,b).

The most stable configuration for dissociative adsorption of H₂O was determined to involve a hydroxide species bridging two surface cations, preferably La³⁺, and a proton associated with a LSM surface oxide ion and directed toward the hydroxide species (Figure 2). Similar configurations of chemisorbed H₂O have been observed by scanning tunneling microscopy studies of the SrO-terminated surface of the layered perovskite Sr₃Ru₂O₇.₄³ In some cases (θ < 0.5, 25−50% Sr), the surface oxide ion relaxed out of the surface, leaving undercoordinated Mn in a similar manner as for the carbonate adsorbates.

Figure 3 shows oxygen chemisorbed as peroxide species bound to LSM surface oxide ions (reaction 3). The O−O bond lengths were 1.46−1.50 Å, that is, slightly longer than the nominal 1.4 Å, which may be ascribed to the additional bonding to the surface cations. Figure 4a−c shows chemisorption of oxygen by forming oxide ions bridging two surface cations (reaction 4) for coverages up to 0.75 monolayer. In the case of full coverage, some oxide ion adsorbates relaxed to peroxide species by associating with LSM surface oxide ions. For some configurations with coverages of 0.5 and higher, restructuring of the surface was observed by outward relaxation and displacement of La³⁺, lowering the coordination to Mn at the surface from four to two (Figure 4e,f). Figure 4d shows the adsorption of an oxygen molecule with a bond length of 1.4 Å. In principle, the (0 0 1) surface contains four additional symmetrically equivalent sites for oxygen bridging Sr−La, but higher coverages resulted in significant restructuring of the surface and thus not considered further.

Bader charge analysis revealed that the bridging oxide ions attained essentially the same charge as the bulk oxide ions of LSM, O−₁.₂₅. In comparison, the charge of oxygen in the dioxide configurations was significantly smaller: O−₀.₇ for the dimer groups in Figure 3 and O−₀.₅ for the O₂ molecule in Figure 4d, indicating that these species can be described as peroxide (O₂²⁻) and superoxide (O₂⁻), respectively.

Figure 3. Chemisorbed oxygen as peroxide species on LSM (0 0 1) with 50% Sr in the surface layer at coverages of a quarter monolayer (a), half monolayer (b), and full monolayer (c).

Figure 4. LSM (0 0 1) with 25% Sr in the surface layer and oxygen chemisorbed as bridging oxide ions: 0.25−0.75 monolayer (a−c), restructured surfaces with a half monolayer (e) and full monolayer (f), and a chemisorbed oxygen molecule (d).

Figure 5. Coverage-dependent adsorption energies for chemisorbed CO₂ (a), H₂O (b), and oxygen as O⁻ (c) and various bridging configurations of O₂ according to Figure 4 (d).
The calculated adsorption energies for LSM with 25, 50, and 100% Sr in the surface layer are shown as a function of adsorbate coverage in Figure 5 with corresponding linear fits. The adsorption energies were slightly less exothermic with increasing Sr content for all adsorbates, particularly at the lowest coverages. The adsorption energy of CO2 showed the strongest coverage dependence, which may be ascribed to its larger size and the number of bonds to La/Sr, that is, steric and chemical interactions, respectively. In comparison, the H2O and O2 adsorbates showed lower interactions both in terms of adsorption energies and structural relaxation. The adsorption energy of the O2 molecule in Figure 4d was −2.82 eV (−1.41 eV per O), that is, in between the values for O2 and O2− at comparable coverages of 0.25−0.5 (Figure 4a,b). The adsorption energies of bridging oxide ions exhibited a complex behavior and a strong dependence on both Sr content and adsorbate coverage. The most exothermic values (θ ≤ 0.5, 25−50% Sr) may to a larger extent reflect the instability of the polar surfaces, as also evidenced by restructuring in some cases (e.g., Figure 4e). Notably, reverse segregation of Sr could be substantiated by considering the segregation energy for Sr combined with the adsorption energy of a bridging oxide ion. A segregation energy of −0.43 eV per Sr from the subsurface to surface was obtained by comparing the slabs with 25 and 50% Sr in the surface layer, while the adsorption energy of O2− was −0.71 eV, more exothermic for the surface with 25% Sr. Accordingly, the most stable configuration was obtained with lower Sr content in the surface layer by including oxygen adsorbates. However, defects and mixed terminations must be considered for the complete understanding of the surface chemistry of LSM.44,45

Table 1 summarizes the thermodynamic parameters for adsorption and the respective site occupancies for the adsorbates. The vibrational frequencies of the adsorbates are provided in Table S1, and the temperature dependence and linear fit of the adsorption entropies are shown in Figure S2. Overall, the obtained adsorption energies are significantly exothermic for all three gases. In the case of CO2, less exothermic chemisorption energies of −1.4 and −1.1 eV were previously obtained for the undoped material based on DFT calculations (using GGA and a different carbonate adsorption geometry) and adsorption isotherms on LaMnO3,35 powders, respectively.25 The present values for the Sr-doped surfaces range from −2.41 to −0.74 eV (θCO2 = 0.25). These values may be compared to the formation enthalpies of La2O2CO3 and SrCO3 from CO2 and the binary oxides, −1.52 and −2.4 eV, respectively.47 Similar CO2 chemisorption energies have been reported for the BaO-terminated BaZrO3 (−2.0 to −2.2 eV).27,48 The obtained adsorption energies for dissociative adsorption of H2O were in the same range as that reported for LaMnO3 (−1.64 eV)50 and other A-site terminated (layered) perovskites; SrTiO3 (−1.1 eV),38 SrZrO3 (−1.5 eV),51 BaZrO3 (−1.4 to −1.5 eV),52,53 and SrRuO2 (−1.3 eV).53 The oxygen adsorption energies correspond well with the value obtained by Piskunov et al. for the 25% Sr-doped (0 0 1) surface, −1.0 eV for O2− and −2.5 eV for O2−1.35 (θO = 0.25).54 It should be noted that several computational studies have been performed for oxygen adsorption on the MnO2-terminated LaMnO3 (0 0 1) surface.34,37,35,56 The strong exothermic adsorption of both H2O and CO2 implies that these may enter competitive regimes. Consequently, the presence of H2O may displace CO2 and prevent carbonate formation on the surface as reported for SrTiO3 and BaZrO3.16,55

For the calculations of equilibrium adsorbate coverages, the peroxide configuration was considered because of the favorable energetics at higher coverages and across Sr contents compared to the bridging oxide ions. The restructuring observed for some of the bridging configurations may reflect permanent changes in the surface that alter the catalytic properties. Moreover, it remains uncertain if the most exothermic adsorption energies for the bridging configuration were associated with other aspects of the computational approach related to charge balance and surface polarity.

3.2. Adsorbate Coverages. The equilibrium adsorbate coverages were sought by minimizing the total Gibbs energy of the system as described in Section 2.2. To show how each energetic term changes with adsorbate coverages, Figure 6 displays the two-dimensional energy landscapes for CO2/O− coadsorption at T = 1073 K, P02 = PCO2 = 1 bar, and 50% Sr-doped surface. Figure 6a shows the total adsorption enthalpy Θads = ΘOΔHadsO + ΘO2ΔHadsO2. As ΔHads for both species is exothermic, the minimum Θads is achieved on the line of ΘO + ΘO2 = 1, with CO2 slightly more favored. The entropic term −TSads goes against surface saturation and contributes a large penalty to the total Gibbs energy with increasing coverages, as shown in Figure 6b. The configurational entropy, −TSconfig is minimized at intermediate total coverage, as both low coverage and saturation are low-entropy states (Figure 6c). The total Gibbs energy of the system is the sum of the previous three terms, with the first two being the dominant terms. In this case, the lowest energy is obtained for ΘO = 0.31 and ΘO2 = 0.29. A similar plot for O2−/H2O coadsorption is shown in Figure S4.

Following this method, the equilibrium surface coverages were surveyed for temperature and oxygen partial pressure.
ranges of 673–1073 K and 0.01–1 bar O₂ and partial pressures of 10⁻¹⁰ to 10 bar for the CO₂ and H₂O coadsorbates on the 50% Sr surface. Figure 7 shows the case for O₂/CO₂ coadsorption. Under the considered conditions, Θₐ is hardly influenced by the presence of CO₂ because of the availability of a significant amount of adsorption sites for both species throughout the pressure ranges (Θ₀). These results show that coadsorption of O₂ and CO₂ is not in competition with each other. Despite the noncompetitive nature of the CO₂ adsorption, CO₂ adsorbates provide extra oxygen-containing surface species that may be involved in the oxygen exchange reactions. There is a significant contribution from CO₂ to Θ₀ even at relatively low pCO₂; 10⁻¹ bar CO₂ increases ΘO by a factor of 1.7 at 673 K and by a factor of 3.5 at 1073 K relative to the CO₂-free case. CO₂ adsorption becomes negligible for partial pressures lower than 10⁻⁷ bar at 1073 K.

Figure 8 shows the calculated adsorbate coverages for O₂/H₂O coadsorption in the same temperature and partial pressure range on the 50% Sr-doped LSM surface. The effect of H₂O on O₂ adsorption qualitatively resembles that of CO₂; that is, ΘO remains almost constant with varying pH₂O. There are major differences as well. Adsorption of H₂O is energetically less favorable compared to that of CO₂ at low coverage but more favorable at high coverage because of weaker adsorbate interactions (Table 1). Consequently, starting from pH₂O = 10⁻¹⁰ bar at 673 K, ΘH₂O is initially lower than ΘCO₂ under equivalent conditions but increases with a steeper slope with increasing partial pressure. A competitive adsorption regime is entered at around pH₂O > 10⁻³ bar with minor suppression of ΘO.

Equivalent coverage plots for the 25% and 100 Sr-doped LSM surfaces are provided in Figures S5–S8. The qualitative trends remain similar to those of the 50% Sr-doped surface, in line with the relatively small changes in adsorption energies as shown in Figure 5. There is a moderate decrease in total...
adsorbate coverages going from the 25% Sr-doped surface to the 100% Sr-doped surface because of the less exothermic adsorption energies with increasing Sr content.

4. DISCUSSION

In this section, we discuss possible connections between surface adsorbate concentrations and the oxygen dissociation rate by comparison with the experimental results from Huang et al. We first assume a simple model for the relationship between the oxygen dissociation rate, \( R_{\text{diss}} \), and the total number of active species on the surface, \( \Theta_{\text{act}} \)

\[
R_{\text{diss}} \propto \Theta_{\text{act}} \exp(-E_d/kT)
\]  

(13)

This model assumes that \( R_{\text{diss}} \) follows an Arrhenius relationship with an activation energy, \( E_d \), that is constant and not affected by coadsorption. The prefactor \( \Theta_{\text{act}} \) represents a nonlinear term because of changes in surface coverage with respect to temperature and partial pressures. In ref 16, the dissociation rate \( R_{\text{diss}} \) is represented by the measured \([^{18}\text{O}^{16}\text{O}]\). Huang et al. obtained apparent activation energies of 0.65 eV in 0.5 atm oxygen, 0.89 eV with the addition of 3000 ppm CO\(_2\) and 0.72 eV with the addition of 2500 ppm CO\(_2\).

Figure 9. Effect of CO\(_2\) and H\(_2\)O on equilibrium \( \Theta_{\text{O-H,O-CO}_2} \) predicted in this work in three gas environments varying with temperature (solid lines) on the 50% Sr-doped surface. The three gas environments are all at \( P_{\text{O}_2} = 0.5 \) atm, with the addition of 3000 ppm H\(_2\)O (blue) and 2500 ppm CO\(_2\) (green). For comparison, \( \Theta_{\text{O}} \) in presence of CO\(_2\)/H\(_2\)O (dashed lines) shows that there is a negligible effect of coadsorption on \( \Theta_{\text{O}} \) under these conditions. The contribution of coverage to the apparent activation energy for each case is fitted and shown by the dashed black lines.

Figure 9 shows \( \Theta_{\text{O-H,O-CO}_2} \) as a function of inverse temperature under the same gas environments on the 50% Sr-doped surface, assuming that \( \Theta_{\text{O-H,O-CO}_2} \) is an appropriate representation of \( \Theta_{\text{act}} \) in eq 13. The Arrhenius relationships are fitted and shown by the dashed black lines. The result shows that changes in \( \Theta_{\text{O-H,O-CO}_2} \) with temperature represents a minor contribution to the apparent activation energy: ~0.16 eV (for pure \( \text{O}_2 \)) and ~0.19 to ~0.23 eV (for coadsorption) in the high-temperature regime (973–1123 K). This effect gradually disappears as temperature goes down and the surface becomes saturated.

Now, we discuss whether \( \Theta_{\text{O-H,O-CO}_2} \) is a good representation of active species contributing to surface dissociation by referring back to measurements in ref 16. Following eq 13, under the same temperature, the ratio of \([^{16}\text{O}^{18}\text{O}]\) in the two gas environments should be the same as the ratio of the respective \( \Theta_{\text{act}} \). In other words, the ratio

\[
\frac{[^{16}\text{O}^{18}\text{O}]}{[^{16}\text{O}^{16}\text{O}]} = \frac{\Theta_{\text{act,O}_2}}{\Theta_{\text{act,O}_2+H_2O}}
\]

where the subscripts \( \text{O}_2 \) and \( \text{O}_2 + \text{H}_2\text{O} \) represent the two gas environments with and without H\(_2\)O addition. The same relationship applies to the comparison with and without CO\(_2\). Comparing the three gas atmospheres in Figure 9, \( \Theta_{\text{O}} \) changes very little with the addition of H\(_2\)O or CO\(_2\) because of the noncompetitive nature of the adsorption. Therefore, if the oxygen exchange mechanism remains unchanged in the presence of H\(_2\)O and CO\(_2\), these results indicate that \( \Theta_{\text{O}} \) is not the only source of active surface species.

The two remaining candidates that we consider for \( \Theta_{\text{O}} \) are \( \Theta_{\text{O+H,O+CO}_2} \) and \( \Theta_{\text{O}_2}\). In Figure 10, we show the ratios as in (a) 0.5 atm \( \text{O}_2 \) plus 3000 ppm H\(_2\)O versus pure \( \text{O}_2 \) and (b) 0.5 atm \( \text{O}_2 \) plus 2500 ppm CO\(_2\) versus pure \( \text{O}_2 \) in comparison to the ratio of the measured oxygen exchange rates. The colored bands represent the uncertainty due to the different Sr contents in the surface layer. Looking at Figure 10a, the ratio of \( \Theta_{\text{O+H,O}} \) goes from 1.2 to 1.50 at 673 K to 1.05 to 1.30 at 823 K. A 1.05–1.5 ratio of \([^{16}\text{O}^{18}\text{O}]\) with and without H\(_2\)O was observed experimentally, which is quantitatively close to the increase in \( \Theta_{\text{O+H,O}} \). In Figure 10b, the ratio between
The present work demonstrates that an increased concentration of oxygen-containing surface species in the presence of small amounts of CO2 or H2O (O162+H2O or O162+CO2) can account for the increase in the oxygen exchange rate according to the homoexchange mechanism. This concentration effect, of course, is not expected to be the only factor that could contribute to the enhanced surface oxygen exchange rate on LSM. It is reasonable to expect that different surface species, such as surface hydroxide and carbonate, can affect the reaction mechanisms in different ways through interactions with the surface and oxygen adsorbates. This could potentially explain some discrepancies between the predicted O162+H2O+CO2 ratio and experimental oxygen exchange rates. Discrepancies can also be ascribed to several limitations of the model, including the use of a single pristine (0 0 1) surface, lack of interactions between coadsorbates, and computational accuracy (particularly the rather large correction applied to the oxygen adsorption energies, see Section 2.1 and the Supporting Information).

We conclude that the ORR is affected by CO2/H2O in the following way when these gases are added in small amounts into O2 gas. First, our predicted adsorption concentrations have shown that trace amounts of CO2/H2O do not hinder surface oxygen adsorption of O2. Second, the simple Arrhenius model, as in eq 13, leads to quantitative agreement with experimental oxygen dissociation rates. This result indicates that the increase of active oxygen species provided by coadsorbed CO2 and H2O can be correlated with promotion of homoexchange. These two points imply that the presence of CO2/H2O in the predicted regime will not impede the ORR. In the regime where dissociative adsorption of oxygen is the rate-limiting step, CO2/H2O coadsorption promotes the overall ORR by providing extra active oxygen species on the surface. In terms of the role of surface coverage and heteroexchange rate on the electrode performance of SOFCs, H2O or CO2 does not take part in the overall fuel cell reactions. Nevertheless, the increased concentration of oxygen species on the cathode in the presence of H2O and/or CO2 may promote the kinetics of intermediate reactions that increase performance.

5. CONCLUSIONS

First-principles calculations and thermodynamic models were used to investigate oxygen, water, and carbon dioxide adsorption on the (La, Sr)O-terminated (0 0 1) LSM surface as functions of temperature and partial pressures. The calculated surface coverages showed that adsorption of oxygen was hardly influenced by trace amounts H2O or CO2 because of the noncompetitive nature of coadsorption. However, CO2 and H2O do contribute significantly to the total number of oxygen-containing surface species, even at low partial pressures. By assuming that these species take part in the oxygen homoexchange reactions, the increase in coverage was...

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2\text{H}_2\text{O} \]

This observation indicates that at least one of the oxygen species in CO2/H2O can exchange with a neighboring peroxide adsorbate and thereby be active in the homoexchange reaction.

The above quantitative comparison shows that it is reasonable to consider \( \Theta_{\text{O}_2+\text{H}_2\text{O}+\text{CO}_2} \) as the prefactor \( \Theta_{\text{act}} \) in \( \text{eq 13} \). This will partly eliminate the nonlinear characteristic of the Arrhenius fitting of the oxygen dissociation rate. In Figure 11a, we reproduce the \( \ln[16\text{O}] \) versus \( 1/\Theta \) plot in ref 16 and we compare it to the coverage-normalized \( \ln[16\text{O}] / \Theta_{\text{O}_2+\text{H}_2\text{O}+\text{CO}_2} \) versus \( 1/\Theta \) plot in Figure 11b for the 50%-Sr doped surface. Here, \( \Theta_{\text{O}_2+\text{H}_2\text{O}+\text{CO}_2} \) is the calculated value from this work under the experimental conditions. Assuming \( 16\text{O} \) \( \Theta_{\text{O}_2+\text{H}_2\text{O}+\text{CO}_2} , \text{exp}(-E/kT) \), we obtain a uniform activation energy of 0.81 eV for all three atmospheres. The good consistencies among all three sets of data after the prefactor normalization indicates that \( \text{eq 13} \) is a plausible model for interpreting experimental surface kinetic data and that the increase in \( \Theta_{\text{act}} \) is possibly the predominant contributor to the enhancement of the oxygen dissociation rate in the presence of CO2 and H2O.

Figures S10 and S11 presents equivalent renormalized dissociation rates for the 25 and 100% Sr-doped surfaces. Similar to the 50% Sr-doped case, the renormalization allows for a uniform activation energy across gas atmospheres. Activation energies of 0.78 and 0.87 eV were obtained for the 25 and 100% Sr-doped surfaces, respectively.

Conclusions

"..."
compared with experimental values of the oxygen exchange rate on LSM. The results suggest that the change in surface coverage of the oxygen-containing species can account for a major part of the measured increase in the oxygen exchange rate in the presence of CO\textsubscript{2} and H\textsubscript{2}O. These results provide a new understanding of the role of surface coverage and coadsorbates on the oxygen exchange rate on LSM surfaces.

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.9b05243.

Chemical potential of O\textsubscript{2}; adsorption entropies; adsorbate interactions; energy contour maps for H\textsubscript{2}O/ O\textsubscript{2} coadsorption; coverage plots for 25\% Sr-doped and 100\% Sr-doped surfaces; and renormalized oxygen dissociation rate on 25\% Sr-doped and 100\% Sr-doped surfaces (PDF)

■ AUTHOR INFORMATION

**Corresponding Authors**

Jonathan M. Polfus — Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; Sustainable Energy Technology, SINTEF Industry, NO-0314 Oslo, Norway; Email: jonathan.polfus@sintef.no

Bilge Yildiz — Department of Nuclear Science and Engineering and Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; Email: byildiz@mit.edu

**Authors**

Jing Yang — Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; Email: jyang@mit.edu

Zuoan Li — Sustainable Energy Technology, SINTEF Industry, NO-0314 Oslo, Norway

Harry L. Tuller — Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.chemmater.9b05243

**Author Contributions**

J.Y. and J.M.P. equally contributing authors.

**Notes**

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

J.Y. and B.Y. thank the support from the Consortium for Advanced Simulation of Light Water Reactors (CASL), an Energy Innovation Hub for Modeling and Simulation of Nuclear Reactors under U.S. Department of Energy Contract no. DEAC05-00OR22725. J.M.P. and Z.L. acknowledge financial support from the national funding organizations (Research Council of Norway, NWO, MINECO) in the framework of the M-ERA.NET project (grant number 258875) “Designing rules for enhancing SURFace KINetics in functional OXides for clean energy technologies” (SURKINOX) and computational resources from Uninett Sigma2 (nn9259k). H.L.T. and B.Y. acknowledge the support for their research from the Department of Energy, Basic Energy Sciences under award number DE-SC0002633 (Chemomechanics of Far-From-Equilibrium Interfaces).

**REFERENCES**


(17) Li, M.; Sun, Z.; Yang, W.; Hong, T.; Zhu, Z.; Zhang, Y.; Wu, X.; Xia, C. Mechanism for the Enhanced Oxygen Reduction Reaction of La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{3-δ} by Strontium Carbonate. *Phys. Chem. Chem. Phys.* 2017, 19, 503–509.


(21) Zhao, Z.; Liu, L.; Zhang, X.; Wū, W.; Tu, B.; Cui, D.; Ou, D.; Cheng, M. High- and Low- Temperature Behaviors of La0.6Sr0.4Co0.2Fe0.8O3-Cathode Operating under CO2/H2O-Containing Atmosphere. Int. J. Hydrogen Energy 2013, 38, 15361–15370.

(22) Lai, S. Y.; Ding, D.; Liu, M.; Liu, M.; Almagir, F. M. Operando and In Situ X-Ray Spectroscopies of Degradation in La0.6Sr0.4Co0.2Fe0.8O3−δ Thin Film Cathodes in Fuel Cells. Chem. Soc. Chem. 2014, 7, 3078–3087.


(34) Cheng, M. High- and Low-Temperature Behaviors of La0.6Sr0.4Co0.2Fe0.8O3-Cathode Operating under CO2/H2O-Containing Atmosphere. Int. J. Hydrogen Energy 2013, 38, 15361–15370.


