Oxygen (O$_2$) reduction reaction on Ba-doped LaMnO$_3$ cathodes in solid oxide fuel cells: a density functional theory study

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Abstract
The oxygen adsorption and subsequent reduction on the {100} and {110} surfaces of 25% Ba-doped LaMnO$_3$ (LBM25) have been studied at the density functional theory (DFT) with Hubbard correction and the results compared with adsorption on 25% Ca-doped LaMnO$_3$ (LCM25) and Sr-doped LaMnO$_3$ (LSM25). The trend in the reduction energies at the Mn cation sites are predicted to be in the order LSM25 < LBM25 < LCM25. In addition, the trend in dissociation energies for the most exothermic dissociated precursors follow the order LBM25 < LSM25 < LCM25. The adsorption energies ($E_{\text{ads}} = -0.56$ to $-1.67$ eV) calculated for the molecular O$_2$ precursors at the Mn cation sites of LCM25, LSM25 and LBM25 are thermodynamically stable, when compared directly with the adsorption energies ($E_{\text{ads}} = -2.14$ to $-2.41$ eV) reported for the stable molecular O$_2$ precursors on the Pt, Ni, Pd, Cu and Ir {111} surfaces. The predicted Gibbs energies as a function of temperature ($T=500$–$1100$ °C) and pressures ($p=0.2$ atm) for the adsorption and dissociation on the surfaces were negative, an indication of the feasibility of oxygen reduction reaction on the {100} and {110} surfaces at typical operating temperatures reported in this work.

Keywords Gibbs free energies · Superoxide · Peroxide · SOFC · LaMnO$_3$

Introduction
The world’s demand for energy, coupled with the finite supply of fossil fuels and the environmental and political drawbacks associated with them, has shifted the focus of energy research to more efficient and sustainable conversion and storage technologies [1].

Solid Oxide Fuel Cells (SOFCs) are electrochemical devices for converting chemical energy into electrical energy and additional heat. Intermediate conversion of heat to mechanical work required by conventional combustion techniques is largely avoided. SOFCs with electrolyte that is ionic conducting presents unique opportunities over other fuel cells, such as cheap constituents, decreased susceptibility to fuel impurities and effectiveness. SOFCs embodies the cleanest, capable and flexible chemical to electrical energy transfer system [2, 3] providing alternatives to broader consumption of hydrogen and carbon-based fuels and regenerating fuel sources [4, 5]. However, for SOFCs to be explored on a bigger commercial scale, they must be less expensive and the electrode fabricated from readily available materials. One approach to cost reduction is the drastic reduction in the operation temperatures, which suppresses cell degradation, thermal stress buildup and improvement in cell lifetimes [6]. Due to their high catalytic reactivity toward the oxygen reduction reaction, noble metal electrocatalyst [7], such as platinum (Pt), is employed as a cathode. However, the cost of platinum represents a fundamental problem for its application.
Perovskite-type oxides such as LaMnO$_3$ have attracted attention for applications built upon their unique electronic and magnetic features. For example, La$_{1-x}$Sr$_x$MnO$_{3-δ}$ is the cathode of choice when the electrolyte material is zirconia in SOFCs [7]. This is attributed to the good electrical conductivity, stability, low cost and efficient catalytic activity for the oxygen reduction reaction [8]. In SOFCs cathode, at dopant concentration ($x = 0.2 \sim 0.3$), La$_{1-x}$Sr$_x$MnO$_{3-δ}$ is reported to be employed as mixed ionic–electronic conducting (MIEC) [9].

For O$_2$ adsorption and subsequent reduction on pure and 25% Ca-doped LaMnO$_3$ (LCM25) {100} and {110} surfaces, Aniagyei et al., [10] reported that adsorption or reduction processes are more favorable at the Mn sites than La and Ca sites at the DFT level with Hubbard correction. The adsorption energies calculated for the {110} surfaces were more favorable and stable than the {100}.

Chen et al., [11] studied the kinetic behavior of the oxygen reduction reaction and diffusion pathways on 25% Sr-doped LaMnO$_3$ (LSM25) cathode surface. From the spin-polarized DFT and molecular dynamics (MD) calculations, O$_2$ adsorption energies were more stable at the Mn sites compared to the Sr sites. La$_{1-x}$Ba$_x$MnO$_3$ is a colossal magnetoresistance (CMR) classical compound [12] with a Curie temperature of 340 K [13]. Dependent on the dopant concentration, the crystal structure moves from orthorhombic through rhombohedral ($x > 0.13$) to cubic ($x > 0.35$). For the magnetic spin alignment, it shows ferromagnetic behavior at Ba concentrations of $x > 0.15$. They are reported to undergo metal-to-insulator transition at $x \approx 0.20$ [13, 14]. La$_{1-x}$Ba$_x$MnO$_3$ has received extensive investigation of its crystallographic and magnetic properties [14, 15], phase transitions [13, 16, 17], and spin dynamics [18]. For the reduction activity on Ba-doped LaMnO$_3$ as cathode materials toward ORR, the best of our information, no theoretical studies have been shown, which makes this theoretical study timely.

In this work, an extension to previous studies [10], Hubbard-corrected DFT approach is applied to study the Gibbs free energies of adsorption of the multiple reaction paths associated with the reduction of oxygen at 25% Ba-doped LaMnO$_3$ {100} and {110} surfaces (LBM25). The oxygen reduction energetics on LBM25 surfaces are compared with LCM25 [10] and LSM25 [see Table S1 and Figure S1 and S2], the main cathode of preference for conventional SOFCs. This is to ascertain whether they could be used as an alternative electrocatalyst for oxygen reduction reaction (ORR) based on their adsorption/reduction energies. The adsorption studies were restricted to the {100} and {110} surfaces of LaMnO$_3$ because they present the most stable surfaces [19, 20].

### Computational details

The calculations were carried out within the Kohn–Sham DFT formalism [21], using a plane-wave basis set as implemented in the Quantum-ESPRESSO [22]. The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) was employed for the exchange and correlation terms [23]. The plane-wave basis set cutoffs for the smooth part of the wave function and the augmented density were set to 40 and 420 Ry, respectively, which ensured convergence of the forces to within 0.01 eV/Å. The Brillouin zone for the bulk LaMnO$_3$ was sampled using a $4 \times 4 \times 4$ Monkhorst–Pack $k$-points mesh [24]. To correct the large self-interaction error inherent in standard DFT-GGA methods for mid-to-late first-row transition metal oxides [25], the DFT + U approach [26] with a U$_\text{eff}$ value of 4.0 eV for Mn ions (mainly Mn$^{3+}$ ions) provides the best results when modeling the LaMnO$_3$ ground-state properties [27]. We have investigated the symmetric $Pm3m$ cubic structure, because it is stable under SOFC operating conditions (above 500 °C in ambient air) [28, 29]. All calculations were spin-polarized to describe accurately the magnetic properties of the LBM25, LSM25 and the triplet ground state of oxygen.

The different possible magnetic orderings at the Mn$^{3+}$ sites in the LBM25 and LSM25 surface structures were considered and found that the ferromagnetic (FM) ordering is 0.3 and 0.2 eV, respectively, more stable than the antiferromagnetic (AFM) ordering. Hence, all the structures investigated in this study have FM spin ordering.

The {100} and {110} surface structures were created from the fully optimized bulk structure using the METADISE code [30], which generates different atomic layer stackings to result in a zero-dipole moment perpendicular to the surface plane, as is required for reliable and realistic surface calculations [31]. The fully relaxed bulk structures were used to create the surfaces to eliminate the presence of fictitious forces during the surface relaxation. The surfaces were modeled using a slab model comprising of eight atomic layers with a vacuum size of 12 Å introduced in the z-direction, which is large enough to avoid any spurious interaction between the periodic slab images.

Similar to previous studies [10], all the surface calculations for the interactions between the molecular oxygen species on the LSM25 and LBM25 surfaces were performed by relaxing the top three layers while keeping the bottom five layers fixed at the bulk parameters. The adsorption energy was calculated according to the following relation:

$$E_{\text{ads}} = E_{\text{surface} + O_2} - (E_{\text{surface}} + E_{O_2})$$

(1)

where $E_{\text{surface} + O_2}$ is the total energy of the substrate–adsorbate system in the equilibrium state, and $E_{\text{surface}}$ and $E_{O_2}$ are the total energies of the substrate (clean surface) and
Results and discussion

Description of Ba-doped LaMnO₃ surfaces

For reduction reaction on SOFC cathodes, the role played by oxygen vacancies present on the surface is critical. The vacant sites are expected to compete against adsorption and dissociation in the mobility of oxygen. To examine the role of the vacant site on the oxygen reduction reactions at the cathode, LB25 surfaces with different layer models are shown in Fig. 1. Summarized in Table 1 are the calculated oxygen vacancy formation energies obtained by substitution of the host La³⁺ cation for Ba²⁺ in the {100} and {110} LaMnO₃ surface models with different layers. The calculated oxygen vacancy formation energies located on the top layer were based on the reaction of

$$\text{La}_0.75\text{Ba}_{0.25}\text{MnO}_3 \rightarrow \text{La}_0.75\text{Ba}_{0.25}\text{MnO}_{3-δ} + \text{O}_2(g)$$

(2)

In previous studies of LaMnO₃ with MnO₂-terminated {100} surface at the GGA+U [32] and hybrid B3LYP [33] levels of theory, a calculated oxygen vacancy formation energy of 2.2 eV was reported. Surfaces model A of

![Image of Ba-doped LaMnO₃ surfaces]

Fig. 1 (Top) A is BaMnO-terminated and B–D are LaMnO-terminated {110} surface models. (Down) MnO₂-terminated (100) LB25 models. Color code: green = La, blue = Ba, purple = Mn, and red = O.

| Surface models | Oxygen-vacancy formation {110} | Oxygen-vacancy formation {100} |
|----------------|-------------------------------|-------------------------------|
| A              | 4.37                         | 2.63                         |
| B              | 3.72                         | 2.97                         |
| C              | 4.10                         | 3.35                         |
| D              | 4.11                         | 3.48                         |
| LaMnO₃        | 4.23                         | 3.60                         |
the MnO₂ terminated {100} and model B of the LaMnO-
minated {110} with the La ion in/near the topmost lay-
ers (Fig. 1) were found to have the lowest oxygen vacancy
formation energies; thus, we chose these two models for
subsequent studies of O₂–LBM25 interactions.

In this work, molecular or dissociative chemisorption
of O₂ on (1 × 1) and (2 × 1) surface models at various cov-
erages of Θ = 0.25 ML and 0.50 ML, where a monolayer
(ML) refers to an oxygen molecule per active surface cation.
Shown in Fig. 2 are the top and side views of the LBM25
{100} and {110} surface models showing the different
adsorption sites explored for O₂ adsorption.

**O₂ adsorption on the oxygen-deficient LBM25
{110} surface**

For O₂ adsorption on the {110} surface with coverages of
Θ = 0.25 ML and 0.50 ML, molecular and dissociative sce-
narios for the selected (1 × 1) and (2 × 1) surface models
were considered. Substitution of host La³⁺ with Ba²⁺ cation
creates a defective surface with a vacant oxygen site. Similar
to the undoped surface [10], different adsorption configu-
ration and modes were exploited at the {110} and {100}
surfaces, that may serve as precursors for O₂ dissociation.
Figure 3 shows the optimized adsorption structures, whiles
the adsorption energies, Löwdin atomic charges, interatomic
bond distances and vibrational stretching frequencies are
presented in Table 2.

For O₂ adsorbed on Mn cation site, the end-on structure
is changed to a side-on structure after optimization (Fig. 3,
A1), with an exothermicity of −2.25 eV. The formed molec-
ular precursor A1 is accompanied by significant charge
transfer (−0.34 e− from the substrate) to the O₂ orbital,
weakening and elongating the d(O–O) to 1.45 Å compared
to gas phase and experimental d(O–O) of 1.23 and 1.21 Å
[34], respectively. For A1, the shortest interatomic distance
d(O–Mn) is 1.838 Å. On the LSM25 surface, O₂ adsorbed
end-on and side-on at the Mn sites, and exothermicities of
1.59 and 2.41 eV were calculated and the d(O–O)= 1.357
and 1.449 Å, respectively (Table S1 and Figure S1). In both
molecular processes, the d(O–O) are elongated by 1.315 and
1.480 Å, respectively. The adsorption energies of −2.14,
−2.41 and −2.25 eV calculated at the Mn cation sites of
LCM25, LSM25 and LBM25 are thermodynamically sta-
ble, when compared directly with the adsorption energies
(E_{ads} = −0.56 to −1.67 eV) reported for molecular O₂ pre-
cursors on the Pt, Ni, Pd, Cu and Ir {111} surfaces [35,
36]. This indicates that LCM25, LSM25 and LBM25 cath-
ode materials may be more efficient for O₂ activation than
the transition metal surfaces. In addition, since molecular
precursors at the Mn cation sites of LCM25, LSM25 and
LB2M are associated with stronger bonds compared to
LaMnO₃ [10], this implies Ca, Sr and Ba as dopants in the
cathode influences the O₂ reduction. The trend in the reduc-
tion energies on the Mn cation sites are predicted to be in
the order LSM25 < LBM25 < LCM25.

For O₂ adsorption on the {110} surface with coverages of
Θ = 0.25 ML and 0.50 ML, molecular and dissociative sce-
narios for the selected (1 × 1) and (2 × 1) surface models
were considered. Substitution of host La³⁺ with Ba²⁺ cation
creates a defective surface with a vacant oxygen site. Similar
to the undoped surface [10], different adsorption configu-
ration and modes were exploited at the {110} and {100}
surfaces, that may serve as precursors for O₂ dissociation.
Figure 3 shows the optimized adsorption structures, whiles
the adsorption energies, Löwdin atomic charges, interatomic
bond distances and vibrational stretching frequencies are
presented in Table 2.

Fig. 2 Schematic representation of the side and top views of the (2 × 1) slab model of (a, b) LBM25 {110} and (c, d) LBM25 {100} supercells
showing the corresponding different adsorption sites explored. Color code: green = La, blue = Ba, purple = Mn, and red = O
For \( \text{O}_2 \) adsorbed on top-La cation, no stable end-on configuration is obtained because it is changed to a side-on structure after optimization (A2, Fig. 3) with an exothermicity of 1.31 eV. The bound \( \text{O}_2 \) molecule experiences a net charge of \(-0.29\) e\(^{-}\) and \(d(\text{O-O})\) elongation of 1.374 Å. The formation of molecular precursor A1 is energetically more favorable than A2 in terms of adsorption energies and stronger bond formation, i.e., shorter \(d(\text{O-Mn}) = 1.838\) Å than \(d(\text{O-La}) = 2.324\) Å showing that Mn are more active than La sites toward oxygen reduction reaction and consistent with experimental observations [37]. In this work, for the \( \text{O}_2 \) molecule adsorbed end-on and side-on at the top-Mn and Sr cation sites on SrMnO-terminated \( \{110\} \) surface, the B (Mn) cation sites were calculated to be more active than A (Sr) cation sites toward oxygen reduction reaction (Table S1). This demonstrates that Mn cation are the favored on both oxygen-deficient LCM25 [10], LSM25 and LBM25 surfaces for adsorption, in agreement with other reported studies on perovskite structures [10, 38, 39].

### Table 2

Calculated adsorption energies (\(E_{\text{ads}}\)), Charge (\(q\)), relevant bond distances (\(d\)) of molecular \(\text{O}_2\) on defective \(\{110\}\) surface of LBM25; \(\text{O-O}\) stretching vibrational frequency (\(\nu\)) of the adsorbed \(\text{O}_2\); and calculated gas-phase \(d(-\text{O}) = 1.229\) Å and the \(\nu(\text{O-O}) = 1558\) cm\(^{-1}\)

| Surface | Config | \(E_{\text{ads}}\) (eV) | \(|q|\) (e\(^{-}\)) | \(d(\text{O-Mn})\) (Å) | \(d(\text{O-La})\) (Å) | \(d(\text{O-O})\) (Å) | \(\nu(\text{O-O})\) (cm\(^{-1}\)) |
|---------|--------|----------------|----------------|-----------------|----------------|----------------|----------------|
| \{110\} | A1     | -2.25         | -0.34          | 1.838           | -              | 1.446          | 641            |
|         | A2     | -1.31 (−1.50) | −0.29          | -               | (2.300)        | 1.374 (1.407)  | 878            |
|         | A3     | −3.78 (−4.40) | −0.46          | 1.883 (1.922)   | 2.377 (2.372)  | 1.495 (1.496)  | 514            |
|         | A4     | -2.96 (−3.34) | −0.53          | -               | (1.507)        | 1.507 (1.500)  | 490            |
|         | D1     | −5.99 (−6.05) | −0.76          | 1.638 (1.649)   | -              | -              | -              |
|         | D2     | −4.80 (−5.49) | −0.89          | -               | 2.241 (1.793)  | -              | -              |
|         | D3     | −7.83 (−7.63) | −0.93          | 1.767 (1.904)   | 2.410 (2.132)  | -              | -              |
| \{100\} | A1     | −0.82         | −0.14          | 1.850           | -              | 1.380          | 861            |
|         | A2     | −1.97 (−2.88) | −0.36          | -               | 1.491 (1.494)  | 497            |
|         | D1     | −3.51 (−4.12) | −0.44          | 1.577 (1.851)   | -              | -              | -              |

The (2\(\times\)1) values are given in parenthesis

\(^a\) The shortest distance between an adsorbed oxygen species and an Mn or La ion \(\{110\}\) surface

\(^b\) The shortest distance between an adsorbed oxygen species and an Mn or La ion \(\{100\}\) surface

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**Fig. 3** Side view of the optimized geometries of oxygen molecule on \((1 \times 1)\) defective LBM25 \{110\}. Color code: green = La, blue = Ba, purple = Mn, and red = O

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\(E_{\text{ads}}\) = adsorption energy, \(\nu\) = vibrational frequency, \(d\) = bond distance.
Analogous adsorption trends are observed for O$_2$ adsorbed side-on at the bridged La–Mn site (A3, Fig. 3). The adsorption energy of $-3.78$ eV is released in that mode, with $d$(O–Mn) and $d$(O–La) at 1.883 and 2.377 Å, respectively. The $d$(O–O) is significantly elongated (1.50 Å). Compared to the LBM25, O$_2$ adsorbed side-on at the bridge Sr–Mn site releases an energy of $-3.31$ eV on the LSM25 $\{110\}$ surface, while a net charge of $-0.51e^-$ is transferred to the O$_2$ orbital in the bond formation process.

When O$_2$ adsorbate is directly incorporated into the surface oxygen vacancy (A4), an energy of $2.96$ eV is released. The $d$(O–O) in the adsorbate are weakened significantly (1.51 Å). Löwdin population analysis shows a significant charge transfer of $-0.53$ e$^-$ to the adsorbate upon incorporation at the surface oxygen vacant site in the LBM25 substrate. Löwdin population analysis shows a significant charge transfer of $-0.64$ e$^-$ to the adsorbate upon incorporation at the surface oxygen vacant site in the LSM25 substrate (see Table S1) compared with a transfer of $-0.53$ e$^-$ to the adsorbate on LBM25 (Table 2) and 0.76 e$^-$ on LCM25 [10] surface. The trend in charge transfer from the surfaces to the adsorbate follows in the order LCM25 < LSM25 < LBM25.

In all the molecular O$_2$ precursors (A1–A4), the elongated O–O bonds were confirmed to have lower stretching vibrational frequencies: 641, 878, 514, and 490 cm$^{-1}$, respectively, compared to the O$_2$ gas-phase stretching frequencies (1558 cm$^{-1}$). Similar to previous studies [10] the adsorbed molecular oxygen species (A1–A3 in Table 2) were classified based on the $d$(O–O) and $\upsilon$(O–O) either as superoxo and peroxo-like species, which were comparable to O$_2^-$ (1.33 Å) and O$_2^{2-}$ (1.44 Å) ions [40, 41]. Calculated vibrational frequencies for the superoxo and peroxide are reliable to O$_2$–CeO$_2$ experimental values [42].

For the dissociated oxide ions O$_2^{2-}$ on the defective surfaces, three possible pathways were exploited with O$_2^{2-}$ ions adsorbing at the oxygen vacant sites and (i) Top-Mn cation (D1), (ii) Top-La cation (D2), and (iii) Bridged Mn and La sites (D3). We found these configurations shown as D1, D2 and D3 in Fig. 3 are much more active. The dissociation energies are $-5.99$, $-4.80$, and $-7.83$ eV, respectively, for D1, D2 and D3 modes. These energies are exothermic than those calculated for their molecular adsorbed counterparts (A1–A4 in Fig. 3). Dissociated configuration D3 has the highest exothermicity. On the SrMnO-terminated $\{110\}$ surfaces, the dissociative configurations (D1, D2 and D3 in Figure S1) have been found to be more stable and have dissociation energies of $-5.98$, $-3.18$ and $-7.03$ eV. The trend in dissociation energies for the most exothermic dissociated precursors follow the order LBM25 < LSM25 < LCM25 [10]. Hence, defective surfaces of LCM25, LSM25 and LBM25 favors dissociative over associative adsorption. Oxygen dissociation on LBM25 is the most plausible in terms of exothermicity.

Similar to adsorption reactions involving the (1 × 1) surfaces, analogous adsorption trends on the (2 × 1) supercell were investigated (Fig. 4). Reported in brackets in Table 2 are the calculated adsorption energies and the optimized interatomic bond distances. For instance, adsorption
energies of − 1.50, − 4.40, and − 3.34 eV on the (2 × 1) surface were calculated for O2 bound side-on at La cation (A2), bridged-LaMn (A3) and end-on at the oxygen vacant sites (A4), compared to − 1.31, − 3.78 and − 2.96 eV, respectively, reported on the (1 × 1) surface. The dissociation energies (D1 and D2) calculated were highly exothermic compared to their (1 × 1) counterparts. The more exothermic adsorption and dissociation energies calculated on the (2 × 1) compared to the (1 × 1) cells could be due to the lower O2 coverage found on the (2 × 1) cell that reduces repulsive lateral interactions between periodic images. This provides larger surface area for the diffusion of the dissociated O2− ions to locate more stable sites.

To provide atomic-level insight into the effect of Ba doping on the electronic structures of LaMnO3 surfaces and their implication for catalytic reactivity, we have plotted the projected density of states (PDOS) for the LBM25 {110}
surface as shown in Fig. 5. From the projected density of states (PDOS) for the undoped defective and LCM25 {110} surface [10], La ions contribute negligible states at the Fermi level compared to the Mn ions. Since the density of states around the Fermi energy level roughly determines the availability of electrons for a given reaction [43], it can be inferred that the catalytic activity of the LaMnO3 {110} surface should be primarily linked to the surface Mn-\(d\) states. This helps to explain why the Mn sites are more active than the La sites for O2 adsorption. It was also reported that Ca doping resulted in a decrease in the Mn-\(d\) states around the Fermi level relative to the undoped surface. As the Mn-\(d\) states dictates the reactivity of the LaMnO3 {110} surface, a decrease in their intensity signifies weaker O2 binding. This helps to explain why the Ca-doped surfaces have weaker O2-binding energies than the undoped surfaces. As shown in Fig. 5, Ba doping also causes a decrease in the intensity of the Mn-\(d\) states, resulting in weaker O2-binding energies (− 2.25 eV) than the undoped defective surface (− 2.32 eV).

**O2 adsorption on defective LBM25 {100} surface**

Similar to adsorption reactions involving the {110} surfaces, analogous adsorption trends on the {100} surfaces were investigated. For O2 adsorbed on top-Mn cation, no stable end-on configuration is observed because it is changed to a side-on structure after optimization. In that configuration, an adsorption energy of 0.82 eV is released. The formed molecular precursor A1 is accompanied by a slight lengthening of the \(d(\text{O–O})\) to 1.28 Å. The \(d(\text{O–Mn})\) is shorter at 1.850 Å for A1.

For O2 directly incorporated into the surface oxygen vacancy (A2, Fig. 6), the adsorption energy of 1.97 eV is released. The incorporation process is accompanied by a net charge gain of − 0.36e− by the adsorbate from the
oxygen-deficient substrate, which weakens the calculated \(d(O-O)\) to 1.49 Å in relation to the gas phase.

On the \{100\} surface, configuration D1 has the highest adsorption energy, shortest interatomic distance \(d(Mn-O)=1.577\) Å and the \(d(O-O)=2.835\) Å, making this configuration the most stable.

On the \((2 \times 1)\) supercell, the direct incorporation into the surface oxygen vacancy releases an energy of 2.88 eV (Fig. 4, A1). However, when adsorbed at the top-Mn site, either in the end-on or side-on configuration, it is dissociated into oxide ions after geometry optimization. One atomic oxygen is adsorbed on top-Mn cation while the other is incorporated into surface vacant site to give D1. The process releases the energy of 4.12 eV. The calculations indicates that adsorption and dissociation processes of O\(_2\) on both pure and oxygen-deficient LCM25, LSM25 and LBM25 at the \{100\} surface are less competitive than that at the \{110\} surface because of a weaker adsorption. This suggests that the \{110\} surface is catalytically more active for O\(_2\) reduction.

**Gibbs free energies \(\Delta G_{ads}(T, p)\) of the O\(_2\) adsorption/dissociation**

To assess the relevance of the calculated adsorption and dissociation energies of the most stable molecular and dissociated configurations at the typical operating temperatures of SOFCs (T = 500–1100 °C) in SOFCs, we have calculated the Gibbs free energies, \(\Delta G_{ads}(T, p)\) using the Gibbs free energy relation

\[
\Delta G_{ads} = G_{surf+adsorbate} - G_{surf} - N\mu_{gas}
\]

where \(N\) represents the number of molecules adsorbed in the reaction. If the enthalpy or the entropy of the solid is not changed considerably by the presence of the adsorbates, these terms cancel out. The vibrational entropy of the adsorbates, \(S_{vib}^{ads}\), and the coverage-dependent configurational entropy, \(\Delta s_{conf}^{\theta}\), only contribute to entropy of the surface/adsorbate. The vibrational entropy of the adsorbates is given by

\[
S_{vib}^{ads} = Nk_B \left\{ \frac{\beta_i}{e^{\beta_i} - 1} \right\} \ln (1 - e^{-\beta \epsilon})
\]

where \(\beta = \frac{1}{k_B T}\) and \(\epsilon = \sum_i h\nu_i\) is the total vibrational energy of the adsorbent obtained from normal-mode analysis DFT calculations [45], and the coverage-dependent configurational entropy may be included as

\[
\Delta s_{conf}^{\theta} = k_B \ln \left( \frac{1 - \theta}{\theta} \right)
\]

where \(\theta\) is the surface coverage. The expression for the Gibbs energy of adsorption then becomes

\[
\Delta G(T, p) = \Delta E_{ads} + \Delta E_{ZPE}^{ads} - dH_{T,0}^{gas} - T \left( \Delta S_{conf}^{\theta} + S_{vib}^{ads} - S_{gas} \right) - Nk_BT \ln \frac{P}{P_0}
\]

with the adsorption energy defined as \(\Delta E_{ads} = E_{surf} + N\mu_{O2}\), \(p = 0.2\) and \(p_0 = 1\) atm. To account for errors in the binding energies of O\(_2\), 1.36 eV/ O\(_2\) obtained from the fitting of experimental formation enthalpy and calculated oxide formation energies [44] is added to the calculated Gibbs free energies for the most stable molecular and dissociated configurations. The zero-point vibrational energy (ZPE) is calculated as the difference between the ZPE correction of the adsorbate on the surface and in the gas phase according to the following equation:

\[
\Delta E_{ZPE} = \left( \sum_{i=1}^{3n} \frac{\hbar \nu_i}{2} \right)_{surf} - \left( \sum_{i=1}^{3n} \frac{\hbar \nu_i}{2} \right)_{gas}
\]

where \(\hbar\) is the Planck constant and \(\nu_i\) are the vibrational frequencies.

Figure 7 shows the predicted Gibbs free energies against temperature plotted for the most stable molecular and dissociative structures of O\(_2\) on the \{110\} and \{100\} surfaces of LBM25. It is evident from the plot that \(\Delta G_{ads}(T, p)\) is always negative, an indication that the oxygen reduction reaction is feasible at the typical operating temperatures. In addition, it is worth stating that \(\Delta G_{ads}(T, p)\) values become more negative with increasing temperature, signifying that oxygen reduction reactions are more possible at higher temperatures, partly explaining why higher temperatures are involved with SOFCs operations. In addition, the \(\Delta G_{ads}(T, p)\) are more negative on the \{110\} compared to \{100\} surfaces; hence, oxygen reduction reactions are more favored on the \{110\} surfaces at higher temperatures.

**Conclusion**

We have studied the adsorption and reduction of O\(_2\) on the \{110\} and \{100\} surfaces of LSM25 and LBM25 as a SOFC cathode material using the Hubbard-corrected DFT approach. The molecular precursors at the Mn cation sites of LCM25 [10], LSM25 and LBM25 are associated with stronger bonds compared to LaMnO\(_3\) [10], this implies Ca, Sr and Ba as dopants in the cathode influence the O\(_2\) reduction. The trend in the reduction energies at the Mn cation sites are predicted to be in the order LBM25 < LBM25 < LCM25. In addition, the trend in dissociation energies for the most exothermic dissociated precursors follow the order LBM25 < LSM25 < LCM25 [10].
Thus, defective surfaces of LCM25, LSM25 and LBM25 favor dissociative over associative adsorption. The dissociated configurations on the \{110\} and \{100\} surfaces of LCM25, LSM25 and LBM25 have higher energies, showing that these adsorbed configurations are thermodynamically the most stable. The predicted $\Delta G_{\text{ads}}(T, p)$ is negative, suggesting that the oxygen reduction reactions on LCM25 and LBM25 are feasible at any of the typical operating temperatures of SOFCs and consistent with the high temperatures employed in operating conditions SOFCs. The $\Delta G_{\text{ads}}(T, p)$ are more negative on the \{110\} compared to the \{100\} surfaces; hence, oxygen reduction reactions are more favored on the \{110\} surfaces at higher temperatures.

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**Availability of data and material** The coordinate of the optimized structures generated in the manuscript is available from the corresponding author on reasonable request.

**Code availability** Not applicable.

**Declarations**

**Conflict of interest** The authors declare that there is no conflict of interest whatsoever regarding the publication of this manuscript.

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