Oxygen (O₂) reduction reaction on Ba-doped LaMnO₃ cathodes in solid oxide fuel cells: a density functional theory study

Albert Aniagyei¹ · Caroline Kwawu² · Ralph Kwakye¹ · Boniface Yeboah Antwi³ · Jonathan Osei-Owusu⁴

Received: 15 July 2021 / Accepted: 10 October 2021 / Published online: 14 October 2021
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Abstract

The oxygen adsorption and subsequent reduction on the {100} and {110} surfaces of 25% Ba-doped LaMnO₃ (LBM25) have been studied at the density functional theory (DFT) with Hubbard correction and the results compared with adsorption on 25% Ca-doped LaMnO₃ (LCM25) and Sr-doped LaMnO₃ (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 (− 2.14 to − 2.41 eV) calculated for the molecular O₂ precursors at the Mn cation sites of LCM25, LSM25 and LBM25 are thermodynamically stable, when compared directly with the adsorption energies ($E_{ads} = -0.56$ to -1.67 eV) reported for the stable molecular O₂ 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 · LaMnO₃

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.

✉ Albert Aniagyei
aaniagyei@uhas.edu.gh

Caroline Kwawu
kwawucaroline@gmail.com

Ralph Kwakye
kwakyer@uhas.edu.gh

Boniface Yeboah Antwi
boni.antwi@yahoo.com

Jonathan Osei-Owusu
oseiowusuansahjoe@gmail.com

¹ Department of Basic Sciences, University of Health and Allied Sciences, Ho, Ghana

² Department of Chemistry, Kwame Nkrumah University of Science and Technology, Kumasi, Ghana

³ Institute of Industrial Research, Council for Scientific and Industrial Research, Accra, Ghana

⁴ University of Environment and Sustainable Development, Somanya, Ghana

Perovskite-type oxides such as LaMnO_3 have attracted attention for applications built upon their unique electronic and magnetic features. For example, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ 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 ($x = 0.2 - 0.3$), $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$ 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, Aniahyei 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.

$\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ 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]. $\text{La}_{1-x}\text{Ba}_x\text{MnO}_3$ 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, to 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_{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 $Pm\bar{3}m$ 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:

$$E_{\text{ads}} = E_{\text{surface}+\text{O}_2} - (E_{\text{surface}} + E_{\text{O}_2}) \quad (1)$$

where $E_{\text{surface}+\text{O}_2}$ is the total energy of the substrate–adsorbate system in the equilibrium state, and E_{surface} and E_{O_2} are the total energies of the substrate (clean surface) and

adsorbate (free O₂ molecule in the spin triplet state), respectively.

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, LBM25 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

Table 1 Calculated oxygen vacancy formation energies (in eV) of LaMnO- {110} and MnO₂-terminated {100} LBM25 surfaces with Hubbard U correction (U_{eff} = 4 eV)

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
LaMnO ₃	4.23	3.60

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

Fig. 1 (Top) A is BaMnO-terminated and B–D are LaMnO-terminated {110} surface models. (Down) MnO₂-terminated {100} LBM25 models. Color code: green = La, blue = Ba, purple = Mn, and red = O

the MnO_2 terminated $\{100\}$ and model B of the LaMnO -terminated $\{110\}$ with the La ion in/near the topmost layers (Fig. 1) were found to have the lowest oxygen vacancy formation energies; thus, we chose these two models for subsequent studies of O_2 –LBM25 interactions.

In this work, molecular or dissociative chemisorption of O_2 on (1×1) and (2×1) surface models at various coverages of $\theta = 0.25$ 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 O_2 adsorption.

O_2 adsorption on the oxygen-deficient LBM25 $\{110\}$ surface

For O_2 adsorption on the $\{110\}$ surface with coverages of $\theta = 0.25$ ML and 0.50 ML, molecular and dissociative scenarios for the selected (1×1) and (2×1) surface models were considered. Substitution of host La^{3+} with Ba^{2+} cation creates a defective surface with a vacant oxygen site. Similar to the undoped surface [10], different adsorption configuration and modes were exploited at the $\{110\}$ and $\{100\}$ surfaces, that may serve as precursors for O_2 dissociation. Figure 3 shows the optimized adsorption structures, while the adsorption energies, Löwdin atomic charges, interatomic bond distances and vibrational stretching frequencies are presented in Table 2.

For O_2 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 molecular precursor **A1** is accompanied by significant charge transfer ($-0.34 e^-$ from the substrate) to the O_2 orbital, weakening and elongating the $d(\text{O}-\text{O})$ to 1.45 Å compared to gas phase and experimental $d(\text{O}-\text{O})$ of 1.23 and 1.21 Å [34], respectively. For A1, the shortest interatomic distance $d(\text{O}-\text{Mn})$ is 1.838 Å. On the LSM25 surface, O_2 adsorbed end-on and side-on at the Mn sites, and exothermicities of 1.59 and 2.41 eV were calculated and the $d(\text{O}-\text{O}) = 1.357$ and 1.449 Å, respectively (Table S1 and Figure S1). In both molecular processes, the $d(\text{O}-\text{O})$ 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 stable, when compared directly with the adsorption energies ($E_{\text{ads}} = -0.56$ to -1.67 eV) reported for molecular O_2 precursors on the Pt, Ni, Pd, Cu and Ir $\{111\}$ surfaces [35, 36]. This indicates that LCM25, LSM25 and LBM25 cathode materials may be more efficient for O_2 activation than the transition metal surfaces. In addition, since molecular precursors at the Mn cation sites of LCM25, LSM25 and LBM25 are associated with stronger bonds compared to LaMnO_3 [10], this implies Ca, Sr and Ba as dopants in the cathode influences the O_2 reduction. The trend in the reduction energies on the Mn cation sites are predicted to be in the order $\text{LSM25} < \text{LBM25} < \text{LCM25}$.

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

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

Table 2 Calculated adsorption energies (E_{ads}), Charge (q), relevant bond distances (d) of molecular (O_2) oxygen on defective {110}-(1×1) surface of LBM25; O–O stretching vibrational frequency (ν) of the adsorbed O_2 ; and calculated gas-phase $d(O-O)=1.229$ Å and the $\nu(O-O)=1558$ cm⁻¹

Surface	Config	E_{ads} (eV)	$ q $ (e ⁻)	$d(O-Mn)^a$ (Å)	$d(O-La)^b$ (Å)	$d(O-O)$ (Å)	$\nu(O-O)$ (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 (1.500)	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 (2×1) values are given in parenthesis

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

For 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 O_2 molecule experiences a net charge of - 0.29 e⁻ and $d(O-O)$ 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 $d(O-Mn)=1.838$ Å than $d(O-La)=2.324$ 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 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].

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 while the reduction energetics at the surface vacant sites follows the order LBM25 < LCM25 < LSM25.

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 $\nu(O-O)$ 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 superoxide and peroxide are reliable to O_2 –CeO₂ experimental values [42].

For the dissociated oxide ions O^{2-} on the defective surfaces, three possible pathways were exploited with O^{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

Fig. 4 Side views of the optimized geometries of oxygen molecule on defective (2 × 1)-{110} (top) and {100} (down) LBM25

energies of -1.50 , -4.40 , and -3.34 eV on the (2×1) surface were calculated for O_2 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 O_2 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 O^{2-} ions to locate more stable sites.

To provide atomic-level insight into the effect of Ba doping on the electronic structures of $LaMnO_3$ surfaces and their implication for catalytic reactivity, we have plotted the projected density of states (PDOS) for the LBM25 $\{110\}$

Fig. 5 Projected density of states of (PDOS) of 25% Ba-doped $LaMnO_3$ (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 $LaMnO_3$ $\{110\}$ 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 O_2 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 $LaMnO_3$ $\{110\}$ surface, a decrease in their intensity signifies weaker O_2 binding. This helps to explain why the Ca-doped surfaces have weaker O_2 -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 O_2 -binding energies (-2.25 eV) than the undoped defective surface (-2.32 eV).

O_2 adsorption on defective LBM25 $\{100\}$ surface

Similar to adsorption reactions involving the $\{110\}$ surfaces, analogous adsorption trends on the $\{100\}$ surfaces were investigated. For O_2 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 (O–O) to 1.28 Å. The d (O–Mn) is shorter at 1.850 Å for A1.

For O_2 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

Fig. 6 Side view of the optimized geometries of oxygen molecule on (1×1) defective LBM25 $\{100\}$. Color code: green=La, blue=Ba, purple=Mn, and red=O

oxygen-deficient substrate, which weakens the calculated $d(\text{O}-\text{O})$ to 1.49 Å in relation to the gas phase.

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

On the (2×1) 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 indicate 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

$$\Delta G^{ads} = G^{surf+adsorbate} - G^{surf} - N\mu_{gas} \quad (3)$$

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, ΔS_{conf}^{θ} , only contribute to entropy of the surface/adsorbate. The vibrational entropy of the adsorbates is given by

$$S_{vib}^{ads} = Nk_B \left\{ \frac{\beta \epsilon}{e^{\beta \epsilon} - 1} \right\} \ln(1 - e^{-\beta \epsilon}) \quad (4)$$

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

$$\Delta S_{conf}^{\theta} = k_B \ln \left(\frac{1 - \theta}{\theta} \right) \quad (5)$$

where θ is the surface coverage. The expression for the Gibbs energy of adsorption then becomes

$$\Delta G(T, p) = \Delta E^{ads} + \Delta E_{ZPE}^{ads} - dH_{T,0}^{gas} - T \left(\Delta S_{conf}^{\theta} + S_{vib}^{ads} - S_{gas} \right) - Nk_B T \ln \frac{p}{p_0} \quad (6)$$

with the adsorption energy defined as $\Delta E^{ads} = E^{(surf+O_2)} - E^{surf} - NE^{O_2}$, $p = 0.2$ 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:

$$\Delta E_{ZPE}^{ads} = \left(\sum_{i=1}^{3n} \frac{h\nu_i}{2} \right)_{surf} - \left(\sum_{i=1}^{3n} \frac{h\nu_i}{2} \right)_{gas} \quad (7)$$

where h is the Planck constant and ν_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 influences the O_2 reduction. The trend in the reduction energies at the Mn cation sites are predicted to be in the order $\text{LSM25} < \text{LBM25} < \text{LCM25}$. In addition, the trend in dissociation energies for the most exothermic dissociated precursors follow the order $\text{LBM25} < \text{LSM25} < \text{LCM25}$ [10].

Fig. 7 Gibbs free energies ΔG (T, p) of the most stable molecular ($^m\text{O}_2$) and dissociative ($^d\text{O}_2$) structures at {110} and {100} surfaces of defective 25% Ba-doped LaMnO_3 (LBM25). Color code: A = ΔG (eV) $^d\text{O}_2$ at LBM25 {110}; B = $^m\text{O}_2$ at LBM25 {110}; C = $^d\text{O}_2$ at LBM25 {100}; D = $^m\text{O}_2$ at LBM25 {100}

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 ΔG^{ads} (T, p) is negative, suggesting that the oxygen reduction reactions on LCM25 [10] 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 ΔG^{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.

Author contributions All the authors contributed equally to the preparation of the manuscript. AA performed the theoretical calculations. The initial draft of the manuscript was written by AA with input and suggestions from all the co-authors. All the authors commented on previous versions and approved the final manuscript.

Funding The authors gratefully acknowledge the UK Royal Society and the Leverhulme Trust for a research grant under the Royal Society-Leverhulme Africa Award Scheme.

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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