The Interaction of Molecular Oxygen on LaO Terminated Surfaces of La$_2$NiO$_4$

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ABSTRACT

Rare-earth metal oxides with perovskite-type crystal structures are under consideration for use as air electrode materials for intermediate to high temperature electrochemical device applications. The surface chemistry of these materials plays a critical role in determining the kinetics of oxygen reduction and exchange reactions. Among various perovskite-structured oxides, certain members of the Ruddlesden-Popper series, e.g. La$_2$NiO$_4$, have been identified as significantly active for surface oxygen interaction. However, the challenge remains to be the identification of the structure and composition of active surfaces, as well as the influence of these factors on the mechanisms of surface exchange reactions. In this contribution, the changes in electronic structure and the energetics of oxygen interaction on surfaces of La$_2$NiO$_4$ are analysed using first principle calculations in the Density Functional Theory (DFT) formalism. As for the surface chemistry, the LaO termination rather than the NiO$_2$ is presumed due to recent experimental evidence for the surfaces of various perovskite structured oxides after heat treatment in oxidizing environments being transition metal free. Our findings substantiate that the LaO terminated surface can indeed participate in the formation of the surface superoxo species. Detailed charge transfer analyses revealed that it is possible for such a surface to be catalytically active owing to the enhanced electronic configurations on neighbouring La sites to surface species. In addition, positively charged oxygen vacancies, relative to the crystal lattice, can act as active sites and catalyse the O-O bond cleavage.

Keywords

Perovskite surfaces, Ruddlesden-Popper phases, oxygen reduction, electro-catalysis, Density Functional Theory.

1. INTRODUCTION

Mixed ionic electronic conducting (MIEC) materials are attracting considerable attention to overcome performance limitations of low to intermediate temperature electrochemical devices for catalytic gas conversion, oxygen separation, and power generation applications. All these applications require selectively active components made up of materials with substantial oxygen ion and electron transport properties accompanied by high interfacial activity for electro-catalytic oxygen reduction and incorporation. Such properties are often found in complex oxides possessing perovskite type crystal structures. The Ruddlesden-Popper (RP) series of compounds, represented by the general formula of A$_{n+1}$B$_n$O$_{3n+1}$ ($n$=1, 2, 3 ...), form a large group of materials with intriguing properties due primarily to distinct crystallographic layers. Here, A and B
cations represent the lanthanides (or rare earth metals) and the first row transition metals respectively. The crystal structure of these series are composed of alternating rock-salt (AO) and \( n \) consecutive perovskite (ABO\(_3\)) layers along the long axis. The first member of one RP series, La\(_2\)NiO\(_4\) is a promising MIEC cathode material possessing fast oxygen transport properties.\(^2\)-\(^6\) La\(_2\)NiO\(_{4+\delta}\) has two structural polymorphs, the phase stability of which are dependent on temperature and oxygen non-stoichiometry (\(\delta\)). At temperatures above 700K, it crystallises as a tetragonal polymorph belonging to \(I4/mmm\) space group symmetry, whilst below 700K, the crystal structure is found to be orthorhombic possessing \(Bmab\) space group symmetry.\(^7\),\(^8\) The most important consequence of the layered nature of the La\(_2\)NiO\(_4\) is the ability to accommodate varying degrees of over-stoichiometry (0 < \(\delta\) < 0.2) through oxygen intercalation into the LaO rock-salt bilayers. Interstitial oxygen ions largely contribute to the conduction of charge carriers via the rapid diffusion mechanism along the apical positions of NiO\(_6\) corner sharing octahedra in the perovskite layers.\(^9\)-\(^13\)

In solid oxide fuel and/or electrolyser cells (SOFCs & SOECs), the most important requirement for achieving high conversion efficiencies at low to intermediate operating temperatures is identified as the facile kinetics of electrode reactions. In particular, the oxygen reduction reaction (ORR) is considered a major rate limiting factor for intermediate temperature operation.\(^14\)-\(^16\) Despite concerted experimental and theoretical efforts, the knowledge as to the actual mechanism of the ORR on such electrode material surfaces is relatively scarce. In addition, the experimental information on the surface structure and composition at operating temperatures of SOFC and steam electrolyser are somewhat uncertain. Although the claims lack experimental validation, it is widely assumed that the outer most layer of the perovskite structured oxide electrodes are generally made up of B-site cations and O anions (\textit{i.e.} “BO\(_2\) terminated”), owing to the anticipated high catalytic activity of the transition metal cation. Only recently, it has been shown that the surfaces of perovskite and perovskite-related oxides are dominated by AO termination at SOFC cathode operating conditions.\(^17\)-\(^21\) The discovery represents a significant challenge for computational science which has to elucidate the chemical mechanisms that take place on that particular surface termination.\(^22\),\(^23\) In addition, theoretical investigations suggest that relative stabilities of surfaces of perovskite related oxides are energetically equivalent for both terminations.\(^24\),\(^25\)

In an earlier investigation employing first principle techniques, the interaction of an oxygen molecule with La\(_2\)NiO\(_4\) surfaces was reported by Zhou \textit{et al}.\(^26\) In their work, the mechanisms of
oxygen adsorption were elucidated on model surfaces cleaved along <100> direction. Hence, all defect free and defective surfaces in that study, included Ni$^{2+}$ cations which further activated the chemisorbed O$_2$ molecule to superoxo or peroxo state by readily donating electrons. In addition, Zhou et al. elucidated that the positively charged oxygen vacancies would significantly increase the O-O bond distance which might lead to oxygen dissociation.

Recently, we used the DFT approach to investigate the oxygen reduction reaction on the SrO-terminated surfaces of SrTiO$_3$ and SrTi$_{0.75}$Fe$_{0.25}$O$_3$. Experimental observations made by Low Energy Ion Scattering (LEIS) spectroscopy measurements, which can determine the elemental composition of the outermost layer,$^{27}$ identified the stable surfaces of these materials at elevated temperatures as predominantly SrO terminated. Our analyses have shown that the oxygen molecule is not activated by the defect free surface and the reaction is highly endothermic (3.4 eV). This is attributed to the rather inert character of the A-site (Sr) cation when participating in the electron exchange with adsorbed species. The low energy defective surfaces characterised by oxygen vacancies, on the other hand, are found to be active for producing superoxo species as a result of interaction between the $d_{z^2}$ atomic orbitals of the subsurface Ti cation (below the oxygen vacancy) and the $\pi^*$ molecular orbital of the O$_2$ molecule.

The objective of the present study is to shed light to our understanding on the reactivity of La$_2$NiO$_4$ surfaces with oxygen by using atomistic simulations. DFT calculations are carried out for diatomic oxygen over the LaO terminated (001) surface. The effect of surface defects, characterised by oxygen vacancies, on the energetics of the oxygen adsorption and dissociation reaction on this particular termination is also elucidated. The catalytic activity of both defect free and defective surfaces are studied on a model structure based on the tetragonal polymorph of La$_2$NiO$_4$. Our purpose is to compare the oxygen dissociation reaction mechanisms on the SrO terminated surface of SrTiO$_3$ and the LaO terminated surface of La$_2$NiO$_4$. Although both surfaces are terminated by their respective A-site cations, with both Sr and La being large and inert cations, there is an important difference in their electronic structure. Sr has the electronic configuration of [Kr]$5s^2$ while La has the electronic configuration of [Xe]$5d^16s^2$. The d-electron occupancy in the valence shell of La allows for polarisation of the shell, including polarisation or partial hybridisation of the 6s orbitals and easier interaction with the $\pi$-shape frontier orbitals of the oxygen molecule. This interesting difference, and the reported data in the literature for the superior performance of La-based perovskites as oxygen electrode materials for SOFC and SOEC, motivated us to elucidate the differences in the reactivity of those surfaces.
2. COMPUTATIONAL METHOD

Electron configurations and energetics of a series of model structures were calculated by using the spin polarised plane wave DFT method with the generalised gradient approximation (GGA) parametrised by Perdew-Berke-Ernzerhof as implemented in the Vienna \textit{ab initio} Simulation Package (VASP).\textsuperscript{29-32} Projector augmented wave (PAW) pseudopotentials with a kinetic energy cutoff of 520 eV were employed.\textsuperscript{33, 34} In order to accurately describe the strong correlation effects for the transition metal (Ni), a rotationally invariant GGA+U approach (as introduced by Dudarev) was used with an effective Hubbard parameter of 6 eV.\textsuperscript{35, 36} A 3 x 3 x 3 Gamma centered \textit{k}-point mesh with Blöchl corrections was used to sample the Brillouin zone when optimizing the tetragonal unit cell.\textsuperscript{37} The VESTA software package was utilised for the analysis and visualisation of the structures and the electron density distributions computed by DFT.\textsuperscript{38}

The La$_2$NiO$_4$ surface is represented by a slab supercell made up of 2 x 2 x 4/3 unit cells, which was utilised for all the simulations to probe the energetics of the surface reaction. In order to obtain a symmetric slab with no net dipole moment perpendicular to its surface, 9 alternately charged planes (3 x (LaO-NiO$_2$-LaO)) are stacked along the <001> axis. A vacuum layer of 12 Å is placed over the slab to avoid interaction between neighbouring supercells. A 3 x 3 x 1 \textit{k}-point mesh was found to be convergent for accurate sampling of the supercell. The coordinates of ions in the bottom two planes were constrained to the optimised bulk positions while the rest are allowed to relax fully. The adsorption of oxygen gas was examined by placing one oxygen molecule per 2 x 2 unit cell surface area, roughly corresponding to a surface coverage of 25%.

Two distinct 2 x 2 surface models were constructed: a defect free slab with stoichiometric number of ions and a defective slab with one oxygen ion removed from each of the top and the bottom layers of the slab. The convergence criteria for electronic self-consistency and ionic relaxation cycles were set as 10$^{-4}$ eV/atom and 10$^{-2}$ eV/Å respectively. Ferromagnetic (FM) ordering was chosen as the initial magnetic moment configuration for all atoms in the model structure. Bader population analysis was performed on the charge density grid to calculate the effective atomic charges.\textsuperscript{39}

The energy barriers for oxygen dissociation were calculated by employing the climbing image nudged elastic band (CI-NEB) method.\textsuperscript{40-45} In order to map the potential energy barriers, six linearly interpolated images were generated as intermediate structures between the two energetically stable start and end configurations, corresponding to the adsorbed and dissociated
states of oxygen on the model surface respectively. Only ions were allowed to relax, with the lattice vectors kept fixed during the NEB calculations.

3. RESULTS & DISCUSSION
Figure 1a depicts the optimised geometry of the La$_2$NiO$_4$ crystal. The lattice parameters of the fully relaxed unit cell of the bulk La$_2$NiO$_4$ crystal structure were calculated as $a = b = 3.904$ Å, $c = 12.539$ Å, and $\alpha = \beta = \gamma = 90^\circ$, which are within 1% error from reported experimental data.$^2$

No noticeable change is observed in the fractional coordinates of the ionic positions in the relaxed structure. The tetragonal distortion (Jahn-Teller distortion) measured by the ratio of bond lengths of Ni-O$_a$ (2.238 Å) to Ni-O$_e$ (1.952 Å) is found as 1.15 (O$_a$ and O$_e$ are used to denote the apical and the equatorial oxygens in the NiO$_6$ octahedron respectively). This causes a change in the surface electronic structure with significant charge redistribution between Ni, La and O$_a$ atoms. The fully relaxed slabs for defect free and defective surfaces, shown in Figures 1b and 1c, followed a well-established trend for cleaved surfaces with contraction in the surface layer and expansion in the sub-surface layer towards vacuum.

![Figure 1](image)

**Figure 1.** (a) La$_2$NiO$_4$ crystal lattice, (b) LaO terminated slab models of defect-free 2 x 2 (001) surface, and (c) defective 2 x 2 (001) surface. Oxygen vacancies are placed on the top and bottom layers of the defective slab in body diagonal fashion to maximise the distance between them. La is depicted green, Ni is depicted grey, O is denoted red.
As described by Tasker, the charged surfaces of ionic solids with a net dipole moment have an infinitely large surface energy. Therefore, these surfaces cannot exist and their natural occurrence require major reconstruction involving foreign species and/or defect restructuring to stabilise them. Tasker categorised charged surfaces into three distinct types according to the stacking sequences and the total electrostatic potentials of subsurface layers. When the sum of electrostatic potentials over anionic and cationic sublattices on individual planes of an ionic crystal is zero, the surface is labelled as type 1 and has no net dipole moment perpendicular to it. If the crystal is made up of charged subsurface layers grouped and stacked in symmetrical configurations, the Madelung sums for the potential of any lattice site becomes finite with a diminishing overall dipole moment perpendicular to its surface. Such surfaces are referred to as type 2 surfaces according to Tasker’s classification. Type 3 surfaces, however, have finite dipole moment values perpendicular to them due to the charged subsurface layers stacked in non-symmetrical fashion.

In this work, both defect free and defective LaO terminated surfaces are obtained by cleaving the bulk crystal along the <001> direction. Since the individual subsurface layers perpendicular to the long axis are not neutral, the slab model is created as a type 2 Tasker surface with 9 alternating layers composed of 3 LaO double layers and 3 NiO$_2$ layers while maintaining the symmetry to eliminate the net dipole moment perpendicular to its surface. Even though the LaO terminated surfaces can also be stabilised by La vacancies, as described for the case of LaAlO$_3$, here we have chosen the cation defect free termination as a simplified model of the real surface.

3.1 Oxygen adsorption on LaO terminated defect-free (001) surface:

Gaseous oxygen is one of the few molecules characterised by a high-spin ground state and low-spin excited state. The reason for this lies in the electronic structure of di-oxygen, which is characterised by two degenerate antibonding $\pi^*$ molecular orbitals formed by out of phase overlap between the 2p atomic orbitals on the oxygen atoms. The $\pi^*$ molecular orbitals are spatially orthogonal with zero overlap which leads to the high stability of the triplet spin state of O$_2$ with a single electron occupying each $\pi^*$ molecular orbital. The O-O bond distance for an isolated O$_2$ molecule is 1.21 Å. The triplet O$_2$ interacts with the surface magnetic moment implying that the adsorption and dissociation reactions would involve various spin state
In order to participate in a chemical reaction, the symmetry of the $\pi^*$ molecular orbitals should be broken either by thermal or irradiative oxidation to the less stable singlet excited state, or through electron transfer to one or both $\pi^*$ molecular orbitals. A single electron transferred to the $O_2$ molecule leads to the highly reactive superoxo state which is an anion radical ($O_2^-$), and two electrons transferred to the $O_2$ molecule lead to the mildly oxidant peroxo state ($O_2^2$). As both the $\pi^*$ molecular orbitals of $O_2$ are a result of out-of-phase overlap of the 2p atomic orbitals on the oxygen atoms, any additional electron occupation of those orbitals leads to repulsion between the oxygen atoms and would be a precursor state for oxygen dissociation. In the superoxo state, the O-O bond length is 1.3~1.4 Å, whilst in the peroxo state, the O-O bond length is 1.4~1.6 Å. The relative orientation of the $O_2$ molecule with respect to the surface also becomes an important factor to determine the energetically most favorable path to transfer charge from the surface to the $\pi^*$ orbitals.

A number of distinct geometric orientations for the $O_2$ molecule are considered in this study. For all cases, the $O_2$ molecule is placed 2 Å above the surface with an initial guess of triplet spin state. The initial magnetic state of the slab, on the other hand, is assumed to be ferromagnetic. Among all calculated adsorption geometries, two energetically favorable orientations with side-on configurations are determined. The first corresponds to the adsorption of $O_2$ to the slip position on a La atom and the second one corresponds to adsorption to a La-La bridge as depicted in Figures 2a and 2b respectively.
Figure 2. (a) Top view of the defect free La$_2$NiO$_4$ slab with adsorbed O$_2$ on the slip position, and (b) on the La-La bridge position. (c) & (d) Electron probability density distribution contours around the adsorbed oxygen. Colour scale: Blue=0, Red=0.15 Å$^3$. (e) & (f) Electron density difference plots for the chemisorbed oxygen. Positive and negative electron density differences are denoted by blue and yellow respectively. The adsorbed O$_2$ molecule is depicted as purple and only the top perovskite layer of the slab is shown for clarity.

The total energies of the La$_2$NiO$_4$ slab with O$_2$ adsorbed to a slip position on La and side on to a La-La bridge position were calculated as -625.94 eV and -625.80 eV respectively. The energies in both geometries are comparable, but the O$_2$ chemisorbed on the slip position is found to be slightly more stabilised (~0.14 eV). The O-O bond length for O$_2$ on the slip position is 1.46 Å. Similarly, the bond length of O$_2$ on the La-La bridge position is 1.33 Å. This suggests that the adsorbed oxygen at bridge position is in the superoxo activated state, while in the slip position it is further activated to the peroxo state. The distances between either of the O and the nearest La atom for each configuration are 2.39 Å and 2.53 Å respectively.
The charges within the slab and the electron transfer to the chemisorbed oxygen molecules on the surface was estimated by applying Bader population analysis (Atoms in Molecules method). Interestingly, the average charge of La in the lattice is found to be +2, the charge of Ni is +1.3, the charge of lattice O is -1.3 and the charges of the oxygen atoms in the oxygen molecule are -0.47 and -0.27 for the La-La bridge case, and -0.69 and -0.58 in the slip position. The Bader charges are lower than the formal charges of La$_2$NiO$_4$ where La, Ni, and O are assumed to have charges of +3, +2, and -2, respectively. The difference between the formal ionic charges and the estimated Bader charges shows the significant degree of covalent bonding within the lattice and resulting from shared electron pairs. It is important to note that not only Ni but also La deviates from its formal ionic charge. Such an effect was not observed in SrTiO$_3$ where the A-site cation Sr has Bader charge corresponding to its formal ionic charge +2.27 The ionicity of the Sr excludes it from the shared electron network of TiO$_2$ and prevents it from mediating possible charge transfer between Ti and any species adsorbed on the SrO surface. In case of La$_2$NiO$_4$ the Bader analysis shows that the La is an active part of the shared lattice electron network. The charge on the oxygen molecule is -0.74 for the La-La bridge and -1.27 for the slip position. Those results show that for the La-La bridge position the oxygen molecule has an electronic structure close to superoxo state while in the slip position its electronic structure is closer to peroxo state. The Bader analysis of the atoms within the lattice suggests the electron density is donated from the electronic structure of the entire lattice and not from a given species on the surface. Analysing the charge density plots in Figures 2c and 2d we can conclude that shared electron density exists between the oxygen atoms from the oxygen molecule and the La atoms on the surface, suggesting that the O$_2$ adsorption is indeed a stable chemisorption state. Such stable chemisorption was not found for SrTiO$_3$, which is another manifestation for the improved catalytic activity of the LaO surface$^{50-53}$ compared to the SrO surface related to the electronic properties of La. Analysis of the electron probability density in Figures 2c and 2d suggests an overlap between the oxygen $\pi^*$ molecular orbital and the d-orbitals of the La atoms.

This assumption is further proved by the electron density difference plots in Figures 2e and 2f where the electron density between the oxygen atoms of the oxygen molecule is reduced and the electron density of the $\pi^*$ molecular orbital is increased. In Figures 2e and 2f positive electron density is denoted in blue and negative electron density is denoted by yellow. It is important to note that electron density is donated not only from the surface La atoms but also from the NiO$_2$ (BO$_2$) network in the subsurface layer, which acts as an electronic reservoir for the dissociative adsorption process, mediated by La atoms in the terminating surface layer.
In addition to the above-mentioned minimum energy geometries for the chemisorption of an oxygen molecule, a variety of possible configurations for the dissociated oxygen atoms were tested. Among these, the minimum energy configurations were found to involve monoatomic oxygen on a bridge site between two La atoms as shown in Figures 3a and 3b. Total energies of the La$_2$NiO$_4$ slab are calculated as -625.84 eV, and -624.24 eV respectively for these configurations, both of which higher than the energy of the chemisorbed O$_2$ on the surface.
**Figure 3.** (a) – (b) Top views of the defect free $\text{La}_2\text{NiO}_4$ slab with dissociated oxygen on La-La bridge positions of the LaO terminated (001) surface. (c) – (d) Electron probability density distribution contours around the dissociated oxygen. Colour scale: Blue=0, Red=0.15 Å$^{-3}$. (e) - (f) Electron density difference plots for the dissociated oxygen. Positive and negative electron densities are denoted by blue and yellow respectively. The dissociated oxygen atoms are depicted as purple.

Figures 3c and 3d show the electron density map of the adsorbed oxygen atoms over the $\text{La}_2\text{NiO}_4$ LaO terminated surface. Both density maps suggest that there is binding interaction between surface La atoms and the adsorbed oxygen atom characterised by electronic density shared between the La and O nuclei. Such interaction was not found in case of SrTiO$_3$. The adsorbed oxygen on the SrTiO$_3$ was highly reactive, with a tendency to recombine into molecular oxygen, and was the main reason why the defect free SrTiO$_3$ could not participate in the oxygen activation reaction. The reason was that Sr atoms could not stabilise the atomic oxygen by electron transfer. However, La on the surface could donate electron density to the atomic oxygen and thus stabilise dissociated oxygen atoms on the surface. Bader analysis indicates the charge of the oxygen atom on the surface is -1 electron. The assumption that La on the surface plays a stabilising role is further supported by the electron density difference plots depicted in Figures 3e and 3f. In both figures it can be seen that negative electron density (denoted with yellow colour) at La atoms points towards the adsorbed oxygen atoms and positive electron density (denoted with blue colour) is localised at the adsorbed oxygen atoms. The electron density difference maps clearly demonstrate the charge transfer from surface La atoms to adsorbed oxygen atoms, stabilising the surface oxygen species.
Figure 4. Results of the transition state analysis between the chemisorbed O$_2$ on the slip position and the dissociated oxygen on the La-La bridge position on defect free surface. The reference energy configuration is the approach of molecular oxygen to the surface. The activation energy for the forward reaction is 1.35 eV while the backward reaction requires 0.25 eV.

In order to probe the energetics of transition states between the chemisorbed O$_2$ at the slip position and the dissociated oxygen, the CI-NEB analyses were performed. The energy diagram is shown in Figure 4. The reference energy is chosen as the energy of the slab with the oxygen molecule 3.3 Å above the surface, at which distance the interaction between the oxygen molecule and the surface can be neglected. As the oxygen molecule approaches the surface, the energy decreases by 0.73 eV, showing that the surface has strong affinity towards oxygen chemisorption. The oxygen molecule is chemisorbed on a La-slip site. This energy calculation verifies our electronic density analysis in Figure 2c, showing that a binding interaction between the surface and the oxygen molecule occurs, and the binding strength corresponds to 0.73 eV. The transition state for the oxygen dissociation has an energy barrier of 1.35 eV which is comparable to the barrier estimated from a similar analysis on the surface of SrTiO$_3^{27}$, and with experimental results reported in the literature.$^{54,55}$ The dissociated oxygen atoms are stabilised compared to the transition state energy by 0.25 eV, which is the main difference from the dissociation mechanism on the SrTiO$_3$ surface where such stabilisation was not observed. The lowest energy is estimated for the chemisorbed oxygen molecule on the LaO surface and while
the LaO terminated La$_2$NiO$_4$ surface can dissociate oxygen, the lower activation barrier for the reverse reaction shows that the surface would tend to favour oxygen evolution.

Figure 5. Results of the transition state analysis between the chemisorbed O$_2$ on the La-La bridge position and the dissociated oxygen on the La-La bridge position on defect free surface. The reference energy configuration is the approach of molecular oxygen to the surface. The activation energy for the forward reaction is 1.095 eV while the backward reaction requires 0.535 eV.

Another possible reaction path is shown in Figure 5 with the oxygen molecule being chemisorbed on the La-La bridge site. Similar to the case represented in Figure 4, the reference energy was chosen to be the oxygen molecule at 3.3 Å above the surface. As a result of the chemisorption, the energy was stabilised by 0.59 eV which is slightly lower than that of the chemisorption at a La slip position (0.73 eV). The oxygen dissociation from this configuration requires an energy barrier of 1.09 eV. The activation barrier for the reverse reaction is 0.53 eV. It is worth noting that the energy of the end product is lower compared to the previous case shown in Figure 4, -0.03 eV and 0.37 eV, respectively. This difference can be attributed to the separation between the two dissociated oxygen atoms on the surface. In the case of the La slip position (Figure 4) the two dissociated oxygen atoms are stabilised by electron transfer from three surface La atoms while in the case of the La-La bridge site (Figure 5), the two dissociated oxygen atoms are stabilised by electron transfer from two surface La atoms. This result shows
that the dissociated oxygen atoms on the La$_2$NiO$_4$ surface tend to occupy distant positions in order to withdraw maximum electron density from the surface.

### 3.2 Oxygen adsorption on LaO terminated defective (001) surface:

Moving on from the ideal surfaces discussed above, we investigated O$_2$ adsorption on defective surface by using a La$_2$NiO$_4$ slab with an oxygen vacancy on its LaO terminated (001) surface. Similar to the previously presented cases for the defect free slab, a number of different initial geometric orientations for the O$_2$ molecule were considered (see the Supporting Information). All possible starting configurations converged to the final end-on O$_2$ configuration as depicted in Figure 6a. One of the oxygen atoms of the molecule occupy the vacant site, while the second one points towards the La-La bridge. The oxygen-oxygen bond within the oxygen molecule is 1.5 Å which suggests that surface-molecule electron transfer has occurred and the oxygen molecule has been activated to the peroxo state. The bond distance between the Ni atom beneath the oxygen vacancy and the oxygen atom from the oxygen molecule is 2.2 Å, which is close to the nominal Ni-O distance at the surface (2.1 Å). Figure 6c shows a cut plane through the total electron density displaying the O-O bond and the electronic interaction between the oxygen molecule, the Ni beneath the oxygen vacancy, and the neighbouring La atoms.
Figure 6. (a) Top view of the defective La$_2$NiO$_4$ slab with O$_2$ adsorbed onto the oxygen vacancy, (b) incorporated oxygen into the vacancy and dissociated oxygen atoms on the La-La bridge position. (c) – (d) Electron probability density distribution contours around the incorporated and adsorbed oxygen. Colour scale: Blue=0, Red=0.15 Å$^{-3}$. (e) - (f) Electron density difference plots for the chemisorbed oxygen. Positive and negative electron densities are denoted by blue and yellow respectively.

The electron density forming the O-O bond within the oxygen molecule can be clearly seen, verifying the oxygen molecule has not yet dissociated. Additional weak interaction can be seen between the Ni and the O atoms which is similar to the Ti-O interaction estimated previously for iron doped SrTiO$_3$. A major difference between the La$_2$NiO$_4$ and SrTiO$_3$ is that the surface La atoms interact with the oxygen molecule, supporting the surface molecule chemisorption. In the case of SrTiO$_3$ such interaction was not observed. We attribute this additional interaction to the electronic structure of La where the additional d-electron in the valence shell leads to polarisation of the valence shell s-orbitals. The Bader population analysis shows that -1.44 electrons are transferred from the surface to the activated molecule (-0.75 electrons for the O in
the vacancy and -0.69 for the O on the La-La bridge). This verifies our assumption that the oxygen molecule is in activated peroxo state. The surface to molecule charge transfer is greater for the defective surface compared to the defect free surface, showing that the surface vacancies can play a significant role in the oxygen activation.

Figure 6e shows the electron density difference map for the oxygen molecule chemisorbed into the vacancy. Blue colour denotes positive electron density difference (i.e. excess electrons relative to the base case), whilst yellow denotes negative electron density difference (i.e. depletion of the electron concentration). The results show the Ni beneath the vacant site loses electrons, which become localised around each oxygen atom. The results resemble the electron density distribution of an oxygen molecule chemisorbed in oxygen vacancy on the SrTiO$_3$ surface. Analysis of the electron density differences show that electron density is transferred between the d$_z^2$ orbital of Ni (or Ti in SrTiO$_3$) and the π* antibonding orbital of the oxygen molecule. An important difference in the La$_2$NiO$_4$ case is that the surface La atoms also take part in the electron density transfer to the oxygen molecule. Such charge transfer was not observed via the surface Sr atoms in the case of SrTiO$_3$.

Figure 6b shows the geometry of the oxygen molecule dissociated on the surface with one oxygen atom incorporated in the perovskite lattice and one oxygen atom on the La-La bridge position. The charge at each oxygen atom is -1.3 which is similar to the charge of the oxygen atoms in the lattice. Figure 6d shows a plane section through the total electron density, passing through the chemisorbed oxygen atom and the oxygen atom on the La-La bridge site. The electron density in Figure 6d verifies the existence of strong La-O interaction characterised by charge transfer in the inter-nuclear region, which suggests a strong binding interaction. The electron density differences plot is shown in Figure 6f. Again, the blue colour denotes positive electron density difference whilst yellow denotes negative electron density difference. The density difference plots show that the oxygen incorporated into the perovskite lattice receives electron density drawn from the entire NiO$_2$ sub-lattice. The oxygen atom chemisorbed on the surface receives electron density from the bridge La atoms at the surface. This leads to a significant stabilisation of the dissociated oxygen on the LaO terminated surface, which was not observed for oxygen absorbed on the comparable SrO terminated SrTiO$_3$ surface.
Figure 7. Results of the transition state analysis between the chemisorbed O$_2$ on the oxygen vacancy and the incorporated/dissociated oxygen on the La-La bridge positions on defective surface. The dissociation of oxygen proceeds with a barrier of 0.28 eV.

In order to identify the transition state between the chemisorbed and dissociated oxygen molecule on the defective surface, and the associated activation barrier, a set of CI-NEB analyses were performed between the geometries in Figure 6a and 6b. The results for the transition state search are shown in Figure 7. The activation barrier for the dissociation of the chemisorbed oxygen was found to be 0.28 eV. The dissociation reaction is exothermic and the energy of the product is 0.93 eV lower than the reactant. The reaction barrier for the reverse reaction is 1.21 eV. The reaction can proceed exothermically because of the electron transfer from the La atoms to the surface chemisorbed oxygen. The activation barrier for oxygen dissociation on the defective La$_2$NiO$_4$ surface is lower compared to the barrier on the defect free La$_2$NiO$_4$ surface, 0.28 eV and 1.09 eV, respectively. Also the activation barrier for oxygen dissociation on the defective La$_2$NiO$_4$ surface is lower compared to the barrier on the defective SrTiO$_3$ surface, 0.28 and 0.5 eV, respectively.

4. CONCLUSION

Following recent experimental reports that the external surfaces of perovskite materials to be AO terminated when exposed to the operating conditions encountered in their application in devices such as SOFC cathodes, we studied the energetics of oxygen adsorption and dissociation reactions on the LaO terminated surfaces of La$_2$NiO$_4$. We have demonstrated that the defect free
(001) surface, with this particular termination, is actually energetically favorable for oxygen adsorption and dissociation. The activation energies for the oxygen dissociation are calculated as about 1 eV by using DFT+U and CI-NEB calculations. In contrast to common assumption, the electronic structure of the LaO terminated surface can promote charge transfer from the surface La atoms to the adsorbed oxygen. This finding, however, cannot be generalised for all cations that occupy the A site in perovskite phases. In our recent study, for example, SrO terminated defect free (001) surface of SrTiO$_3$ was found to be energetically not favorable for oxygen adsorption and dissociation. This strongly suggests that the electronic structure of the A-site cations plays a very important role in promoting charge transfer to surface adsorbates. In the case of Sr, the valence shell is built by 5s electrons. That atomic orbital is easily ionized leading to the Sr$^{2+}$. The closed shell Sr$^{2+}$ does not interact with chemisorbed oxygen molecules and therefore does not provide electron density that would facilitate the oxygen dissociation reaction. In the case of La, however, the valence shell is built by the 6s and one 5d electrons. The additional d-electron in the valence shell leads to the polarisation of the 6s valence orbitals. Thus, La can facilitate the oxygen chemisorption and destabilise the oxygen molecule by surface to molecule charge transfer. We believe that this comparison sheds light to our understanding on why the superior catalytic activity in oxygen reduction reactions is observed in La perovskite oxides. These findings have far reaching implications in the fundamental understanding of the interaction of oxygen with complex metal oxide surfaces.

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21
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