

Mechanism for enhanced oxygen reduction kinetics at the (La,Sr)CoO_{3-δ}/(La,Sr)₂CoO_{4+δ} hetero-interface†

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The recently reported fast oxygen reduction kinetics at the interface of (La,Sr)CoO_{3-δ} (LSC₁₁₃) and (La,Sr)₂CoO_{4+δ} (LSC₂₁₄) phases opened up new questions for the potential role of dissimilar interfaces in advanced cathodes for solid oxide fuel cells (SOFCs). Using first-principles based calculations in the framework of density functional theory, we quantitatively probed the possible mechanisms that govern the oxygen reduction activity enhancement at this hetero-interface as a model system. Our findings show that both the strongly anisotropic oxygen incorporation kinetics on the LSC₂₁₄ and the lattice strain in the vicinity of the interface are important contributors to such enhancement. The LSC₂₁₄(100) surface exposed to the ambient at the LSC₁₁₃/LSC₂₁₄ interface facilitates oxygen incorporation because the oxygen molecules very favorably adsorb onto it compared to the LSC₂₁₄(001) and LSC₁₁₃(001) surfaces, providing a large source term for oxygen incorporation. Lattice strain field present near the hetero-interface accelerates oxygen incorporation kinetics especially on the LSC₁₁₃(001) surface. At 500 °C, 4 × 10² times faster oxygen incorporation kinetics are predicted in the vicinity of the LSC₁₁₃/LSC₂₁₄ hetero-interface with 50% Sr-doped LSC₂₁₄ compared to that on the single phase LSC₁₁₃(001) surface. Contributions from both the anisotropy and the local strain effects are of comparable magnitude. The insights obtained in this work suggest that hetero-structures, which have a large area of (100) surfaces and smaller thickness in the [001] direction of the Ruddlesden–Popper phases, and larger tensile strain near the interface would be promising for high-performance cathodes.

1. Introduction

The slow rate of oxygen reduction at the cathode has been the primary limitation to the performance of solid oxide fuel cells (SOFCs) at intermediate temperatures (500–700 °C),^{1–5} which is important for materials stability and system cost.^{1,3,5,6} This has led to an extensive search for highly active cathode materials that accelerate the kinetics of the oxygen reduction reaction (ORR).

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Broader context

The high efficiency and fuel flexibility of Solid Oxide Fuel Cells (SOFCs) render them attractive as a sustainable energy conversion technology. There is growing interest in the design of dissimilar interfaces at the nano-scale to enable high-performance SOFC cathodes with fast oxygen reduction reaction (ORR) kinetics at lower temperatures than their traditional operation temperature of 800 °C. A motivating example for this purpose has been the hetero-structure made of the (La,Sr)CoO_{3-δ} and (La,Sr)₂CoO_{4+δ} phases with highly active interfaces. Two previous experimental reports have observed 10³ to 10⁴ times enhancement in ORR kinetics at 500–550 °C arising from the interface of these two phases. However, these empirical observations have not yet provided a fundamental understanding of why these interfaces are so highly active to ORR. Here we use first-principles based calculations to quantitatively demonstrate two important mechanisms that can govern the unusually high ORR activity of this hetero-interface system; the strongly anisotropic oxygen adsorption and incorporation kinetics on the (La,Sr)₂CoO₄(100) surface and the lattice strain effect near the interface. Our findings provide new insights for designing novel interfaces in high-performance cathodes. Furthermore, these results are applicable broadly to other systems where oxide interfaces are critical in charge transfer kinetics, as batteries, catalysis, and sensors.

Traditionally, perovskite type transition metal oxides (ABO_3) have been widely investigated as SOFC cathodes.^{2,3,7-10} More recent studies highlight the potential of layered materials, such as the Ruddlesden–Popper (RP) family of $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$, as desirable cathodes due to their fast and anisotropic oxygen incorporation and transport properties.^{6,11-14} Interestingly, Sase *et al.* demonstrated from Secondary Ion Mass Spectrometry (SIMS) that the oxygen surface exchange rate at the hetero-interface of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3/(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ thin films is enhanced by about 10^3 times at 500°C compared to that on the single-phase $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ surfaces.¹⁵ Following up on this study, Crumlin *et al.*, using electrochemical impedance spectroscopy measurements, reported also an ORR activity enhancement of up to about 10^3 to 10^4 times at 550°C on the thin film $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$ cathodes whose surfaces are decorated with $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ islands (and thus with a high density of $\text{LSC}_{113}/\text{LSC}_{214}$ interfaces).¹⁶ While it is evident that the interfacial regions are contributing to this unusually high ORR activity, the governing mechanism behind these empirical observations has not been identified to date. Obtaining a microscopic level understanding for such behavior is important for designing novel interfaces for very high-performance SOFC cathodes. In this paper, we hypothesize two possible mechanisms for the ORR enhancement on this hetero-structure; the first is the anisotropically fast O_2 incorporation into the $\text{LSC}_{214}(100)$ surface present at this interface (as is the configuration reported in both ref. 15 and 16), and the second is the effect of lattice strain on the oxygen reduction reactions near the hetero-interface.

In support of our first hypothesis, several compositions belonging to the first member of the RP series, A_2BO_4 , were shown to exhibit fast anisotropic oxygen exchange and diffusion kinetics.^{6,12,13,17-23} For example, on $\text{La}_2\text{NiO}_{4+\delta}$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$, 10^2 to 10^3 times larger oxygen interstitial diffusion and surface exchange coefficients along the ab plane ((001) plane) than on the c plane ((100) plane) were reported.^{17,19,21,22} Similar reports for $(\text{La,Sr})_2\text{CoO}_{4+\delta}$ are scarce to date. We have previously shown a fast anisotropic oxygen interstitial transport along the ab plane in $\text{La}_2\text{CoO}_{4+\delta}$ computationally.¹³ There are no reports in the literature yet on its surface exchange kinetics on each major plane. The $\text{LSC}_{214}(100)$ surface can play an important role as an oxygen source boundary condition by the energetically favorable O_2 adsorption enabling fast ORR kinetics at the $\text{LSC}_{113}/\text{LSC}_{214}$ interface. In fact, this surface is exposed to air in both Sase *et al.*'s work¹⁵ and Crumlin *et al.*'s work¹⁶ since

they both deposited the LSC_{214} on top of LSC_{113} in creating a highly textured hetero-interface.

In support of our second hypothesis, lattice strain was recently shown to alter the oxygen defect chemistry as well as the oxygen reaction and diffusion kinetics on perovskite oxides. Strain fields are often induced by the lattice mismatch near a dissimilar interface. As shown in Fig. 1, the $(\text{La,Sr})\text{CoO}_3/(\text{La,Sr})_2\text{CoO}_4$ layered structure (constructed using density functional theory (DFT), see Section 2) imposes a $+1.9\%$ planar strain in the (001) plane of LSC_{113} , and a -0.8% planar strain in the (001) plane of LSC_{214} . These theoretical values are expected to give an upper boundary of the magnitude of strain near the $\text{LSC}_{113}/\text{LSC}_{214}$ hetero-interface. Lattice strain is shown (by works including those of the authors here) to have a significant impact on facilitating oxygen ion transport,²⁴⁻²⁸ vacancy formation,²⁹⁻³² and surface adsorption^{27,30} – specific to this paper's scope are the oxygen vacancy formation, oxygen adsorption and oxygen incorporation kinetics on the $(\text{La,Sr})\text{CoO}_3$ films.^{27,30,33} $\text{La}_2\text{CoO}_{4+\delta}$ has not been a subject of similar studies to date, and we address the potential effects of strain also in this material as part of this paper.

Another factor that can affect the ORR activity near the $\text{LSC}_{113}/\text{LSC}_{214}$ interface is the redistribution of oxygen defects and dopants. Very recently, Gadre *et al.*, based on DFT calculations, proposed that the enhancement of interfacial ORR activity in this system could be caused by significant Sr interdiffusion from LSC_{113} into LSC_{214} .³⁴ The large extent of Sr enrichment in LSC_{214} was expected to induce the formation of a large amount of oxygen vacancies and accelerate the oxygen incorporation kinetics.³⁴ While this is a reasonable hypothesis, in our ongoing experimental work³⁵ we do not find any evidence for a detectable amount of Sr segregation in LSC_{214} near the $\text{LSC}_{113}/\text{LSC}_{214}$ interface. Furthermore, it is not clear how the increased amount of oxygen vacancies in LSC_{214} can enhance the ORR activity by several orders of magnitude since the interstitial path into LSC_{214} and similar RP phase compounds is already very fast. Therefore, in this study, we focus on the interstitial oxygen incorporation and transport as the dominant ORR path on LSC_{214} with a Sr doping level $\leq 50\%$,^{36,37} rather than a vacancy dominated oxygen incorporation process.

In this paper, we quantitatively probe the two above-discussed mechanisms for the reported enhancement of the ORR activity at the hetero-interface of $\text{LSC}_{113}/\text{LSC}_{214}$. In Section 2, the computational approach and method details are described. In

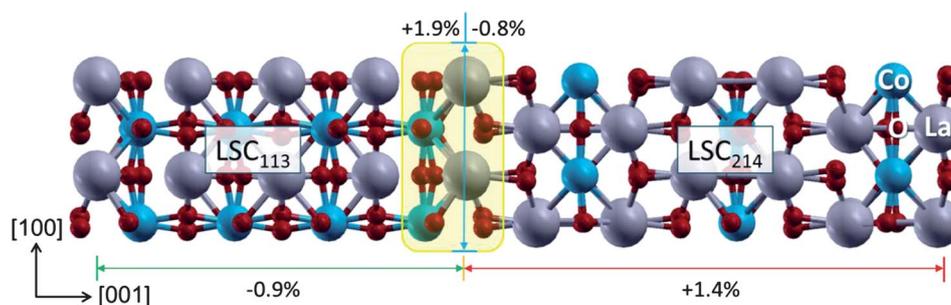


Fig. 1 DFT model of the $(\text{La,Sr})\text{CoO}_3$ (LSC_{113})/ $(\text{La,Sr})_2\text{CoO}_4$ (LSC_{214}) structure, and the theoretically estimated strain states induced near this interface.

Section 3, first the anisotropic oxygen adsorption, dissociation/incorporation and diffusion on LSC_{214} as a function of Sr content, and then the strain effects on the oxygen incorporation and migration kinetics on both LSC_{113} and LSC_{214} are assessed. We integrate these *two individual effects* on each single phase, and estimate the ORR activity enhancement that they *together* can impose near the $\text{LSC}_{113}/\text{LSC}_{214}$ hetero-interface. Finally, in Section 4, we summarize our major observations and conclusions.

2. Computational method and model

2.1. Ground-state structures and energies

We performed plane wave DFT calculations using the Vienna *ab initio* simulation package (VASP).³⁸ We employed the generalized gradient approximation (GGA) parameterized by Perdew and Wang³⁹ along with the projector augmented wave (PAW)⁴⁰ method to describe ionic cores. To avoid the self-interaction errors that occur in the traditional DFT for strongly correlated electronic systems, we employed the DFT + U method within Dudarev's approach⁴¹ accounting for the on-site Coulomb interaction in the localized d orbitals, with an effective $U - J = 3.3$ eV taken from the previous reports for LaCoO_3 ^{27,30} and $\text{La}_2\text{CoO}_{4+\delta}$.¹³ For La, Co, and O, the standard PAW/PW91 potentials were used for our calculations, while for Sr, Sr_{sv} potential was applied. All calculations used a plane wave expansion with a cutoff of 400 eV and included spin polarization. Our test calculation confirmed that the energy cutoff of 400 eV was well converged within 5 meV in total energy, compared to the one with 600 eV. Geometries were relaxed using a conjugate gradient algorithm until the forces on all unconstrained atoms were less than $0.03 \text{ eV } \text{\AA}^{-1}$.

The lattice constants of the fully relaxed bulk La_2CoO_4 model are 3.90 \AA (a, b) and 12.6 \AA (c), which are in good agreement with the experimentally reported values.⁴² To replicate the interfacial strain conditions that the thin films are subjected to at the $\text{LSC}_{113}/\text{LSC}_{214}$ interface, a 2D-planar compressive (tensile) lattice strain was imposed by contracting (elongating) the simulation cell in the $[100]$ and $[010]$ directions and relaxing the cell configuration and dimension in the $[001]$ direction for LSC_{214} (LSC_{113}) in a slab model configuration. The bulk structure of LSC_{214} was cleaved along the (100) and (001) planes to construct surfaces that are represented by slabs of ~ 10 and 11 \AA thick, respectively, containing 6 atomic asymmetric layers with the

bottom two layers constrained to bulk lattice positions. For all calculations, a vacuum spacing of $\sim 10 \text{ \AA}$ was placed in the direction of the surface normal. This vacuum spacing, equivalent to the slab thickness, is converged to within 0.5 meV per atom compared to analogous calculations using larger vacuum gaps of 15 and 20 \AA . When examining adsorption, molecules were placed on only one side of the slab. To avoid the fictitious dipole moment, dipole corrections^{33,34} were applied in computing all of the energies reported here.^{43,44} O_2 adsorption calculations were performed for one molecule per surface unit cell, corresponding to a surface coverage of 25% with four equivalent adsorption sites. A $2 \times 2 \times 1$ Monkhorst-Pack k -point mesh was used, which was sufficient to give well converged results. Fig. 3(a) and (c) shows the top and side views of the $\text{LSC}_{214}(100)$ unit cell. The details of $\text{LSC}_{113}(001)$ slab model are described in our previous report.²⁷ To obtain the $\text{LSC}_{113}/\text{LSC}_{214}$ hetero-structure, we merged the two single-phase structures in a multilayer configuration (Fig. 1) and fully relaxed both the lattice vectors and atomic positions. For this calculation, we increased the energy cutoff to 600 eV for expanding the wave function and used T points in the Brillouin zone.

2.2. Reaction and migration energy barriers

The climbing image nudged elastic band (CI-NEB) method⁴⁵ was employed to calculate the migration and incorporation energy barrier of oxygen on and in LSC_{214} . Initial approximations to reaction paths were obtained by linear interpolation between the energy minima configurations. Three intermediate images were used for all NEB calculations, which was sufficient to map the minimum energy path (MEP) accurately. The NEB simulations were conducted with fixed lattice vectors.

2.3. Reaction kinetics at the interface

In order to estimate the relative enhancement in the ORR kinetics near the LSC_{113} and LSC_{214} interface compared to the single phase of LSC_{113} , we compute the ratio, $\frac{k_{113/214}^*}{k_{113}^*}$. The surface reaction rate constants, k^* , are determined by the O_2 adsorption and dissociation processes, considered to take place consecutively here, to ultimately incorporate oxygen into the subsurface of each phase.

The oxygen incorporation path on the single phase LSC_{113} is shown in Fig. 2(a);²⁷ O_2 adsorbs onto the $\text{LSC}_{113}(001)$ surface,

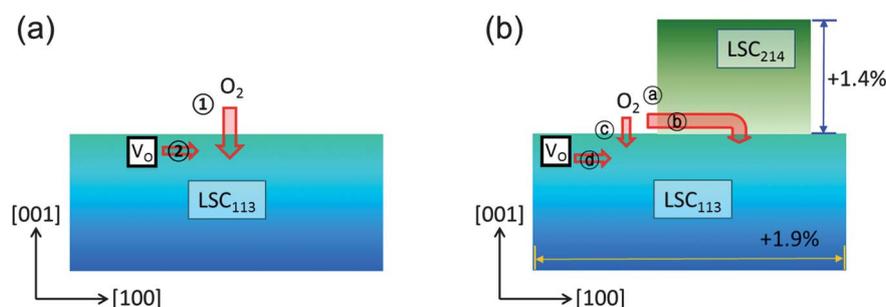


Fig. 2 Illustration of the oxygen incorporation paths (a) on the single phase LSC_{113} and (b) near the $\text{LSC}_{113}/\text{LSC}_{214}$ hetero-interface. The latter includes both path I (a \rightarrow b) and path II (c \rightarrow d).

and then is incorporated and dissociated by the assistance of a migrating surface oxygen vacancy. For the LSC₁₁₃/LSC₂₁₄ hetero-structure, there are two parallel paths for oxygen incorporation as shown in Fig. 2(b); path I (a → b) and path II (c → d). In path I, oxygen adsorbs onto the LSC₂₁₄(100) surface, then dissociates, incorporates, and migrates through the LSC₂₁₄ into the LSC₁₁₃. A path that starts with the O₂ adsorption on the LSC₂₁₄(001) surface followed by diffusion along the [001] direction is ignored due to the very high energy barriers involved, as will be discussed later. Path II is the same as the oxygen incorporation path on the single phase LSC₁₁₃. As described in Fig. 1, the presence of lattice strain is expected near the interfaces of this hetero-structure (Fig. 2(b)). In the next sections, we assess the energetics of each unit process along these oxygen incorporation paths, with and without strain, to estimate the enhancement of ORR activity. Here we describe how the energetics and kinetics of each process are treated in this analysis, especially how we get to the effective k^* for each path shown in Fig. 2.

The adsorption energy, E_{ads} , of O₂ was defined as

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

where E_{total} is the total energy of the system with the adsorbed O₂, E_{surf} is the total energy of the bare surface, and E_{O_2} is the total energy for the O₂ in the gas phase. With this definition, negative adsorption energies correspond to energetically favored states.

The oxygen vacancy and interstitial formation energies, E_{vac} and E_{int} , were calculated as

$$E_{\text{vac}} = E_{\text{defect}} - E_0 + \frac{1}{2}E_{\text{O}_2}, E_{\text{int}} = E_{\text{defect}} - E_0 - \frac{1}{2}E_{\text{O}_2} \quad (2)$$

where E_{defect} is the total energy of the system with a point defect (oxygen vacancy or interstitial) and E_0 is the total energy of the defect-free system. Smaller formation energy favors the formation of oxygen vacancies or interstitials.

Oxygen incorporation kinetics into the surface of an SOFC cathode are formulated as:⁴⁶

$$j = -k^* \delta c|_{\text{surface}} \quad (3)$$

where j is the flux, c the concentration, and k^* the effective surface incorporation rate constant of oxygen. The k^* is used as a quantitative measure of ORR kinetics here and is approximately calculated as:⁴⁷

$$k^* \approx A_k \times \exp\left\{-\frac{(E_{\text{ads}} + E_{\text{dis}})}{k_B T}\right\} \quad (4)$$

where A_k is the prefactor, E_{ads} the O₂ adsorption energy, E_{dis} the O₂ dissociation energy, k_B the Boltzmann constant, and T the temperature. For LSC₂₁₄, the most favorable surface dissociation for O₂ involves adsorption in a surface vacancy near the rock-salt layer and dissociation *via* interstitial incorporation from that site. Therefore, E_{dis} is treated as the superimposition of oxygen vacancy formation energy (E_{vac}) and the oxygen incorporation energy barrier (E_{inc}) (see Section 3.1). For LSC₁₁₃, the O₂ dissociation process is governed by the availability and mobility of oxygen vacancies on the surface.^{27,47} Therefore, E_{dis} is composed of the oxygen vacancy formation energy (E_{vac}) and oxygen vacancy migration energy (E_{mig}) on the surface.^{27,48}

3. Results and discussion

3.1. Anisotropic oxygen adsorption, dissociation and incorporation on (La,Sr)₂CoO₄

We assess the results on both undoped La₂CoO₄ (as a model reference system) and 50% Sr-doped (La_{0.5}Sr_{0.5})₂CoO₄ (the same as the experimentally demonstrated composition^{15,16}). In each model, the LSC₂₁₄(100) surface has only one type of termination which includes both the A-site and the B-site cations exposed to the environment. For the LSC₂₁₄(001) surface the CoO₂ termination layer is considered, and it is equivalent to the CoO₂-terminated LSC₁₁₃(001) that has been theoretically⁴⁹ found as the most stable surface on perovskite-type cobaltites.^{50–52}

3.1.1. La₂CoO₄. The most stable adsorption structures of O₂ on both the (100) and (001) surfaces of undoped LSC₂₁₄ are shown in Fig. 3(a) and (b), respectively. An O₂ molecule adsorbs onto the bridge site of LSC₂₁₄(100) between La atoms in the vicinity of the interstitial path between the LaO planes. Surface oxygen vacancies are not expected to be present on the undoped LSC₂₁₄,^{36,37,53} and do not play a role in the O₂ adsorption and dissociation on the (100) surface. Interestingly, the adsorption energy in this configuration is -3.24 eV, indicating a very strong adsorption of O₂ onto this surface. On the other hand, the O₂ adsorption energy on LSC₂₁₄(001) is -0.24 eV, which is considerably weaker. As expected, this value and the adsorption configuration (with the O₂ atop a Co atom in a tilted fashion^{27,30}) are very close to the one on LSC₁₁₃(001).²⁷ The adsorption energy difference between (100) and (001) surfaces on undoped LSC₂₁₄ is 3 eV, favoring that on the former.

O₂ adsorption on LSC₂₁₄(100) is followed by rotation and dissociation of O₂ that directly lead to O incorporation as an interstitial into the rock-salt layer, as shown in Fig. 3(c) and the insets of Fig. 3(d). The dissociated O replaces the lattice oxygen of the surface by kicking it off into an interstitial site between the LaO planes in the subsurface region (Fig. 3(c)). This is analogous to the interstitialcy path that governs the oxygen migration in the bulk of this material.¹³ The energy barrier for this incorporation process on the undoped LSC₂₁₄(100) is 0.77 eV (Fig. 3(d)), which is lower than the one on the LSC₁₁₃(001) surface (1.31 eV) that is governed by the availability and mobility of surface oxygen vacancy.²⁷ Therefore, the O₂ dissociation kinetics alone on the LSC₂₁₄ surface are expected to present an additional enhancement by 0.54 eV compared to that on the LSC₁₁₃ surface.

Similarly to the other A₂BO₄ materials,^{6,12,13,17–23} we quantitatively show here that oxygen diffuses anisotropically in LSC₂₁₄¹³ (Fig. 3(e)). The oxygen migration barrier along the [100] direction (by interstitialcy mechanism) in the bulk LSC₂₁₄ is 0.61 eV, which is significantly lower than 1.95 eV in the [001] direction. The oxygen transport on the LSC₂₁₄(100) surface in the [001] direction is even more unfavorable with an energy barrier of ~ 3 eV (Fig. 3(f)). In LSC₂₁₄, therefore, oxygen most favorably diffuses along the [100] direction *via* the interstitialcy path.¹³ The kinetics of oxygen diffusion in LSC₂₁₄, however, do not significantly accelerate the overall ORR kinetics compared to LSC₁₁₃ because the migration barrier of oxygen in bulk LSC₁₁₃ (0.69 eV)²⁷ is similar to the one along the fast interstitialcy route in LSC₂₁₄. Since the focus is on the “surface incorporation rate of

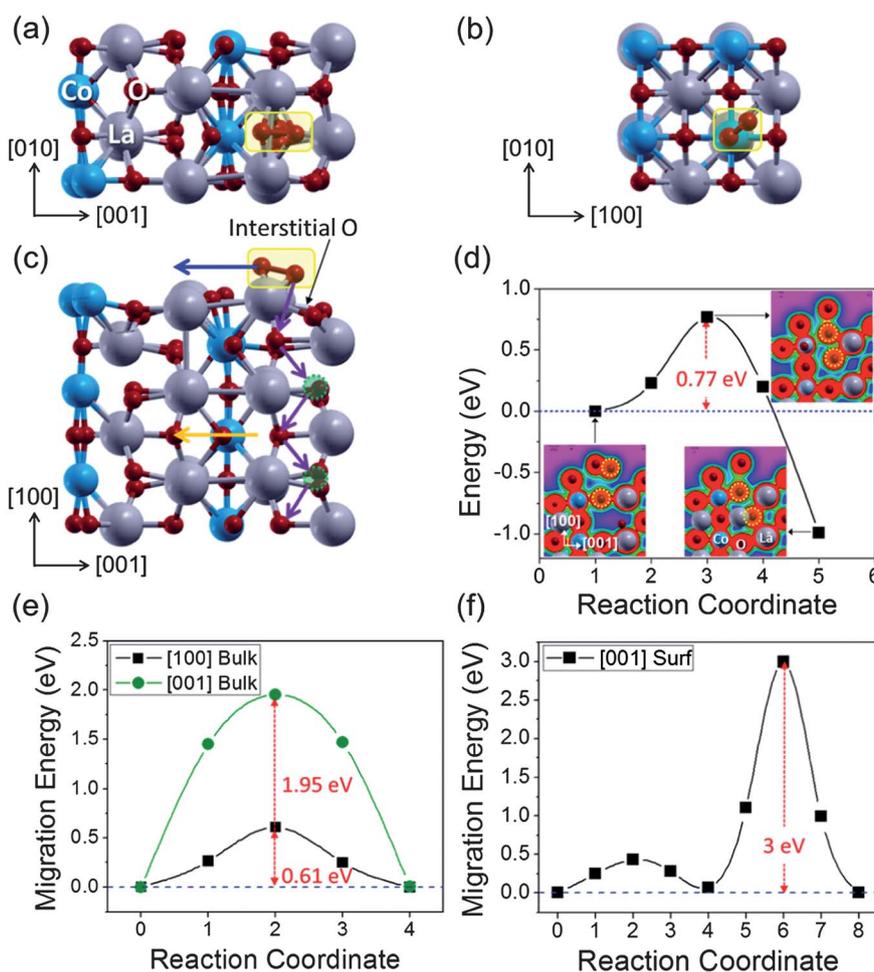


Fig. 3 Top view of (a) $\text{La}_2\text{CoO}_4(100)$, (b) $\text{La}_2\text{CoO}_4(001)$, (c) side view of La_2CoO_4 model unit cell which schematically shows the oxygen migration pathways along the [001] on the surface (blue arrow) and in the bulk (yellow arrow), and along the [100] direction into the bulk (purple arrow), and (d) the relative energy of the system for O_2 dissociation/incorporation on La_2CoO_4 along the [100] direction. The yellow boxes in (a–c) show the adsorbed oxygen molecule on each surface. Charge density plots for the initial, transition, and final states are shown in the insets of (d) for oxygen incorporation. The relative energy of the system is shown for (e) O migration along the [100] direction (purple arrows in (c)) and along the [001] direction (orange arrow in (c)) in the bulk La_2CoO_4 ; and for (f) O migration on $\text{La}_2\text{CoO}_4(100)$ surface (blue arrow in (c)). The barrier of 3 eV in (f) corresponds to the migration of oxygen across the AO–AO rock-salt layers on the $\text{La}_2\text{CoO}_4(100)$ surface (Fig. S1 in the ESI†).

oxygen” on $\text{LSC}_{214}(100)$, oxygen diffusion in the bulk along the [001] direction was not included into the quantitative estimate of the relative enhancement of ORR kinetics based on k^* . Furthermore, at the hetero-interface of $\text{LSC}_{113}/\text{LSC}_{214}$, the fast diffusion path in the [100] direction is in direct contact with LSC_{113} , thus oxygen can directly incorporate into LSC_{113} without the diffusion step across the rock-salt layers along the [001] direction in LSC_{214} . Lastly, even if a small number of migration steps along the [001] direction near the interface take place, the overall “resistance” of this very short path would be small despite the relatively large energy barrier. These points justify that diffusion along the [001] direction is not a significant contributor to the ORR assessment.

3.1.2. $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$. For assessment of the oxygen incorporation kinetics on the 50% Sr-doped LSC_{214} , one must know the most stable Sr distribution in the structure. We compared the energetic stability of LSC_{214} with a uniform

distribution of Sr and with a cation ordered structure. In the latter, double layers of SrO and LaO are 1 : 1 ordered perpendicular to the c axis as shown in Fig. 4(a) and (c). This layered structure of the A-site cations has also been observed in similar RP phase systems.^{54–61} Our DFT calculations showed that this cation ordered LSC_{214} is energetically more stable than the one with uniform distribution of Sr, by 0.04 eV per formula unit (f.u.) (see Fig. S2 in the ESI†). We therefore evaluated the oxygen adsorption, dissociation, and incorporation processes on the cation ordered LSC_{214} model. Multiple pathways for these processes were considered and quantitatively investigated (see Fig. S4 in the ESI†).

Although oxygen incorporation into $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ is not mediated by exchange with surface and subsurface vacancies (as noted in Section 1), it is reasonable to expect the presence of oxygen vacancies on the (100) surface with a high Sr content.^{36,37,53} The vacancy and interstitial formation energies calculated here on various positions on the surface and in the

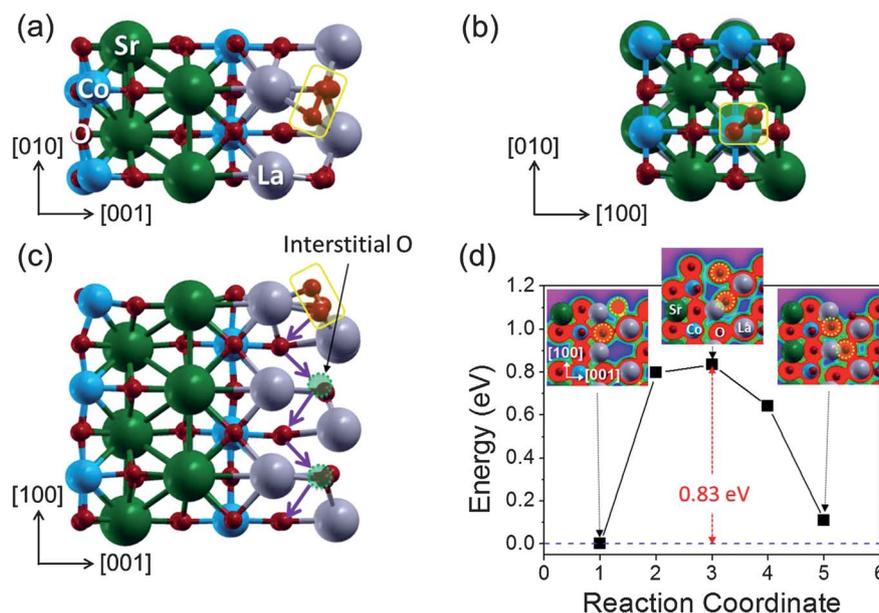


Fig. 4 Top view of (a) $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4(100)$, (b) $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4(001)$, (c) side view of $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ model unit cell which schematically shows the oxygen incorporation and migration pathway along the $[100]$ direction into the bulk (purple arrow), and (d) the relative energy of the system for oxygen incorporation into $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ along the $[100]$ direction. The yellow boxes in (a), (b) and (c) show the adsorbed oxygen molecule on each surface. Adsorption is into an oxygen vacancy on the AO–AO rock-salt layer in (a) and (c). Charge density plots for the initial, transition, and final states for oxygen incorporation are shown in the insets of (d).

bulk LSC_{214} justify this (see Fig. S3 in the ESI[†]). In the bulk, oxygen interstitials are most dominantly favored, with a formation energy of $E_{\text{int}} = 0.22$ eV, over oxygen vacancies with $E_{\text{vac}} = 2$ eV. Thus, oxygen incorporation into and diffusion in the bulk $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$ take place *via* oxygen interstitials, similarly to the case of undoped LSC_{214} . On the $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4(100)$ surface, however, the surface oxygen interstitial is not stable. Oxygen rather preferentially binds on the bridge site between La atoms on the rock-salt layer; this is 0.52 eV more favorable than the binding onto the interstitial site on the (100) surface. The vacancy formation energy on this surface varies between 2.15–3.60 eV depending on the vacancy site considered. Without surface oxygen interstitials, it is possible that the surface vacancies (with formation energy of 2.15 eV) can exist on the AO–AO rock-salt layers at elevated temperatures. Although their concentration is not expected to be very high, their presence is considered crucial upon surveying the oxygen reaction pathways on the surface.

Among the oxygen incorporation pathways considered on $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4(100)$, the one in which an O_2 first adsorbs into a surface vacancy on the rock-salt layer (position 2 in Fig. S3(c) in the ESI[†]), followed by oxygen dissociation and incorporation into an interstitial site in the rock-salt layer, is energetically the most favorable (Fig. 4(c)). This is unlike the case on the undoped $\text{LSC}_{214}(100)$ where the most preferred O_2 adsorption site is the bridging site between La atoms on the rock-salt layer. Although the adsorption on $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4(100)$ is into a vacancy, the dissociation is into an interstitial site between the rock-salt layers, as shown in the insets of Fig. 4(d), and would be followed by interstitialcy diffusion. 2.15 eV is required for vacancy formation and 0.83 eV for the oxygen dissociation and incorporation barrier. The energy barrier for this incorporation

process on 50% Sr-doped $\text{LSC}_{214}(100)$ is slightly higher than that on undoped $\text{LSC}_{214}(100)$ (0.77 eV) and on the $\text{LSC}_{113}(001)$ surface (0.70 eV).²⁷ This suggests that the increase of Sr content on LSC_{214} does not further facilitate oxygen incorporation.

Upon doping Sr into La sites, the adsorption strength on the $\text{LSC}_{214}(100)$ surface reduces relatively, while the adsorption energy and configuration on the $\text{LSC}_{214}(001)$ surface remains almost the same (due to lack of A-site cations on that surface). Despite the adsorption into an oxygen vacancy on the 50% Sr-doped $\text{LSC}_{214}(100)$, the adsorption energy is -2.02 eV, and this is 1.22 eV weaker than the case on the undoped one. This decreases the adsorption energy difference between the (100) and (001) surfaces from 3 eV for undoped LSC_{214} to 1.82 eV for 50% Sr-doped LSC_{214} , respectively (Table 1), but the difference of 1.82 eV that represents the anisotropy of oxygen adsorption is still very significant. The relative reduction in the O_2 adsorption strength upon Sr doping can be explained as follows. On an undoped $\text{LSC}_{214}(100)$, significant surface relaxations take place to accommodate the adsorbing oxygen. On the 50% Sr-doped surface, however, the relatively large Sr atoms inhibit the relaxation of the top layer of the (100) surface and retain a rigid structure (Fig. 4(a)) upon O_2 adsorption. Overall such strongly

Table 1 Adsorption energies of an oxygen molecule on the (100) and (001) surfaces of 0% and 50% Sr-doped LSC_{214} . The ‘Difference’ represents the anisotropic adsorption strength that favors the (100) surface

E_{ads} (eV)	La_2CoO_4	$(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$
(100)	−3.24	−2.02
(001)	−0.24	−0.20
Difference	3.00	1.82

enhanced adsorption onto the (100) surface of LSC_{214} can provide a large flux of oxygen as an increased source term for the oxygen incorporation kinetics on $\text{LSC}_{214}(100)$, and is one possible reason for the ORR enhancement at the hetero-interface of $\text{LSC}_{113}/\text{LSC}_{214}$.^{15,16}

Our results suggest that doping of Sr into LSC_{214} hinders the oxygen adsorption and incorporation process relative to the undoped LSC_{214} due to structural reasons. However, electron transfer properties of Sr-doped LSC_{214} at finite temperatures are actually expected to help the overall reaction kinetics. Furthermore, for both 0% and 50% Sr-doped LSC_{214} , the anisotropically strong adsorption of O_2 onto $\text{LSC}_{214}(100)$ plays a more important role than the anisotropic oxygen dissociation and incorporation into LSC_{214} for the ORR enhancement near the $\text{LSC}_{113}/\text{LSC}_{214}$ hetero-interface.

3.2. Strain effect on the oxygen incorporation on $(\text{La,Sr})\text{CoO}_3$ and $(\text{La,Sr})_2\text{CoO}_4$ near the hetero-interface

3.2.1. $(\text{La,Sr})\text{CoO}_3$. As described in Fig. 1 and 2, $\text{LSC}_{113}(001)$ is in theory up to +1.9% tensile strained in the [100] and [010] directions near the $\text{LSC}_{113}/\text{LSC}_{214}$ interface. Thus, we can include here the effect of strain on oxygen adsorption, and vacancy formation and migration on the $\text{LSC}_{113}(001)$ surface, which we previously assessed.^{27,30} We remind that the oxygen dissociation and incorporation kinetics are limited by the availability and mobility of oxygen vacancies on the surface of LSC_{113} , as well as on other similar perovskite cathodes.^{27,48} As the tensile strain increases up to the limit of elastic stretching, both the oxygen molecule adsorption and oxygen vacancy formation become more favored, as shown in Fig. 5(a).²⁷ Increasing planar tensile strain weakens the in-plane Co–O bonds by decreasing the Co *d* and lattice O *p* orbitals' hybridization, which consequently causes strengthening of the chemisorption of O_2 onto Co. An oxygen vacancy is more easily formed due to the weakening of the in-plane Co–O bonds upon tensile strain. The energy barrier for oxygen vacancy migration on $\text{LSC}_{113}(001)$ is significantly lowered in the [110] direction with the increase of strain, as shown in Fig. 5(b),²⁷ because of the increased space available in the migration path of oxygen. We will use this strain dependence later to quantify the acceleration of the ORR kinetics near the hetero-interface of $\text{LSC}_{113}/\text{LSC}_{214}$ in Section 3.3.

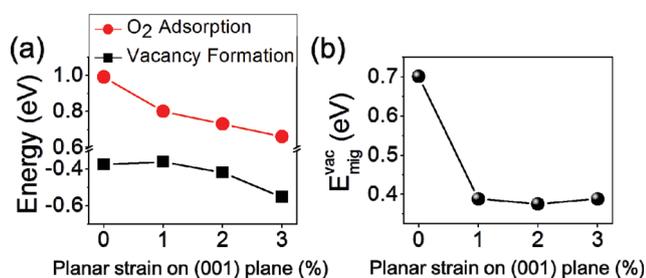


Fig. 5 (a) Tensile planar strain dependence of (a) O_2 adsorption and oxygen vacancy formation energies, and of (b) the migration energy barrier of oxygen vacancy in the [110] direction on undoped $\text{LSC}_{113}(001)$ surface. (Adapted from ref. 27.)

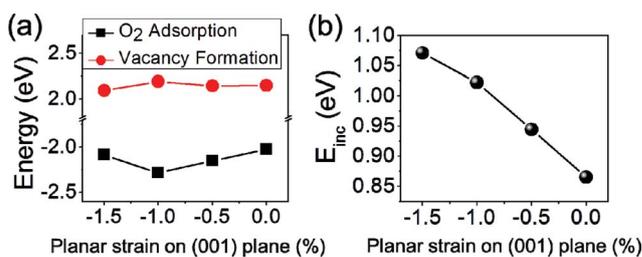


Fig. 6 Strain dependence of (a) O_2 adsorption and oxygen vacancy formation energies, and (b) the energy barrier of oxygen incorporation into 50% Sr-doped $\text{LSC}_{214}(100)$ surface.

We note that because the $\text{LSC}_{113}(001)$ surface investigated here is CoO_2 -terminated, the Sr-dopant level does not introduce significant quantitative differences to our results, especially with regards to the relative effects of strain. Thus, all the LSC_{113} results reported and used in this paper are taken on undoped LSC_{113} .

3.2.2. $(\text{La}_{0.5}\text{Sr}_{0.5})_2\text{CoO}_4$. The theoretically estimated strain in LSC_{214} near the $\text{LSC}_{113}/\text{LSC}_{214}$ hetero-interface is -0.8% of the compressive planar strain on the (001) plane, which leads to $+1.4\%$ tensile strain relaxation in the [001] direction (Fig. (1)). Experimentally, in a multilayer $\text{LSC}_{113}/\text{LSC}_{214}$ heterostructure the largest strain that is measured in LSC_{214} layers is $+1\%$ tensile strain along [001],³⁵ which arises from a -1.5% compressive planar strain on the (001) plane. The latter case is considered here to represent the maximum feasible strain in such a structure for the evaluation of strain effects on LSC_{214} . As shown in Fig. 6(a), the strain dependence of O_2 adsorption and vacancy formation is very weak, with changes of only 0.06 eV and 0.05 eV, respectively, at -1.5% compared to the unstrained state. The strain response of oxygen incorporation into LSC_{214} along the [100] direction (Fig. 4(c)) is more significant, with a reduction of the incorporation energy barrier up to 0.21 eV. The strain dependence of the oxygen incorporation energy is correlated to the increase in the width of the entrance channel for the oxygen interstitial (measured as the distance across the rock-salt layer) (Fig. S5 in the ESI†). Overall, the strain dependence on the single phase LSC_{214} surface is weaker than the one on the single phase LSC_{113} surface (Fig. 5).

3.3. Quantification of the enhancement of oxygen reduction kinetics near the $\text{LSC}_{113}/\text{LSC}_{214}$ hetero-interface

Here we integrate the individual effects of anisotropy and lattice strain (for each single phase), described in Sections 3.1 and 3.2 above, to quantitatively estimate the relative enhancement in the ORR kinetics expected near the $\text{LSC}_{113}/\text{LSC}_{214}$ hetero-interface. In Section 1, we showed the theoretical lattice strain near the hetero-interface (Fig. 1). The actual strain induced in the LSC_{113} and LSC_{214} layers in a multilayer configuration in our ongoing experimental work was found by X-ray diffraction.³⁵ The experimentally determined strain states along the [100] and [001] directions are consistent qualitatively (in sign) with those predicted by the DFT calculations in this paper. In estimating the maximum effect of lattice strain on the relative ORR kinetics enhancement, we use the largest strain values that are

Table 2 Unit reaction energies on the unstrained and strained LSC₁₁₃ and LSC₂₁₄. The strain range near the LSC₁₁₃/LSC₂₁₄ hetero-interface is based on our measurements on a multilayer configuration made of LSC₁₁₃ and LSC₂₁₄³⁵

Unit process energies (eV)	E_{ads}	E_{vac}	E_{inc}	E_{mig}
Unstrained LSC ₂₁₄ (100)	-2.02	2.15	0.87	—
Unstrained LSC ₁₁₃ (001)	-0.38	0.99	—	0.70
-1.5% strained LSC ₂₁₄ on (001) plane	-2.09	2.09	1.07	—
+0.8% strained LSC ₁₁₃ on (001) plane	-0.36	0.83	—	0.44

experimentally found: -1.5% compressive planar strain on the (001) plane of LSC₂₁₄ and +0.8% tensile planar strain on the (001) plane of LSC₁₁₃. These planar strain values are deduced from the measured +1.0% tensile strain in LSC₂₁₄ and -0.6% compressive strain in LSC₁₁₃ in the [001] direction, using 0.25 as the Poisson ratio typical for most oxides.

We compare the overall oxygen reduction kinetics at/near the LSC₁₁₃/LSC₂₁₄ hetero-interface (Fig. 2(b)) with those on the single phase LSC₁₁₃ (Fig. 2(a)) on the basis of the strain- and anisotropy-dependent energetics of unit processes discussed in Section 3.2. The paths for oxygen incorporation near the hetero-interface were described in Fig. 2 and Section 2.3. Table 2 summarizes all energies used for this quantitative comparison reported next.

As explained in Section 2, in order to estimate the relative enhancement of oxygen reduction kinetics, we calculate the ratio of the k^* on the LSC₁₁₃/LSC₂₁₄ hetero-structure to that on the single phase LSC₁₁₃. Using eqn (4), the k^* via the oxygen incorporation path I (Fig. 2(b)) is:

$$k_{113/214-I}^* \approx \left[v_1 \times \exp \left\{ - \frac{(E_{\text{ads}}^{214} + E_{\text{vac}}^{214} + E_{\text{inc}}^{214})}{k_B T} \right\} \right]_{113/214} \quad (5)$$

Using eqn (4), the k^* via the path II (Fig. 2(b)) is:

$$k_{113/214-II}^* \approx \left[v_2 \times \exp \left\{ - \frac{(E_{\text{ads}}^{113} + E_{\text{vac}}^{113} + E_{\text{mig}}^{113})}{k_B T} \right\} \right]_{113/214} \quad (6)$$

All pre-factors in eqn (5) and (6) are incorporated into v_1 and v_2 , respectively. The $k_{113/214}^*$ for the LSC₁₁₃/LSC₂₁₄ hetero-structure is the sum of $k_{113/214-I}^*$ and $k_{113/214-II}^*$.

For the single phase unstrained reference state of LSC₁₁₃, k_{113}^* is:

$$k_{113}^* \approx \left[v_3 \times \exp \left\{ - \frac{(E_{\text{ads}}^{113} + E_{\text{vac}}^{113} + E_{\text{mig}}^{113})}{k_B T} \right\} \right]_{113} \quad (7)$$

where all prefactors are incorporated into v_3 . We assume that the prefactor terms, v_1 , v_2 , and v_3 are approximately the same on the single phase LSC₁₁₃ and the LSC₁₁₃/LSC₂₁₄ hetero-structure.

The ratio $\frac{k_{113/214}^*}{k_{113}^*}$ that represents the relative enhancement of ORR kinetics at/near the LSC₁₁₃/LSC₂₁₄ interface compared to that on the single phase LSC₁₁₃ is calculated using eqn (5)–(7) and Table 2. At 500 °C, representative of Sase *et al.*'s^{15,18} O-SIMS measurement conditions, $\frac{k_{113/214}^*}{k_{113}^*}$ is found as 4×10^2 .

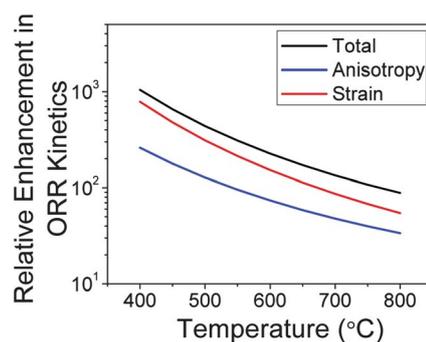


Fig. 7 The relative enhancement of ORR at/near the LSC₁₁₃/LSC₂₁₄ interface, quantified as $\frac{k_{113/214}^*}{k_{113}^*}$ as a function of temperature. The deconvoluted contributions of the LSC₂₁₄ anisotropy and the lattice strain in LSC₁₁₃ and LSC₂₁₄ (together) are also shown.

We deconvolute the effect of anisotropy and the effect of strain in this total enhancement factor by subtracting the factor with no strain from the total $\frac{k_{113/214}^*}{k_{113}^*}$ noted above as:

$$\left[\frac{k_{113/214}^*}{k_{113}^*} \right]_{\text{strain}} = \frac{k_{113/214}^*}{k_{113}^*} - \left[\frac{k_{113/214}^*}{k_{113}^*} \right]_{\text{no strain}} \quad (8)$$

We note that the $\left[\frac{k_{113/214}^*}{k_{113}^*} \right]_{\text{no strain}}$ is equivalent to the LSC₂₁₄ anisotropy effect alone at this hetero-structure. Fig. 7 shows these results in the 400–800 °C range, and as expected the relative acceleration in ORR is more significant at the lower temperatures. At 500 °C, the contribution to the overall enhancement factor from the LSC₂₁₄ anisotropy is 10^2 times. The contribution from lattice strain (considered both in LSC₁₁₃ and LSC₂₁₄ together) at 500 °C is 3×10^2 times. On the basis of these results, we think that both the LSC₂₁₄ anisotropy and the strain effect especially in LSC₁₁₃ could have acted equally importantly as two possible sources to accelerate the ORR kinetics on the LSC₁₁₃/LSC₂₁₄ hetero-structure that was reported experimentally in ref. 15 and 16.

4. Conclusion

Using DFT + U calculations, we demonstrated that, at the LSC₁₁₃/LSC₂₁₄ interface, the LSC₂₁₄(100) surface serves as an energetically favorable window for oxygen adsorption and incorporation. In addition to this, the lattice strain near the hetero-interface facilitates oxygen incorporation especially on LSC₁₁₃. These two factors together accelerate the ORR kinetics by 4×10^2 times at 500 °C. This finding explains to a large extent the experimental results of ref. 15 and 16 at 500–550 °C, and predict the RP phase anisotropy and the strain effects as two equally important sources of ORR activity enhancement reported for the LSC₁₁₃/LSC₂₁₄ hetero-structure. These results, however, quantitatively underestimate the $\times 10^3$ to 10^4 enhancement reported experimentally. Both computational and experimental uncertainties may contribute to this difference.

However, we believe that an important reason for this difference is the assessment of the single phase LSC₁₁₃ and LSC₂₁₄ separately in this work rather than an explicit representation of this LSC₁₁₃/LSC₂₁₄ interface. Recent experimental work in our group has shown that LSC₂₁₄ is electronically activated when it interfaces the LSC₁₁₃, and this electronic activation is expected to facilitate charge transfer from the surface to the oxygen adsorbates in the reduction process.³⁵ This effect cannot be captured in our current DFT models. Nevertheless, such electronic activation of LSC₂₁₄, concurrent with the anisotropically high oxygen incorporation into LSC₂₁₄, is thought to be another key mechanism that additionally contributes to the fast ORR near the LSC₁₁₃/LSC₂₁₄ interface. Besides these sources, we cannot ignore that other factors such as space charge effects⁶² and a change in the electronic structure^{52,63} near the hetero-interface may also contribute to the ORR enhancement. Insights gained from our results can guide the design of novel perovskite/Ruddlesden–Popper composites for faster ORR kinetics. Hetero-structures with a large area of the (100) surfaces and smaller thickness in the [001] direction of the RP phase, and with tensile strain fields are expected to provide faster ORR kinetics for high-performance SOFC cathodes.

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