PAPER
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Effect of structure on oxygen diffusivity in layered oxides: a combined theoretical and experimental study
1. Introduction

Atomic and ionic diffusion in solids has received growing interest over the past few decades as solid state electrochemical systems such as batteries and fuel cells become efficient and effective means of generating and storing electrical energy derived from chemical energy.5–6 Diffusion in solids is of particular interest in solid state batteries (lithium ions)7,8 and solid oxide fuel cells (oxygen ions),9–11 as higher diffusivity correlates with higher electrolyte and electrode performances. In the case of oxygen diffusion, there exist two types of oxygen defects – oxygen vacancies and interstitials – that can support oxygen diffusivity. Oxygen ions adjacent to vacant sites enable oxygen ions to hop from normally occupied to adjacent unoccupied sites in the lattice, while interstitials can diffuse via two different mechanisms, viz., via interstitial (from normally occupied to a nearby empty interstitial site) and interstitially (interstitial ion displacing a normally occupied ion into an adjacent empty interstitial site) mechanisms.12 Unlike fluorite and perovskite oxides, which can normally only accommodate oxygen vacancies (UO2+x) as an exception13, layered oxides can accommodate both types of defects,14–17 thus offering an advantage in their ability to operate at high oxygen partial pressures via oxygen interstitial/interstitialcy diffusion and at low oxygen partial pressures via oxygen vacancy diffusion.

A common form of layered oxide is A2B2O5 – also known as the 214 phase (term n = 1 of the Ruddlesden–Popper series A_{n+1}B_{n+1}O_{2n+2}) – including nickelates, cobaltates, and cuprates in which Ni, Co, and Cu occupy the B-site, respectively. Nickelate and cobaltate 214 phases exhibit the K2NiF4 or T structure, with alternating stacks of rock-salt AO- and perovskite ABO3-layers. Because copper can accommodate three different oxygen coordinations, as shown in Fig. S1, three different crystal structures exist for the 214 cuprates. For layered cuprates with large A-site cations, such as lanthanum or strontium, copper is octahedrally coordinated by six oxygen atoms \( \text{T}-\text{A}_2\text{Cu}_4\text{O}_{12} \). With small A-site cations, such as praseodymium or cerium, copper forms square-planar coordination \( \text{T}^{-}\text{A}_2\text{Cu}_4\text{O}_{14} \), and in between the two...
phases there is the T\* structure, a hybrid of T and T', in which copper forms pyramidal coordination blocks with oxygen.\textsuperscript{18}

These three structures may share similar chemistries, but show very distinct characteristics. For example, T'-structured Pr\textsubscript{2}CuO\textsubscript{4} has an extremely low oxygen diffusivity of \(7.2 \times 10^{-13}\) cm\(^2\) s\(^{-1}\) at 700 °C.\textsuperscript{19} The incorporation of the larger Sr\textsuperscript{2+} cations on the A-site leads to the T\* structure, as in Pr\textsubscript{1.6}Sr\textsubscript{0.4}CuO\textsubscript{4}, which exhibits a significantly higher oxygen diffusivity of \(6.7 \times 10^{-10}\) cm\(^2\) s\(^{-1}\) at 700 °C.\textsuperscript{20} T'-structured La\textsubscript{2}CuO\textsubscript{4} exhibits an even higher oxygen diffusion coefficient \(D^f\) of around \(1 \times 10^{-8}\) cm\(^2\) s\(^{-1}\).\textsuperscript{21} However, it is unclear whether the difference in diffusivity comes from the crystal structure, since both the cation chemistry and size are changing. Increasing acceptor/donor concentrations will likely lead to larger numbers of oxygen vacancies/interstitials. Different diffusion mechanisms also affect how fast oxygen can migrate. Oxygen diffusion in Pr\textsubscript{2}CuO\textsubscript{4} or T- La\textsubscript{2}CuO\textsubscript{4} is believed to be through oxygen interstitiality mechanisms, while in acceptor-doped Pr\textsubscript{1.6}Sr\textsubscript{0.4}CuO\textsubscript{4}, diffusion is \textit{via} the oxygen vacancy mechanism. Different cation sizes can affect local charge distribution, lattice parameter and lattice strain, thereby affecting diffusivity. There is no direct comparison of oxygen diffusivities among these structures as each cation chemistry is stable in only one structure. This study aims to answer the question of how different structures of identical cation chemistry affect diffusion and investigate underlying mechanisms by combining experimental (structural control and oxygen isotope exchange) and theoretical (density functional theory) methods.

2. Experimental methods

2.1 Thin film preparation

T and T'-structured La\textsubscript{2}CuO\textsubscript{4} thin films of \(\sim 30\) nm thickness were grown by pulsed laser deposition (PLD). After loading single crystal LaAlO\textsubscript{3} (LAO) substrates (MTI Corporation) and a bulk target of desired composition (refer to Experimental section in Kim, \textit{et al}.\textsuperscript{17}), the PLD chamber was pumped down to a base pressure of \(3 \times 10^{-6}\) Torr, and then the substrate was heated to 600 °C. A Coherent COMPex Pro 205 KrF excimer laser of 248 nm wavelength with 260 mJ per pulse at 1 Hz was used to ablate the bulk targets. The surface of each target was pre-ablated with 300–3000 pulses before every deposition. The chamber was maintained at 10 mTorr oxygen pressure during deposition.

2.2 Structural characterization

2.2.1 X-ray diffraction. X-ray diffraction (XRD) measurements for thin films were performed using Rigaku Smartlab with high resolution PB-Ge(220)\(\times 2\) package. Alignment to the symmetric substrate (single crystal LAO with (001) orientation) peak was performed prior to each scan.

2.2.2 TEM analysis. TEM samples from layered cuprate thin films were prepared by using FEI Nova NanoLab focused ion beam. To eliminate any charge effect and protect the sample surface from Ga\textsuperscript{+} ion beam damage, 90 nm of Au and 30 nm of Pt/Pd (80/20) were deposited on the sample by DC sputtering.

Additional protective layers of polymer resin and 5 nm of Pt/Pd (80/20) were subsequently deposited, and finally 1.7 μm of Pt was deposited by gas injection system (GIS). The sample was Ga\textsuperscript{+} ion milled at 30 kV, at various currents. A tungsten (W) omniprobe was used to pick up the milled plate and attach it on a Mo TEM grid. After the sample attachment on the grid, fine milling was conducted at low currents by reducing the milling current gradually. The atomic structures of the La\textsubscript{2}CuO\textsubscript{4} thin films were investigated using HAADF (High-Angle Annular Dark Field) and BF (Bright Field) images obtained by FEI Titan scanning/transmission electron microscope (STEM) at accelerating voltage of 300 kV. Here, a 300 kV electron beam is focused down to a spot with probe size of <0.1 nm, and scanned across the thinned sample.

2.3 Oxygen diffusivity measurement

2.3.1 Oxygen isotope exchange experiment. Schematic illustrations of the experiment is shown in Fig. 1(a) and (b). A 90 nm thick gold blocking layer was deposited on top of a PLD-deposited T- or T'-La\textsubscript{2}CuO\textsubscript{4} thin film except for a narrow area masked by a thin kapton tape. After removing the tape, the film was annealed at 673 K for five hours in air to stabilize the gold layer. A custom-built oxygen isotope exchange setup as shown in Fig. S2\textsuperscript{*} was used. The sample is placed inside a quartz tube, then a high vacuum pump system consisting of Edwards EXT70 turbomolecular pump, RV3 rotary vane pump, and ECC120 turbomolecular pump controller is used to pump down to 5.0 \(\times 10^{-6}\) Torr range. The tube is then filled with ultra high purity oxygen to 0.5 atm = 506.625 hPa and the furnace is slid on tracks so that the sample is located at the center of the furnace and annealed for at least 10 times longer than the isotope exchange exposure period at 500, 550, and 600 °C. The sample is then quenched to room temperature by sliding the furnace away from the sample chamber and exposing the sample tube to a fan to further cool the specimen. The tube is then pumped down again to 5.0 \(\times 10^{-6}\) Torr, then filled with \(^{18}\)O\textsubscript{2} gas (99%, Sigma Aldrich) to the same pressure of 0.5 atm = 506.625 hPa. The process is then repeated for each exchange experiment. The diffusion profiles of the oxygen isotope are subsequently analyzed by secondary ion mass spectrometry (SIMS).

2.3.2 Secondary ion mass spectrometry. Oxygen isotope diffusion profiles in T- and T'-structured La\textsubscript{2}CuO\textsubscript{4} thin films were analyzed by IONTOF TOF. SIMS 5 (Münster, Germany) Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) as illustrated in Fig. 1(c) and (d). First, a 30 nA beam of 3 keV Cs\textsuperscript{+} ions was rastered to etch the gold layer. Then, secondary ion images were obtained with a 0.2 pA beam of 30 keV Bi\textsuperscript{+} ions.

3. Computational methods

3.1 Bulk T- and T’-structures

We modeled bulk T- and T'-structured La\textsubscript{2}CuO\textsubscript{4} (space group = \(I4/mmm\)) using a \(2 \times 2 \times 2\) supercell composed of 112 atoms with DFT calculations. DFT calculations were performed using VASP\textsuperscript{22,23} with projected augmented wave (PAW) pseudopotentials from the VASP database and generalized gradient

Additional protective layers of polymer resin and 5 nm of Pt/Pd (80/20) were subsequently deposited, and finally 1.7 μm of Pt was deposited by gas injection system (GIS). The sample was Ga\textsuperscript{+} ion milled at 30 kV, at various currents. A tungsten (W) omniprobe was used to pick up the milled plate and attach it on a Mo TEM grid. After the sample attachment on the grid, fine milling was conducted at low currents by reducing the milling current gradually. The atomic structures of the La\textsubscript{2}CuO\textsubscript{4} thin films were investigated using HAADF (High-Angle Annular Dark Field) and BF (Bright Field) images obtained by FEI Titan scanning/transmission electron microscope (STEM) at accelerating voltage of 300 kV. Here, a 300 kV electron beam is focused down to a spot with probe size of <0.1 nm, and scanned across the thinned sample.

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approximation (GGA) of Perdew–Burke–Ernzerhof (PBE). An energy cutoff of 700 eV and a 3 × 3 × 1 Monkhorst–Pack k-point mesh were used after convergence tests. Atom positions were relaxed until all forces were less than 0.005 eV Å⁻¹. Lattice constants of La₂CuO₄ used in this study are a = b = 3.803 Å and c = 13.15 Å for the T-structure and a = b = 4.005 Å and c = 12.55 Å for the T’-structure.18,25 The probable strain and its effect on defect formation energies by the lattice mismatch between T- and T’-structured La₂CuO₄ thin films and LaAlO₃ substrates are so small that they were not taken into account in this study (explained in more detail in the ESI Fig. S3 and S4†).

### 3.2 Oxygen defect formation energies

To calculate the change in enthalpy when oxygen vacancies or interstitials are generated in La₂CuO₄, O atoms were removed from or added to the perfect La₂CuO₄ supercell, and then relaxed as done for the perfect La₂CuO₄ supercell. The defect formation or generation energy in the field of computational chemistry – when an oxygen defect of charge q is inserted in bulk La₂CuO₄ is defined as:

\[
E_{\text{defect}} = E_{\text{defect}}^{\text{tot}} - E_{\text{tot}}^{\text{perfect}} + \sum n_O \mu_O + q\left( E_F + E_{\text{VBM}}^{\text{perfect}} + \Delta V_{\text{avg}} \right)
\]

(1)

where \(E_{\text{defect}}^{\text{tot}}\) is the total energy of a relaxed supercell containing oxygen defect with charge q, and \(E_{\text{tot}}^{\text{perfect}}\) is the total energy for the perfect crystal using an equivalent supercell. The integer \(n_O\) indicates the number of O atoms that have been removed from (or added to) the supercell to form the defect, and \(\mu_O\) is the oxygen chemical potential. The electrochemical potential for electrons is the Fermi energy, \(E_F\), which is measured from the valence band edge maximum (VBM). To calculate the \(E_F\) relative to VBM, we employed the DFT + Hubbard U (DFT+U) approach within spin-polarized density functional theory by applying \(U_{\text{eff}}\) \((U - J) = 3 \text{ eV for ferromagnetic (FM) spin ordered La}_2\text{O}_3 \text{ and 8 eV for type-II antiferromagnetic (AFM-II) spin ordered Cu.}^{27}\) As shown in Fig. S5,† we found that the value of \(E_F\) relative to VBM does not change with respect to the \(U_{\text{eff}}\) value applied on Cu, even though band gaps similar to experimental values (1–2 eV (ref. 28)) could be obtained in a range of 4 eV < \(U_{\text{eff}}\) for Cu < 8 eV. Therefore, we conclude that \(U_{\text{eff}}\) value is not a critical factor for calculating the oxygen defect formation energy of La₂CuO₄. \(E_{\text{VBM}}^{\text{perfect}}\) is the VBM of the perfect supercell, which is obtained by \(E_{\text{tot}}^{\text{perfect}} - E_{\text{tot}}^{\text{perfect},+1}\), where \(E_{\text{tot}}^{\text{perfect},+1}\) is the total energy of the +1 charged perfect supercell. \(\Delta V_{\text{avg}}\) is the difference in average potentials \(V_{\text{avg}}\) far from the defect relative to the perfect supercell, i.e., \(\Delta V_{\text{avg}} = V_{\text{avg}}^{\text{defect}} - V_{\text{avg}}^{\text{perfect}}\), where \(V_{\text{avg}}^{\text{defect}}\) and \(V_{\text{avg}}^{\text{perfect}}\) are the average potentials of the defective and perfect supercells, respectively. The last two terms in eqn (1), \(q(E_{\text{VBM}}^{\text{perfect}} + \Delta V_{\text{avg}})\), are
the same as $E_{\text{corr}}$, a correction term that accounts for finite k-point sampling in the case of shallow impurities, or for elastic and/or electrostatic interactions between supercells, introduced in ref. 29 and 30. The calculation of the correction term is explained in Fig. S6 in ESI.†

To describe the defects in experimentally prepared T- and T'-La$_2$CuO$_4$, we chose single and paired oxygen defects in eight unit cells of T- and T'-La$_2$CuO$_{4\pm\delta}$ [i.e., $\delta = 1/64$ and 1/32]. Oxygen defects in T- and T'-La$_2$CuO$_{4\pm\delta}$ were created by removing/adding an oxygen atom in the perfect T- and T'-La$_2$CuO$_4$ structures. The formation energy of each oxygen defect was calculated relative to the perfect LCO crystal, using eqn (1). For examination of defect structures LCO was grown as a single-phase T-structure on LaAlO$_3$ substrate (Fig. 3(b)) is not as epitaxial compared to the T-LCO lms grown on the LCCO15 seed layer/LaAlO$_3$ (2 nm) to LCO (1.5 nm thick) to LCO (5 nm thick). Both films have c-axis perpendicular to the substrate.

3.3 Activation energy for diffusion

The nudged elastic band (NEB) routine$^{33-35}$ along with the climbing image method$^{34}$ implemented in VASP, was used with DFT calculations to predict the lowest energy pathway for oxygen diffusion in T- and T'-LCO. The initial and final configurations of diffusion pathways were optimized as done for the relaxation of the structures containing doubly charged defects. Eight images of intermediate atomic configurations were generated with constant spacing between the initial and final configurations. A spring constant of 5.0 eV Å$^{-2}$ and energy cutoff of 700 eV were used. The ionic relaxations were conducted until all forces were less than 0.005 eV Å$^{-1}$, and the electronic convergence was terminated at an energy difference of 10$^{-4}$ eV.

4. Results and discussion

4.1 Structural characterization

XRD spectra of La$_2$CuO$_4$ (LCO) thin films grown by PLD on single crystal LaAlO$_3$ (100) substrates with and without seed layer (deposited between substrate and desired film) are shown in Fig. 2. LCO grows as a single-phase T-structure on LaAlO$_3$ without seed layer, but forms a T'-structure when deposited on top of a thin seed layer of La$_{1.85}$Ce$_{0.15}$CuO$_4$ (LCCO15). Both films are grown c-axis oriented perpendicular to the substrate.

T- and T'-structured LCO thin films without and with the LCCO15 seed layer on LaAlO$_3$ substrates were further investigated by STEM-HAADF and -BF images, as shown in Fig. 3. As can be seen in Fig. 3(a) and S3,† the T-structured LCO thin film grows epitaxially on the LaAlO$_3$(001) substrate and perpendicular to the substrate (parallel to c-axis of the LCO film), which agrees with the results from HRXRD analyses in Fig. 2. The T'-structured LCO film grown on the LCCO15 seed layer/LaAlO$_3$ substrate (Fig. 3(b)) is not as epitaxial compared to the T-LCO film without seed layer, presumably due to lattice mismatch (refer to ‘strain in LCO thin film’ section in ESI†). However, the film is highly crystalline with near-uniform structure and with preferred orientation (c-axis perpendicular to the substrate as analyzed with respect to the locations of La, Cu and O atoms), agreeing with the results from HRXRD in Fig. 2.

The difference in the positions of some oxygen atoms between T- and T'-LCO are clearly observed in the STEM-BF images of Fig. 3; the STEM-BF image of oxygen atoms in apical sites in T-LCO shows brighter line contrast along a- or b-axis of the thin film (denoted with blue dotted lines in Fig. 3(a)) than that of oxygen atoms in equatorial sites, while T'-LCO shows little difference in the STEM-BF contrast of oxygen atoms between O-and CuO$_2$-planes as can be seen in Fig. 3(b). This contrast difference in T- and T'-LCO confirms that T- and T'-LCO thin films form on LAO(001) substrates without and with LCCO15 seed layer.

4.2 Oxygen diffusivities of T- and T'-La$_2$CuO$_4$

The oxygen diffusivities of both T- and T'-LCO thin films are studied to examine the effect of structure on diffusivity with films of the same cation chemistry but different structures. The two structures of LCO are prepared on insulating LAO substrates with and without a LCCO15 seed layer as described in Section 4.1. Cation diffusion is so slow for heavy atoms such as La and Ce that studies have been conducted at 900 °C and above. $^{36-39}$ By extrapolating the diffusivity temperature dependence down to 600 °C, D of La and Ce comes out to be less than 10$^{-24}$ cm$^2$ s$^{-1}$. The highest temperature our samples experienced was at 600 °C for less than two hours (including deposition and isotope exchange experiments), and total diffusion length, $L = \sqrt{D \times t}$, comes out to be less than 1 Å. Therefore, it is valid to assume that there is not sufficient Ce diffusion from the seed layer (~1.5 nm thick) to LCO (~30 nm thick) to affect oxygen diffusion behavior.
Oxygen diffusion in the $ab$-plane is faster than along the $c$-axis as evidenced in the isostructural nickelates, and will dominate the performance in polycrystalline bulk materials used for practical purposes. Therefore, diffusion in the $ab$-plane for the two structures is compared with films oriented $c$-axis perpendicular to the substrate. After the $^{18}$O isotope exchange is completed, the isotope profiles are obtained by SIMS as described in experimental methods and Fig. 1. Oxygen isotope concentration–distance profiles for T- and T'-LCO are plotted in Fig. 4(a) and (b). The $^{18}$O isotope density in both thin films decreases along the direction of in-plane diffusion. The distribution of the $^{18}$O isotope in the T-LCO thin film extends further from the origin than in the T'-LCO thin film over the same period of time, indicating that the $^{18}$O isotope exhibited a higher diffusivity in T-LCO than in T'-LCO.

Values for $D_{ab}^*$ (oxygen diffusion coefficient along $ab$-plane) are extracted by fitting the data with the aid of Crank’s solution for diffusion in a semi-infinite medium. The fits to the data in Fig. 4 resulted in $D_{ab}^* = 1.06 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for T-LCO and $D_{ab}^* = 1.30 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for T'-LCO at 600 °C showing that the oxygen diffusivity for the T-structure is approximately ten times higher than that in the T'-structure.

**Fig. 3** Scanning transmission electron microscopy (STEM) – high angle annular dark field (HAADF) and – bright field (BF) images of (a) T-La$_2$CuO$_4$ (LCO) thin film on LaAlO$_3$ (LAO) substrate and (b) T'-La$_2$CuO$_4$ thin film on LCCO15 seed layer/LAO substrate. Green, blue, and red circles in each image are inserted in order to identify the atomic positions of La, Cu, O atoms in T- or T'-structured LCO, respectively.

**Fig. 4** $^{18}$O isotope concentration profiles measured by ToF-SIMS after oxygen isotope exchange for one hour at $aO_2 = 0.5$ atm and 600 °C for (a) T- and (b) T'-La$_2$CuO$_4$ thin films.
Oxygen tracer diffusion experiments were performed at two additional temperatures, 500 and 550 °C, with the derived diffusion coefficients plotted in Fig. 4. The temperature dependence of diffusivity can be expressed as

$$D = [\text{def}] \frac{1}{6} d^2 \nu_0 \exp \left( \frac{\Delta S}{k_B} \right) \exp \left( -\frac{E_m}{k_B T} \right)$$

where [def] is the migrating defect concentration, $Z$ the number of potential defect migration sites, $d$ the jump distance, and $\nu_0$ the attempt frequency. The extracted pre-exponential terms and activation energies for diffusion (i.e., migration enthalpy $E_m$) for T- and T'-LCO are $2.21 \times 10^3$ cm$^2$ s$^{-1}$ and $1.07 \times 10^3$ cm$^2$ s$^{-1}$, and $1.79 \pm 0.03$ eV and $1.03 \pm 0.24$ eV, respectively. Because $Z$, $d$, and $\nu_0$ cannot differ by more than few factors between T- and T'-LCO, we can deduce that T-LCO has several orders of magnitude more oxygen defects than T'-LCO. It is notable that while the magnitude of oxygen tracer diffusion is larger for T-LCO in this temperature range due to the large number of defects, it nevertheless exhibits a higher activation than that of T'-LCO. Extrapolating the diffusivity fits, T-LCO will have smaller diffusion coefficients below 415 °C. This represents the first direct comparison of oxygen diffusivity between T- and T'-structures with the same cation chemistry. Previous comparisons of oxygen diffusivities obtained for the T- and T'-structured layered cuprates were derived from studies on cuprates with different chemical compositions.\textsuperscript{19}

4.3 Oxygen defect formation energies

In oxygen diffusion-mediated materials, a higher oxygen diffusion coefficient ($D_{ab}^{\text{O}}$) is generally correlated with a lower activation energy for diffusion ($E_a$).\textsuperscript{43} However, we observe that while the T-structured LCO shows faster oxygen diffusion, it nevertheless exhibits a higher activation barrier compared to T'-structured LCO. In an attempt to explain this unexpected relationship, we examine the respective defect chemistries of T- and T'-structured LCO, utilizing DFT calculations (described in Computational methods section) to identify the dominant type(s) of oxygen defects contributing to diffusion and their relative concentrations in the two structures.

4.3.1 Case of single defects. Fig. 6 shows atomic configurations in T- and T'-LCO, and the positions of different oxygen defects in the structures. In both structures, two distinct oxygen vacancy sites exist, the so-called apical and equatorial oxygen sites for the T-structure, and the O- and Cu$_2$O$_2$-plane sites for the T'-structure. Out of two interstitial sites in T-LCO, only one – shown in Fig. 6(a) – is thermodynamically feasible,\textsuperscript{44} which is also confirmed by our calculations. There is only one interstitial site in T'-LCO. The defect formation energy of each defect type was examined with different defect charges, i.e., neutral, singly- and doubly-charged. As summarized in the tables in Fig. 6, oxygen interstitials are highly likely to be formed in T-LCO regardless of their charge. Among oxygen interstitials with different charges, doubly-charged interstitials show the lowest formation energy, suggesting that doubly-charged oxygen interstitials predominantly form in T-LCO. Likewise, oxygen interstitials prefer to be generated in T'-structured LCO (Fig. 6(b)), while oxygen vacancy formation is also highly feasible in the O-plane. Two types of oxygen defects are therefore predicted to exist in the T'-structured LCO. Considering that the formation energy of oxygen interstitials in T-LCO is much lower than in T'-LCO (nearly twice lower), the oxygen interstitial concentration naturally formed in T-LCO is predicted to be much higher than in T'-LCO. For example, at 600 °C, exp \left( -\frac{E_I}{k_B T} \right) is $7.95 \times 10^{15}$ and $2.01 \times 10^7$ for doubly-charged oxygen interstitials in T- and T'-LCO, respectively.

4.3.2 Case of defect pairs. In order to examine whether oxygen defect pairs can be formed in local regions, defect pair formation energies for VO$^{2-}$–Vo$^{2-}$ and IO$^{2-}$–Io$^{2-}$ in T- and T'-LCO were calculated and are shown in Fig. 7 and 8. Since interactions between closely-located defect pairs predominate in their impact on formation and defect migration energies, we only consider defect pairs at 1$^{\text{st}}$ and 2$^{\text{nd}}$ nearest neighbor distances. Furthermore, the formation of oxygen vacancy pairs is considered only around equatorial oxygen sites in T-LCO, or oxygen sites in O-plane in T'-LCO because oxygen vacancy formation is more stable at these sites as summarized in the tables in Fig. 6. As summarized in the tables in Fig. 7, T-LCO strongly favors a second oxygen interstitial in the 1$^{\text{st}}$ nearest neighbor position (position I in Fig. 7(b)) to form a pair, given the highly negative formation energy of Io$^{2-}$–Io$^{2-}$ pair. Oxygen vacancy pairs, on the other hand, hardly form in T-LCO, regardless of the locations of the defect pairs. This result is in accordance with the formation energy of a single oxygen defect shown in Fig. 6(a); T-LCO

![Oxygen tracer diffusion coefficients along the ab-plane ($D_{ab}$) for T- and T'-LCO thin films at $aO_2 = 0.5$ atm as a function of inverse temperature (1/T).](image-url)
thermodynamically prefers to form a high concentration of interstitials while incapable of accommodating oxygen vacancies. For $T^0$-LCO, both $V_{O}^{2+}$ to $V_{O}^{2+}$ (Fig. 8(a)) and $I_{O}^{2+}$ to $I_{O}^{2+}$ pairs (Fig. 8(b)) have negative formation energies, and therefore local regions with both oxygen vacancy and interstitial pairs can exist. Among several configurations with different neighbors, the 2nd nearest neighbor (position 1 in Fig. 8) is the most energetically favorable for vacancy defects. For interstitial defects, the 1st nearest neighbor pair is the most energetically favorable. Note that this is only considering oxygen interstitials; oxygen atoms on O- and CuO$_2$-planes as well as lanthanum and copper atoms are closer than the 1st nearest interstitial.

4.4 Oxygen diffusion path

To find the minimum energy path (MEP) for oxygen diffusion along the $ab$-plane in $T$- and $T^0$-structured La$_2$CuO$_4$, diffusion
Energy barriers were calculated using NEB methods as explained in Computational methods for every possible migration pathway taken by oxygen vacancies or interstitials in the structures. For the NEB calculations, only doubly charged oxygen interstitials and vacancies were considered given that they are thermodynamically favored to be generated, according to the defect deformation energies reported in Section 4.3. The diffusion pathways along the ab-plane were considered only when oxygen point defects migrate via first- or second-nearest neighbor sites, as indicated in Fig. 9–12. Some examples of energy landscapes calculated along diffusion coordinates of defects in T- and T'-structured La₂CuO₄ were shown in Fig. S7.†

4.4.1 T'-structured La₂CuO₄. Fig. 9 shows energy barriers for the migration of a doubly charged oxygen interstitial in the ab-plane via interstitialcy (paths A and B) and the direct interstitial (path C) migration mechanisms in T'-structured La₂CuO₄.‡ Among paths A, B and C, paths A and B show lower energy barriers for migration (1.81 and 1.87 eV), which agree closely with the experimentally estimated value of 1.79 eV in Fig. 5. The energy barrier is also comparable to that of IO₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋щен.objects/10.1039/b204253j/fig08a.png' height='100' width='100' align='left'>Fig. 8 Images: atomic configurations of T'-LCO showing the locations of (a) VO₀²⁺₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋щен.objects/10.1039/b204253j/fig08b.png' height='100' width='100' align='left'>Fig. 9 Energy barriers for the migration of doubly charged oxygen interstitials in T'-LCO via interstitialcy (paths A and B) and direct interstitial mechanism (path C). Energy barrier values of 1.55, 1.91, 1.87, and 2.12 eV for A, B, and C paths, respectively, were calculated by DFT, while the experimental energy barriers for A, B, and C paths were 1.81, 1.87, and 2.83 eV, respectively. **Fig. 10** shows energy path for oxygen moves along the ab-plane with the path labeled A. This suggests that in T'-structured LCO, oxygen diffusion dominantly occurs via interstitialcy migration of doubly charged oxygens; A and B pathways are available for unpaired interstitials while only path A dominates when two interstitials are paired.

4.4.2 T'-structured La₂CuO₄. Fig. 11(a) shows energy pathways for doubly charged oxygen vacancy migration along five possible pathways (1’ to 5’) for a single oxygen vacancy created in T'-structured La₂CuO₄. Paths 1’, 2’, 4’, 5’ except 3’ contribute to ab-plane diffusion; among them, path 2’ appears to be most confined to ab-plane diffusion, not only because oxygen vacancies are created and move on the O-plane (most favorable sites for vacancies) (refer to Fig. 6(b)), but also because it exhibits the lowest energy barrier for migration (2.09 eV). However, the calculated value is much higher compared to the experimentally estimated energy barrier for diffusion (1.03 eV in Fig. 4).

In the case of interstitial atoms (Fig. 11(b)), the direct interstitial mechanism along the ab-plane (path C’) shows a minimum energy barrier for diffusion (1.94 eV), unlike the interstitialcy mechanism in T-La₂CuO₄ (path A in Fig. 9). However, this value is also much higher than the experimental value.

For oxygen vacancy pairs (Fig. 12(a)), the energy barrier for oxygen movement via path 2’ does not show a discernible change in comparison with that of a single vacancy (Fig. 11(a)), regardless of the relative position of VO₀²₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋щен.objects/10.1039/b204253j/fig08a.png' height='100' width='100' align='left'>Fig. 8 Images: atomic configurations of T'-LCO showing the locations of (a) VO₀²⁺₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋щен.objects/10.1039/b204253j/fig08b.png' height='100' width='100' align='left'>Fig. 9 Energy barriers for the migration of doubly charged oxygen interstitials in T'-LCO via interstitialcy (paths A and B) and direct interstitial mechanism (path C). Energy barrier values of 1.55, 1.91, 1.87, and 2.12 eV for A, B, and C paths, respectively, were calculated by DFT, while the experimental energy barriers for A, B, and C paths were 1.81, 1.87, and 2.83 eV, respectively. **Fig. 10** shows energy path for oxygen moves along the ab-plane with the path labeled A. This suggests that in T'-structured LCO, oxygen diffusion dominantly occurs via interstitialcy migration of doubly charged oxygens; A and B pathways are available for unpaired interstitials while only path A dominates when two interstitials are paired.

4.5. Summary

The defect formation energies (Eₓ) and migration energies (Eₘ) calculated by DFT, as well as pre-exponential terms (Dₒ) and activation energies (Eₒₐ) of diffusion from oxygen isotope exchange experiments for T and T’ structures of LCO are summarized in Table 1. Oxygen vacancy formation energies for T-La₂CuO₄ are positive (see Fig. 6), and therefore are excluded from the table. The oxygen interstitial formation energy for the T-structure is found to be highly negative (–2.83 eV). This implies the ready formation of a high concentration of oxygen interstitials already at reduced temperatures, and thus oxygen
diffusion is predicted to be limited only by the migration barrier. This is confirmed by the agreement between the activation energy of diffusion $1.79 \pm 0.03 \text{ eV}$ from the isotope exchange experiment and the calculated migration energy of $1.81 \text{ eV}$. It should be noted that this is unlike the case of traditional mixed ionic and electronic conducting (MIEC) oxides in which the overall diffusion activation energy includes a contribution from thermally activated defect formation, given a low initial defect concentration at reduced temperatures and increase in oxygen vacancies at higher temperatures.

Oxygen vacancy formation energies for $\text{T-La}_2\text{CuO}_4$ are negative and comparable to that of oxygen interstitials. However, since the vacancy migration energies are significantly

<table>
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<th>Path</th>
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<th>Direction</th>
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<tr>
<td>A</td>
<td>1.87</td>
<td>Interstitial, a-b</td>
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<tr>
<td>B</td>
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<td>Interstitial, a-b</td>
</tr>
<tr>
<td>C</td>
<td>2.20</td>
<td>Interstitial, a-b</td>
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Fig. 9 (a) Three (A, B and C) diffusion pathways of doubly charged oxygen interstitials ($\text{IO}^{2-}$) along the $ab$-plane in T-$\text{La}_2\text{CuO}_4$. Paths A and B represent interstitialcy migrations, and path C is a direct interstitial migration pathway. (b) Atomic configurations of T-LCO perpendicular to $ab$-plane (oxygen diffusion plane) showing A, B and C paths. Yellow and cyan circles denote oxygen interstitial and lattice oxygen atom participating in the interstitialcy migration, respectively. Green, blue, red circles are La, Cu, O atoms, respectively, that do not directly participate in the migration. Table: diffusion energy barriers of doubly charged oxygen interstitials along paths A, B and C, shown in figures (a) and (b).

<table>
<thead>
<tr>
<th>2nd $\text{IO}^{2-}$ position</th>
<th>Path</th>
<th>Barrier (eV)</th>
<th>Direction</th>
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<tr>
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<td>A</td>
<td>1.96</td>
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<tr>
<td>I</td>
<td>B</td>
<td>3.44</td>
<td>Interstitial, a-b</td>
</tr>
</tbody>
</table>

Fig. 10 (a) Two (A and B) diffusion pathways of doubly charged oxygen interstitials (marked with ‘I’ indicated by yellow circle) along ab-plane in T-LCO, when an additional oxygen interstitial (2nd $\text{IO}^{2-}$) exists in the nearest neighbor (marked with ‘I’ in pink circle). Paths A and B are interstitialcy migration pathways. (b) Atomic configurations of T-LCO perpendicular to ab-plane (oxygen diffusion plane) showing the paths A and B. 2nd $\text{IO}^{2-}$ is present in position I (refer to Fig. 7). Yellow, pink and cyan circles denote $1^{st}$ $\text{IO}^{2-}$, 2nd $\text{IO}^{2-}$, and a lattice oxygen atom participating in the migration. Green, blue, red circles are La, Cu, O atoms, respectively, that do not directly participate in the migration. Table: diffusion energy barriers of doubly charged oxygen interstitials along paths A and B shown in figures (a) and (b).
Fig. 11  (a) Left: five (1 to 5) diffusion pathways of doubly charged oxygen vacancy (V$_{O}^{2+}$) along ab-plane or c-axis in T’-La$_2$CuO$_4$+. Paths 1’ and 2’ are migration on O-plane along ab-plane, paths 3’ is along c-axis between O- and CuO$_2$-planes, and paths 4’ and 5’ are on CuO$_2$-plane along ab-plane. Right: table of energy barriers of oxygen vacancy-mediated diffusion via 1’ to 5’ pathways. (b) Left: three (A’, B’ and C’) pathways of doubly charged oxygen interstitials (I$_{O}^{2-}$) along ab-plane in T’-La$_2$CuO$_4$+. A’ and B’ paths are interstitialcy migration, C’ path is direct interstitial migration. B’ and C’ paths are purely related to ab-plane migration. Right: diffusion energy barriers of doubly charged oxygen interstitial along A’ to C’ pathways. Bottom: atomic configurations of T’-LCO showing A’, B’ and C’ paths. Yellow and cyan circles denote oxygen interstitials and lattice oxygen atoms participating in the interstitialcy migration, respectively. Green, blue, red circles are La, Cu, O atoms, respectively, that do not directly participate in the migration.

Fig. 12  (a) Left: diffusion pathway 2’ of doubly charged oxygen vacancy (marked with “O” in yellow circle, 1$^{st}$ V$_{O}^{2+}$) on O-plane in T’-LCO, when an additional oxygen vacancy (2$^{nd}$ V$_{O}^{2+}$) exists in close distances (positions 1 to 4 in pink circles). Table: diffusion energy barriers of oxygen via 1$^{st}$ V$_{O}^{2+}$ movement along path 2’, when there are 2$^{nd}$ V$_{O}^{2+}$ in positions 1 – 4 (refer to Fig. 8(a)). (b) Left: diffusion pathway C’ of doubly charged oxygen interstitials (marked with “I” in yellow circle, 1$^{st}$ I$_{O}^{2-}$) in T’-LCO, when an additional oxygen interstitial (2$^{nd}$ I$_{O}^{2-}$) exists in the first and second nearest neighbors (positions 1 and 2 in pink circles). Table: diffusion energy barriers of oxygen via 1$^{st}$ I$_{O}^{2-}$ movement along path C’, when 2$^{nd}$ I$_{O}^{2-}$ exists in position 2 (refer to Fig. 8(b)). Bottom right: atomic configurations of T’-LCO perpendicular to ab-plane (oxygen diffusion plane) showing the path C’, when 2$^{nd}$ I$_{O}^{2-}$ is present in position 2 (refer to Fig. 8(b)). Yellow, and pink circles denote 1$^{st}$ I$_{O}^{2-}$ and 2$^{nd}$ I$_{O}^{2-}$, respectively. Green, blue, red circles are La, Cu, O atoms, respectively, that do not directly participate in the migration.
higher than that of the pair-wise interstitial diffusion, the net diffusion is dominated by oxygen interstitials. This, again, is confirmed by comparing the migration energy of interstitial pairs (1.06 eV) as calculated by DFT and the activation energy of diffusion 1.03 ± 0.24 eV as obtained from the experiment. Because of much lower interstitial formation energy for T-LCO, the amount of oxygen interstitials is likely much greater in T-LCO compared to T’-LCO, thus much larger pre-exponential term in diffusivity.

In summary, oxygen diffusion in T-LCO is dominated by large concentration of oxygen interstitials migrating via interstitialcy mechanism, while T’-LCO has several orders of magnitude lower concentrations of oxygen defects and oxygen diffusion is via direct interstitial mechanism as interstitial pairs with significantly lower migration barrier compared to T-LCO. For both structures, thermal activation is determined solely by the corresponding migration energies. This is consistent with our earlier findings of surprisingly low reduction/oxidation enthalpies that result in defect concentrations being insensitive to temperature excursions at a given $aO_2$.

5. Conclusions

The effect of structure on oxygen diffusion was successfully separated from those induced by variations in cation chemistry by successfully growing two different structures of La$_2$CuO$_4$ in thin film form with the aid of buffer layers. Oxygen diffusivity as derived from isotope exchange studies with the aid of SIMS profiling is faster in T-than in T’-structured La$_2$CuO$_4$, while the activation energy of diffusion is surprisingly lower for the T’-structure. Oxygen defect formation energies and migration energies were calculated by DFT for both types of oxygen defects in the T and T’ structures. Oxygen interstitials are the dominant defect species for both structures. Oxygen diffusion is through interstitialcy mechanism in T-LCO, but is through direct interstitial mechanism in pairs in T’-LCO. The magnitude of diffusivity is dominated by the density of available mobile defects, and is therefore higher in the T-structure which exhibits considerably lower defect formation energies. The activation energies for diffusion as derived from oxygen isotope exchange experiments are directly correlated with the activation energies of migration calculated by DFT, explaining the lower activation energy for diffusion in the T’-structure. This provides an insight into creating models for diffusion mechanisms in layered structures with multiple defect species by combining experimental and computational approaches.

Conflicts of interest

There are no conflicts to declare.

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