

# Strain-Dependent Surface Defect Equilibria of Mixed Ionic-Electronic Conducting Perovskites

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makes the LSF surface more reducible than the compressed counterpart. These two observations were then validated using firstprinciples calculations. Finally, with the aid of thermodynamic analyses, we showed that the strain-dependent surface defect equilibria of LSF can be captured by bulk-like ideal solution defect models with shifted oxygen chemical potentials. The findings and methodology presented in this study enable quantitative determination of the surface defect chemistry, which is crucial to understanding and designing functional surfaces for efficient conversions of energy and fuels.

# INTRODUCTION

Mixed ionic and electronic conducting (MIEC) perovskitetype oxides,<sup>1</sup> such as  $La_{1-x}Sr_{x}CoO_{3-\delta}$  (LSC) and  $La_{1-x}Sr_{x}Co_{1-y}Fe_{y}O_{3-\delta}$  (LSCF), are among the state-of-the-art materials used in solid oxide cells and water electrolysis due to their high catalytic activities and high ionic/electronic conductivities. Recent advances in synthesizing atom-precise thin-film systems<sup>2</sup> have further boosted the functionalities of the MIEC perovskites via strain engineering.<sup>3,4</sup> For example, tensile strains have been found to enhance oxygen evolution kinetics in LSC for both low-temperature<sup>5</sup> and high-temperature<sup>6</sup> electrochemical applications. To date, the reactivity on the MIEC perovskite oxides is often related to the bulk properties of the materials, such as bulk diffusivity,<sup>7</sup> eg band filling,<sup>8</sup> and the position of the O 2p band center.<sup>9</sup> While these bulk descriptors provide valuable insights, surface defects (such as oxygen vacancies<sup>10</sup> and polarons<sup>11</sup>) should also be critical as they can act as decisive reactive centers during the (electro)chemical reactions.<sup>12-16</sup> Therefore, a deep understanding of the surface defect chemistry in the MIEC perovskites and its response under lattice strain is essential for rationally optimizing the functionalities of a broad range of electrochemical applications.

For bulk point defects, thermodynamic formulations have been established to understand the defect equilibria under external stimuli (such as gas atmospheres,<sup>17–19</sup> electrical polarization,<sup>20</sup> and lattice strain<sup>21</sup>). Nevertheless, the defect chemistry near the surface region has remained open. As the surface composition<sup>22</sup> and structure<sup>13</sup> can deviate significantly from the bulk, bulk defect chemistry is often not sufficient to describe the surface defects.<sup>23</sup> For example, it has been generally observed in perovskites and CeO<sub>2</sub>-based materials that the surface is much more defective than the bulk.<sup>24–28</sup> The possible presence of surface space-charge regions,<sup>29</sup> surface precipitates,<sup>30</sup> and surface dipoles<sup>31</sup> further contrasts the bulk and surface defect behaviors.

Although the strain-dependent surface defect chemistry can be inferred from *ex situ* surface characterizations,<sup>32</sup> it at best represents a "snapshot" of the entire defect equilibrium diagram, not to mention the likely surface evolution<sup>33</sup> prior

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**Figure 1.** Well-defined strain states and surface structure/chemistry of the epitaxial LSF thin films. (a) X-ray RSMs of the (103) reflection of the asprepared LSF films grown on LSAT and KTO single crystal substrates. Note that the film peak has the same  $Q_x$  values as that of the substrate, confirming identical in-plane lattice constants. (b) LEED pattern with the primary electron beam energy of 30 eV and (c) O *K*-edge XAS map showing the p(1 × 1) structure of the LSF (001) surface with homogeneous chemistry.

to the ex situ measurements. Therefore, to enable a more complete understanding of the surface defect chemistry and its strain dependency, one needs to reliably quantify the equilibrated surface defect concentrations in situ in a wide range of temperatures, gas pressures, and strain states. While significant advances have been made to enable in situ defect characterization, most techniques<sup>34–37</sup> are still bulk sensitive, making it difficult to isolate the surface defect chemistry. In this sense, near ambient pressure X-ray absorption spectroscopy (NAP-XAS) provides a powerful platform to probe the surface chemistry both *in situ* and *in operando*.<sup>38,39</sup> Since the sampling depths for the total/partial electron yield (TEY/ PEY) NAP-XAS measurements are smaller than 5 nm,<sup>40,41</sup> the electronic structures revealed by PEY- and TEY-XAS should directly reflect the defect chemistry at the materials surfaces. As an example, the seminal work by Mueller et al.<sup>42</sup> successfully utilized NAP-XAS to identify the surface redox center for oxygen exchange reactions in a series of MIEC perovskites.

Here, we investigate the strain-dependent surface defect equilibria on (001)-terminated epitaxial  $La_{0.6}Sr_{0.4}FeO_3$  (LSF) thin films. We chose LSF as model systems due to their broad applications in solid oxide fuel/electrolysis cells<sup>43,44</sup> and chemical looping.<sup>45</sup> Moreover, the well-studied defect chemistry<sup>18</sup> and strain-defect coupling<sup>46</sup> in bulk LSF further facilitates the comparison between the bulk and surface defect behaviors. We introduced well-defined strain states into LSF films from heteroepitaxy<sup>33</sup> and probed the surface defect chemistry of the differently strained LSF during O<sub>2</sub> incorporation/evolution reactions (OIR/OER):

$$O_2 \rightleftharpoons 2O^{2-} + 4h^{\bullet} \tag{1}$$

As shown in eq 1, the OIR/OER in LSF is accompanied by the formation and annihilation of electron holes  $(h^{\bullet})$ .<sup>18</sup> Recent studies have further established the correlation between the oxygen exchange rate and the electron hole concentration<sup>15</sup> on

the LSF surface. Therefore, a fundamental understanding of the surface equilibria of electron holes is critical to rationally engineer the OIR/OER kinetics on the LSF-based (electro)catalysts. To date, the surface electron hole evolution in LSF during OIR/OER is still under debate, where both iron<sup>47</sup> (i.e.,  $Fe^{3+} \rightleftharpoons Fe^{4+}$ ) and  $oxygen^{42}$  (i.e.,  $O^{2-} \rightleftharpoons O^{-}$ ) have been proposed as the redox centers. In this work, we aim to address these fundamental questions regarding the strain-dependent surface defect chemistry in LSF: Whether and how would lattice strain affect the redox center and the equilibrium concentration of the electron holes on the LSF surfaces during OIR/OER?

To answer these questions, we used electron-yield NAP-XAS to probe the near-surface  $(<5 \text{ nm})^{40,41}$  electronic structures on the differently strained LSF films at 400 °C in a wide range of oxygen partial pressures  $(pO_2)$ . In the remaining of the paper, we use the term "surface" to refer to the near-surface region rather than the very top surface atomic layer. As a result, we found that the Fe L-edges between the differently strained LSF films are almost identical, whereas O K-edges exhibit considerable differences. These observations indicate that for all the strain states examined in this work, the surface electron holes have strong oxygen character. The NAP-XPS observations were also supported by first-principles calculations, which suggest the electron holes in LSF are mainly located in oxygen states regardless of the strain state. By analyzing the O K-edge spectra, we then present a quantitative determination of the strain-dependent surface equilibria of electron holes on coherently strained LSF thin films. We found that tensile strain reduces the concentration of surface electron holes at any given pO<sub>2</sub>, suggesting that the tensile-strained LSF surface is more reducible compared to the compressive counterpart. Such strain-dependent reducibility was also verified by density functional theory (DFT) calculations. Finally, with the aid of thermodynamic analyses, we demonstrated that the strain-



**Figure 2.** O *K*-edge absorption spectra. (a) *In situ* O *K*-edge XAS spectra collected from LSF/LSAT in various  $pO_2$  at 400 °C. (b) Overlay of the shaded pre-edge regions in (a). Note that the feature "A" systematically decreases upon lattice reduction. (c) Comparison of the O *K*-edge between LSF/LSAT and LSF/KTO at different  $pO_2$ . Note that the LSF/KTO surface has a much lower pre-edge intensity than the LSF/LSAT, indicating that the tensile-strained LSF surface is more reducible than their compressive counterparts. All the XAS spectra were collected using the PEY mode; see Methods for more details.

dependent surface defect equilibria can be largely captured by ideal-solution-based defect models (i.e., without defect-defect interactions) with shifted oxygen chemical potentials.

## RESULTS AND DISCUSSION

Characterization of the LSF Films. Coherently strained epitaxial LSF films were grown onto two different types of (001)-oriented single crystal substrates: La<sub>0.18</sub>Sr<sub>0.82</sub>Al<sub>0.59</sub>Ta<sub>0.41</sub>O<sub>3</sub> (LSAT), and KTaO<sub>3</sub> (KTO) using pulsed laser deposition (PLD). The film thickness was determined to be 15 nm using X-ray reflectivity (Figure S1). In this paper, we will denote these two types of samples as LSF/LSAT and LSF/KTO, respectively. As shown in Figures S2 and S3, these two types of samples have similar surface composition and roughness. X-ray diffraction reciprocal space maps (RSMs) for the as-prepared LSF films are shown in Figure 1a and Figure S4. As illustrated, both types of LSF thin films maintained identical in-plane lattice parameters (featured by the same  $Q_x$ ) as that of the respective substrates, indicating that the films are fully strained. As discussed in the previous study,<sup>33</sup> the two types of LSF samples represent two opposite strain states: -1.3% compressive (LSF/LSAT) and +1.7% tensile (LSF/KTO).

To characterize the surface structure and chemistry of the LSF films, we conducted low-energy electron diffraction (LEED) and X-ray photoemission electron microscopy

(XPEEM) measurements. For these measurements, we grew LSF films onto the (001)-oriented Nb-doped SrTiO<sub>3</sub> substrate (i.e., LSF/STO) using the same growth condition. This change of the substrate material was necessary to provide sufficient electronic conductivity and thus enable LEED and XPEEM experiments on epitaxial LSF films, which cannot be done on insulating LSAT and KTO based samples owing to charging effects. Despite the different strain states, we expect that the surface structure/chemistry of the LSF/LSAT and LSF/KTO can be inferred from that of LSF/STO since all these samples have the same lattice orientation<sup>33</sup> and similar surface composition and roughness (Figures S2 and S3). For consistency with the experimental conditions for the surface redox studies (to be discussed below), we preannealed the LSF/STO sample in  $2 \times 10^{-7}$  Torr O<sub>2</sub> at 400 °C for 10 min before the measurements. As shown in Figure 1b, the LEED pattern (30 eV) shows a characteristic  $p(1 \times 1)$  perovskite (001) surface structure with a four-fold symmetry. Furthermore, by collecting X-ray absorption spectroscopy (XAS) maps around the O K-edge, La M-edge and Fe L-edge (Figure 1c and Figure S5), we show that the LSF sample has a homogeneous surface chemistry within the spatial resolution of XAS mapping ( $\sim$ 50 nm).

**NAP-XAS Measurements.** The representative O *K*-edges and Fe *L*-edge NAP-XAS spectra for the LSF films are shown in Figures 2 and 3. First, as highlighted by the shaded region in



**Figure 3.** Fe *L*-edge absorption spectra. (a) Representative *in situ* Fe *L*-edge absorption spectra of LSF/LSAT collected in different  $pO_2$  at 400 °C. (b) Overlay of the Fe  $L_3$ -edges in (a) showing the invariant peak position and constant peak ratio of the two  $L_3$  features. (c) Comparison of the Fe  $L_3$ -edge between LSF/LSAT and LSF/KTO at various  $pO_2$ . Note that the Fe *L*-edge absorption spectra are essentially insensitive to lattice strain. All the XAS spectra were collected using the TEY mode; see Methods for more details.

Figure 2a, the main change in the O K-edge spectra during oxygen redox reactions takes place in the pre-edge. A zoom-in view of the O K pre-edge region is shown in Figure 2b, where the three distinct features are labeled as "A", "B", and "C". The pre-edge feature "A" corresponds to the transition from O 1s to the ligand hole  $\underline{L}$  in the  $3d^5\underline{L}$  configuration in LSF.<sup>42,48</sup> The intensity of feature "A" decreased with decreasing pO<sub>2</sub> in the gas environment, indicating a filling of the ligand band, which corresponds to a reduction of LSF.<sup>42</sup> The two features between 529 and 532 eV (feature "B" and "C") can be assigned to the unoccupied  $t_{2g}\downarrow$  and  $e_g\downarrow$  states, respectively.<sup>42,48</sup> The increase of the  $t_{2g}\downarrow$  peak upon lattice reduction has been attributed to a change in covalency.<sup>42</sup> As the  $e_g\downarrow$  state is convoluted with the O<sub>2</sub> gas absorption peak,<sup>42</sup> we cannot unambiguously identify its intensity evolution.

Unlike the O *K*-edges, the Fe *L*-edges remained largely invariant during the experiments (see Figure 3a). As highlighted by the dashed lines, the positions of the Fe  $L_3$ absorption spectra remained constant within the reproducibility of the photon energies (±0.1 eV). Meanwhile, while there is a change in peak width at the high-energy tail of the Fe  $L_3$  edge, the intensity ratio between the two Fe  $L_3$  peaks—the fingerprint of different oxidation states of iron<sup>49</sup>—remained constant (evident from the superimposed spectra in Figure 3b). These observations suggest a constant valence state of the lattice Fe during the oxygen redox reactions. By comparing the Fe  $L_3$ -edge spectra of LSF to that of the reference spectra (Figure S7), we assign the lattice Fe to be 3+ valence state, with a  $3d^5$  configuration. Note that the constant Fe<sup>3+</sup> valence state in LSF is drastically different from that of SrFeO<sub>3-x</sub>.<sup>50</sup>

Next, we turn to the strain dependency of the surface defect chemistry, where we compare the O K-edge and Fe L-edge between LSF/LSAT and LSF/KTO at different pO2. For O Kedge (Figure 2c), it can clearly be observed that the tensile strained LSF (LSF/KTO) has a smaller pre-edge feature "A" than that of the compressively strained LSF (LSF/LSAT) at any given pO<sub>2</sub> examined in this study. Due to the very similar surface composition of these two types of LSF samples (Figures S2 and S6), the O K-edge difference can be safely regarded to originate from a difference in the LSF defect chemistry rather than surface Sr concentration difference.<sup>42,48</sup> Therefore, the reduced ligand hole concentration on the LSF/ KTO surface confirms that the biaxial tensile strain makes the LSF surface more reducible than the compressive surfaces. By comparing these two samples to LSF/STO, which is almost stress free,<sup>33</sup> we further confirmed that the strain dependency is monotonic (Figure S8). On the other hand, the Fe L-edge absorption is insensitive to lattice strain for the whole  $pO_2$ range examined in this study (Figure 3c). Therefore, combining Figures 2 and 3, we confirm that surface electron holes have strong oxygen character for both compressive and tensile strained LSF. Similar phenomena have also been reported by Mueller et al. on their polycrystalline (stress-free) LSF thin films during electrochemical reactions.<sup>42</sup> Here, we



Figure 4. Strain-dependent defect chemistry in LSF revealed by DFT. (a) Schematics of the LSF unit cell employed in the DFT calculation (side view). Biaxial strain is applied in the in-plane directions (i.e., *a* and *b* axes), while the out-of-plane *c* axis is set to be relaxed. (b) Change in formation energy ( $\Delta E_f$ ) for both oxygen vacancies in the FeO<sub>2</sub> (site 1) and La<sub>0.5</sub>Sr<sub>0.5</sub>O (site 2) stacking layers as a function of biaxial lattice strain. Here a more negative  $\Delta E_f$  value indicates easier oxygen vacancy formation. Note that both types of oxygen vacancies are more favorable under lattice tension. The solid lines in (b) indicate the parabola fitting to the DFT calculation results. (*c*-d) Comparison of the Bader charge of (c) lattice oxygen and (d) lattice Fe in stoichiometric LaFeO<sub>3</sub> and La<sub>0.5</sub>Sr<sub>0.5</sub>FeO<sub>3</sub> as a function of biaxial lattice strain. Note that the electron hole induced by Sr doping is mostly centered on the oxygen site.

demonstrate that the oxygen being the redox-active species also applies to the epitaxially grown and biaxially strained LSF films.

Finally, with the aid of bulk-sensitive partial fluorescence yield (PFY) mode XAS (Figure S9) and electrical conductivity measurements (Figure S10), we confirmed that the phenomena presented in Figures 2 and 3 (i.e., oxygen-centered electron holes and tensile-strain enhanced reducibility) are not only limited to the surface layers, but are rather general and can apply to the entire LSF film.

**First-Principles Calculations.** Having experimentally probed the oxygen character of the electron holes in LSF and their strain dependency, we further validate our observations with *ab initio* calculations. In this section, we use DFT calculations to demonstrate that (i) oxygen vacancy

formation in LSF is energetically more favorable under tensile in-plane strain and (ii) electron holes in LSF are preferentially located on the oxygen site, regardless of strain state.

Due to the challenges in stabilizing biaxial strains at the surface atomic layer in the DFT calculations, here we focus on the strain-dependent bulk defect properties in LSF. The calculation is still insightful, as we have discussed in the previous section that the strain effects on LSF's electronic structure and reducibility are qualitatively the same for both the surface (Figures 2 and 3) and bulk (Figures S9 and S10). The cell used in the DFT calculations is shown in Figure 4a (side view). As illustrated,  $La_{0.5}Sr_{0.5}FeO_3$  composition was selected for the calculations in order to reduce the size of the simulation cell. Consistent with experimental conditions, the cell is under in-plane biaxial strain (i.e., lattice strain applied in



**Figure 5.** Bulk defect chemistry and defect models for LSF. (a) Comparison of the defect model with the bulk defect equilibria in LSF pellet. The scattered data points (600–800 °C) are digitized from ref 18. The solid lines represent the best fit for the scattered data points using eq 7. The dashed line indicates the extrapolated bulk defect equilibria in LSF at 400 °C, which was obtained by extrapolation. (b) Logarithm of the fitted  $K_{ox}$  values (from eq 8) between 600 and 800 °C as a function of the reciprocal temperatures. The dashed line indicates the linear fitting ( $R^2 = 1$ ) for the  $K_{ox}$  from which the  $K_{ox}$  value at 400 °C was extrapolated. (c) Optical spectra of the stress-free LSF/MgO film at 700 °C in various pO<sub>2</sub>. Note that the more oxidized LSF film exhibits suppressed transmittance, which is also evident from the optical images (inset). (d) Comparison of the defect model with the bulk defect chemistry of the stress-free LSF film (LSF/MgO). The scattered points represent the defect concentrations quantified by the optical measurements. The lines represent the defect model, which has the same color coding as in (a). Note that the bulk defect chemistries of the stress-free LSF film largely follow the defect model within the error bars. The error estimation for the optical quantification is shown in Figure S13.

the *a* and *b* axes in Figure 4a) and fully relaxed in the out-ofplane direction (*c* axis). For completeness, we calculated the strain-dependent oxygen vacancy formation energies for the oxygen sites in both the FeO<sub>2</sub> and the La<sub>0.5</sub>Sr<sub>0.5</sub>O layers. These two types of oxygen atoms are labeled as site 1 and site 2 in Figure 4a, respectively.

We first compare the strain-dependent formation energies for both types of oxygen vacancies. The absolute energy changes in oxygen vacancy formation energies as a function of strain is presented in Figure S11. For better visualization, the relative change in the defect formation energies,  $\Delta E_{tr}$  are presented in Figure 4b.  $\Delta E_{f}$  represents the difference in the oxygen vacancy formation energy between strained and fully relaxed unit cells. As such, negative  $\Delta E_{f}$  values indicate that specific strain states would facilitate oxygen vacancy formation compared to the strain-free case. As illustrated, the oxygen vacancies in both the FeO<sub>2</sub> and  $La_{0.5}Sr_{0.5}O$  layers exhibit monotonic strain dependency and are energetically more favorable under biaxial lattice tension. The DFT calculation results thus explain the experimentally observed reducibility difference between the differently strained LSF samples (Figure 2 and Figures S8 and S10). Our findings are also supported by previous DFT studies in  $La_{0.75}Sr_{0.25}FeO_3$ .<sup>46</sup>

To elucidate the nature of the electron hole in LSF, we further compare the electronic structure between  $LaFeO_3$  and  $La_{0.5}Sr_{0.5}FeO_3$ . The comparison is informative because Fe cations in  $LaFeO_3$  have a well-defined  $Fe^{3+}$  valence state (3d<sup>5</sup> configuration).<sup>48</sup> Meanwhile, substituting  $Sr^{2+}$  ions onto  $La^{3+}$  sites within the  $LaFeO_3$  lattice serves to introduce electron holes into the system.<sup>48</sup> By comparing the Bader charges<sup>51</sup> between stoichiometric  $LaFeO_3$  and  $La_{0.5}Sr_{0.5}FeO_3$ , we systematically show the evolution of the hole state with both chemical

composition and strain state. As illustrated in Figure 4c,d, for all the strain states examined in this study (-1.5%, 0%, and +1.5%), Sr doping in LaFeO<sub>3</sub> mainly affects the Bader charge for oxygen (with more than 0.07 increase), while the Bader charges of Fe are essentially unchanged (with less than 0.02 decrease). These findings clearly indicate the electron holes generated by Sr doping are mainly localized on the oxygen site regardless of lattice strain, which agrees well with our NAP-XAS results discussed earlier. The strong oxygen character of the electron holes in LSF can be also seen in the orbital-resolved density of states (Figure S12). In accordance with our findings, previous simulations for LaFeO<sub>3</sub><sup>52</sup> also found that the localization of electron holes on the O site (i.e., yielding an O<sup>-</sup>) is energetically more favorable than on the Fe site (i.e., yielding an Fe<sup>4+</sup>).

**Defect Models for LSF.** Prior to this study, Mizusaki et al. proposed an ideal-solution-based defect model to describe the bulk defect equilibria in LSF based on the assumption of Fe<sup>4+</sup> polarons.<sup>19</sup> Nevertheless, from the experimental and simulation results discussed above, we have shown that the electron holes are mainly centered on the oxygen site. In this section, we present a modified defect model considering this more appropriate oxygen-centered electron hole. In accordance with the scope of this work, we limit our discussion to the high pO<sub>2</sub> regime where the oxygen exchange in LSF is charge compensated by electron holes, which corresponds to an oxygen nonstoichiometry range ( $\delta$ ) in La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3- $\delta$ </sub> of 0 <  $\delta$  < 0.2 (ref 18).

We propose that the OIR/OER (eq 1) in LSF can be expressed using Kröger–Vink notation as

$$\frac{1}{2}O_2 + V_0^{\bullet\bullet} + O_0^{\times} \rightleftharpoons 2O_0^{\bullet}$$
<sup>(2)</sup>

where  $O_0^{\times}$ ,  $V_0^{\bullet\bullet}$ , and  $O_2$  denote a neutral lattice oxygen, a doubly positively charged oxygen vacancy, and gas phase oxygen, respectively. To account for the strong oxygen character of the electron hole in LSF,  $O_0^{\bullet}$  denotes a relatively positively charged oxygen ion (i.e., an O<sup>-</sup> in absolute charges). Hence, eq 1 indicates that the oxygen incorporation reaction is charge compensated by the oxidation of the surface lattice oxygen (and vice versa). Please note that the adoption of the  $O_{O}^{\bullet}$  symbol here is not meant to indicate that electron holes in LSF have no partial Fe character. In fact, theoretical studies have suggested that hole states in LSF originate from the hybridization between O 2p and Fe 3d electronic states.53 Nevertheless, since both NAP-XAS and DFT revealed a preferred hole localization on oxygen, we keep the current format to highlight the strong oxygen character of the hole state for simplicity. After all, compared to the case of  $SrFeO_{3-x}$ where both the Fe L-edge and O K-edge absorption spectra demonstrated significant evolution during lattice redox, 50,54 electron holes in LSF are definitely much more localized on oxygen.

Using the framework described above, the equilibrium constant  $K_{ox}$  for eq 2 is given by

$$K_{\text{ox}} = [O_{\text{O}}^{\bullet}]^2 \times [O_{\text{O}}^{\times}]^{-1} \times [V_{\text{O}}^{\bullet\bullet}]^{-1} \times pO_2^{-1/2}$$
(3)

where [] indicates the concentration of each species in units of moles per mole of La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3- $\delta$ </sub>. Based on this definition, it follows that  $[V_O^{\bullet\bullet}] = \delta$ , which is the oxygen nonstoichiometry in La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3- $\delta$ </sub>. For charge and site conservation, one needs to consider:

$$[\mathrm{Sr}'_{\mathrm{La}}] = 2[\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}] + [\mathrm{O}_{\mathrm{O}}^{\bullet}] \tag{4}$$

$$[O_O^{\bullet}] + [O_O^{\times}] + [V_O^{\bullet\bullet}] = 3$$
(5)

where  $[Sr'_{La}] = 0.4$  corresponds to the Sr concentration in LSF. Combining eqs 3–5, we can correlate the pO<sub>2</sub> to the oxygen nonstoichiometry ( $\delta$ ):

$$pO_2 = (0.4 - 2\delta)^4 \times (2.6 + \delta)^{-2} \times \delta^{-2} \times K_{ox}^{-2}$$
(6)

and the hole concentration  $([O_0^{\bullet}])$ :

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$$pO_{2} = [O_{0}^{\bullet}]^{4} \times (2.8 - [O_{0}^{\bullet}]/2)^{-2} \times (0.2 - [O_{0}^{\bullet}]/2)^{-2} \times K_{\text{ox}}^{-2}$$
(7)

The defect model described in eq 6 was then used to fit the bulk oxygen nonstoichiometry data in LSF pellets at temperatures between 600 and 800 °C (data digitized from ref18). As shown in Figure 5a, the fitting results are in good agreement with the experimental data, which yields the validity of our defect model. The van't Hoff plot for the fitted equilibrium constant  $K_{ox}$  is presented in Figure 5b, which shows a linear relation between ln  $K_{ox}$  and the reciprocal temperatures. We can thus obtain the standard enthalpy and entropy change for the oxygen incorporation/evolution reactions ( $\Delta H_{ox}$  and  $\Delta S_{ox}$ ) in eq 2 from the van't Hoff plot as

$$\ln K_{\rm ox} = -H_{\rm ox}/RT + S_{\rm ox}/R \tag{8}$$

where *R* denotes the gas constant and *T* is the temperature. The bulk thermodynamic parameters obtained are  $\Delta H_{ox}^{\text{bulk}} = -111.2 \pm 0.2 \text{ kJ mol}^{-1}$  and  $\Delta S_{ox}^{\text{bulk}} = -90.2 \pm 0.2 \text{ J mol}^{-1} \text{ K}^{-1}$ . Note that these parameters are different from the values derived from the Fe<sup>4+</sup> model<sup>18</sup> as we are considering different defect reactions. Based on these parameters, we can extrapolate the equilibrium constant  $K_{ox}$  for bulk LSF to a temperature of 400 °C (i.e., the temperature we conducted all the NAP-XAS experiments), which is shown by the black open square circle in Figure 5b. Then, using eq 7, we can construct the bulk defect equilibrium diagram at 400 °C (Figure 5a, dashed line).

To demonstrate that the bulk defect chemistry of the LSF films used in this study also follows the defect model that is derived from the LSF pellets (Figure 5a), we conducted *in situ* optical measurements on a 120 nm stress-free LSF film that is grown on the MgO substrate (LSF/MgO, for which the strain analysis is shown in Figure S4). The representative optical transmittance spectra are shown in Figure 5c, which summarized the optical properties of the LSF/MgO film under equilibrium with different  $pO_2$  at 700 °C. Note that the optical transmittance increased as the sample gets reduced, indicating that the reduced LSF film has weaker light absorbance, which agrees with previous studies on LSF.55 The optical property evolution during the oxygen redox can be also visualized from the inset images in Figure 5c, where the oxidized LSF film appears to be darker due to its strong light absorbance. Previous studies have demonstrated that the magnitude of light absorption at 1.25 eV scale linearly with the electron hole concentrations in  $La_{1-x}Sr_xFeO_3^{55}$  (Figure S13). Therefore, by comparing the change in the optical absorbance (proportional to the absorption coefficient) at 1.25 eV (methods described in Figure S14), we estimated the bulk hole concentrations in the stress-free LSF film at different temperatures and pO2, and the results are summarized in Figure 5d. As illustrated, the quantified bulk hole concen-



Figure 6. Quantifying surface hole concentration from O K-edge spectra. Representative O K-edge spectra showing the (a) saturated and (b) depleted surface hole concentration  $[O_0^{\circ}]$ . All the spectra in (a, b) are collected at 400 °C except for the LSF/MgO spectrum in (b), which is collected at 500 °C to fully reduce the sample. (c) Comparison of the O K-edge absorption spectra from a LSF surface with intermediate  $[O_0^{\circ}]$  to the two end-member spectra in (a, b). The two solid circles highlight the presence of isosbestic points in the O K-edge spectra. (d) Difference spectra for plot (c) with respect to the depleted  $[O_0^{\circ}]$  state. The shaded region indicates the area S used in eq 9 to calculate the surface hole concentration.

trations in the LSF film (LSF/MgO) can be largely captured by the defect model within the error bars.

**Strain-Dependent Surface Defect Equilibria.** Finally, we demonstrate that the surface defect equilibrium diagram in LSF can be largely described using a "pO<sub>2</sub>-shifted" bulk defect model. To do so, we first describe the methods that we developed to quantify the surface hole concentration ( $[O_0^{\bullet}]$ ) from the feature "A" in the O *K*-edge absorption spectra (Figure 2b). Second, we compare the strain-dependent surface defect equilibria to the bulk defect model.

As shown in Figure 5a, the concentration of electron holes in  $La_{0.6}Sr_{0.4}FeO_{3-\delta}$  ([O<sub>0</sub>]) exhibits saturation/depletion behaviors at sufficiently high and low pO<sub>2</sub>, respectively. Such phenomena can be understood from eq 3. Under highly

oxidizing conditions, the saturated hole concentration is determined by the Sr doping concentration:  $[O_0^{\circ}]_{saturated} = [Sr'_{La}] = 0.4$  Meanwhile, at sufficiently low  $pO_2$ , the hole concentration is depleted:  $[O_0^{\circ}]_{depleted} = 0$ , since charge compensation of Sr-doping is fully provided by oxygen vacancies. Considering these facts, we can quantify the surface  $[O_0^{\circ}]$  from O *K*-edge spectra by using the two O *K*-edge spectra under strongly oxidizing and strong conditions (i.e.,  $[O_0^{\circ}]_{saturated}$  and  $[O_0^{\circ}]_{depleted}$ ).

To verify the existence of these two extreme O *K*-edge spectra, we collected the O *K*-edge from LSF samples at different strain states and under opposite cases of  $pO_2$ . In addition to LSF/KTO and LSF/LSAT, we also collected the O *K*-edge spectra from the fully relaxed LSF/MgO film. As



**Figure 7.** Constructing the strain-dependent surface defect equilibria at 400 °C. (a) Schematics of the experimental sequence in changing  $pO_2$  during the NAP-XAS measurements to quantify the surface hole concentrations. (b) Quantified surface hole concentrations of LSF/LSAT and LSF/KTO at 400 °C in different  $pO_2$ . In accordance with plot (a), the closed and open cycles represent measurements in the oxidation (from low  $pO_2$  to high  $pO_2$ ) and reduction (from high  $pO_2$  to low  $pO_2$ ) directions, respectively. (c, d) Fitting the surface defect concentration with the defect model (eq 7), where the fitting results are shown by the dashed lines. The solid lines represent extrapolated bulk defect chemistry at 400 °C (see Figure 6a). As indicated by the arrows, the surface defect equilibria can be largely captured by the bulk defect model with shifted oxygen chemical potentials.

illustrated in Figure 6a,b, there is a great overlap in the preedge regions (i.e., feature "A" in Figure 2b) when the LSF films are under strongly oxidizing/reducing conditions. Note that these saturated/depleted pre-edge features are independent of the  $pO_2$  and lattice strain. The perfect overlay of the pre-edges thus confirms the presence of the completely oxidized/reduced O K-edge spectra and also confirms that the oxygen gas absorption<sup>42</sup> does not affect the surface hole quantification in our experiments. For calibration, we compare the completely oxidized O K-edge (Figure 6a) to the reference bulk spectra.<sup>4</sup> As shown in Figure S15, the calibrated surface saturated hole concentration ([ $O_O^{\bullet}$ ]<sub>saturated</sub>) is 0.4 ± 0.1, which is in excellent agreement with the nominal value of 0.4. For the fully reduced O K-edge spectra (Figure 6b and Figure S16), the pre-edge feature completely vanishes and also overlaps quite well. We thereby assign it to represent the depleted surface hole concentration of  $[O_O^{\bullet}]_{depleted} = 0.$ 

Having demonstrated the two end-member O K-edge spectra for LSF with the  $[O_0^{\bullet}]_{saturated}$  and  $[O_0^{\bullet}]_{depleted}$  states, we now describe the methods to normalize the absorption

spectra, which is essential in quantifying the surface  $[O_0^{\bullet}]$  from the XAS spectra. Conventionally, the O K-edge spectra are normalized to the regions that are far above the absorption edge.<sup>42,56</sup> However, as different oxygen pressures contribute differently to the postedge region (Figure S17), we cannot adopt this normalization method in this study. Instead, we normalize the spectra to the isosbestic point (i.e., common intersection point) at  $\sim$ 529.5 eV, which is demonstrated in Figure S18. The presence of the isosbestic points in the O Kedge spectra of LSF during oxygen incorporation reactions has also been confirmed in the previous study.<sup>42</sup> Since the isosbestic point is in the pre-edge region, the O2 gas-phase absorption effect is minimal (Figure S17), which is evident also from the perfect overlay of the fully oxidized O K-edge spectra in Figure 6a. Representative normalized O K-edge spectra at various pO<sub>2</sub> are summarized in Figure S19.

To quantify the surface  $O_0^{\circ}$  concentrations, we superimpose the normalized O *K*-edge spectra at an intermediate  $[O_0^{\circ}]$  state with the fully oxidized/reduced O *K*-edge spectra in Figure 6c. The two common intersection points at around 527 and 529.5 eV are highlighted with the solid circles. We then subtract the reference  $[O_O^{\bullet}]_{depleted}$  state from the spectra-of-interest, and the resulting difference spectra is shown in Figure 6d. Finally, using the difference spectra, we calculate the integrated area *S* between the two common points (shown by the solid circles) in Figure 6d, which is schematically shown by the shaded region. The area *S* thus directly reflects the contribution of the surface electron holes. Since the intensity of the ligand hole absorption feature is linearly correlated to the hole concentration in LSF (Figure S15), we can calculate the surface hole concentration by comparing the obtained area *S* to that of the saturated hole state  $[O_O^{\bullet}]_{saturated}$  ( $S_{saturated}$ , the area under the dotted lines in Figure 6d):

$$[O_{O}^{\bullet}] = [O_{O}^{\bullet}]_{\text{saturated}} \times (S/S_{\text{saturated}}) = 0.4 \times (S/S_{\text{saturated}})$$
(9)

Using eq 9, we quantify the  $[O_0^{\bullet}]$  on the LSF/LSAT and LSF/ KTO surfaces as a function of pO2 at 400 °C. To check whether the sample surface is in equilibrium with the environment, we conduct the measurements both in the reduction direction (i.e., transition from high  $pO_2$  to low  $pO_2$ ) and in the oxidation direction (from low  $pO_2$  to high  $pO_2$ ). The sequence in changing the pO<sub>2</sub> during the NAP-XAS experiments is schematically presented in Figure 7a. The quantified  $pO_2$ - $[O_0^{\bullet}]$  relations for both LSF/LSAT and LSF/ KTO are summarized in Figure 7b. As the  $[O_0^{\bullet}]$  values measured in the oxidation (open symbols) and reduction (closed symbols) directions are similar, we confirm that the sample surface was in equilibrium with the gas atmospheres at least for  $pO_2 > 10^{-4}$  Torr. Note that since the PEY mode XAS is used for the quantification, Figure 7b represents the defect equilibria in the top  $\sim 2$  nm of the LSF film.<sup>42</sup>

We then fit the surface  $pO_2$ - $[O_0^{\bullet}]$  relation with the bulk defect model (eq 7), and the results are shown by the dashed lines in Figure 7c,d. For the high  $pO_2$  region ( $pO_2 > 10^{-4}$ Torr) where we confirm the sample is in equilibrium with the gas atmosphere, we find that the surface  $O_0^{\bullet}$  can be well captured by the defect model. On the other hand, for  $pO_2 <$  $10^{-4}$  Torr, we note that the measured surface hole concentrations somewhat deviate from the defect model. The deviation is more pronounced for the tensile-strained LSF (LSF/KTO). However, given the slow oxygen exchange kinetics at low oxygen partial pressures<sup>57</sup> and the uncertainties in the surface hole quantification, we cannot unambiguously conclude whether the observed phenomena are from defectdefect interactions.<sup>58</sup> Further study is required to address this question, and we thus keep it open in the present study. In any case, it is obvious that the surface defect equilibria in LSF are drastically different from that of the CeO<sub>2</sub>-based materials, where the surface defect concentrations demonstrate a much weaker  $pO_2$  dependence than the bulk.<sup>24,26</sup> As such, the LSF surface defect chemistry is more "bulk-like" than in case of CeO<sub>2</sub>. Since the bulk defect model in eq 7 is based on ideal solution assumptions, the bulk-like surface defect equilibria in LSF indicates that the averaged defect-defect interactions on the LSF surfaces are weaker than that of CeO<sub>2</sub>.<sup>27,5</sup>

To facilitate the comparison between the surface and bulk defect chemistry in LSF, we also plot the extrapolated bulk defect equilibria for the stress-free LSF at 400 °C (see Figure 5a) in Figure 7c,d with the solid lines. As illustrated, the surface hole concentrations for both LSF/LSAT and LSF/ KTO are considerably smaller than the values predicted by the bulk defect chemistry at any given  $pO_2$ , indicating a higher

concentration of oxygen vacancies on the surface. In accordance with our observations, a similar phenomenon (i.e., a more reduced surface) has also been reported qualitatively for both the powder<sup>25</sup> and thin-film<sup>60</sup> LSF in previous studies. Notably, even the compressive-strained LSF surface is more reducible than the extrapolated stress-free bulk. This observation is very interesting because both our (Figure 4b) and previous<sup>46</sup> calculations have shown that lattice compression would suppress the oxygen vacancy formation in bulk LSF. The highly enhanced surface reducibility can be due to the different defect thermodynamics between the surface and bulk. In support of this hypothesis, our DFT calculations have revealed a lower oxygen vacancy formation energy at the LSF surface compared to that in the bulk (Figure S20 and Table S1). Reduced surface oxygen vacancy formation energy from DFT calculations has also been reported on other related perovskites systems  $^{28,61,62}$  (e.g., LaCoO<sub>3</sub>). At this point, however, we cannot determine whether the highly reduced LSF surface originate from the modified  $\Delta H_{ox}$  or  $\Delta S_{ox}$ (see eq 8) values in the near-surface regions or a combination of both. We aim to address to this question in future studies by extending the current investigation to different temperatures.

Moreover, we find that the strain-dependent surface defect equilibrium diagram can be largely described by a "pO<sub>2</sub>shifted" bulk (extrapolated). As shown by the arrows in Figure 7c,d, the defect equilibria on the compressive and tensile strained LSF surfaces can be well reproduced by shifting the bulk equilibria toward the high  $pO_2$  direction by 2 and 5 orders of magnitude, respectively. Shifting the Brouwer diagram toward higher  $pO_2$  corresponds to a variation in the thermodynamic parameters (i.e., a reduction in  $K_{ox}$ , see eqs 7 and 8) for the oxygen incorporation/evolution reactions. The strain-induced "pO2-shifted" defect equilibria in LSF can also be inferred from the electrical conductivity measurements, where the pO2-dependent electrical conductivity of LSF/KTO can be largely reproduced by shifting that of LSF/STO toward high  $pO_2$  (Figure S10). These findings are in excellent agreement with a recent study by Schmid et al.,<sup>15</sup> where they found that the oxygen release reaction rate on the LSF surface can be best described assuming a "pO2-shifted" Brouwer diagram. While such a shift in the oxygen chemical potential for the surface defect equilibria was hypothesized in Schmid's study, here we provide direct experimental evidence on the same material.

#### CONCLUSION

In summary, we presented a generalizable methodology to quantify surface defect equilibria and constructed the straindependent surface defect equilibrium diagram of LSF, a model MIEC perovskite. In situ O K-edge and Fe L-edge NAP-XAS measurements provided direct evidence that electron holes that participate in the high-temperature OIR/OER have strong oxygen character, both for compressive- and tensile-strained LSF. In support of this finding, ab initio defect modeling confirmed that electron holes in LSF are mainly located on oxygen sites regardless of strain state. In addition, we showed both experimentally and computationally that tensile strained LSF is more reducible than compressive strained LSF. For thermodynamic analysis, we developed an OO-based defect model for LSF and validated it with the bulk defect chemistry of both LSF pellets and LSF thin films. By comparing the surface defect equilibria with the defect model, we showed that the LSF surfaces under both tensile and compressive strains are

considerably more reducible than the extrapolated bulk values for stress-free LSF. Moreover, the surface defect equilibria can be largely captured by a bulk-like, ideal-solution-based defect model, which is drastically different than that of the CeO<sub>2</sub> case.<sup>24,26</sup> As a result, the transition from bulk defect equilibria to strain-dependent surface defect equilibria is equivalent to a shift in  $pO_2$  (i.e., the oxygen chemical potential) by as much as 5 orders of magnitude at 400 °C. The insights into the straindependent surface defect equilibria can help elucidate the mechanisms of surface oxygen exchange kinetics and guide the rational design of oxygen-incorporation (electro)catalysts in solid oxide cells, sensors, and chemical-looping processes. By using fluorescence yield XAS and microfabricated electrochemical cells,<sup>26,63</sup> we expect the current framework can also help to elucidate other defect-related phenomena in MIEC systems, including those occurring at solid-solid and solidliquid interfaces.

# METHODS

Sample Preparation and Characterization. La<sub>0.6</sub>Sr<sub>0.4</sub>FeO<sub>3</sub> (LSF) thin films were deposited using pulsed laser deposition (PLD) with a KrF ( $\lambda$  = 248 nm) excimer laser. As substrates, (001)oriented 10 mm  $\times$  5 mm  $\times$  0.5 mm LSAT and KTO single crystals (MTI Corporation, one-side polished) were employed in this work to prepare differently strained LSF films. During PLD deposition, the backside substrate temperature was kept at 850 °C (which approximately corresponds to 650 °C surface temperature) in an oxygen pressure of 20 mTorr. By applying 3500 laser pulses (2 Hz, 1.5 mJ/cm<sup>2</sup>) to the LSF target, a LSF film of 15 nm thickness was grown on the substrates. After the PLD deposition, the films were cleaned with deionized (DI) water to remove potential surface Sr precipitates.<sup>64</sup> Reciprocal space mapping (RSM) was collected with Rigaku SmartLab X-ray diffractometer using Cu K-Alpha1 radiation. To maximize the RSM signal from the film, an asymmetric configuration [103-] is employed for the measurement. More details on the sample characterizations (such as thin-film compositional and strain states analysis) can be found in ref 33.

**Near-Ambient Pressure X-ray Absorption Spectroscopy.** near-ambient pressure X-ray absorption spectroscopies (NAP-XAS) were collected using the partial electron yield (PEY) mode at Beamline 9.3.2 of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, using the total electron yield (TEY) mode at the IOS (23-ID-2) beamline of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory. For the PEY measurement, a kinetic energy of 150 eV was set for the detected electrons to avoid overlap with the Auger and other photoelectron peaks.

For both experiments, the sample was placed on a ceramic heater, with a K-type thermocouple mounted onto the sample surface for temperature measurements. Prior to the XAS experiment, each sample was cleaned in 0.3 Torr  $O_2$  to remove the adventitious carbon on the surface (Figure S21). At each oxygen pressure, O K-edge and Fe L-edge absorption spectra were collected after the sample was allowed to equilibrate with the gas environment for 15 min. For data processing, the background of the NAP-XAS spectra was removed using linear fitting. For the Fe L-edge, the spectra were normalized to the strongest absorption feature between 710 and 711 eV. The O K-edge spectra were normalized to the isosbestic point at around 529.5 eV (Figures S18 and S19).

X-ray Photoemission Electron Microscopy and Low-Energy Electron Diffraction. X-ray photoemission electron microscopy (XPEEM) and low-energy electron diffraction (LEED) measurements were conducted at the XPEEM/LEEM endstation of the ESM beamline (21-ID) of the National Synchrotron Light Source II. The experiments were performed at room temperature after the LSF film was annealed in  $10^{-5}$  Torr O<sub>2</sub> at 400 °C for 10 min, without exposing the sample to air. To enhance the sample electrical conductivity, the LSF film was grown on the (001)-oriented Nb-doped SrTiO<sub>3</sub>

substrate (MTI corporation) for these measurements, using the same growth parameters as other samples used in this study.

**Density Functional theory (DFT).** DFT calculations were performed with the Vienna Ab Initio Simulation Package (VASP<sup>65</sup>). An energy cutoff of 500 eV was used with PBE functional and the generalized gradient approximation. A Hubbard *U* correction of 4.0 eV was applied to Fe. All calculations were spin-polarized. Defect formation energies in the bulk were calculated using a  $2 \times 2 \times 2$  La<sub>0.5</sub>Sr<sub>0.5</sub>FeO<sub>3</sub> supercell (8 formula units with a  $4 \times 4 \times 4$  *K*-point grid). For biaxially strained calculations, the lattice parameters were fixed in *x* and *y* directions, while the *z* direction was allowed to relax freely (Figure 4a). Surface calculations were performed for FeO-terminated (001) surface with 10 atomic layers and 20 Å of vacuum (Figure S20). Atoms of the five bottom layers were fixed, while the top surface was allowed to relax. A  $1 \times 1 \times 1$  *K*-point grid was used.

In Situ Optical Characterization. To measure the total transmittance at controlled temperatures and atmospheres, we used a custom-made spectrophotometer which was described in detail previously.<sup>66</sup> For the optical measurements, we grew by PLD a 120 nm LSF film onto the two-side polished MgO (001) substrate of 10 mm × 5 mm × 0.5 mm dimensions (MTI corporation), using the same growth parameters as other samples. The gas composition of the atmosphere inside the flow cell was controlled by a constant flow (at rate of 140 sccm) of premixed gases. Gas mixtures of pure O<sub>2</sub> and Ar were used for measurements in the 10<sup>-1</sup> to 750 Torr pO<sub>2</sub> range and a gas mixture of CO/CO<sub>2</sub>/Ar for the lower pO<sub>2</sub> range.

## ASSOCIATED CONTENT

## **③** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.2c00614.

Details of the experimental and computational procedure, XAS analysis, DFT calculations, electrical conductivity measurements, optical spectra analysis, and additional sample characterizations (PDF)

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## **Author Contributions**

J.W., A.K.O., and B.Y. conceived the experiment design. J.W. prepared the samples and analyzed the data. J.W., A.K.O, E.J.C., I.W., and A.H. carried out the NAP-XAS experiments. J.W. and J.T.S. conducted the XPEEM and LEED measurements. J.Y. conducted the DFT calculations. D.K. conducted the optical measurements. A.N. conducted the Van der Pauw measurements. J.W. wrote the manuscript, and all authors contributed to its revision. B.Y. supervised the project.

#### Notes

The authors declare no competing financial interest.

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