Effect of Atmospheric CO₂ on Surface Segregation and Phase Formation in La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} Thin Films

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Abstract

The effects of atmospheric CO₂ on surface segregation and phase formation in La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF-6428) were investigated. (001)-oriented LSCF-6428 thin films were deposited on lattice matched (110)-oriented NdGaO₃ (NGO) substrates by Pulsed Laser Deposition (PLD). Using the synchrotron technique of Total Reflection X-ray Fluorescence (TXRF), it was found that the kinetics of Sr surface segregation was enhanced when annealing at 800°C in a high CO₂ partial pressure, as compared to a similar anneal in a CO₂-free atmosphere, with the oxygen partial pressure being constant in both cases. Hard X-ray Photoelectron Spectroscopy (HAXPES) measurements showed that the contribution of the surface carbonate to surface oxide phases increased significantly for the sample annealed in the high-CO₂ atmosphere. Atomic Force Microscopy (AFM) studies showed enhanced surface phase formation during the high-CO₂ partial pressure anneal. Density functional theory (DFT) calculations provide a thermodynamic basis for the enhanced kinetics of surface segregation in the presence of atmospheric CO₂.

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1. Introduction

40% strontium doped lanthanum cobalt iron oxide, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF-6428), is a commonly used perovskite-type material for cathodes in solid oxide fuel cells (SOFCs). The advantages of LSCF-6428 lie in its mixed ionic and electronic conductor (MIEC) behavior and its excellent thermal expansion coefficient (TEC) match with the electrolyte, which is often yttria stabilized zirconia (YSZ) and gadolinium doped ceria (GDC) [1]. In spite of these advantages, when operated at working temperature of SOFCs (typically, $>800^\circ\text{C}$), LSCF-6428 suffers from long-term stability issues [2-5]. This has negative implications for long-term usage of these cathode materials.

Strontium segregation to the surface of LSCF-6428 during annealing at elevated temperatures in the form of strontium oxide (SrO) and strontium carbonate (SrCO_3) has been reported previously [6, 7]. Oh et al. reported that the formation of Sr-rich precipitates was enhanced with increasing temperature and oxygen partial pressure [6]. Davis et al. reported SrCO_3 formation on LSCF-6428 thin films after annealing at 800°C in air, using hard x-ray photoelectron spectroscopy (HAXPES) [7]. The formation of SrCO_3 was attributed to the presence of CO_2 in the atmosphere. It was speculated that SrO is formed at the surface due to Sr surface segregation, leading to the formation of SrO by reaction with atmospheric oxygen. Reaction of SrO with atmospheric CO_2 leads to the formation of SrCO_3 . It is also possible that CO_2 will directly react with the enhanced Sr concentration at the surface of LSCF-6428 in the presence of O_2 to form SrO and SrCO_3 . The formation of these surface phases will be deleterious to the electrochemical performance of the device not only because SrO and SrCO_3 are both electrical insulators, but also because formation of these surface phases reduces the effective LSCF-6428 surface area for oxygen incorporation, which is an important step in oxygen reduction reaction (ORR) process. The anode exhaust gas in SOFCs undergoing an anode gas recycle process can contain as much as 30% CO_2 produced by hydrocarbon fuels [8]. Any gas leakage from the anode side resulting from crack formation in the seals, electrolyte or interconnects will risk exposing the cathode to this high CO_2

concentration. For this reason, a 30% CO₂ gas phase concentration is chosen as the high-CO₂ concentration in this study.

Different CO₂ partial pressures were applied for real-time TXRF studies at typical SOFC working temperature 800°C, aiming to probe the kinetics of Sr segregation at the surface of LSCF-6428 thin films. AFM studies were performed to examine morphological changes on the surface and DFT calculations were used to explain the mechanism of the segregation.

2. Material and Methods

In this study, LSCF-6428 thin films were grown epitaxially on single crystal lattice matched substrates to get a smooth surface/gas interface suited for grazing incident angle x-ray studies. Epitaxial LSCF-6428 thin films were deposited on lattice matched 10×10×0.5 mm³ single crystal (110) NdGaO₃ (NGO, CrysTec) substrates by pulsed laser deposition (PLD) at the Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwestern National Laboratory (PNNL). The films were deposited using a LSCF 6428 target, at an oxygen partial pressure of 10 mTorr, and with the substrate heated to 550°C. The heteroepitaxy of (001) LSCF-6428 || (110) NGO was confirmed by x-ray diffraction (XRD) analysis (Figure 1a). Figure 1b shows a cross-section of a focused ion beam (FIB) assisted cross-section of the thin film, showing that the heteroepitaxial film was ~ 250 nm in thickness.

Real-time total reflection x-ray fluorescence (TXRF) measurements were carried out at the X23A2 beamline at the National Synchrotron Light Source-I (NSLS-I) at Brookhaven National Laboratory (BNL). TXRF is a non-destructive method to probe the surface composition of materials. The technique does not require ultra-high vacuum, and thus allows *in-situ* high temperature studies of samples exposed to different atmospheres. The X23A2 beamline is equipped with a Vortex four-element detector with a resolution of approximately 220eV at 6keV [9]. In these experiments, each of the four elements in LSCF was first ‘windowed’ by capturing their corresponding fluorescence peaks summed by four single channel analyzers (SCA). The data was then input into a multiple channel analyzer (MCA). The materials used to ‘window’ each element were a LaAlO₃ target for La, a SrTiO₃ target for Sr, a Co₂O₃ sheet for Co, and a

Fe₂O₃ sheet for Fe. The fluorescence lines used for window each element were L α_1 for La, and K α_1 for Sr, Fe, and Co.

Figure 2 shows the schematic of the TXRF setup. A specially designed stainless steel chamber was used that allows incoming and outgoing x-ray beams as well as the fluorescence signals from the sample to go through its Kapton window. The x-ray fluorescence signals are collected using a fluorescence detector facing the Kapton window of the chamber. The chamber is capable of heating a sample up to 1000°C with flowing gases. This chamber was fixed onto a Huber goniometer that can tilt the sample relative to the beam during the experiments.

Before taking measurements, the chamber was first flushed with the desired gas composition with a volume 15 times larger than the chamber volume to ensure that all residual gases in the chamber are removed. The gas compositions for the two experiments were 30% CO₂ - 21% O₂ - 49% N₂ for the ‘high CO₂’ concentration experiments and 21% O₂ - 79% N₂ for the ‘CO₂-free’ experiments. In both cases, the oxygen partial pressure was 0.21 atm. After the environment achieved desired gas phase composition, the sample was heated to 800°C in 40 minutes. The chamber was then kept heated at 800°C for 9 hours. Scanning the incoming x-ray over a range of incidence angles starting with a grazing angle and collecting the fluorescence signals for all the elements carried out depth profiling of all the elements. Each such scan lasted for ~ 45 minutes. At large incident angles, the x-ray beam penetrates deep into the sample and the detector gets signals from the substrate as well as from the thin film. As the incident angle is reduced, the depth from which the signal is collected reduces. Below a certain angle, known as the critical angle θ_c , the x-ray beam is totally reflected and only the topmost ~10 nanometers of the thin film fluoresces giving the surface composition of the film.

After the real-time TXRF measurements, the samples were cooled down to room temperature. Atomic force microscopy studies were carried out on the post-annealed samples using a Bruker Dimension 3000 AFM.

Hard x-ray photoelectron spectroscopy (HAXPES) measurements on the post-annealed TXRF samples were carried out in Beamline X24A at the NSLS. Incident photon energy of 2140 eV was used, and the energy was calibrated using the 3d binding energy of silver (Ag 3d_{5/2}=368.27 eV) measured from a silver foil. The strontium 3d peak is a doublet from spin orbit splitting into

3d_{3/2} and 3d_{5/2}. Curve fitting was carried out in the same manner as reported by van der Heide [4]. To distinguish between surface phases, Sr 3d_{5/2} peaks corresponding to 133.0 and 134.0 eV energies, were attributed to surface strontium oxide (SrO) and surface strontium carbonate (SrCO₃), respectively [4].

3. Results

In the TXRF experiment, the incoming photon energy was set above the Sr K-edge. Figure 3 shows a typical raw data set of photon counts versus incident angle for Sr and La. The photon intensity of the i^{th} component, $I_i(\gamma)$, is a function of the incident angle γ , and is proportional to the concentration of the i^{th} component in the material, $N_i(\gamma)$:

$$N_i(\gamma) \propto I_i(\gamma) \quad [1]$$

Defining the proportionality constants for Sr and La as a and b , gives:

$$N_{Sr} = a \times I_{Sr} \quad [2]$$

$$N_{La} = b \times I_{La} \quad [3]$$

At any x-ray incident angle, the A-site Sr concentration, $R_{Sr/(Sr+La)}$, can then be represented by measured intensities I_{Sr} and I_{La} as:

$$R_{Sr/(Sr+La)} = \frac{N_{Sr}}{N_{Sr} + N_{La}} = \frac{I_{Sr}}{I_{Sr} + C \times I_{La}}, \quad [4]$$

where C is a constant defined as:

$$C = \frac{b}{a} \quad [5]$$

The constant C can now be expressed in terms of the measured intensities, I_{Sr} and I_{La} , and $R_{Sr/(Sr+La)}$ as:

$$C = \frac{I_{Sr}(1 - R_{Sr/(Sr+La)})}{R_{Sr/(Sr+La)} I_{La}} \quad [6]$$

We know that for LSCF-6428, $R_{Sr/(Sr+La)} = 0.4$ in the bulk. With increasing incident angle of x-ray beam the La and Sr signals asymptotically reach the bulk value (Figure 3) as the surface contribution gets to be vanishingly small with increasing depth from which information is collected. Using these bulk intensities, and the value of $R_{Sr/(Sr+La)}$ in the bulk, C can be calculated using Eq. 6. Knowing C and the measured intensities, I_{Sr} and I_{La} , $R_{Sr/(Sr+La)}$ can then be plotted for all angles using Eq. 4.

Processed data for the *in-situ* TXRF measurements for LSCF-6428 thin films at 800°C are plotted as $R_{Sr/(Sr+La)}$ versus the incident angle of the x-ray beam. Figures 4a and 4b show the results for the ‘high CO₂’ and ‘CO₂-free’ cases, respectively. The total high-temperature exposure time in both experiments was ~ 9 hours. Since information on surface segregation is present in the data collected at incident angles below the critical angle, data is presented only for incident angles close to the θ_c .

Figure 5 shows the Sr 3d peaks measured by HAXPES, for an as-deposited sample, as well as the post-annealed samples in CO₂-free and high CO₂ atmospheres. The peaks have been fit to three separate 3d_{3/2} and 3d_{5/2} doublets, corresponding to surface SrO, surface SrCO₃ and bulk perovskite phases. The figure shows that while there is some surface phases form in the as-deposited sample, the high temperature exposures clearly lead to enhanced surface phase formation. The figure also shows that the surface carbonate to surface oxide contributions is much more enhanced for the high-CO₂ case.

4. Discussion

The critical angle, θ_c , for LSCF-6428 at 800°C for an incident x-ray beam with energy of 16.3 keV is calculated to be 0.17 degrees. To understand surface segregation, it is best to start at the dashed line in Figure 4 that marks the critical angle and look at the trends going towards lower

angles to the left. This gives the profile of Sr/(Sr+La) ratio going from the bulk towards the surface of the thin film.

It is interesting to note in Figure 4 that the as-deposited film is actually Sr-poor (La-rich) at the surface. However, in both cases, Sr segregation to the surface of the LSCF-6428 thin films occurs on annealing, with the amount of Sr segregation increasing with annealing time at 800°C (Figures 4a and 4b). In both cases, by the end of the anneal, the surface Sr enhancement exceeds the bulk value of 0.4, in spite of the original as-deposited surface being Sr-poor. In the high-CO₂ atmosphere, the Sr surface segregation appears to reach a stable value after 2 hours of annealing, and does not change appreciably during the subsequent annealing time. In contrast, for the CO₂-free case, Sr continues to segregate to the surface even after 9 hours of annealing. This is a clear indication that the kinetics of Sr surface segregation is enhanced in high-CO₂ case. It should be mentioned that no changes were observed on the B-site cation sublattice and the ratio of Co to Fe signals remain unchanged during annealing.

For the formation of surface SrCO₃ in the high CO₂ case, two possible mechanisms are proposed. The first can be pictured as a two-step process. The first step is the formation of a surface SrO phase by the reaction of enriched surface Sr with atmospheric oxygen (Eq. 7). This is followed by the formation of a surface SrCO₃ phase by reaction of the SrO with atmospheric CO₂ (Eq. 8).

At 800°C, the equilibrium CO₂ partial pressure for SrCO₃ formation (by Eq. 8) is 1.7×10⁻³ atm [7]. Since the high-CO₂ partial pressure of 0.3 atm is well above the equilibrium value, the formation of SrCO₃ is thermodynamically favored. The formation of SrCO₃ removes the reactant, SrO in the second step (Eq. 8), which is also the product in the first step (Eq. 7). By removing the product, the kinetics of Sr surface segregation in step 1 is enhanced.

The second mechanism does not require an initial formation of SrO to form SrCO₃, provided of course that the gas-phase CO₂ partial pressure is high enough. In this case, the Sr in the lattice reacts with gas phase O₂ and CO₂ to form SrCO₃ directly (Eq. 9).

The composition of the LSCF is chosen to be different from LSCF-6428 to reduce the number of unit cells required for the composition and hence reduce computation time for the density functional theory (DFT) calculations. However, it is believed that the trends are still valid for the LSCF-6428 case. The DFT calculations performed here pertain to calculating Gibbs free energy changes for the overall reaction given in Equation 9 and are independent of the mechanistic details of $SrCO_3$ formation. One could potentially conceive of separating the overall reaction given in Equation 9 into two sub-steps, one involving the formation of SrO from $La_{0.75}Sr_{0.25}Co_{0.25}Fe_{0.75}O_3$, and a second involving formation of $SrCO_3$ from SrO through Equation 8. It is important to note while $SrCO_3$ formation is observed, it is not possible in the set of experiments reported in the present work to distinguish between direct formation of $SrCO_3$ from the perovskite and the formation of $SrCO_3$ from SrO originally ex-solved from the perovskite phase through surface segregation and precipitation.

The standard Quantum Espresso software package [10] was utilized to compute the ground state energy. Ultrasoft pseudopotentials and generalized gradient approximation (GGA) for the exchange-correlation functional with the on-site Hubbard repulsion U (GGA + U) [11] corrections were used in this calculation. We applied Standard Coulomb repulsion parameter of $U = 5$ eV and exchange parameter of $J = 1$ eV to the 3d orbitals of the B-site transition metals including Fe and Co [12]. The energy cutoff was set to be 450 eV. The spin polarization effects were fully applied in the simulation. Figure 6 shows a representative supercell with the periodic boundary conditions applied along all the three x, y and z directions. The supercell was built for $La_{0.75}Sr_{0.25}Co_{0.25}Fe_{0.75}O_3$ containing a total of 40 atoms. Monkhorst-Pack k-point mesh was set to be $2 \times 2 \times 2$ in the first Brillouin zone for the total energy calculations [13]. The computed equilibrium lattice constant of such a cubic perovskite oxide was 3.91 Å, which is consistent with the experimental value of 3.925 Å for $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ [14]. A large vacuum of 10 Å is used and the atoms on the bottom layer were fixed at their bulk geometry to mimic the surface phase.

The crystal structure of $SrCO_3$ is orthorhombic [15]. The chemical potential for CO_2 calculated was simply adopted from the NIST Webbook [16]. Since it is well known that the vibrational

entropy changes of solids in these types of heterogeneous catalytic reactions are much smaller than the gas-phase entropy and the configurational entropy contributions, only the configurational entropy was considered.

Four separate cases were calculated. Two oxygen vacancy concentrations in LSCF, corresponding to $\delta = 0$ and 0.125, were considered, each exposed to two CO₂ partial pressures of 3.6×10^{-4} atm (CO₂ partial pressure in atmospheric air) and 0.3 atm. In all cases, the free energy change of Eq. 9 is presented in PO₂ versus T plots (Figure 7). The dashed lines in the figures are the loci of $\Delta G = 0$. To the left of the dashed line (blue area), $\Delta G < 0$, implying there is a thermodynamic driving force for SrCO₃ formation. To the right of the dashed line (red area), $\Delta G > 0$, it implies that SrCO₃ formation is not stable. The results show that for both vacancy concentrations, increasing CO₂ the partial pressure moves the dashed line move towards high temperature values, thereby increasing the temperature range over which SrCO₃ formation is stable. This again indicates CO₂ in the atmosphere provides additional thermodynamic driving force for the forward reaction in Eq. 9, and thus enhances the kinetics of Sr surface segregation. These two mechanisms both indicate enhanced kinetics and at this point it is not possible to distinguish which is prevalent.

Interestingly, Figure 7 shows that increasing the oxygen vacancy concentration also moves the dashed line to the right, thereby increasing the range of SrCO₃ stability. Although the exact reason for this is not known, it is speculated that the introduction of vacancies destabilizes the perovskite phase, making it easier to form surface phases. Of course, given that the simulated composition is not identical to the actual composition, and that the near surface oxygen vacancy concentration is not known; the DFT results should not be taken as quantitatively accurate. Nevertheless, the results do explain the trends that are experimentally observed.

For the CO₂-free case, the formation of some SrCO₃ surface phase (Figure 5b) is unexpected. This can be possibly attributed to trace CO₂ in the gases. The purities of the gases used in the experiments are: oxygen > 99.5%, nitrogen > 99.9995%, and carbon dioxide > 99.95%.

Interestingly, Figure 4 shows that the highest Sr/(Sr+La) ratio in the CO₂-free case (above 0.5) is higher than that in high-CO₂ case (below 0.5). Since after 9 hours of annealing, the Sr segregation is still evolving for CO₂-free case, while it seems to saturate for the high-CO₂, a

relevant question is whether the saturation in high-CO₂ case is due to significant reduction in the perovskite surface due to surface phase formation.

In order to address this issue, AFM analyses of the sample surfaces after annealing were carried out. The AFM images are shown in Figures 8a and 8b. The figures shows that the surface precipitates in 30% CO₂ case are significantly larger than those in the CO₂-free case, resulting in surface area coverage ratio of 61.3% versus 12.2%, respectively. This supports the conjecture that in the high-CO₂ case, the surface is indeed highly covered by the newly formed surface phases. These surface phases can act as a diffusion barrier, thereby reducing the effective area for Sr surface segregation and reaching a steady state after 2 hours of annealing.

5. Conclusions

This study demonstrates that the presence of CO₂ in the atmosphere enhances the kinetics of surface Sr segregation in LSCF-6428 thin films at 800°C. The results suggest that the formation of SrCO₃ increases segregation kinetics and allows Sr surface segregation to reach a steady state significantly faster. It appears that this steady state is not due to the surface reaching thermodynamic equilibrium, but due to blocking of the perovskite surface by the surface phases.

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References

- [1] H. Ullmann, N. Trofimenko, F. Tietz, D. Stover, and A. Ahmad-Khanlou, Correlation between thermal expansion and oxide ion transport in mixed conducting perovskite-type oxides for cathodes, *Solid State Ionics* 138 (2000) 79–90.
- [2] S.P. Simner, M.D. Anderson, M.H. Engelhard and J.W. Stevenson, Degradation Mechanisms of La–Sr–Co–Fe–O₃ SOFC Cathodes, *Electrochemical and solid-state letters*, 9 (2006) A478-A481.
- [3] E. Bucher and W. Sitte, Long-term stability of the oxygen exchange properties of (La, Sr)_{1-z}(Co, Fe) O_{3-δ} in dry and wet atmospheres, *Solid State Ionics*, 192(1), pp 480-482. (2011).
- [4] P.A.W. Van Der Heide, Systematic x-ray photoelectron spectroscopic study of La_{1-x}Sr_x-based perovskite-type oxides, *Surface and interface analysis* 33 (2002) 414-425.
- [5] S.R. Bishop, K.L. Duncan and E.D. Wachsman, Surface and bulk defect equilibria in strontium-doped lanthanum cobalt iron oxide, *Journal of the Electrochemical Society* 156 (2009) B1242-B1248.
- [6] D. Oh, D. Gostovic, and E.D. Wachsman, Mechanism of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ Cathode Degradation, *Journal of Materials Research* 27 (2012) 1992-1999.
- [7] J.N. Davis, Y. Yu, D. Cetin, K.F. Ludwig, U.B. Pal, S. Gopalan, and S.N. Basu, Surface Segregation and Phase Formation in Thin Films of SOFC Cathode Materials, *Proceedings of Energy Technology 2014: High-temperature Material Systems for Energy Conversion and Storage*, TMS, (2014) 247-258.
- [8] Y. Tanaka, A. Momma, K. Sato and T. Kato, Improvement of Electrical Efficiency of Solid Oxide Fuel Cells by Anode Gas Recycle, *ECS Transactions*, 30 (2011) 145-150.
- [9] J. C. Woicik, B. Ravel, D. A. Fischer, and W. J. Newburgh, Performance of a four-element Si drift detector for X-ray absorption fine-structure spectroscopy: resolution, maximum count rate, and dead-time correction with incorporation into the ATHENA data analysis software, *Journal of synchrotron radiation*, 17 (2010) 409-413.
- [10] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, et al., QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials., *J. Phys. Condens. Matter*. 21 (2009) 395502.

- [11] A. Liechtenstein, V. Anisimov, J. Zaanen, Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators, *Phys. Rev. B.* 52 (1995) 5467–5471.
- [12] Y.-L. Lee, J. Kleis, J. Rossmeisl, D. Morgan, Ab initio energetics of $\text{LaBO}_3(001)$ ($\text{B}=\text{Mn}$, Fe , Co , and Ni) for solid oxide fuel cell cathodes, *Phys. Rev. B.* 80 (2009) 224101.
- [13] H. Monkhorst, J. Pack, Special points for Brillouin-zone integrations, *Phys. Rev. B.* 13 (1976) 5188–5192.
- [14] J.S. Hardy, J.W. Templeton, D.J. Edwards, Z. Lu, J.W. Stevenson, Lattice expansion of LSCF-6428 cathodes measured by in situ XRD during SOFC operation, *J. Power Sources.* 198 (2012) 76–82.
- [15] <http://www.handbookofmineralogy.org/pdfs/strontianite.pdf>
- [16] <http://webbook.nist.gov/>

Figures

Figure 1. (a) XRD and (b) FIB-SEM of (001) LSCF-6428 thin film on (110) NGO substrate.

Figure 2. Schematic of a typical TXRF measurement showing fluorescence peaks corresponding to the different elements in LSCF.

Figure 3. Typical TXRF raw data for LSCF-6428 thin film. The dashed line marks the position of the critical angle.

Figure 4. Real-time TXRF data for LSCF-6428 plotted as Sr/(Sr+La) ratio versus x-ray beam incident angle. The plots are from data collected at (a) 800°C in 30% CO₂, 21% O₂ and 49% N₂ for 9 hours and 7 minutes and at (b) 800°C in 21% O₂ and 79% N₂ for 8 hours and 51 minutes.

Figure 5. Sr 3d peaks of a) 30% CO₂-annealed, b) CO₂-free annealed and c) as-deposited films obtained by HAXPES measurements. The data is fit to a combination of a surface oxide (SrO), a surface carbonate (SrCO₃) and a bulk perovskite (LSCF) phase.

Figure 6. Representative 2X2X2 supercell of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Co}_{0.25}\text{Fe}_{0.75}\text{O}_3$ used for the DFT calculations.

Figure 7. Calculated phase diagrams for the above reaction plotted as $\log(p\text{O}_2)$ versus temperature, where a) $\delta=0$, $p\text{CO}_2=360 \text{ ppm}$, b) $\delta=0$, $p\text{CO}_2=0.3 \text{ atm}$, c) $\delta=0.125$, $p\text{CO}_2=360 \text{ ppm}$, and d) $\delta=0.125$, $p\text{CO}_2=0.3 \text{ atm}$.

Figure 8. AFM 3-D images of the surface of post-annealed LSCF-6428 samples in a) high-CO₂ environment and b) CO₂-free environment.