In Situ Oxygen Surface Exchange Coefficient Measurements on Lanthanum Strontium Ferrite Thin Films via the Curvature Relaxation Method

Qing Yang, "Theodore E. Burye, "Richard R. Lunt," and Jason D. Nicholas*"a

a Chemical Engineering & Materials Science Department, Michigan State University, 428 South Shaw Lane, 2527 Engineering Building, East Lansing, MI 48824, U.S.A.

b Department of Physics and Astronomy, Michigan State University, 567 Wilson Road, 4210 Biomedical Physical Science Building, East Lansing, MI 48824, U.S.A

* Phone: (517) 355-1615, Email: jdn@msu.edu, Web: https://www.egr.msu.edu/nicholasgroup/

Abstract

Here, an in situ curvature relaxation ($\kappa R$) method was used to measure chemical oxygen surface exchange coefficients ($\tilde{k}$'s) under well-characterized stress, temperature, and oxygen partial pressure conditions. These $\tilde{k}$'s were measured by analyzing the transient curvature of yttria stabilized zirconia supported $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ thin films reacting to oxygen partial pressure step changes. The sputtered thin film $\tilde{k}$'s measured here were consistent with extrapolated bulk sample $\tilde{k}$'s, but larger than those reported for pulsed laser deposited thin films. This is the first time the curvature response of a system has been used to characterize thin film oxygen surface exchange kinetics. The simultaneous measurement of film stress and $\tilde{k}$ provided by the curvature relaxation method may help explain the large $\tilde{k}$ discrepancies observed in the literature.

Keywords: Curvature Relaxation; Oxygen Surface Exchange; Lanthanum Strontium Iron Oxide; LSF; Strain; Stress; Thin Film; Mechano-Chemical Coupling; Mechano-Chemically Active
1. Introduction

Due to the presence of multivalent cations and accommodating crystal structures, many mixed ionic electronic conducting (MIEC) materials can alter their bulk oxygen vacancy concentration \( (c_{O}) \) by changing their cation oxidation state. For the MIEC material lanthanum strontium iron oxide (LSF), these changes can be summarized via the defect reaction:

\[
2Fe_{Fe}^{	ext{a}} + O_{o}^{	ext{g}} \rightarrow \frac{1}{2} O_{2} + V_{O}^{2+} + 2Fe_{Fe}^{	ext{a}}
\]  

[1]

at temperatures below 625°C and oxygen partial pressures \( (pO_{2})s \) ranging from 1 to \(~1\times10^{-7}\ atm [1, 2]. Internal redox reactions such as this allow MIEC oxides to: a) catalyze the removal of \( NO_x \), \( CO \), and unreacted hydrocarbons from combustion gas streams [3], b) sense oxygen partial pressures for fuel-efficient engine operation [4], c) catalyze the dissociation of \( H_2O \) or \( CO_2 \) for alternative fuel production[5, 6], d) act as anti-oxidants in the human body [7, 8], e) separate oxygen for gas purification applications [9], and f) serve as catalytically-active solid oxide fuel cell electrode materials [10], among other uses.

In addition to altering cation and anion defect concentrations, these internal redox reactions can affect overall lattice strain. For instance, in lanthanum strontium ferrite [11], cerium oxide [12-14], lanthanum strontium cobaltite [15, 16], lanthanum strontium chromate [17], lanthanum manganate [18], lanthanum strontium cobalt iron oxide [16, 19], barium strontium cobalt iron oxide [20], and strontium iron titinate [21] the operation of reactions such as Equation 1 results in lattice expansion as the oxygen nonstoichiometry \( (\delta) \) increases. This mechano-chemical coupling can be summarized as a chemically induced strain \( (\epsilon_c) \) given as:

\[
\epsilon_c = \frac{\Delta l}{l} = \alpha_c \Delta \delta
\]  

[2]

where \( l \) is sample length, \( T \) is the temperature, and \( \alpha_c \) is the chemical expansion coefficient.

Here, this mechano-chemical coupling was used to measure the chemical oxygen surface exchange coefficient \( (\tilde{k}) \) of \( La_{0.6}Sr_{0.4}FeO_{3-\delta} \) (LSF-64). This was achieved by analyzing the curvature response of LSF-64 thin film | yttria stabilized zirconia (YSZ, \( Y_{1.5}Zr_{0.84}O_{1.92} \)) bilayers equilibrating to step changes in \( pO_2 \). This curvature relaxation \( (\kappa R) \) method can be used to measure the \( \tilde{k} \) of any mechano-chemically coupled thin film. It has the benefit of being an \textit{in situ} (and potentially \textit{in operando}) technique that does not require electrodes. It also simultaneously measures film stress and \( \tilde{k} \). This last attribute is especially important because through the operation of equilibria like that in Equation 1, stress can alter the oxygen vacancy and/or electronic species concentrations that determine \( \tilde{k} \) [22-24]. Therefore, the simultaneous measurement of film stress and \( \tilde{k} \) provided by the \( \kappa R \) method may help explain the large differences in \( \tilde{k} \) observed for nominally identical composition and testing conditions (up to 10,000 times for LSF-64 at 650°C) [25, 26].

2. Materials and Methods
2.1 The Mathematics of Determining \( \tilde{k} \) via Bilayer Curvature Relaxation

For a mechano-chemically active film constrained by an invariant, mechano-chemically inactive substrate, changes in film oxygen vacancy concentration result in film stress and film
strain that alter the bilayer curvature [27, 28]. Films with thicknesses 1) less than \( \frac{1}{100} \) of the characteristic thickness \( L_C \) given as:

\[
L_C = \frac{\bar{D}}{\kappa}
\]  

(where \( \bar{D} \) is the bulk chemical oxygen diffusivity [9, 29]), and 2) less than \( \frac{1}{1000} \) of the thickness of an elastically deforming substrate [30], maintain uniform through-thickness stress and oxygen vacancy concentrations; even as the films equilibrate with their surroundings (the oxygen ions in the bulk are so mobile that they can eliminate oxygen concentration gradients quicker than the surface exchange process can produce them, and the film is so thin compared to the substrate that a plane stress situation exists in the film). Accordingly, temporal changes to \( \kappa \) are solely controlled by \( \tilde{k} \). Thus, it is possible to extract \( \tilde{k} \) from the curvature response of LSF | YSZ bilayers equilibrating to small step changes in \( pO_2 \) using the well-known solution for oxygen transport into/out of a surface-controlled membrane:

\[
\frac{c_v - c_{v_{\infty}}}{c_{v_{\infty}} - c_{v_0}} = \frac{\delta - \delta_0}{\delta_{\infty} - \delta_0} = 1 - \sum_{i=1}^{n} A_i \exp\left( -\frac{t \tilde{k}_i}{h_f} \right)
\]  

where \( c_v, c_{v_{\infty}}, \) and \( c_{v_0} \) are the instantaneous, initial, and new-\( pO_2 \)-equilibrated oxygen vacancy concentrations in the film, \( \tilde{k}_i \) is the surface exchange coefficient for a portion of the film with an area fraction \( A_i \), \( t \) is time, and \( h_f \) is the film thickness [31-35].

Equation 4 has the same form as that used to extract \( \tilde{k} \) from electrical conductivity relaxation (ECR) experiments [32-35]. The difference between the \( \kappa R \) and ECR techniques is that the latter uses electrical conductivity changes to measure \( \Delta \delta \), while the former uses film stress changes. Specifically, for a film thickness to substrate thickness ratio \( \leq \frac{1}{1000} \), the film stress \( \lambda \) is related to the bilayer curvature \( \kappa \) via Stoney’s Equation:

\[
\lambda = \frac{\kappa E_s h_s^2}{6h_f(1-v_s)}
\]  

where \( E_s \) is the substrate Young’s modulus, \( h_s \) is the substrate thickness, and \( v_s \) is the substrate Poisson’s ratio [30]. To determine the relationship between \( \kappa \) and \( \delta \) for a linear elastic bilayer, Hooke’s Law and Equation 2 can be combined with Equation 5 to yield:

\[
\Delta \delta = \left( \frac{E_s h_s^2 (1-v_f)}{6\rho_f E_f h_f (1-v_s)} \right) \Delta \kappa
\]  

where \( \rho_f, v_f, \) and \( E_f \) are the film relative density, the film Poisson’s ratio, and the film Young’s modulus, respectively. Assuming the product in parentheses remains constant and non-zero during a small step change in atmospheric \( pO_2 \), Equation 4 can be rewritten using Equation 6 as:

\[
\frac{\kappa - \kappa_0}{\kappa_{\infty} - \kappa_0} = 1 - \sum_{i=1}^{n} A_i \exp\left( -\frac{t \tilde{k}_i}{h_f} \right)
\]  

Equation 7 indicates that the \( \kappa R \) method can reliably be used to measure \( \tilde{k} \) as long as \( h_f \) is known, the film is dense, the film and substrate both deform elastically, and the film chemical expansion coefficient, Poisson’s Ratio, and Young’s Modulus are roughly constant over each \( pO_2 \) step (as is the case here) [36-39]. As shown in Equation 7, quantitative knowledge of the film’s elastic properties and/or chemical expansion coefficient is not required to measure \( \tilde{k} \) in a
\( \kappa R \) experiment. That said, as shown in Equation 6, a large film chemical expansion coefficient, a large film Young’s Modulus, and a small film Poisson ratio are desirable because they result in large, easily-resolvable, \( pO_2 \)-induced equilibrium bilayer curvature changes.

2.2 Sample Fabrication

Here, LSF-64 was chosen as an archetypal material due to its large chemical expansion coefficient of \( \alpha_c = 0.01994 \) [40], single-phase behavior over the 25-800°C and \( 1 \times 10^{-12} \leq pO_2 \leq 1 \) atm range when in an unstressed state [40], \( pO_2 \)-independent Young’s modulus and Poisson’s ratio over the 25-725°C and \( 1 \times 10^{-4} \leq pO_2 \leq 0.1 \) atm range [36], and importance as a model solid oxide fuel cell cathode material [41]. LSF-64 powder was synthesized via the glycine nitrate process (GNP) [42] using a 1:1 metal nitrate: glycine ratio. A 3-inch sputtering target was prepared by hot pressing GNP-prepared LSF-64 powder in a nitrogen atmosphere using a graphite die. The hot pressing temperature was ramped to 300°C at 20°C/min, held there for 30 minutes, ramped to 600°C at 20°C/min, ramped to 1200°C at 10°C/min, held there for 120 minutes, and finally ramped to room temperature at a nominal cooling rate of 10°C/min.

One side polished (1 inch diameter, 200 \( \mu m \) thick) single crystal, 100-YSZ wafers (MTI Corp., Richmond, CA) were used as substrates for thin film LSF-64 deposition. Single crystal YSZ was chosen as a substrate material due to its chemical inertness (LSF-YSZ cation intermixing and/or interphase formation only occurs above 1000°C in air) [43], its high yield stress (>400 MPa below 800°C in air) [38], and its constant oxygen vacancy concentration and \( pO_2 \)-independent elastic moduli over the 25-800°C and \( 1 \times 10^{-25} \leq pO_2 \leq 1 \) atm range [39]. The surface roughness of the YSZ substrate deposition surface was 1 nm according to manufacturer specifications. Prior to thin film deposition, the YSZ substrates were annealed at 1100°C for 60 minutes to relieve residual stress within the substrates. Annealed wafers tested from 25-800°C showed no curvature changes with heating, indicating the success of the annealing schedule in relieving the residual substrate stress. In preparation for LSF-64 thin film deposition, substrates were mounted in a high vacuum (\( 1 \times 10^{-5} \) Pa, base pressure) sputtering chamber using double-sided tape on the underside of the substrates. LSF-64 was subsequently DC plasma-sputtered on these substrates using an Ar background pressure of 210 Pa, and a deposition rate of 1.2-3 nm/min at room temperature.

3. Experimental

3.1 Curvature Relaxation Measurements

After sputtering, the bilayer samples were placed on a platform inside a sealed quartz reactor and heated in a vertically mounted tube furnace. The outer cover of this quartz reactor contained a three meter long spiral of ⅛” quartz tubing (1.2 meters of which was in the furnace hot zone) used to preheat the incoming gas. From 25-725°C a thermocouple placed at the sample location did not record a temperature change when the gas flow was switched between 100 sccm of air (with a thermal conductivity between 26.18 and 67.85 mW/(m*K) from 25-725°C) [44] and 100 sccm of nitrogen (with a thermal conductivity between 25.8 and 67.7 mW/(m*K) from
25-725°C) [45], indicating the effectiveness of the gas preheating setup for use with the atmospheres utilized here. Prior to \( \kappa R \) experiments, LSF-64 | YSZ samples were annealed within the testing setup for 1 hour at 600°C in air to crystallize the as-deposited LSF-64 films.

Bilayer \( \kappa R \) experiments were conducted using the multi-beam optical stress sensor (MOSS) depicted in Figure 1. This device measured the bilayer curvature using the CCD detected inter-spot spacing \( (d) \), the initial inter-spot spacing \( (d_0) \), the detector inclination \( (\phi) \), the sample-to-detector distance \( (L) \) and the geometric relationship:

\[
\kappa = \left( \frac{\cos\phi}{2L} \right) \left( 1 - \frac{d}{d_0} \right)
\]  

Values for \( d_0 \) and the ratio in the first set of parentheses were obtained by taking MOSS measurements on flat and \( \kappa =0.1 \text{ m}^{-1} \) mirrors placed in the sample location prior to initial sample heating. To observe high temperature LSF | YSZ curvature relaxation, a four-way valve was used to abruptly switch between 100 sccm of research grade air (with a \( pO_2 = 0.21 \)) and a 90 sccm research grade nitrogen - 10 sccm research grade air mixture (with a \( pO_2 = 0.021 \)). An oxidizing to reducing oxygen partial pressure ratio of 10 (a standard \( pO_2 \) step size used in ECR experiments [46, 47]) was utilized here. Previous studies on lanthanum strontium cobaltite (which is isomorphous to LSF) have shown that the assumption of linear exchange kinetics implicit in Equations 4 and 7 is valid for oxidizing to reducing oxygen partial pressure ratios less than 20 [48]. The reactor volume was determined to be \( \sim 10 \text{ mL} \) through flush-time dominated \( \kappa R \) experiments at temperatures from 625-725°C. These flush time dominated \( \kappa R \) experiments had an activation energy of 0.1eV. This is in line with the 0.07 eV predicted by Otter et al. [49] for a flush time limited continuously stirred reactor. The \( \sim 10 \text{ mL} \) sample chamber reactor volume (a reactor size commonly used in ECR experiments) [49, 50] and the 100 sccm gas flow rates used in the \( \kappa R \) experiments set the reactor flush time to < 2.5 seconds above 450°C, according to Equation 16 of den Otter et al. [49]. Flush-time corrections to Equation 7 available in the literature [49] were not necessary for experiments at and below 525°C, because the film \( \kappa \)'s were below \( 2\times10^{-6} \text{ cm/sec} \) and hence within the “fast flushing” regime identified by den Otter et al. [49]. The total duration of each curvature relaxation experiment was at least 5 times the largest fitted time constant \( (\tau_i) \):

\[
\tau_i = \frac{\kappa_f}{h_f}
\]

for that relaxation. \( \kappa \) values were determined by performing a least-squares regression fit of Equation 7 to normalized curvature relaxation data using the Origin © computer program.

3.2 Sample Structural Characterization

Film thickness and microstructural measurements were conducted on bilayer fracture surfaces using a Zeiss Auriga scanning electron microscope (SEM) operated at 30 kV and 50 pA. Prior to SEM analysis, \( \sim 1.5 \text{ nm} \) of Pt was sputtered onto LSF-64 | YSZ fracture surfaces to prevent electrical charging. Multiple areas of multiple samples were imaged to obtain statistically significant film thickness measurements. Film and substrate phase purity analyses were conducted for \( 20^\circ < 2\theta < 80^\circ \) using a 0.005\(^\circ \) step size, a 0.1 second per step hold time,
and a nickel-filter-equipped Bruker Davinci x-ray diffractometer (XRD) operated at 30 kV and 15 mA.

4. Results and Discussion

Figure 2 shows the microstructure of a κR-tested LSF-64 film on a YSZ substrate. The LSF-64 films exhibited a uniform thickness of 250 ± 3 nm across each YSZ wafer. Literature measurements [26] have shown that the LSF-64 characteristic thickness, \(L_c\), is 200 \(\mu\)m at 725°C and increases with decreasing temperature. Therefore, the κR-tested LSF-64 films were completely surface controlled and amenable to analysis via Equation 7.

Figure 3 shows diffracted x-ray intensity scans for bare YSZ wafers, as-sputtered LSF-64 wafers, and κR-tested bilayers. The only observable planes in the YSZ wafers were the (200) and (400) planes, consistent with the (100)-oriented single crystal nature of the substrates. Figure 3 also shows the evolution of the thin film crystallinity. The as-deposited LSF was initially amorphous, which was expected for the room temperature sputter deposition conditions utilized here. Curvature monitoring during initial LSF | YSZ sample heating to 600°C (not shown) indicated that the initially amorphous LSF films transformed into crystalline LSF between 550 and 600°C. All the major XRD peaks listed in LSF-64 Powder Diffraction File (PDF) [51] card numbers 01-082-1961 and 01-072-8133 are present in Figure 3, indicating that the sputtered LSF-64 films were made of randomly-oriented polycrystals. The observed x-ray peak intensity ratios differed from the reference patterns, indicating preferred grain orientation within the films. Specifically, the LSF (012), (113), (202), (024), (overlapping 300,214,018), (overlapping 220, 208), and (overlapping 134,128) XRD intensities were 40%, 5%, 15%, 25%, 20%, 10%, and 5% of the (104/110) peak, respectively, compared to 16%, 1%, 21%, 57%, 40%, 14%, and 12% in the reference patterns. LSF-64 grain size determinations made using the Scherrer Equation [52] on the (104/110), (024), and (202) XRD peaks resulted in grain sizes of 54, 40, and 36 nm, respectively. The observed grain size and XRD line intensity trends are consistent with the (104/110) oriented grains/domains growing at the expense of the (024) and (202) oriented grain/domains during a ferroelastic \(R\bar{3}m\) phase transformation known to occur in bulk materials [53] at film stresses reached at temperatures below 475°C upon sample cooling.

Figure 4 shows representative normalized curvature relaxation data for a LSF-64 | YSZ sample at 525°C. All relaxations displayed well-resolved relaxations with significant differences between final and initial curvatures. Experiments at low temperature and in the presence of intentional vibrations indicated that index of refraction changes along the MOSS laser beam path caused by high-temperature convective gas currents were the main source of signal noise in the κR measurements. Figure 4 also shows that the measured relaxation behavior was well fit by Equation 7 when two relaxation processes, each with their own time constant (\(\tau_i\)), were employed. The Equation 7 pre-exponential terms were roughly constant at \(A_1 = 0.7 \pm 0.05\) and \(A_2 = 0.3 \pm 0.05\) across all 525-475°C reduction and oxidation cycles.

Table 1 shows the LSF oxygen surface exchange and equilibrium film stress levels at a given temperature remained constant with redox cycling. This reproducibility indicates that
events capable of complicating the $\kappa R$ analysis such as film cracking, film delamination, and LSF ferroelastic domain switching (which is known to occur in bulk LSF-64 above $\sim 120$ MPa at room temperature) [53] did not occur to a significant extent during the $\kappa R$ measurements. The low Table 1 film stress levels and roughly constant values of $A_1$ and $A_2$ also support this interpretation. As is commonly observed [35, 48], $\tilde{k}$ was always faster on oxidation than on reduction due to greater initial concentrations of oxygen vacancy and/or electronic species in reduced material undergoing oxidation than in oxidized material undergoing reduction. Figure 5 shows two distinct time constants, suggesting that either a) two processes or b) the same process occurring with different rates over different parts of the surface were active. The nearly identical activation energies for $\tilde{k}_1$ and $\tilde{k}_2$, shown in Figure 6, suggests the latter option occurred here. This behavior has been observed in ECR experiments on both epitaxial thin films [32, 34, 35] and single crystals [33]. In these literature studies, multiple time constants have been attributed to differing rates of oxygen incorporation into either a) surfaces with different crystallographic orientations, or b) surfaces with distinct bulk and grain boundary contributions. It is likely that similar effects are occurring in the LSF-64 films studied here, and this possibility will be examined in a future publication.

Figure 6 shows how the sputtered LSF-64 $\tilde{k}$’s obtained here via $\kappa R$ compared to the LSF-64 $\tilde{k}$’s available in the literature. The sputtered film $\tilde{k}$’s had 475-525°C activation energies on oxidation (1.3 eV, 1.1 eV, and 1.4 eV for $\tilde{k}$, $\tilde{k}_1$, $\tilde{k}_2$ respectively) and reduction (1.2 eV, 1.1 eV, and 1.2 eV for $\tilde{k}$, $\tilde{k}_1$, $\tilde{k}_2$ respectively), close to the 1.3 eV activation energy observed for bulk LSF-64 by tenElshof et al. [26]. These ~1.3 eV activation energies, which were very different than the 0.36 eV expected for an atmospheric flushing process [49], indicate that none of the observed time constants were related to reactor flushing limitations. The sputtered films tested here had $\tilde{k}$, $\tilde{k}_1$, and/or $\tilde{k}_2$ values that were consistent with low-temperature extrapolations of bulk LSF-64 $\tilde{k}$ values [2, 26], and inconsistent with literature pulsed laser deposited LSF-64 films [25, 54]. The close $\tilde{k}$ agreement between the sputtered films and bulk samples may be because the non-epitaxial, polycrystalline sputtered films tested here at relatively low stress levels (i.e. $\leq 120$ MPa) without electrodes more closely resembled the structure and stress state of the bulk LSF-64 samples [2, 25] than the epitaxial pulse laser deposited thin films [25, 54] previously measured via ECR in the literature (these literature films may have had a different surface structure or stress state because of the electrodes used to measure them, their epitaxial nature, and/or a different stress/strain history).

Lastly, Figure 7 shows the average $p_{O_2}$—equilibrated stress values for the various temperatures and atmospheres. The linear dependence of film stress on temperature is another indication that the films remained elastic over the measured temperature range. The measured equilibrium film stresses in air were consistent with the film-substrate CTE mismatch, assuming stress free grains formed at 600°C, a 475-525°C YSZ CTE ranging from 9.4 to 9.6 ppm/K [55], a 475-525°C LSF-64 Poisson’s Ratio of 0.34 [36], a 475-525°C LSF-64 Young’s Modulus ranging from 105 to 110 GPa [36], and a 475-525°C LSF CTE of 14.0 ppm (which is the polycrystalline CTE reported for both $La_{0.7}Sr_{0.3}FeO_{3-\delta}$ and $La_{0.5}Sr_{0.5}FeO_{3-\delta}$ in this temperature range in
The ~15 MPa in chemical stress generated upon switching from a $P_{O_2}$ of 0.21 and 0.021 atm is lower than the 30 MPa predicted from Equation 2 and Hooke’s Law, given a bulk LSF-64 biaxial modulus of 160 GPa [56], a bulk LSF-64 chemical expansion coefficient of 0.01994 [37], and a bulk LSF-64 $\Delta \delta$ of 0.01 upon switching between a $P_{O_2}$ of 0.21 and 0.021 [1]. However, this slight disagreement is not surprising given that differences in elastic, oxygen storage, and thermo-chemical properties between thin film and bulk samples of the same composition may exist. Disagreement has also been found in ceria thin films [28], where chemical stress scaled with grain size, and films with 36-54 nm grain sizes exhibited film stresses 1-2 times the values predicted using bulk material properties.

5. Conclusions
An electrode-free curvature relaxation method that can be used to simultaneously measure film stress and chemical oxygen surface exchange coefficients in situ has been demonstrated here for the first time. The $\tilde{k}$ values obtained using this technique on sputtered La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ films were consistent with low-temperature bulk La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ $\tilde{k}$ extrapolations. Further, the observed chemical stresses were consistent with predictions made using bulk material properties. Given the unique advantages of the curvature relaxation method and the fact that many MIEC materials are mechano-chemically coupled, this method could find wide application in the characterization of MIEC catalysts, sensors, gas separation membranes, solid oxide fuel cell electrodes, and other ion-exchange materials.

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7. List of Symbols and Acronyms

- $A_l$: Area Fraction
- $\alpha_c$: Chemical Expansion Coefficient
- CTE: Coefficient of Thermal Expansion
- $c_v$: Bulk Oxygen Vacancy Concentration
- $d$: MOSS CCD Detected Inter-spot Spacing
- $d_0$: MOSS Initial Inter-spot Spacing
- $\bar{D}$: Bulk Chemical Oxygen Diffusivity
- $\delta$: Oxygen Nonstoichiometry
- ECR: Electrical Conductivity Relaxation
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<thead>
<tr>
<th>Symbol</th>
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<tr>
<td>$E_f$</td>
<td>Film Young’s Modulus</td>
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<td>$E_S$</td>
<td>Substrate Young’s Modulus</td>
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<td>$\varepsilon_c$</td>
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<td>$\kappa R$</td>
<td>Curvature Relaxation</td>
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<td>LSF</td>
<td>Lanthanum Strontium Iron Oxide</td>
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<td>$525^\circ C$</td>
<td>$55.6$</td>
</tr>
<tr>
<td>$500^\circ C$</td>
<td>$80.3$</td>
</tr>
<tr>
<td>$475^\circ C$</td>
<td>$105$</td>
</tr>
</tbody>
</table>

Note: $k$ values were obtained using single relaxation time fits, while $k_1$ and $k_2$ were obtained using dual relaxation time fits. The indicated $\lambda$ values are those at the end of the indicated relaxation. The ending (i.e., equilibrium) $\lambda$ for an oxidation cycle was the starting $\lambda$ for the subsequent reduction cycle, and vice-versa. Samples were always reduced before being oxidized. The reported $\lambda$ values are relative to those at $600^\circ C$ in air, where the LSF-64 film was assumed to crystallize into stress-free grains. Red. denotes reduction and Oxid. denotes oxidation.
Figure 1. Multi-beam Optical Stress Sensor (MOSS) curvature measurement schematic
Figure 2. Scanning electron micrograph of a kR-tested La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ | Y$_{0.16}$Z$_{0.84}$O$_{1.92}$ fracture surface
Figure 3. X-ray diffraction scans of uncoated substrates (top), LSF sputtered substrates (middle), and kR-tested LSF sputtered substrates (bottom). Note that the YSZ (200) and YSZ (400) peaks extend off the chart. LSF-64 assignments were made using La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ Powder Diffraction File card number 01-082-1961 and Y$_{0.16}$Zr$_{0.84}$O$_{1.92}$ Powder Diffraction File card number 01-070-8272 [51].
Figure 4. The normalized $La_{0.6}Sr_{0.4}FeO_{3-\delta} \mid Y_{0.16}Zr_{0.84}O_{1.92}$ $\kappa R$ curve for the 1st oxidation cycle at 525°C. The gray and black lines correspond to one and two relaxation times, respectively.
Figure 5. The $\kappa R$ data of Figure 4 plotted on a semi-log plot to indicate that two relaxation times, $\tau_1$ and $\tau_2$, are present.
Figure 6. $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ $\kappa R \tilde{k}$ values compared with $\tilde{k}$ values from the literature [2, 25, 26, 54]. Squares and diamonds denote bulk $\tilde{k}$ values, while triangles, circles, and stars denote thin film $\tilde{k}$ values. Like Figure 4, $\tau_1$ denotes the fast process and $\tau_2$ denotes slow process. The error and standard deviation in the $\kappa R \tilde{k}$ values are less than the size of the symbols.
Figure 7. Equilibrium $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ film stress levels as a function of temperature and oxygen partial pressure. Open symbols denote values after reduction, and closed symbols denote values after oxidation. The error is less than the size of the symbols.
References
$\frac{\kappa - \kappa_0}{\kappa_\infty - \kappa_0}$

$525^\circ C$ on Oxidation

$1 - A_1 \text{Exp}(-t/\tau_1)$

$1 - A_1 \text{Exp}(-t/\tau_1) - A_2 \text{Exp}(-t/\tau_2)$

$A_1 (1 - \text{Exp}(-t/\tau_1))$

$A_2 (1 - \text{Exp}(-t/\tau_2))$
Figure(s)

$\ln \left( 1 - \frac{1}{k_{\infty} - k_0} \right)$

$525^\circ C$ on Oxidation

Time (sec)

$\tau_1$

$\tau_2$
Figure(s)