Porous Thick Film Lanthanum Strontium Ferrite Stress and Oxygen Surface Exchange Bilayer Curvature Relaxation Measurements

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Here, the chemical oxygen surface exchange coefficient and film stress of porous La0.6Sr0.4FeO3-δ (LSF64) thick films were simultaneously measured in situ between 275–375 °C and 275–700 °C, respectively, using a bilayer curvature measurement technique. The magnitude and activation energy of the porous LSF64 thick film oxygen surface exchange coefficients were consistent with those from large grained, bulk samples. However, unlike large-grained, dilatometry-tested bulk LSF64 samples that only exhibited measurable chemical stress above 525 °C, the fine-grained, curvature-tested porous LSF64 thick films studied here exhibited measurable chemical stress over the complete temperature range from 275 to 700 °C. Further, the porous LSF64 thick films exhibited a kink in their Arrhenius chemical stress behavior (displaying activation energies of 0.07 eV below 525 °C and 0.5 eV above 525 °C), suggesting a distinct lattice-dominated chemical stress response above 525 °C and a distinct grain-boundary-dominated chemical stress response below 525 °C.

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Oxygen-exchange-capable mixed ion electronic conducting (MIEC) materials are widely used in electrochemical devices such as solid oxide fuel cells (SOFCs), catalysts, and gas separation membranes. However, debate exists on the oxygen surface exchange rates of even the most-common MIEC materials. For instance, chemical oxygen surface exchange coefficient (κ) discrepancies greater than 4 orders of magnitude are reported at identical temperature and oxygen partial pressure conditions for the MIEC material La0.6Sr0.4FeO3-δ (LSF64).10–13 Similarly, large κ discrepancies have been observed for other MIEC materials such as lanthanum strontium cobalt iron oxide14–17 and reduced cerium oxide.18–21 Since recent studies have shown that strain can alter κ,20–21 it is likely that some of these observed κ discrepancies are due to differences in MIEC stress state. Unfortunately, simultaneous κ and stress state measurements on MIEC materials are largely absent from the literature. Here, the stress and oxygen surface exchange coefficients of porous LSF64 thick films atop single crystal (Y2O3)0.13(ZrO2)0.87 (YSZ) substrates were simultaneously measured in situ using a new bilayer curvature measurement technique.

Theoretical Background

Porous thick film stress measurement.— Stresses in dense thin films (i.e. those with film to substrate thickness ratios less than 1:1000) can be rigorously extracted from bilayer curvature measurements using Stoney’s Equation:

\[
\delta_{St} = \frac{\kappa M_f h_f^3}{6h_i}
\]

where \(\delta_{St}\) is the thickness averaged film stress predicted from Stoney’s Equation, \(\kappa\) is the bilayer curvature, \(h_i\) is the substrate thickness, \(h_f\) is the film thickness, and \(M_f\) is the substrate biaxial modulus defined as \(E_i/(1 - \nu_i^2)\) where \(E_i\) is substrate Young’s modulus and \(\nu_i\) is the substrate Poisson’s Ratio.22,23 Stoney’s equation is convenient because the thickness averaged film stress (\(\delta_{St}\)) (which is the same as the stress at each point in the film due to the film’s thinness) can be extracted from bilayer curvature measurements without knowledge of the film elastic properties.

In contrast, stresses in dense thick films can be rigorously extracted from bilayer curvature measurements using the equation:

\[
\lambda(\zeta) = \frac{a}{b} - \frac{M_f h_f}{b M_h S} \left(1 + \frac{h_f^4 M_f^4}{h_i^4 M_h^4} - \frac{6h_f^4 M_f^4}{h_i^4 M_S^4}\right) \]

where

\[
a = \left(1 + \frac{h_f^4 M_f^4}{h_i^4 M_h^4} + \frac{h_f^4 M_f^4}{h_i^4 M_S^4} + \frac{h_f^4 M_f^4}{h_i^4 M_f^4} + \frac{h_f^4 M_f^4}{h_i^4 M_f^4}\right)
\]

\[
b = \left(1 + \frac{h_f^4 M_f^4}{h_i^4 M_h^4}\right)
\]

\(\zeta\) is the film-normal distance from the substrate mid-plane, \(M_f\) is the film biaxial modulus, and the other variables have their previously defined meanings.22,23 As seen upon inspection, film to substrate thickness ratios ≤1:1000 cause Equation 2 to collapse to Equation 1, and the thinner the film, the less \(\zeta\)-variation in the film stress. (Note, Equations 1–4 ignore stress complications caused by edge effects. As discussed in Freund and Suresh,22 these edge effects only become significant when film thickness to width ratios are >50. For reference, a 5 μm film on a 1 inch diameter wafer has a film thickness to width ratio of 0.0002.)

Although Equations 2–4 were used to estimate the film stresses here, calculations made using Equations 2–4 indicate that dense and porous LSF64 films even several microns thick are well described by Equation 1 when deposited on commercially available single crystal YSZ substrates. For instance, stress predictions made using Equations 2–4 and literature 500 °C LSF64 and YSZ24 elastic property data in air indicate that dense, 5 μm thick LSF64 films on 200 μm thick YSZ single crystal wafers have film stresses that range from 97.4% of \(\delta_{St}\) at the film-air interface, to 97.7% of \(\delta_{St}\) at the film-substrate interface. Similar stress predictions on 50% porous films can be made by treating the porous films as homogeneous bodies with \(M_f\) values that are ~15% of their dense values (50% porous samples of alumina, hydroxyapatite, ceria, and other ceramic materials26–29 all display \(M_f\) values that are ~15% of their dense values). These
predictions indicate that 5 μm thick, 50% porous LSF64 films on 200 μm thick YSZ single crystal wafers exhibit film stresses that range from 97.5% of $\delta_{S}$ at the film-air interface, to 97.6% of $\delta_{S}$ at the film-substrate interface. These calculations indicate that the average thick film stresses extracted from curvature measurements on (5 μm thick LSF64 porous film | 200 μm thick YSZ single crystal substrate) bilayers are well described by Stoney’s Equation and therefore largely insensitive to LSF64 thick film elastic properties (or small, oxygen-pressure-induced changes therein).

Porous thick film oxygen surface exchange coefficient measurement.— Films for reliable oxygen surface exchange measurements must be thin enough so that oxygen incorporation into, or removal from, the films (which involves oxygen exchange and bulk diffusion in a series pathway) is controlled by surface exchange alone.\textsuperscript{30,31} Mathematically, this requires $h_\ell$ to be less than 1/100th the material’s characteristic thickness ($L_C$) defined as:

$$L_C = D/k = R_3\sigma_{V_3}$$ \hspace{1cm} [5]

where $D$ is the oxygen diffusion coefficient, $R_3$ is the electrical surface resistance, and $\sigma_{V_3}$ is the oxygen vacancy ionic conductivity.\textsuperscript{34–36} When surface exchange dominates over bulk diffusion, the oxygen vacancy concentration remains spatially uniform within the bulk of the material, even as $\delta$ changes. For a material with a single oxygen surface mechanism responding to an instantaneous change in oxygen partial pressure ($p_{O_2}$), the change in $\delta$ is given by the well-known solution to Fick’s Second Law:

$$\frac{\delta - \delta_0}{\delta_\infty - \delta_0} = 1 - \exp\left(-\frac{kt}{h_f}\right)$$ \hspace{1cm} [6]

where $\delta$ is the instantaneous film oxygen nonstoichiometry, $\delta_0$ is the initial film oxygen nonstoichiometry, $\delta_\infty$ is the new-$p_{O_2}$-equilibrated film oxygen nonstoichiometry, $t$ is time, and the other variables have their previously defined meanings.\textsuperscript{34}

Since the total electrical conductivity ($\sigma$) of LSF64 is dominated by the electronic conductivity,\textsuperscript{11} and the electronic conductivity is linearly proportional to $\delta$ via the LSF64 mechano-chemical defect reaction: \textsuperscript{12,35}

$$2Fe^{\delta+}_F + O_2^{\gamma} \rightarrow 1/2O_2(g) + V_\gamma^{\delta+} + 2Fe^{\delta+}_F$$ \hspace{1cm} [7]

(assuming a $p_{O_2}$-independent electron mobility), many authors have used the equation:

$$\frac{\sigma - \sigma_0}{\sigma_\infty - \sigma_0} = \frac{\delta - \delta_0}{\delta_\infty - \delta_0} = 1 - \exp\left(-\frac{kt}{h_f}\right)$$ \hspace{1cm} [8]

to extract $k'$s by fitting the electrical conductivity relaxation (ECR) response of dense LSF64 thin films equilibrating to sudden $p_{O_2}$ changes.\textsuperscript{11,12,36} Similarly, other authors have used the expression:

$$\frac{\sigma - \sigma_0}{\sigma_\infty - \sigma_0} = 1 - \exp\left(-\frac{kt}{\frac{V_v}{\alpha_c}}\right)$$ \hspace{1cm} [9]

where $V_v$ is the volume fraction porosity, $\alpha_c$ is the specific pore surface area, and the other symbols have their previously defined meanings, to extract $k'$s by fitting the ECR response of porous MIEC films with average particles sizes $\ll L_C$.\textsuperscript{37}

Instead of using the total electrical conductivity to monitor $\delta$ changes (by assuming $p_{O_2}$-independent mobilities), the bilayer curvature relaxation technique uses $k$ to monitor $\delta$ changes (by assuming $p_{O_2}$-independent elastic biaxial moduli). Specifically, in mechano-chemically active materials, $\delta$ changes induce chemical strain ($\epsilon_c$) quantified by the relation:

$$\epsilon_c = \frac{\Delta l}{l} = \alpha_c \Delta \delta$$ \hspace{1cm} [10]

where $l$ is sample length, $T$ is the temperature, and $\alpha_c$ is the coefficient of chemical expansion (CCE).\textsuperscript{38} If a mechano-chemically active film behaves in a linear elastic manner, this chemical strain induces a change in the film stress ($\Delta k_\ell$) that is given by Hooke’s Law:

$$\Delta k_\ell = M_f \epsilon_c$$ \hspace{1cm} [11]

Relating this amount of chemical strain to the oxygen nonstoichiometry via Equation 10 yields:

$$\Delta k_\ell = M_f \alpha_c \Delta \delta$$ \hspace{1cm} [12]

For the case of a mechano-chemically active thick film on a mechano-chemically inactive substrate, the change in film stress is linearly proportionally to the change in bilayer curvature. This is seen by plugging Equations 1, 2 and 10 into Equation 12 to yield:

$$\Delta k_\ell \left[ \frac{a}{b} \delta_{S} - \delta_{S} \delta_{S} + \frac{1}{h_f} \frac{M_f}{h_f} \left( 1 + \frac{h_f}{h_S} \frac{M_f}{M_S} \right) - \frac{6h_f}{h_f} \frac{M_f}{M_S} \right] = \left[ \frac{M_f}{\alpha_c} \right] \Delta \delta$$ \hspace{1cm} [13]

Assuming the bracketed quantities in Equation 13 remain constant and non-zero during small step changes in atmospheric $p_{O_2}$, Equation 8 can be rewritten using Equation 13 to describe the curvature relaxation of a dense thick film | inert substrate bilayer as:

$$\frac{k - k_0}{k_\infty - k_0} = \frac{\delta - \delta_0}{\delta_\infty - \delta_0} = 1 - \exp\left(-\frac{kt}{h_f}\right)$$ \hspace{1cm} [14]

where $k$ is the instantaneous bilayer curvature, $k_0$ is the initial bilayer curvature, $k_\infty$ is the new-$p_{O_2}$-equilibrated curvature, and the other variables have their previously defined meanings. Similarly, Equation 9 can be rewritten can be rewritten using Equation 13 to describe the curvature relaxation of a porous thick film | inert substrate bilayer as:

$$\frac{k - k_0}{k_\infty - k_0} = \frac{\delta - \delta_0}{\delta_\infty - \delta_0} = 1 - \exp\left(-\frac{kt}{\frac{V_v}{\alpha_c}}\right)$$ \hspace{1cm} [15]

Since most materials change lattice parameter when altering their oxygen content, curvature measurements are capable of providing in situ, electrode-free, simultaneous $k$ and $\lambda$ measurements for a variety of oxygen-exchange materials.

Dense sample thermal and chemical expansion coefficient measurement.— Past literature studies\textsuperscript{39,40} have separated out thermal and chemical expansion from bulk dilatometry experiments using the relation:

$$\frac{\partial \varepsilon_{T+\delta C}}{\partial T}\bigg|_{p_{O_2}} = \alpha_T + \alpha_C \frac{\partial \delta}{\partial T}\bigg|_{p_{O_2}}$$ \hspace{1cm} [16]

where $\varepsilon_{T+\delta C}$ is the dilatometry-measured thermo-chemical strain, $\alpha_T$ is the coefficient of thermal expansion (CTE), and the other variables have their previously defined meanings. This approach has been used here on bulk dilatometry-measured samples to measure the LSF64 thermal and chemical expansion coefficients.

Experimental

Thick film sample preparation.— Phase pure La$_{0.6}$Sr$_{0.4}$FeO$_{3\delta}$ (LSF64) powder was produced using the glycine-nitrate combustion process (GNP)\textsuperscript{41} followed by calcination in air. Specifically, stoichiometric metal nitrates (>99% pure, Alfa Aesar) were dissolved in Milli-Q deionized water and mixed with glycine powder (>99% pure, Sigma-Aldrich) in a 1:1 ratio. The solution was then transferred to a stainless steel vessel, heated on a hot plate at 400°C, and finally transformed to an ash-like powder after combustion. The resulting powder was then calcined in a dedicated alumina crucible (AD-998, Coorstek) at 1000°C for 1 hour using 5°C/min nominal heating and cooling rates.

Porous LSF64 thick films were manufactured using colloidal spray deposition followed by sintering. Specifically, colloidal suspensions were produced by ball milling 6.5 g of LSF64 powder, 0.3 g of dibutyl phthalate dispersant (Sigma-Aldrich), 52.5 g of 3 mm (Y$_2$O$_3$)$_{0.05}$(ZrO)$_{0.95}$ milling media (Tosoh USA), and ∼18 ml
of isopropanol (Sigma-Aldrich), in a 60 mL polyethylene bottle (VWR) at 70 rpm for 24 hours. After ball milling, the suspensions were diluted with additional isopropanol to a 1 weight percent solids loading, 1/6 of which was spray deposited using an airbrush (Iwata-Medea) onto the unpolished sides of one-side-polished, 1 inch diameter, 200-μm-thick, single crystal, (100)-oriented (Y₂O₃)₀.₁₃(ZrO₂)₀.₈₇(YSZ) substrates (University Wafer) preheated to 100°C. As done previously for experiments with 8 mol% YSZ substrates,¹³ to relieve residual stress within the YSZ wafers the 13 mol% YSZ substrates used here were pre-annealed at 1100°C for 1 hour with nominal heating and cooling rates of 5°C/min. 13 mol% YSZ substrates were chosen to present. At temperatures between 275°C and 900°C the samples began to sinter. This resulted in reactor flush times ranging from 1.8 seconds to 3.2 seconds for at least 5 times the observed sample relaxation time constant. The Origin software program was used to plot the normalized curvature relaxation data and fit the values of k using Equation 15.

**Thick film structural and morphological characterization.**—The crystal structure and phase purity of the calcined LSF64 powder and the LSF64 films before and after bilayer κ measurements were analyzed using a Davinci X-ray diffractometer (Brucker) operated at 30 kV and 15 mA with a copper filament and a Ni filter for 2θ = 20° < 2θ < 80° with a 0.005° step size and a 0.1 sec/step dwell time.

In order to characterize morphological and microstructural parameters (V₀ and S₀) of the porous films, a post-k-tested bilayer sample was fractured, epoxy impregnated (EpoThin, Buehler) and polished down to a 1 μm finish using SiC sandpaper and diamond lapping films (Allied High Tech). A Zeiss Auriga Focused Ion Beam-Scanning Electron Microscope (FIB-SEM) with an x-y spatial resolution of 1 nm was used to image a series of 2D microstructural cross-sections. The z spacing between adjacent x-y FIB-SEM slices was 25 nm. FIB polishing was conducted using a final milling probe current of 600 pA. SEM micrographs were taken using a 30 kV electron excitation voltage and a 4.2 nm working distance. Due to the electrically conductive nature of the LSF, no sputtered top-coat layers were needed. Using the procedures detailed in Yang,⁴⁴ the 2D serial SEM images were aligned, cropped and segmented into binary images. The Mimics software program (Materialize) was then used to 1) create a 3D reconstruction from the 2D images and to 2) determine the V₀ and S₀ values needed to extract k using Equation 15. For all the samples, the 25 nm z resolution was less than 1/150 of the particle size, ensuring 3D reconstruction V₀ and S₀ errors less than 5%.⁴⁵

**Bulk sample preparation and characterization.**—Dilatometry was used to measure the thermo-chemical expansion of dense, large-grained, bulk LSF64 samples. To prepare these samples, 95% dense, 76.2 mm diameter cylindrical pellets were prepared by hot pressing ~200 g of the calcined GNP LSF64 powder in a graphite die at 60 MPa and 1200°C for 120 minutes under nitrogen. Rectangular bars 2.5 mm × 2.5 mm × 7.65 mm in dimension were then cut from the hot pressed samples and loaded into a Netzsch DIL 402 C dilatometer along the longitudinal axis and analyzed in air or a 2.1% O₂-97.9% N₂ mixture. Linear dilatometry was performed with a 50 sccm flush rate in air from room temperature to 1050°C at a heating rate of 1°C/min, a 10 minute hold, and a nominal cooling rate of 1°C/min. Dilatometry was also used to measure the sintering kinetics of porous LSF64 samples. First, porous, 12.7 mm diameter cylindrical pellets were prepared by uniaxial cold pressing calcined GNP LSF64 powder in a stainless steel die at 13 MPa. The resulting porous, 9.25 mm-long pellet was then loaded into the dilatometer and subjected to the same sintering schedule as the porous thick films described previously (i.e. 1050°C for 1 hour, with heating and cooling rates of 5°C/min). After dilatometer testing, fracture surface SEM of these dilatometry-analyzed LSF64 samples was performed using the analysis conditions described previously.

**Results and Discussion**

**Bulk samples.**—Figure 2 shows thermo-chemical expansion curves for dense, large-grained LSF64 in air (pO₂ = 0.21) and 10 times diluted air (pO₂ = 0.021) atmospheres. Equation 16, \( \frac{V₀}{V} \), data from Mosleh et al.,¹¹ and the Figure 2 data were combined to extract a 25–1000°C LSF64 α₀ = 12.4 ppm/K, a 525–1000°C LSF64 (α₀|pO₂=0.021) = 0.0101, and a 525–1000°C LSF64 (α₀|pO₂=0.021) = 0.00867. These α₀ and α₀ values are comparable to literature reports on similar LSF compositions, such as La₀.₃Sr₀.₇FeO₃₋ₓ (with a 500–900°C α₀ = 11.052 ppm/K and a 500–900°C α₀ = 0.01994)⁴⁶ and La₀.₃Sr₀.₇FeO₃₋ₓ (with a 25–500°C α₀ = 12.98 ppm/K and a 650–900°C α₀ = 0.017–0.047).⁴⁷ Line intercept grain size determinations (not shown) indicated that these dense dilatometry samples had grain sizes of 1.7 ± 0.2 μm. As shown in Figure 2, no mechano-chemical coupling was detected in these large grained LSF64 samples below ~550°C.

Figure 3 shows the sintering behavior of the porous LSF4 samples. Upon heating from 25 to ~800°C, these samples exhibited linear thermal expansion, and at 800°C the samples began to sinter. This
Thermo-chemical
tures of the
remained microstructurally stable during bilayer
700
400
and contained well-necked particles with an average diameter of
3028
Journal of The Electrochemical Society
(a) Photograph of the top surface of a
Figure 4.
Bulk, dense LSF64 sample dilatometry under
LSF64 film.
(b) SEM image of the top surface of
Figure 3.
Bulk, porous LSF64 sample dilatometry in air (pO
κ
100 200 300 400 500 600 700 800 900 1000
μ
2 µm
4.7 µm
1.3 µm
Thermal
Thermo-

Figure 2. Bulk, dense LSF64 sample dilatometry under pO
κ
0.21 (black) and pO
κ
0.021 (gray). Dashed line denotes thermal expansion fits to the
data made using Equation 16 and the oxygen nonstoichiometry data of Mosleh et al.11 Note that chemical expansion only occurs above ~525°C in these large grained, dense samples.
suggests that the porous LSF64 films later tested from 275–700°C remained microstructurally stable during bilayer κ experiments.

Porous thick films.— Figure 4 shows representative microstructures of the κ-tested LSF64 films. As indicated from the FIB-SEM analyses, these 4.6 ± 0.6 μm thick porous films were crack-free and contained well-necked particles with an average diameter of 400 ± 10 nm. This particle size is much below the >200 μm 25–700°C L_C values measured for LSF64,45,46 ensuring a surface con-
trolled porous LSF64 thick film κ-response and the legitimate use of Equation 15 to extract k. The sample porosity was 50.7% and the sample surface area per unit volume was 0.024 mm⁻¹. Microstructural analyses on halves and quarters of the microstructural volume shown in Figure 4c yielded V_T and S_V values within 5% of each other, indicating the reconstructed volumes were sufficiently large to be microstructurally representative. The high film porosity ensured an open, well-percolated pore network that facilitated rapid gas exchange with the atmosphere.

Figure 5 shows X-ray diffraction (XRD) patterns for a) the GNP-produced LSF64 powder after calcination, b) the as-deposited LSF64 thick film atop a YSZ substrate, and c) a κ-tested LSF64 thick film atop a YSZ substrate. XRD peak indexing indicated that both the raw LSF64 powder and the constrained films were polycrystalline and contained only phase pure LSF64. The fact that the (200) and (400) YSZ planes were stronger in the as-deposited porous film XRD spectra than in the sintered, κ-tested porous film XRD spectra was an indication of the higher relative density of the sintered, κ-tested LSF films.

Figure 6 shows representative curvature relaxation spectra for LSF64|YSZ bilayers subjected to multiple pO
κ cycles between 0.21 and 0.021 atm. The faster relaxation kinetics at higher temperature is a manifestation of Arrhenius oxygen surface exchange behavior. The reproducibility of the equilibrium curvature levels with pO
κ cycling shown in Figure 6 (and exhibited by all the samples at each individual temperature during a particular thermal segment) indicates that the induced oxygen nonstoichiometry changes were reversible and that no irreversible stress events such as film cracking and/or delamination occurred during the κR experiments.

The well resolved mechano-chemical coupling behavior observed in the porous thick film curvature data of Figure 6 at temperatures significantly below 525°C contrasts with the bulk sample dilatometry behavior shown in Figure 2. To some extent, this is due to the higher mechano-chemical coupling sensitivity of the curvature measurements compared to the dilatometry measurements (using Equation 11, Equations 2–4, the bilayer dimensions, and the 300°C elastic constants of LSF6424 and YSZ,46 it is possible show that the
0.001 m⁻¹ 300°C equilibrium curvature difference in Figure 6 corresponds to a chemical strain of 3 × 10⁻⁶ that is within the Figure 2 noise. However, this may also be due to the larger grain size of the dilatometry-tested bulk samples which would be expected to produce less grain-boundary-induced strain (the dilatometry-tested samples had an average grain size of 1.7 ± 0.2 μm while the porous thick films which had a grain size that was too large for analysis via the Williamson-Hall Method,⁴⁰ i.e. > ~80 nm, and less than the size of the FIB-SEM reconstructed particle sizes, i.e. <400 nm).

In contrast to previous sputtered LSF64 thin film κR measurements where two distinct surface exchange time constants (perhaps representing oxygen incorporation directly into the bulk and grain boundaries, respectively) were observed,⁴¹ here only one time constant was observed. This may be due to the significantly smaller surface area of exposed grain boundaries (i.e. larger grain size) of the porous films tested here, compared to the previously measured sputtered films (which had an average grain size of 43 nm).⁴²

Figure 7 shows that porous LSF64 thick film κ measurements were generally reproducible with thermal cycling between 275 and 700°C. This indicates that degradation events that could affect k (such as phase transitions,⁴³ ferroelastic domain switching,⁴⁴ irreversible cation surface segregation,⁴⁵ etc.) did not occur to a significant extent during thermal cycling between 275 and 700°C. Further, as indicated by a single, 500 sccm k activation energy of 1.3 eV below 375°C, and identical k values for the 100 and 500 sccm flow rates below 325°C, flush time limitations were not present below 375°C when a 500 sccm gas flow rate was used. This is consistent with the <0.67 second reactor volume flush times discussed previously and the >5 second time constant measured at and below 375°C under a 500 sccm gas flow rate. Above 375°C, the measured k's exhibited an activation energy of 0.2 eV for both the 100 sccm and 500 sccm flow rates, respectively, which is close to the apparent 0.07 eV activation energy estimated to result when reactor flush time limitations dominate.⁴⁶ Therefore, only the k’s between 275 and 375°C are reported here.

Figure 8 compares the LSF64 k’s reported here to others available in the literature. The 275–375°C 1.3 eV porous thick film k activation energy measured here is consistent with the 1.3 eV activation energy reported by ten Elshof et al. for bulk LSF64 measured by ECR and similar to the 1.1–1.4 eV activation energies reported by Yang et al.⁴⁷ for sputtered LSF64 thin films measured by κR. This similarity may be because all of those samples were polycrystalline and non-epitaxial in nature.

Figure 9 shows that the equilibrium stress levels displayed by the porous LSF64 thick films were similar those in bulk samples (i.e. close to zero) but generally lower than those in the sputtered LSF64 films of Yang et al.⁴⁷ This may be part of the reason the k’s exhibited an activation energy of 1.3 eV below 375°C and identical k values for the 100 and 500 sccm flow rates below 325°C, flush time limitations were not present below 375°C when a 500 sccm gas flow rate was used. This is consistent with the <0.67 second reactor volume flush times discussed previously and the >5 second time constant measured at and below 375°C under a 500 sccm gas flow rate. Above 375°C, the measured k’s exhibited an activation energy of 0.2 eV for both the 100 sccm and 500 sccm flow rates, respectively, which is close to the apparent 0.07 eV activation energy estimated to result when reactor flush time limitations dominate.⁴⁶ Therefore, only the k’s between 275 and 375°C are reported here.

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stress magnitudes in the porous thick films. Instead, it seems likely that the 1 hour 1100°C bare wafer substrate annealing schedule used here was not effective at removing all the residual stress from the 13 mol% YSZ wafers and that residual stress relaxation within the YSZ substrates during LSF64 sintering at 1050°C caused the substrates to alter their curvature. Despite the unexpected porous thick film LSF64-YSZ bilayer sample equilibrium film stress magnitudes, the reproducible equilibrium stresses exhibited with multiple \( p_{O_2} \) cycles in Figure 6 (and observed in all 275–700°C experiments) indicate that substrate stress relaxation did not occur during the isothermal \( k \) measurements.

Figure 10 shows the difference in the equilibrium porous LSF64 thick film stress between \( p_{O_2} = 0.21 \) and \( p_{O_2} = 0.021 \) (i.e. the chemical stress, \( \lambda_c \)) as a function of temperature. The Figure 10b Arrhenius plot displays a pronounced kink at 525°C. A similar 525°C \( \lambda_c \) kink has also been observed in pulse laser deposited LSF64 thin films. Curiously, this chemical expansion kink happens at the same temperature as the chemical expansion onset temperature in Figure 2. Together, this data suggests that LSF64 exhibits a distinct lattice-dominated chemical stress response above 525°C and a distinct grain-boundary-dominated chemical stress response below 525°C.

The application of Equation 12 and the assumption of temperature-independent \( M_f \) and \( \alpha_c \) values allows the activation energies for oxygen vacancy formation (\( \Delta G_f \)) to be extracted from the chemical stress activation energies shown in Figure 10b. The assumption of temperature-independent \( M_f \) values is a good one, since LSF64 \( M_f \) values only change gradually by \( \sim 15\% \) between 275 and 700°C and can therefore not account for the exponential changes shown in Figure 10b. The assumption of temperature-independent \( \alpha_c \) values below 500°C is more suspect, since no \( \alpha_c \) data at these temperatures exist in the literature. However, assuming that \( \alpha_c \) remains constant from 275–500°C (i.e. assuming that only \( \delta \) differences produce \( \lambda_c \) differences, as been assumed in studies on ceria and anatase) results in a grain boundary \( \Delta G_f = 0.07 \text{ eV} \) and a lattice \( \Delta G_f = 0.5 \text{ eV} \). These \( \Delta G_f \) values show it is much easier to form oxygen vacancies at the LSF64 grain boundaries than inside the LSF64 lattice.

**Conclusions**

Here, a curvature relaxation technique was used to measure the chemical oxygen surface exchange coefficients and stress states of a porous thick film for the first time. The porous \( \text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3 \) thick films studied here displayed mechano-chemical coupling at all tested temperatures from 275–700°C. As shown in Figure 8, this allowed \( k \) measurements to be made below 400°C (i.e. at next generation SOFC operating temperatures) for the first time. Consistent with their low film stress, the porous LSF64 films displayed \( k \) values consistent with low-temperature extrapolations of bulk LSF64 samples. The LSF64 films also displayed a temperature-induced transition from grain boundary dominated chemical expansion to lattice dominated chemical expansion. This is the first time such a chemical stress transition has been observed.

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**List of Symbols**

- \( \alpha_c \): Coefficient of chemical expansion (CCE)
- \( \alpha_T \): Coefficient of thermal expansion (CTE)
- \( \delta \): Instantaneous film oxygen nonstoichiometry
- \( \delta_0 \): Initial film oxygen nonstoichiometry
- \( \delta_\infty \): New-\( p_{O_2} \), equilibrated film oxygen nonstoichiometry
- \( \Delta \): Change in
- \( d \): CCD-detected average inter-spot spacing
- \( d_0 \): Spacing between the parallel laser beams striking the sample
- \( D \): Oxygen diffusion coefficient
- \( \varepsilon_c \): Chemical strain
- \( \varepsilon_{T+C} \): Dilatometry-measured thermo-chemical strain
- \( E_S \): Substrate Young’s modulus
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