Practical Considerations for Reliable Stress and Oxygen Surface Exchange Coefficients from Bilayer Curvature Relaxation Measurements

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Abstract

The curvature relaxation technique is a new electrode-free method for simultaneously measuring a material's chemical oxygen surface exchange coefficient and stress state under controlled atmosphere and temperature conditions. Provided certain conditions are met, this *in situ* / *in operando* technique can be used to accurately measure the oxygen surface exchange coefficients and stress states of dense, porous, thin, or thick film oxygen exchange materials. The present paper provides a detailed, practical discussion of these conditions and compares the curvature relaxation technique to alternative oxygen surface exchange coefficient measurement approaches.

Keywords

Oxygen Surface Exchange; Curvature Relaxation; Chemical Strain; Chemical Stress; Mechano-Chemical Coupling; Thin Film; Mechano-Chemically Active;

1. Introduction

Materials capable of quickly exchanging oxygen with the surrounding atmosphere are used in a variety of electrochemical devices such as solid oxide fuel cells (SOFCs),¹⁻⁵ catalytic reactors,^{6,7} gas sensors,⁸ solar thermochemical fuel generators,^{7,9} and gas separation membranes.^{10,11} Many of the best performing oxygen exchange materials, such as those in Table 1, are mixed ionic electronic conducting (MIEC) materials that facilitate oxygen exchange through an internal change in cation oxidation state. For example, the oxygen exchange reaction in the MIEC material lanthanum strontium iron oxide (LSF) is:

where, in the forward direction, lattice oxygen (O_o^x) leaves the lattice to produce oxygen gas ($O_{2(g)}$) by creating an oxygen vacancy ($V_o^{\bullet\bullet}$) and filling two iron-bound electron holes ($2Fe_{Fe}^{\bullet}$).^{12,13} A material's intrinsic ability to exchange oxygen is often quantified by its chemical oxygen surface exchange coefficient, k , which is the rate constant for a dominant oxygen exchange reaction like Equation 1.

Unfortunately, large disparities exist in the reported oxygen surface exchange coefficients of even the most common MIEC materials. For instance, literature reports indicate that there is a 2 orders of magnitude variation, a 3 order of magnitude variation, and a 4 order of magnitude variation in the 650°C k of $Ce_{0.9}Gd_{0.1}O_{1.95-8}$,¹⁴ lanthanum strontium cobalt iron oxide ($La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-8}$)^{15,16}, and $La_{0.6}Sr_{0.4}FeO_{3-8}$ (LSF64),^{13,17-19} respectively. Many authors have suggested that some of this k variation may be caused by varying MIEC stress/strain states,²⁰ with density functional theory simulations predicting that experimentally-achievable thin film biaxial tensile strains of 1-2%²¹ can enhance ionic transport coefficients by up to 1000 times.^{22,23} However, techniques capable of simultaneously measuring a material's k and stress state have been

missing from the literature. The present work provides practical advice for utilizing a new curvature relaxation (κR) technique^{19,24} that simultaneously measures a material's thickness-averaged stress state and oxygen exchange coefficient under *in situ/in operando* conditions.

2. Theoretical Considerations

2.1 Oxygen Surface Exchange Coefficient Measurements

The κR technique relies upon the lattice strain induced by changes in the oxygen nonstoichiometry, δ , occurring as a result of oxygen exchange reactions like Equation 1. Specifically, dense¹⁹ or porous²⁴ films of mechano-chemically active materials (i.e. those that exhibit a change in strain due to a change in δ) such as those in Table 1 are produced on inert substrates, heated, and subjected to small, sudden oxygen partial pressure (pO_2) changes. As shown in Figure 1a, in response to a new pO_2 , mechano-chemically active films bonded to inert substrates will strain as they adjust their oxygen nonstoichiometry, leading to a relaxation of the bilayer sample curvature that tracks the rate of oxygen exchange in the MIEC film.

Dense MIEC films with thicknesses less than $\sim 1/100^{\text{th}}$ of their characteristic thickness (L_C):

$$L_C = D/k = R_S \sigma_{V_O} \quad [3]$$

(where D is the bulk chemical oxygen ion diffusivity, R_S is the electrical surface resistance, and σ_{V_O} is the bulk oxygen ion conductivity) have fast oxygen diffusion within the film compared to the rate at which oxygen leaves or enters the film via the surface exchange process. This ensures that no through-thickness δ gradients develop (even as the film equilibrates and the film δ changes).^{25,26} Hence, oxygen exchange in these films is completely controlled by oxygen surface exchange, allowing k to be determined by fitting the observed curvature relaxation to the solution to Fick's Second Law for oxygen transport into or out a surface-controlled membrane:

$$\frac{\kappa - \kappa_0}{\kappa_\infty - \kappa_0} = \frac{c_v - c_{v_0}}{c_{v_\infty} - c_{v_0}} = 1 - \sum_{i=1}^n A_i \exp\left(-\frac{tk_i}{h_f}\right) \quad [4]$$

where κ , κ_0 , and κ_∞ are the instantaneous, initial, and new pO_2 -equilibrated sample curvatures, c_v , c_{v_0} , and c_{v_∞} are the instantaneous, initial, and new pO_2 -equilibrated oxygen vacancy concentrations in the film, δ , δ_0 , and δ_∞ are the instantaneous, initial, and new pO_2 -equilibrated oxygen nonstoichiometries, 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.^{19,27-31} Figure 1b shows an example of using Equation 4 to fit measured κR data.

Similarly, highly porous, well-necked MIEC films with particle sizes (P) less than $\sim 1/100^{\text{th}}$ of L_C can have their k determined from the expression:

$$\frac{\kappa - \kappa_0}{\kappa_\infty - \kappa_0} = \frac{c_v - c_{v_0}}{c_{v_\infty} - c_{v_0}} = 1 - \exp\left(-\frac{kt}{\frac{1-V_V}{S_V}}\right) \quad [5]$$

where V_V is the volume fraction porosity, S_V is the specific pore surface area, and the other symbols have their previously defined meanings.^{24,32} (See Nicholas³³ for a derivation of Equations 4 and 5).

Dense MIEC films with thicknesses greater than $\sim 1/100^{\text{th}}$ of L_C and porous MIEC films with particle sizes greater than $\sim 1/100^{\text{th}}$ of L_C have their curvature response controlled by both oxygen surface exchange into/out of the MIEC (quantified by k) and bulk transport within the MIEC (quantified by D). κR measurements on films with these geometries have not yet been attempted due to the inherent difficulty in accurately measuring both k and D from a single sample,^{26,34} and the fact that an oxygen vacancy concentration gradient through the thickness of the film complicate the existing relationships used to extract film stress from the bilayer curvature. However, with additional work, simultaneous k and D measurements on thick dense films or large grained porous films should be possible.

2.2 Film Stress Measurements

At any time in a κR experiment, the measured curvature can be converted into a biaxial film stress (λ). In fact, this has been done in many past equilibrium *in situ* wafer curvature studies that were not configured to derive meaningful materials property data from transient (i.e. relaxation) curvature data.³⁵⁻⁴⁰ Specifically, for dense MIEC films with film to substrate thickness ratios $\leq 1:1000$ this is accomplished using Stoney's Equation:

$$\bar{\lambda} = \kappa \frac{M_S h_S^2}{6h_f} \quad [6]$$

where $\bar{\lambda}$ is the thickness-averaged film stress, h_S is the substrate thickness and M_S is the substrate biaxial modulus defined as $E_S/(1 - \nu_S)$ where E_S is substrate Young's modulus and ν_S is the substrate Poisson's Ratio.^{36,41} More generally, the biaxial stress for a dense film with an arbitrary $h_f: h_S$ ratio can be extracted from the bilayer curvature using the relationship:

$$\lambda(z) = \kappa \frac{M_S h_S^2}{6h_f} \left[\frac{a}{b} - \frac{M_f h_f}{b M_S h_S} \left(1 + \frac{h_f^3 M_f}{h_S^3 M_S} \right) - \frac{6h_f}{h_S^2} \frac{M_f}{M_S} z \right] \quad [7]$$

where

$$a = \left(1 + 4 \frac{h_f}{h_S} \frac{M_f}{M_S} + 6 \frac{h_f^2}{h_S^2} \frac{M_f}{M_S} + 4 \frac{h_f^3}{h_S^3} \frac{M_f}{M_S} + \frac{h_f^4}{h_S^4} \frac{M_f^2}{M_S^2} \right) \quad [8]$$

$$b = \left(1 + \frac{h_f}{h_S} \right) \quad [9]$$

z 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.^{36,41} As seen by inspecting Equation 7, $h_f: h_S$ ratios $\leq 1:1000$ cause Equation 7 to collapse to Equation 6, and smaller $h_f: h_S$ ratios lead to less z -variation in film stress. Thankfully, even for dense films less than a few microns thick on $200 \mu\text{m}$ thick yttria stabilized zirconia (YSZ) single crystal wafers, the errors in thickness-

averaged film stress introduced by using Equation 6 instead of Equation 7 are typically less than a few percent.²⁴ While Equations 6 and 7 can be used to determine the biaxial stress state within dense films as a function of thickness, they can only be used to estimate the thickness-averaged film stresses present in porous films containing microstructural features capable of locally concentrating or dissipating the average film stress.

3.0 Practical Considerations

3.1 Curvature Measurement

3.1.1 In Situ/In Operando Curvature Measurement Setup

Figures 2 and 3 provide schematic and photographic documentation of the experimental setup presently used to conduct κ R measurements. In this setup, a k-Space Associates (kSA, Dexter, MI) multi-beam optical sensor (MOS) generates a multi-spot (typically a 3 x 3) laser array with an inter-spot spacing of d_o and array dimensions of 3-5 mm by passing light from a 25 mW fiber-coupled diode laser through 2 inclined etalons, each at right angles to each other. The laser-beam array then passes through a beam splitter, exits the kSA MOS optical housing, reflects off a table mounted 45° mirror, passes through a quartz window and into a vacuum-evacuated fused silica tube, travels up into a vertically-mounted tube furnace, passes through another quartz window into the sample chamber, and then reflects off the polished surface of a multilayer sample. After reflecting off the sample with array-averaged incidence and reflection angles of θ , the laser beam array passes once again through the quartz window and into the vacuum evacuated fused silica support tube, travels down the tube and out of the furnace, passes through the bottom quartz window and into ambient air, reflects off the table-mounted 45° mirror, enters the kSA MOS optical housing, reflects off the beam splitter, and finally reflects off a rotatable mirror (which can

be used to keep the array on the CCD as the sample curves, but often isn't necessary due to manual pitch and yaw knobs on the assembly holding the inner fused silica support tube) before passing through a bandpass filter and entering the CCD detector. As shown in Figure 1, a convex sample curvature causes the beams of the reflected array to diverge, while a concave sample curvature causes the beams of the reflected array to initially converge. Based on basic geometrical relationships, the sample curvature is calculated from the CCD-detected inter-spot spacing (d) using the relationship:

$$\kappa = \left(\frac{\cos\theta}{2L} \right) \left(1 - \frac{d}{d_o} \right) \quad [10]$$

where L is the sample to CCD distance, and the other variables have their previously defined meanings. The inter-spot spacing is determined by capturing a CCD image with a frame-grabber and using proprietary k-Space algorithms to fit the observed laser beam positions. Before each measurement, d_o is determined by measuring d when a flat mirror ($\kappa=0$) is placed in the sample location. Subsequently, $\frac{\cos\theta}{2L}$ is determined by adjusting $\frac{\cos\theta}{2L}$ until the software correctly measures curvature of a mirror with a known curvature (typically $\kappa=1/10$ m).

3.1.2 Curvature Measurement Sensitivity

For correct curvature measurements of concave samples via Equation 10, L must be less than the reflected array convergence distance. Thankfully, this is never a problem given the small κ of commercially available wafers (the wafers typically appear flat to the human eye and can be made even flatter through a recommended high temperature anneal of the as-received wafers). The inter-spot spacing CCD detector can be placed close to the sample to increase the d of concave samples or further from the sample to increase the d of convex samples. Literature studies have reported that resolvable room-temperature curvature changes of $\sim 0.0006 \text{ m}^{-1}$ are possible with

convenient L and ϕ values of 66 cm and 3° , respectively.³⁸ One benefit of using a multi-beam laser array (instead of a single laser beam) to measure sample curvature is that with a multi-beam array only the inter-spot spacing, d , and not the absolute laser spot positions on the CCD are required for an accurate curvature measurement. This ensures that curvature measurements conducted with a multi-beam array are less sensitive to vibrations and hence do not require active vibration-damping controls to obtain a good curvature signal to noise ratio.

As demonstrated by the signal to noise ratio in Figure 1a, high-temperature curvature changes of $\sim 0.001 \text{ m}^{-1}$ are resolvable with the κR setup described here (with $L=100 \text{ cm}$ and $\theta=3^\circ$). One key to obtaining good curvature resolution at elevated temperature is to limit laser beam travel through high temperature gases (temperature-induced index of refraction fluctuations and/or gradients within the gas alter d .) In the present κR setup, laser beam travel through high temperature gasses is limited by resting the sample on an inner support tube that has been vacuum evacuated to $\sim 0.2 \text{ Pa}$. Another key to obtaining well-resolved, high-temperature curvature measurements is to deploy a notch filter (a 10 nm wide notch filter is presently used) that keeps the laser-spots discernable by limiting the amount of stray blackbody radiation entering the CCD. Optimization of the CCD camera settings (gain, background threshold, etc.) may also be needed to ensure that all the kSA MOS laser spots remain distinguishable from the background. With a conventional red (660 nm) laser array, these techniques ensure that $\sim 0.001 \text{ m}^{-1}$ resolution curvature measurements are possible from room temperature until $\sim 900^\circ\text{C}$ (higher temperatures may be possible using smaller wavelength kSA MOS lasers).

3.2 Controlled Atmosphere Test Rig Design

3.2.1 Controlled Atmosphere Reactor Design & Gas Handling

As shown in Figure 4, a custom built, two-piece fused silica reactor consisting of an outer cover and an inner support tube is used to establish a controlled atmosphere around the sample while maintaining optical access. The outer reactor cover consists of a closed end, 27 mm inner diameter, 30 mm outer diameter fused silica tube bonded to a female Pyrex 34/45 tapered ground joint (Technical Glass Products; Painesville Twp, OH). The reactor design is such that the fused silica portion of the reactor is exposed to high temperatures, while the Pyrex portion of the test rig rests outside the furnace hot zone. A ~3 m long gas preheating coil made from 6.35 mm diameter fused silica tubing wraps around the outer cover and directs preheated gas onto a κR sample, which rests approximately 6 mm below the closed end of the outer reactor cover when the test rig is fully assembled. Approximately 1.2 m of the gas-preheating coil exist in the furnace hot zone.

The inner sample support tube consists of a 20 mm inner diameter, 25 mm outer diameter fused silica tube axially bonded to a 19 mm inner diameter, 22 mm outer diameter fused silica tube. The thinner, 22 mm diameter end of this tube is then tucked inside an upward facing male 34/45 tapered Pyrex joint (Technical Glass Products; Painesville Twp, OH) and bonded to a fused silica window (Technical Glass Products; Painesville Twp, OH) inclined at 4° to the tube axis normal. This 4° inclination ensures that any back-reflections from the fused silica window do not enter the CCD detector within the MOS. A second 4° inclined fused silica window is bonded to the upper portion of the inner support tube, and, as mentioned previously, the portion of the inner support tube between the two quartz windows is vacuum evacuated. A 6.35 mm diameter gas port in the Pyrex joint approximately 10 mm above the fused silica window provides an exit path for the process gas.

The inner tube is designed so that enough distance between the bottom of the male ground glass joint and the top of the exit gas port exists for the inner support tube to be secured by a custom-made aluminum mounting block. As shown in Figure 3, this aluminum mounting block is bolted to a positioning system made up of a x translation stage (NT66-430, Edmund Optics; Barrington, NJ), a y translation stage (NT66-430, Edmund Optics; Barrington, NJ), a pitch goniometer (GON65-1, Newport Optics; Irvine CA) a yaw goniometer (GON65-u, Newport Optics; Irvine CA), a 90° mounting bracket (07-TSR-204 CVI Melles Griot; Albuquerque, NM), and an optical post assembly (07-DUP-011/07-DSQ-003, CVI Melles Griot; Albuquerque, NM). This inner tube positioning system is used to make the inner tube coaxial with the kSA MOS laser beam array that is reflected off a 45° mounted (NT59-002, Edmund Optics; Barrington, NJ) $\lambda/20$ Zerodur mirror (NT43-420-533, Edmund Optics; Barrington, NJ) attached to a micrometer stage (NT66-427, Edmund Optics; Barrington, NJ) that is designed to axially translate with original laser beam array exiting the MOS.

A removable ~10 mm long piece of a 19 mm inner diameter, 25.4 mm outer diameter 99.8% alumina tube (Coorstek; Golden, CO) rests atop the flat, ground surface at the top of the inner support tube. This alumina spacer ensures that κR samples do not become silica contained through direct contact with the inner support tube, and several ~6 mm deep, ~2 mm wide axial-normal oriented notches on top of the alumina spacer ensures adequate gas mixing beneath the sample (since some studies have shown that Si from a quartz reactor tube can degrade a material's k at 600°C,⁴² when utilizing a silica test rig it is a good idea to minimize κR analysis temperatures, check for reproducible k values via multiple switching events with time, and/or perform post-mortem X-ray Photoelectron studies to detect Si surface contamination). κR samples rest in an unclamped manner atop the alumina spacer and vacuum grease seals the test rig ground glass joint.

To prevent atmospheric backflow into the κR fused silica test rig, cooled exit gas is bubbled through a gas bubbler filled with vacuum pump oil.

Controlled atmosphere κR gas mixtures are typically either bought outright or made in-house via gas mixing. For example, in past SOFC cathode material κR studies, a 0.21 atm oxygen partial pressure gas has been obtained directly from a compressed air tank, while a 0.021 atm oxygen partial pressure mixture is obtained by combining 10 sccm of mass flow controller (MC-500SCCM-D-DB15K, Alicat Scientific; Tuscon, AZ) dispensed air and 90 sccm of mass flow controller (MC-500SCCM-D-DB15K, Alicat Scientific; Tuscon, AZ) dispensed nitrogen.^{19,24} In all cases, the sample atmosphere is quickly switched between the two gas streams using a four-way ball valve (SS-45YF4, Swagelok; Solon, OH).

3.2.2 The Need for Controlled Atmosphere Gas Preheating

Adequate gas preheating is essential for reliable κR measurements. In fact, inadequate gas preheating can lead to sample curvature fluctuations that overwhelm the mechano-electrochemical coupling response of a sample equilibrating to a new pO_2 ; thereby making k measurements through the use of Equations 4-5 impossible.

As shown in Figure 5, gas pre-heating problems often display themselves as 1) an initial curvature response that overshoots an equilibrium values and 2) a sample curvature response that occurs regardless of whether a mechano-chemically active layer is present, or not. These curvature fluctuations occur because inadequately pre-heated gas with a temperature different than that initially around the sample (which occurs as a result of the different thermal conductivities of the original and new gas mixtures) preferentially cools, or warms, one side of the sample (due to non-uniform gas currents within the sample chamber). In the case of switching between 100 sccm of

air (with a 25-725°C thermal conductivity between 26.18 and 67.85 mW/(m*K))⁴³ and 100 sccm of nitrogen (with a thermal conductivity between 25.8 and 67.7 mW/(m*K) from 25-725°C),⁴⁴ a thermocouple placed at the sample position can detect a temperature change of several degrees when the atmosphere is switched. However, when the gas-preheating spirals described in Section 3.2.1 are employed, no temperature changes are detected by a thermocouple at the sample location when the atmosphere is changed from nitrogen to air (at least not at temperatures $\leq 725^\circ\text{C}$ and flow rates ≤ 500 sccm), and the observed curvature relaxations are similar in shape to those in Figure 1.

3.3 Measurable k Values

The k values that can be obtained from typical κR samples range from 2×10^{-5} to 5×10^{-10} cm/sec. The upper k limit is set by the film thickness (or the particle thickness in the case of a porous film) and the reactor flush time (τ_f). This is because for a dense film:

$$k_i = h_f / \tau_i \quad [11]$$

where τ_i is the characteristic time for individual relaxation process i in the film, and the other variables have their previously defined meanings. The error-free use of Equations 4 and 5 require that the reactor atmosphere be flushed “instantly” so that the observed relaxation corresponds solely to the response of the material (instead of the material responding much quicker than the reactor gas volume is exchanged, in which case the sample would act as a reactor flush time sensor). Mathematical analyses available in the literature have shown that, assuming the sample is surface controlled (i.e. h_f or $P \ll 0.03L_c$), τ_f needs to be less than 3 times that of the largest sample time constant τ_i to reliably determine k using Equations 3 and 4.⁴⁵ For a continuously

stirred reactor, τ_f depends upon the reactor volume (V_r) the gas flow rate (Φ) and the reactor temperature in Kelvin (T_r) according to:

$$\tau_f = \frac{V_r T_{STP}}{\Phi T_r} \quad [12]$$

where T_{STP} is 298 K.⁴⁵ Thus, a 10 mL reactor flushed with 100 sccm of 600°C gas has a τ_f of 2.0 seconds, allowing Equations 3 and 4 to reliably measure $k < 2 \times 10^{-5}$ cm/sec values on 100 nm films.

As shown in Figure 6, flush time compromised k 's can be identified experimentally using two methods (experimental identification of flush-time compromised k values is especially important in those cases where V_r is unknown, complicated gas flow patterns prevent the reactor being modeled as a continuously stirred reactor, and/or slow gas transport through the pores of a porous film are a potential cause for concern). The first method involves increasing the reactor gas flow rate by at least 3 times and determining whether k changes. If it does not, the sample is not flush time limited.⁴⁵ The second method involves analyzing the k activation energy, since a true k will behave in an Arrhenius manner (with an activation energy typically of at least a few tenths of an eV), while a flush time compromised k will remain essentially constant with temperature (with an apparent activation energy close to 0.07 eV in accordance with Equation 12 for typical SOFC operating temperature ranges).

The lower k limit is set by the temperature stability of the kSA MOS optics (which is controlled by the room's heating, ventilation, and air conditioning characteristics) and the patience of the system operator. For reference, since KR experiments need to be conducted for at least five times the largest sample τ_i to ensure reliable fitting of the measured KR curves,⁴⁵ a 100 nm thick sample requiring a 24 hour curvature relaxation would have a k of 5×10^{-10} cm/sec.

3.4 Materials Considerations

3.4.1 Requisite Substrate Properties

Single crystal wafers make the best substrates for κR experiment because 1) they typically have larger fracture stresses than polycrystalline substrates, 2) they cannot plastically deform via grain boundary sliding, 3) they can be oriented and cut to exhibit directionally independent elastic properties in the plane of the substrate, and 4) they can easily be polished to yield optically flat and reflective surfaces (which facilitates subsequent thin film deposition or laser array reflection). In addition, single crystal wafers can also be left unpolished on one side, which simplifies thin film curvature measurements by preventing two sets of laser array reflections (one set from the exposed thin film surface and one from the exposed substrate surface).

Ideally, substrate materials should be commercially available in widths that larger than the typical 3-5 mm laser beam array. One inch (25.4 mm) diameter wafers are widely available, but smaller diameter wafers may be utilized when pulse laser deposited thin film thickness uniformity is a concern. Substrate materials should also remain chemically inert over the entire temperature and p_{O_2} range of interest when in contact with the mechano-chemically active film, the process gas, and the sample carrier support tube (as shown in Figure 4, a spacer can be used at the end of the support tube to help prevent contamination of the substrate by the support tube). To ease interpretation of the film stress vs. temperature data, it is also a good idea to select substrate materials that remain single phase over the entire temperature and p_{O_2} range experienced by the sample. Since Equations 4 and 5 are derived using Hooke's Law,^{19,24} the substrate material should remain linear elastic during the course of the κR experiment. The substrate material should also be mechano-chemically inactive to ensure that oxygen vacancy concentration changes in the film are the only source of bilayer curvature relaxation. In this regard, substrate materials containing

cations potentially existing in multiple oxidation states should be treated with extreme caution, since they have the potential to undergo internal, mechano-chemically-active oxygen exchange reactions such as those in Equation 1. Since M_S values are needed to extract the film stress via Equation 6, the Young's Modulus and Poisson ratio of the substrate material should be known for the temperatures and p_{O_2} conditions of interest (As shown by Equations 4 and 5, neither M_S or M_f are needed if only a film k is desired). Further, the substrate's biaxial modulus should be constant over the intended p_{O_2} step size to ensure that oxygen vacancy concentration changes in the film are the only source of bilayer curvature relaxation. Lastly, knowledge of the substrate thermal expansion properties can be helpful in understanding the observed equilibrium bilayer curvature vs. temperature behavior.

Based on these requirements, corundum ($\alpha\text{-Al}_2\text{O}_3$), spinel (MgAl_2O_4), and cubic YSZ ($(\text{Y}_2\text{O}_3)_x(\text{ZrO}_2)_{1-x}$ where $x > 0.09$ to avoid the long-term destabilization of the cubic phase into the tetragonal phase)⁴⁶ are all recommended as substrate materials. All of these materials are commercially available in appropriately oriented, one inch diameter, single crystal wafers with either one side polished (useful for either thin or thick film κR experiments) or two side polished (useful only for thick film κR experiments) configurations from suppliers such as Crystec, GmbH (Berlin, Germany), Marketch (Port Townsend, WA, USA), MTI Corp. (Richmond, CA, USA) or University Wafer (Boston, MA, USA). All of these materials have high chemical stabilities^{47,48} and high melting points ($>2000^\circ\text{C}$)^{46,49} that limit chemical reactions or interdiffusion with many film materials (if film-substrate chemical interactions do occur, chemical barrier layers of cerium oxide or other materials can be utilized). All of these materials are single phase solids from 25-2000°C,^{46,49} all of them are mechano-chemically inactive,⁵⁰⁻⁵³ and all of them have high 25-800°C single-crystal yield stresses greater than 400 MPa.⁵⁴⁻⁵⁶ In addition, both polycrystalline and single

crystal elastic property data from 25-1000°C in air exists for corundum,^{57,58} spinel,^{59,60} and cubic YSZ.⁶¹⁻⁶⁴ Further, literature studies suggest that the 25-1000°C majority defect concentrations in bulk corundum,⁶⁵⁻⁶⁷ spinel,^{51,68} and cubic YSZ are identical in air and hydrogen, with the result that their elastic constants in air and hydrogen only differ by a few percent^{61,64,65} (the fact that these elastic constants vary so little over the >20 orders of magnitude p_{O_2} difference between air and hydrogen suggests they will be constant over the ≤ 1 order of magnitude p_{O_2} difference used in the typical κR experiment). Lastly, temperature-dependent single-crystal thermal expansion data in air for corundum,⁶⁹ spinel,⁶⁹ and cubic YSZ⁶³ is also available in the literature.

Regardless of the substrate material, all κR wafers should be annealed at high temperature prior to use, so that residual stresses within the wafers may be removed. If this is not done, the relaxation of these residual stresses during a κR experiment may cause wild bilayer-curvature vs. temperature behavior and/or prevent long-term, isothermal equilibrium curvature values from being achieved. The success of a particular substrate annealing schedule can be evaluated by measuring the curvature changes of bare, unclamped wafers as a function of temperature (which ideally should exhibit no curvature change vs. temperature). Annealing for 20 hours at 1450°C has been sufficient to relieve residual stress within 200 μm thick YSZ wafers purchased from Crystec, MTI, and University Wafer.

3.4.2 Requisite Film Properties

In order to obtain k from a κR experiment via Equations 4 or 5, the film must 1) display first order (i.e. linear) oxygen surface exchange kinetics, 2) remain linear elastic during the oxygen exchange process, 3) have a biaxial elastic modulus that remain constant over the p_{O_2} step size, and 4) strain enough to produce measurable bilayer curvature changes. The first condition is

usually met as long as the p_{O_2} difference between the initial and final gas is less than an order of magnitude.^{70,71} However, to ensure the film exhibits first order kinetics, it is advisable to use smaller step sizes and/or confirm that identical k 's are obtained using various p_{O_2} step sizes (for instance oxidizing p_{O_2} /reducing p_{O_2} ratios of 2, 5 or 10). The second condition is met by analyzing materials below their yield stress. The small grain size and surface constraints present in thin film geometries are beneficial in that they often raise the yield stress above that observed in bulk materials.⁷² However, ferroelastic phase transitions, high-temperature grain boundary sliding, and other film stress relaxation mechanisms that invalidate the use of Equations 4 and 5 may occur for some film materials under some conditions. Therefore, before extracting oxygen surface exchange coefficients from κR data, bilayer linear elasticity should always be confirmed by ensuring that reproducible and time-independent equilibrium stresses are achieved with multiple p_{O_2} switching events (as shown in Figure 1a). Attempts to detect the onset of yielding should also be made by searching for slope changes in equilibrium film stress vs. temperature plots and/or a sudden deviation from the equilibrium film stresses predicted via literature CTE and elastic property data, as observed in Yang and Nicholas.⁷³ It is important to note that κR measurements may still be possible on materials which have yielded, so as long as p_{O_2} switching results in stresses that are less than or equal to the previously achieved maximum stress (many mechano-chemically active materials behave in a linear elastic manner as they are unloaded and then reloaded to the previously achieved maximum stress⁷⁴). The third condition is also met by keeping the p_{O_2} step size small. Thankfully, the 25-800°C biaxial moduli of most mechano-chemically active materials are essentially constant for a p_{O_2} step size of 10.^{61,64,75,76} As evidenced from Equations 4- 6, one of the beauties of the κR technique is that film elastic constant values are not required to obtain either the oxygen surface exchange coefficient or the film stress. The fourth condition is met by studying

film materials with a high chemical expansion coefficient, α_c (materials with a α_c greater than 0.01, such as the high performance oxygen exchange materials in Table 1, typically work well), utilizing a sensitive curvature measurement setup (such as that described in Section 3.12), and depositing films that are both thin enough to ensure a roughly constant stress through the thickness of the film and thick enough to produce detectable curvature changes with p_{O_2} switching.

3.5 Bilayer Geometry Considerations

The bilayer curvature changes expected for a given temperature or p_{O_2} change can be calculated from known solutions in the literature,^{36,77} provided the bilayer geometry, the necessary film, and the necessary substrate materials properties (elastic and thermo-chemical expansion coefficients) are specified (see <https://www.egr.msu.edu/nicholasgroup/> or Nicholas³³ for MatLab code providing film stress vs. temperature predictions). Larger $h_f:h_s$ ratios allow the film to “tug” more on the underlying substrate (giving larger equilibrium curvature differences for a given p_{O_2} step size), while smaller $h_f:h_s$ ratios collapse Equations 7-9 to Stoney’s Equation (Equation 6) and allow the film stress to be calculated without knowledge of the film elastic properties. Calculations made using available literature solutions^{36,77} (and subsequently corroborated by experiments)^{19,24,78} have shown that (for typical mechano-chemical film and inert substrate materials combinations) films ~100 nm to ~5 μm in thickness on 200 μm thick substrates give well-resolved bilayer curvature changes when a 1 order of magnitude p_{O_2} step size is used. As discussed in Section 2.2, the small $h_f:h_s$ ratios of these samples also collapse Equations 7-9 to Stoney’s Equation (Equation 6) without much error; eliminating large through-film-thickness stress gradients that could complicate κR fitting by invalidating the use of Equations 4 and 5.

Although not yet experimentally verified, calculations made using available literature solutions^{36,77} suggest that well-resolved bilayer curvature changes may be possible for samples with films as thin as ~ 10 nm when testing film materials with large chemical expansion coefficients (such as those in Table 1), utilizing substrates ~ 150 μm thick (wafers much thinner than this will likely be too fragile for handling and are not commercially available), and/or increasing the p_{O_2} step size (ensuring, of course, that the surface exchange process remains linear and the film and substrate elastic constants remain constant by checking that the same k is obtained for a variety of p_{O_2} step sizes). κR experiments utilizing Equations 4 and 5 should also be possible for films thicker than 5 μm , provided that 1) the $h_f:h_s$ ratio is kept below ~ 40 and 2) the dense film thickness or porous film particle size (not grain size) is less than $1/100^{\text{th}}$ of the characteristic thickness defined in Equation 3. Comparison with the characteristic thickness (which is available in the literature for many materials)¹⁰ ensures that the film's electrochemical response is complete surface controlled (if the film is truly surface-controlled, k should remain constant as the film thickness is varied, all else being equal).

In all cases, the diameter of the bilayer should be much larger than the film thickness to allow edge effects to be ignored. As discussed in Freund and Suresh,³⁶ edge effects typically only alter the stress state of material within ~ 50 film thicknesses of an edge, suggesting that 98% and 99.996% of a 5 μm and 100 nm thick film, respectively, on a 25.4 mm wide substrate experience the thickness-averaged small-strain stress states predicted by Equations 6-9. That being said, a combination of large films strains (typically greater than a few tenths of a percent), large substrate diameter to substrate thickness ratios, and/or large film strains may invalidate the assumptions of linear elasticity and spherical bilayer curvature used to derive Equations 6-9.³⁶ Therefore, Chapter 2 of Freund and Suresh should be consulted to identify sample geometries that will ensure the

bilayers remain in the linear elastic regime, and substrates with smaller substrate diameter to substrate thickness ratios should be utilized if needed. In all cases, circular substrates are recommended to avoid the complicated stress states that may exist near sharp corners.

3.6 System Costs

An itemized κ R system parts list, showing that the total cost for a full κ R setup is around \$90k, is provided in Table 2. Sample fabrication costs such as the ~\$100 for each single crystal substrate, film deposition costs, etc. are not included in Table 2. Table 3 shows that the costs for a κ R setup compare favorably with other oxygen surface exchange measurement techniques.

The κ R setup cost in Table 2 are calculated assuming that four mass flow controllers (at \$4950 each) are used to produce two κ R gas mixtures (each with a different p_{O_2} , $p_{O_2} = 0.21$ and 0.021 , for instance) from two unmixed gas tanks (one nitrogen tank and one air tank, for instance). If only a few κ R experiments are to be conducted, cost savings may be realized by only purchasing two mass flow controllers and ordering premixed gases (each with a different oxygen partial pressure) directly from a supplier. For tests on oxygen exchange materials that operate in air, cost savings may also be realized by replacing stainless steel tubing with plastic tubing and replacing stainless steel fittings with brass fittings. However, due to the oxygen permeability of most plastics and the chemical reactivity of brass, stainless steel tubing and fittings are recommended when using low p_{O_2} or reactive gas mixtures.

4.0 Comparison to Alternative Techniques

As shown in Table 3, the κ R technique is presently one of the cheapest electrode-free k measurement techniques. Electrode-free k measurement techniques are needed because the high

surface area, closely-spaced interdigitated electrodes required to measure films with low electrical conductivity can lead to 1) inadvertent strain engineering of the film c_v and k via electrode-film CTE mismatch induced strain and the operation of mechano-chemically active reactions such as Equation 1,^{20,23} and 2) artificial k enhancement caused by electrode-catalyzed oxygen incorporation at the film-electrode-gas triple phase boundary⁷⁹ (in films with high electrical conductivity, electrode use is not a problem because the electrodes can be placed far apart and made to cover only a small fraction of the exposed film surface). The κ R technique is also the only technique presently able to simultaneously measure a material's stress state and oxygen surface exchange coefficient. Further, the κ R technique has the added convenience of allowing *in situ* or *in operando* measurements.

The κ R technique is limited by the fact that, like the Electrical Conductivity Relaxation (ECR), Coulombic Titration, Electrical Titration, Gravimetric Relaxation, Optical Relaxation, Atmospheric Relaxation, and Strain Relaxation techniques, k values can only be measured on materials that exhibit a change in their bulk oxygen vacancy concentration with p_{O_2} at the temperatures of interest (thankfully most high performance oxygen exchange materials are not in their Brouwer diagram electrolytic domains and therefore exhibit a change in oxygen content with a change in p_{O_2}). Like the ECR technique, gas flushing and gas preheating problems typically set an upper limit on the measurable k values of $\sim 2 \times 10^{-5}$ cm/sec (higher k values can be inferred, to some extent, by extrapolating low-temperature data). The κ R technique is also limited by the fact that it requires the film to be mechano-chemically active (i.e. it must exhibit a lattice strain when it changes its oxygen concentration). Thankfully, most materials exhibit a lattice distortion when oxygen is removed. The biggest limitations of the κ R technique are that the technique requires 1) that oxygen exchange be the only source of p_{O_2} -induced mechanical relaxation in the film, and 2)

that the film remain well-bonded to the substrate. Thankfully, as discussed in Section 3.4.2 inelastic relaxation processes can be detected by monitoring the long-term equilibrium curvature, comparing the k 's obtained from multiple relaxations under identical conditions, and searching for sudden kinks in equilibrium stress vs. temperature plots. Film delamination and/or cracking can also be detected by sudden kinks in equilibrium stress vs. temperature plots.

5.0 Conclusions

In conclusion, the curvature relaxation technique is a new, electrode-free method for simultaneously measuring a material's film stress and chemical oxygen surface exchange coefficient under *in situ* or *in operando* conditions. In its present form, it can be used on dense or porous, thin or thick film materials, provided the $h_f:h_s$ ratio is low enough to allow application of Stoney's Equation, and the film thickness (in the case of dense films) or particle size (in the case of porous films) is much less than the material's characteristic thickness. It is presently among the cheapest electrode-free techniques for measuring oxygen surface exchange coefficients, and the only technique yielding simultaneous k and stress data. Further, since most materials strain in response to a change in composition, the curvature relaxation technique promises to be an important tool in establishing the links between mechanics and electrochemistry in a variety of solid state battery, fuel cell, memristor, ion exchange, and catalytically-active materials. The technique will also provide instrumental in determining if it is possible to strain-engineer ionic transport properties.

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Table 1. Common Mechano-Chemically Active Oxygen Exchange Materials

Material	Measured Temperature (°C)	Chemical Expansion Coefficient, α_c
$Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$	700-900	0.14 ^{80,81} †
CeO_2	800	0.10 ^{81,82}
$La_{0.3}Sr_{0.7}FeO_{3-\delta}$	650-875	0.017-0.047 ⁸³
$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$	700-900	0.031 ^{84,85}
$La_{1-x}Sr_xCoO_{3-\delta}$ $0.2 \leq x \leq 0.8$	600-900	0.023-0.024 ^{84,86}
$SrFe_{1-x}Ti_xO_{3-\delta}$ $0.25 \leq x \leq 0.7$	23	0.03 ⁸⁷
$Ba_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$	600-900	0.026-0.016 ⁸⁸
$La_{1-x}Sr_xCrO_{3-\delta}$ $0.16 \leq x \leq 0.3$	1000	0.024 ⁸⁹
$LaMnO_{3-\delta}$	600-1000	0.024 ⁹⁰
†For $0 \leq \delta \leq 0.05$. Although nonlinear above 0.05, α_c is always ~linear for $\Delta\delta \leq 0.01$ ⁸⁰		

Table 2. κ R System Equipment and Vendor List

Component (Total Cost)	Vendor	Item #	Item Description	Approx. Item Cost
Controlled Atmosphere Test Rig (\$1163)	Technical Glass Products (Painesville Township, OH)	20X25	22 mm ID-25 mm OD Fused Silica Tubing for Inner Support Tube, 5 cm long	\$32
		27X30	27 mm ID-30 mm OD Fused Silica Tubing for Outer Support Tube, 5 cm long	\$25
		4X6.35	4 mm ID-6.35 mm OD Fused Silica Tubing for Outer Support Tube Gas Preheating, 3 m long	\$50
		1X0.125	Three Fused Silica Windows	\$16
		STJ34-45M	34/45 Fused Silica Joint	\$30
	Coorstek (Golden, CO)	65825-01.0000	19mm ID-25 mm OD 99.8% Pure Al ₂ O ₃ Tube, 25 mm long	\$10
	Michigan State Glassblower	Custom	Controlled Atmosphere Test Rig Assembly Labor Costs	\$1000
Controlled Atmosphere Test Rig Holder (\$2,085)	Edmund Optics (Barrington, NJ)	NT66-430	X-Translation Stage for Test Rig Alignment	\$375
		NT66-430	Y-Translation Stages for Test Rig Tube Alignment	\$375
	Newport Optics (Irvine, CA)	GON65-L	Lower Goniometer for Test Rig Tube Alignment	\$500
		GON65-U	Upper Goniometer for Test Rig Alignment	\$500
		AJS100-0.5	Goniometer High Precision Small Knob Adj. Screw	\$25
		AJS100-0.5H KD.75	High Precision Hex Adjustment Screw, Large Actuator Knob	\$30
	CVI Melles Griot (Albuquerque, NM)	07-DUP-011	Stable Rod Post with Removable Base	\$80
		07-DSQ-003	1/4-20 Standard Stable Rod Carrier	\$65
		07-TSR-204	Short Right Angle Bracket with 1/4-20 Holes	\$65
	Michigan State Machine Shop	Custom	Controlled Atmosphere Test Rig Mounting Bracket	\$70
Optical Table Components (\$2,225)	Edmund Optics (Barrington, NJ)	NT43-420-522	50 cm OD $\lambda/20$ Flat Zerodur Mirror	\$245
		NT58-671	Right Angle Post Clamp for the Zerodur Mirror	\$15
		NT59-002	45° Mounting Adapter for the Zerodur Mirror	\$30
		NT59-751	Optical Post for the Zerodur Mirror	\$10
		NT58-976	Optical Post Holder for the Zerodur Mirror	\$10
		NT66-427	Translation Stage for the 45° Mirror	\$375
	Thor Labs (Newton, NJ)	PBI11112	100 x 64 x 6 cm Optical Breadboard	\$1500
	Sorbothane (Kent, OH)	0510151-70-10	Four 70 Durometer 6 cm OD Non-Skid Hemispheres	\$40
Furnace (\$7,000)	Applied Test Sys. (Butler, PA)	3210-3.00-12-12	1200°C Split Tube Furnace, Furnace Controller, RS-232 Comm., and Over-Temperature Controller	\$6,500
	McMaster-Carr (Chicago, IL)	Various	Unistrut Bars and Brackets for a Vertical Furnace Support System	\$500
Gas Handling Components (\$21,860)	Alicat (Tucson, AZ)	MC-500SCCM-D-DB15K	Four 0-500 sccm Mass Flow Controllers with Built in Logic and Pre-calibrated Gas Selection	\$19,800
	Swagelok (Solon, OH)	SS-45YF4	Stainless Steel Four Way Ball Valve	\$430
		Various	Stainless Steel Tubing, Unions, Tees, Valves	\$1000
	VWR (Batavia, IL)	55850-702	Two Stainless Steel Two Stage Regulators	\$460
	Airgas (Lansing, MI)	16071600	Nitrogen, Research Grade, 99.9995% Pure	\$110
		16049780	Compressed Air, Chromatographic Grade	\$60
MOS System (\$54,500)	k-Space (Dexter, MI)	MOS	Preassembled 25 mW, 660 nm Laser Multi-beam Optical Stress Sensor with Control Software and On-site Installation. No Automatic Mirror Tracking.	\$54,500
Total System Cost (in 2012 U.S. Dollars): \$88,833				

Table 3. A Comparison of Common Methods Used to Determine Oxygen Surface Exchange Coefficients

Method	Conductivity Relaxation	Permeation	Coulombic Titration	Electrical Titration	Curvature Relaxation	Impedance Spectroscopy	Gravimetric Relaxation	Optical Relaxation	Atmospheric Relaxation	Strain Relaxation	Isotope Exchange Depth Profiling
Involves measuring the:	electrical conductivity of a sample equilibrating to an atmospheric pO_2 change	surface dominated through-sample surface resistivity	pO_2 around a sample equilibrating to an externally imposed pO_2 change	pO_2 monitoring around a sample equilibrating to an electrically imposed $c_{V_O^{\bullet\bullet}}$ change	curvature of a bilayer equilibrating to an atmospheric pO_2 change	electrochemical impedance response of a material, possibly with blocking electrodes	weight change of a sample equilibrating to an atmospheric pO_2 change	optical properties of a sample equilibrating to an atmospheric pO_2 change	gas composition around a sample equilibrating to a change in atmospheric O_2 isotope ratios	lattice parameter of a material equilibrating to an atmospheric pO_2 change	$c_{O^{2-}}^*$ - depth profile of a sample equilibrating to a change in atmospheric O_2 isotope ratios
Described in Refs:	91,92	93,94	95	96,97	19,24	98,99	100,101	102,103	104	105,106	107,108
Measured k variant	$\tilde{k}$	$\tilde{k}$	$\tilde{k}$	$\tilde{k}$	$\tilde{k}$	$k_{O^{2-}}^q$	$\tilde{k}$	$\tilde{k}$	$k_{O^{2-}}^*$	$\tilde{k}$	$k_{O^{2-}}^*$
Obtains k through	Fick's 2 nd Law solution fitting	Wagner Equation	Fick's 2 nd Law solution fitting	Fick's 2 nd Law solution fitting	Fick's 2 nd Law solution fitting	Equivalent Circuit Modeling	Fick's 2 nd Law solution fitting	Fick's 2 nd Law solution fitting	Fick's 2 nd Law solution fitting	Fick's 2 nd Law solution fitting	Fick's 2 nd Law solution fitting when k & D are co-limiting
Electrode-free?	No	No	Yes	No	Yes	No	Yes	Yes	Yes	Yes	Yes
Suitable for <i>in situ</i> , bulk sample or thick film analyses?	Yes, if the material has a change in charged defect concentration	Yes below ~500°C. Glass seal complications typically prevent higher temperature experiments	Yes, but sealing problems often cause complications above ~500°C.	Yes below ~500°C. Glass seal complications typically prevent higher temperature experiments	Yes, if the material is mechano-chemically active and it behaves as a linear elastic solid	Yes	Yes	Yes, if the material has optical defects influenced by a change in defect concentration	Yes	Yes, if the material is mechano-chemically active and it behaves as a linear elastic solid	No. The need for high vacuum conditions during depth profiling prevents <i>in situ</i> measurements
Suitable for <i>in situ</i> , thin film analyses?			No. Voluminous samples are required to noticeably alter gas composition				No. Voluminous samples are required to noticeably alter weight		No. Voluminous samples are required to noticeably alter gas composition		

Equipment Costs	\$	\$	\$	\$	\$\$	\$\$	\$\$	\$\$	\$\$\$	\$\$\$	\$\$\$\$
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$k_{O_2-}^q$, $k_{O_2-}^*$ and $\tilde{k}$ = electrically determined, tracer determined, and chemically determined (ambipolar) k , respectively. c_{O_2-} = [total lattice oxygen], $c_{O_2-}^*$ = [oxygen tracer], $c_{V_O^{\bullet\bullet}}$ = [oxygen vacancy], R_s = oxygen exchange surface resistance, R = ideal gas constant, T = temperature in kelvin, F = Faraday's Constant, I = current, and V = voltage. Here, oxygen defects are assumed to be the only mobile ions. \$ denotes system costs less than ~\$50,000, \$\$ denotes system costs between ~\$50,000-\$100,000, \$\$\$ denotes system costs between ~\$100,000-\$500,000, and \$\$\$\$ denotes system costs above \$500,000.

Figure 1. Representative (a) κR curves for a LSF64 film on a 100-oriented YSZ wafer with cycling between a 10% air - 90% N_2 mixture and 100% air, from Yang⁷⁸ and (b) normalized and fitted κR curve for a LSF64 film on a 100-oriented YSZ wafer with switching from a 10% air - 90% N_2 mixture to 100% air showing that two oxygen exchange process are active, from Yang and Nicholas¹⁹ (reprinted with permission from Elsevier).

Figure 2. Schematics of the *kSA MOS Setup* used to perform κR experiments for a) dense film/dense substrate bilayers, and b) porous film/dense substrate bilayers. Note that when studying dense films, as in part a), the *kSA MOS* laser beams are reflected off the film surface. In contrast, when studying porous films, as in part b) the *kSA MOS* laser beams are reflected off the substrate surface. These schematics are not drawn to scale and are drawn with arbitrary bilayer curvature.

Figure 3. Pictures of the curvature relaxation setup a) with and b) without the outer quartz tube removed.

Figure 4. Schematic of the controlled atmosphere test rig. The shaded gray region represents the disposable alumina spacer used to support the sample.

Figure 5. Sample curvature vs. time for a sputtered 100 nm thick LSF64 film on a 200 μm thick 100-oriented YSZ substrate (top) and a bare 200 μm thick 100-oriented YSZ substrate (bottom) when switching between 20 sccm of N_2 (0-300 sec) and 20 sccm of air (300-5000 sec) without adequate gas preheating. See Figure 1 for the sample curvature vs. time behavior of a LSF64|YSZ sample with adequate gas preheating.

Figure 6. Real (white) and apparent (gray) oxygen surface exchange coefficients for a porous 4.7 μm LSF64 film on a 200 μm thick 100-oriented YSZ substrate taken under various gas flow rates. As indicated by the change in slope of the 500 sccm gas flow measurements, reliable k measurements could not be obtained above 375°C due to reactor flush time limitations. The reliability of the 500 sccm measurements is confirmed by their low temperature agreement with the 100 sccm measurements (reprinted with from Ref. ²⁴ with permission from the Electrochemical Society).

List of Symbols and Acronyms

A_i	Area fraction
α_c	Chemical expansion coefficient
α_T	Coefficient of thermal expansion (CTE)
c_v	Instantaneous bulk oxygen vacancy concentration
$c_{v\ o}$	Initial pO_2 -equilibrated oxygen vacancy concentration
$c_{v\ \infty}$	New pO_2 -equilibrated oxygen vacancy concentration
δ	Instantaneous film oxygen nonstoichiometry
δ_0	Initial film oxygen nonstoichiometry
δ_∞	New pO_2 -equilibrated film oxygen nonstoichiometry
d	CCD-detected average inter-spot spacing
d_o	Spacing between the parallel laser beams striking the bilayer
D	Oxygen diffusion coefficient
ECR	Electrical conductivity relaxation
E_S	Substrate Young's modulus
$Fe\dot{e}_{Fe}$	Iron-bound electron holes
h_f	Film thickness
h_s	Substrate thickness
Φ	Gas flow rate
k	Surface exchange coefficient
κ	Instantaneous bilayer curvature
κ_0	Initial bilayer curvature
κ_∞	New pO_2 -equilibrated bilayer curvature

κR	Curvature relaxation
λ_f	Film stress
$\bar{\lambda}$	Thickness averaged film stress
$\bar{\lambda}_{st}$	Thickness averaged film stress predicted from Stoney's Equation
L	Sample to CCD camera distance
L_C	Characteristic thickness
LSF64	$\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$
M_f	Film biaxial modulus
M_S	Substrate biaxial modulus
MIEC	Mixed Ionic Electronic Conducting
MOS	Multi-beam Optical Sensor
$O_{2(g)}$	Oxygen gas
O_o^x	Lattice oxygen
pO_2	Oxygen partial pressure
P	Particle size
R_S	Intrinsic oxygen surface exchange resistance
$\sigma_{V_O^{\bullet}}$	Oxygen vacancy ionic conductivity
sccm	Standard Cubic Centimeters per Minute (i.e. mL/min)
SOFC	Solid Oxide Fuel Cell
S_V	Specific pore surface area
θ	MOS laser beam array angle of reflection
τ_i	Time constant
t	Time

T	Temperature
T_r	Reactor temperature in Kelvin
ν_f	Film Poisson's Ratio
ν_s	Substrate Poisson's Ratio
$V_o^{\bullet\bullet}$	Oxygen vacancy
V_r	Reactor volume
V_v	Volume fraction porosity
YSZ	Yttria Stabilized Zirconia
z	Film-normal distance from the substrate mid-plane

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