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Nonlinear Impedance Analysis of La$_{0.4}$Sr$_{0.6}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ Thin Film Oxygen Electrodes

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The rate of oxygen reduction/evolution on oxide surfaces continues to limit the performance of intermediate temperature (500–800°C) solid oxide fuel cells (SOFCs) and electrolysis cells (SOECs).1 La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF), and particularly the composition La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF-6428), exhibits a good balance of kinetic activity, ionic and electronic transport properties, and chemical stability, resulting in its prevalence as an oxygen electrode.2–4 Electrochemical measurements on LSCF-6428, including conductivity relaxation,5–7 coulometry,4,6 and impedance techniques2,7,8 have underscored the importance of bulk oxygen vacancies in governing rates of O$_2$ reduction and evolution. However, a clear understanding of how these vacancies contribute to the mechanism and rate-limiting step(s) of O$_2$ exchange remains elusive.

The thermodynamic understanding of La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-\delta}$ derives largely from measurements of equilibrium oxygen nonstoichiometry ($\delta_0$) upon exposure to different oxygen environments and temperatures.9–11 In the limit of high B-site iron content (y > 0.6), workers have interpreted this $\delta_0 - \rho_{O_2} \sim T$ relationship using a p-type point-defect model originally developed for LSF (LSCF, with y = 1),12 where electrons are localized on iron centers of discrete charge and defects are considered dilute.9,13 For Co-rich compositions (y < 0.4), a metallic model used to describe LSC (LSCF, with y = 0) yields better agreement.4 While La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3}$ exhibits semiconducting behavior over a wide range of $\rho_{O_2}$ and temperature, the observed $\delta_0 - \rho_{O_2}$ relationship deviates substantially from both p-type and metallic models under oxidizing conditions ($\rho_{O_2} > 10^{-2}$, lower temperature). The cause for this departure from a p-type model is unclear, though some workers have sought to hybridize p-type and metallic models to describe LSCF.11 Others speculate that LSCF’s surface is more reducible than its bulk, based on first-principles calculations13 and an experimentally observed increase in oxygen nonstoichiometry with pellet surface area under oxidizing conditions.9

Oxygen exchange kinetics for LSCF have been studied using electrical conductivity relaxation (ECR) and isotope exchange methods (IE) on dense pellets,5,14 and electrochemical impedance spectroscopy (EIS) on porous electrodes.7 However, interpretation of these measurements in terms of kinetics can be very challenging due to an inherent convolution of kinetics and transport. In the case of ECR and IE, the major difficulty is deconvoluting time constants associated with kinetics and bulk diffusion. Interpretation of EIS response of porous electrodes additionally requires consideration of both surface and bulk transport. Since these techniques are limited to small perturbations from equilibrium, they are insensitive to differences in nonlinearity between transport and kinetic rate laws, leading to non-unique fits of kinetic/transport models. As a result, little consensus exists for the mechanism or rate law of oxygen reduction on porous LSCF-6428.

One path toward isolating surface kinetics and material thermodynamics is to study dense thin film electrodes where transport rates are fast and the active volume of the electrode is known. While thin film studies have proved crucial in furthering understanding of mixed ionic and electronic conducting (MIEC) electrodes, many thin films exhibit behavior different from their bulk counterparts. For example, in the case of La$_{1-x}$Sr$_x$Co$_{0.2}$O$_{3-\delta}$ (LSC), the reducibility of thin films differs from bulk thermodynamic measurements.15,16 Although cause of this behavior is not fully understood, non-uniform distribution of the cation dopant (Sr, in this case) offers a possible explanation. For the sake of clarity, we define three manifestations of cation inhomogeneity: precipitation, where the cation forms a secondary metal-oxide phase; segregation, equilibrium cation rearrangement, possibly due to space-charge or strain effects; and stratification, long-range (> Debye length), non-equilibrium cation inhomogeneity caused by electrode processing. Depth-profile secondary ion mass spectroscopy (DP-SIMS) and nonlinear impedance analysis suggest at least part of this effect may result from Sr sequestration.17,18 In the case of LSCF-6428, in situ total-reflection X-ray fluorescence (TXRF) suggest there may be an inherent bias-independent thermodynamic driving force for surface Sr segregation and possibly precipitation into non-perovskite phases.19 X-ray photoelectron spectroscopy (XPS) of LSCF-6428 polished pellets20 and LSCF-8228 200 nm pulsed laser deposited (PLD) films21 show evidence of Sr segregation at the gas-solid interface. Low energy ion scattering (LEIS) revealed a nearly Sr and O-saturated surface monolayer for polished pellets and films alike when annealed above 600°C.22,23

A further challenge facing analysis of thin film electrodes is their typically rapid changes in performance with time relative to porous...
coefficients. While the data in Figure 1 alone cannot accurately resolve Bi, NLEIS is sensitive to small passive harmonics associated with nonlinear rates. These measured harmonics are particularly sensitive to the electrode's thermodynamic and kinetic properties—both of which are expected to have very distinct (and specific) nonlinear behavior. By comparing the measured EIS and NLEIS responses of LSCF-6428 thin films to models describing these phenomena, this study seeks to better understand the factors governing electrode performance and degradation.

Theory

Empirical thermodynamic model.—The impedance response of thin film MIEC electrodes depends on the thermodynamic relationship between the electrochemical driving force and defect concentrations. As shown in Figure 1, for LSCF-6428 at the high pO2 relevant to SOFC cathodes, the Log δO2 = Log pO2 relationship deviates substantially from both p-type and metallic models.4 Due to the sensitivity of our impedance models to this behavior, we instead adopt an empirical relationship between δ and pO2 based on Kuhn et al.'s measurements:

\[ \ln[\delta] = -B_0 - B_1 \ln[f_{O2}] - B_2 \ln[f_{O2}]^2, \]

where δ is the oxygen nonstoichiometry (which in general deviates under dynamic conditions from δ0), fO2 is the oxygen fugacity in the solid, and Bi are empirical coefficients. While the data in Figure 1 alone cannot accurately resolve B2, NLEIS is sensitive to small differences in the nonlinearity of the thermodynamic model, and thus spectra are expected to exhibit a dependence on B2.

The thermodynamic factor, \( A = -1 \frac{\ln f_{O2}}{\ln 10} \), is a useful quantity for describing the ease of vacancy formation upon changing fO2 and the non-ideality of the solution for a dilute, ideal solution, \( A = 1 \).3 In the limit of gas-solid equilibrium (where \( \delta \ll \delta_0 \)), we define \( A_0(\delta_0) \equiv A(\delta)|_{f_{O2}=1} \approx A_0 - \delta_0 f_{O2} \).

Thin film electrode model.—Assuming a sufficiently thin electrode (where gradients in electrode composition are negligible along an axis perpendicular to the film surface), accumulation of oxygen vacancies in the film must balance the surface reaction rate of oxygen consumption \( r_{O2} \) at the gas-electrode interface (\( \delta = L \)) and the measured ionic current \( i \) at the electrode-electrolyte interface (\( \gamma = 0 \)),

\[ \frac{L}{V_m} \frac{\partial \delta}{\partial t} = \frac{i}{2F} |_{\gamma=0} - 2 r_{O2} |_{\gamma=L}, \]

where \( L \) is the electrode thickness, \( V_m \) the molar volume of the electrode, and \( F \) is Faraday's constant. The driving force for \( O_2 \) reduction/oxidation at the gas-electrode surface can be expressed in terms of the deviation of the oxygen chemical potential in the solid from equilibrium with the gas:

\[ \psi = \frac{1}{2} \ln \left[ \frac{f_{O2}}{p_{O2}} \right] = \frac{\mu_{O2}^{\text{solid}} - \mu_{O2}^{\text{gas}}}{2RT} \]

To ensure \( r_{O2} = 0 \) at equilibrium, we use an empirical rate law based on non-equilibrium thermodynamics to describe the surface kinetics,

\[ r_{O2} = k_{O2}(T) p_{O2}^{\delta_0}(1 - e^{2\delta}) \]

where \( k_{O2}(T) \) is the rate coefficient and \( n \) is the empirical vacancy reaction order. Note that in the limit of \( \delta \to \delta_0 \), the prefactor \( k_{O2}(T) p_{O2}^{\delta_0} \) corresponds to the equilibrium exchange rate, \( R_{O2} \). This empiricism does not explicitly consider the dependence of the forward rate on electronic carrier concentration. Under the assumption that the forward rate is independent of electronic carrier concentration, the parameter \( n \) corresponds to the reaction order with respect to bulk vacancy concentration, i.e. a reaction mechanism limited by single-vacancy-site chemisorption of \( O_2 \) corresponds to \( n = 1 \), while the dissociative adsorption of \( O_2 \) onto two adjacent vacancy sites corresponds to \( n = 2 \).25 In contrast, if the reaction is limited by electron availability (as in a p-type semiconductor, for example) Eq. 4 forces this \( p_{O2} \) dependence into the \( \delta^2 \) term, precluding a simple mechanistic interpretation of \( n \).

For a galvanostatic impedance measurement at zero bias, the current density \( j = j \cos(\omega \psi) \) is a periodic signal with amplitude \( j \) and angular frequency \( \omega \). Assuming equilibrium of ion transfer within the electrolyte and across the electrode/electrolyte interface, the electrode voltage relates directly to the thermodynamic driving force:

\[ V = \frac{RT}{2F} \psi \]

Linear impedance response.—For a small-amplitude current perturbation, a linear approximation for the impedance predicted by Eqs. 1–5 is valid. The resulting impedance \( Z(\omega) \) is analogous to that of a resistor and capacitor in parallel:

\[ Z(\omega) = \frac{V}{i} = \frac{2R_c}{1 + j\omega C}, \]

where the characteristic resistance (\( R_c \)) is defined as the maximum value of the absolute imaginary impedance, \( |Z(\omega)| \), and the characteristic time constant (\( \tau = 2RC \)) is defined as the reciprocal characteristic “peak” angular frequency, where \( |Z(\omega)| \) is maximum (i.e. where \( \omega = \omega(\omega_0) = \infty \)). For the above model, the characteristic resistance is sensitive only to the surface kinetics.

\[ R_c = \frac{RT}{2\pi F^2 R_{O2}} \]

As shown by Kawada et al., the storage capacity of oxygen vacancies in the thin film results in a chemical capacitance, \( C_0 \).15 The volume-specific capacitance, \( VSC \), is an intrinsic thermodynamic property of the material and thus tied to the aforementioned thermodynamic models.

\[ VSC = C_0 = \frac{8F^2}{V_m} \frac{\partial \delta}{\partial p_{O2}^{\text{eq}}} \approx \frac{4F^2}{V_m RT} \delta_0 \]

Nonlinear impedance response.—Assuming a moderate-amplitude current perturbation, we expect the steady-periodic response of the cell to be resolvable in a finite power series in the
Table I. Definitions of dimensionless variables and their corresponding dimensional scaling factors.

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<th>Quantity</th>
<th>Dimensional Form</th>
<th>Dimensionless Form</th>
<th>Dimensional Scaling Factor</th>
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<td>Time</td>
<td>$t$</td>
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<td>$\omega_c = \frac{1}{T}$</td>
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<tr>
<td>Perturbation Frequency</td>
<td>$\tilde{\phi}$</td>
<td>$\sigma = \frac{\tilde{\phi}}{\omega_c}$</td>
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<tr>
<td>Current Amplitude</td>
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<td>$\alpha = \frac{\tilde{i}}{\tilde{V}}$</td>
<td>$i^* = 4F\rho_{O_2}$</td>
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<tr>
<td>Potential</td>
<td>$V$</td>
<td>$\psi = \frac{\tilde{V}}{\tilde{V}}$</td>
<td>$V^* = \frac{F\delta}{RT}$</td>
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where $\alpha$, $\tau$, and $\sigma$ are the dimensionless current density amplitude, time, and current perturbation frequency, respectively, defined in Table I, and $\psi_{\beta,m}$ and its complex conjugate $\psi^*_{\beta,m}$ are the complex Fourier voltage coefficients associated with the $\alpha^\beta$ contribution to the $k^{th}$ voltage harmonic.26 This work focuses on $U_{\ell,k}$, the lowest $\alpha$-order contribution to the $k^{th}$ voltage harmonic $\psi_{k,m}$, rescaled to the impedance such that the absolute imaginary component $|U_{\ell}(\sigma \rightarrow 1)| = 1$:

$$U_{\ell,k}(\sigma) = 4^k\psi_{k,m}(\sigma)$$

Experimental

Film fabrication and characterization.—Epitaxial (001)-oriented thin films (20–70 nm) of La$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3}$ were deposited on a YSZ substrate with a ~5 nm gadolinium-doped ceria protective interlayer (GDC) via pulsed laser deposition (PLD). The films were characterized with high resolution X-ray diffraction (HRXRD), confirming the pseudocubic epitaxy of LSCF, and with atomic force microscopy (AFM), giving the film thickness and root-mean-square roughness values of 0.237–0.323 nm, as detailed by Lee et al.24 On each YSZ/GDC substrate, the LSCF electrodes were patterned into multiple neighboring microelectrodes with diameters ranging from 50 to 200 μm.

Electrochemical measurements.—Silver mesh and paint were used as the counter electrode. As shown in Figure 2, a microprobe station (Karl Soss, Germany) was used to asymmetrically heat the cell to 600 °C (Linkam TS1500, UK heating stage) while making electrical contact with the counter electrode and a single microelectrode via tungsten carbide probes. Atmospheric gas blends of 100%, 10%, and 1% O$_2$ (bal. Ar) were passed over the cell at 100 scm. The electrode temperature was confirmed by placing a thermocouple on the GDC surface upon each change in gas environment.

Linear electrical impedance spectroscopy (EIS) was performed using a Solartron 1260 impedance analyzer, 5 mV perturbation amplitude, and 1 mHz to 1 MHz frequency range. Nonlinear impedance spectroscopy (NLEIS) was performed using the testing apparatus detailed in reference.26 During a single NLEIS frequency sweep (lasting ~4 hours), 12 current perturbation amplitudes ($\tilde{i}$) were used for each frequency ($\tilde{\omega}$) corresponding to a ~2 mV (yielding a nearly linear voltage response) to ~30 mV voltage perturbation (producing clear 2nd and 3rd voltage harmonics). Due to rapid increases in the electrode’s time constant and the low-frequency-limitations (~5 mHz) of NLEIS, the “slower” 1% and 10% measurements could only be performed within the first several hours of testing. Increasing the temperature beyond 600 °C further exacerbated cell instability. Unless otherwise stated, all subsequent data come from a single 20 nm by 200 μm microelectrode at 600 °C.

Results and Analysis

Linear impedance.—Figure 3 shows an example EIS spectrum collected in 100% O$_2$ at 600 °C. Over the duration of a single EIS frequency sweep (~5 minutes), the impedance agrees well with the equivalent circuit representation described by Eq. 6. High-frequency features are small and are therefore included with the ohmic electrolyte resistance in the extrapolated series resistance as shown in the inset. The semicircular shape of the impedance and lack of a high-frequency Warburg feature support the assumption of a vacancy diffusion-equilibrated film limited by the surface oxygen reaction.

Figure 4 shows the extracted $R_c$ and $VSC$ of a single microelectrode at 600 °C as a function of time and $p_{O_2}$; open symbols correspond to the linear portion of the NLEIS impedance. Barringer the 50 to 68 hour interval, $R_c$ increases with measurement duration. Conversely, the $VSC$ shows a strong $p_{O_2}$ dependence and otherwise remains stable despite large fluctuations in resistance. All microelectrodes tested share this behavior of $R_c$ variability and $VSC$ stability. However, the trends of $R_c$ shown in Figure 4a (e.g. increasing vs. decreasing with time) are not in phase with concurrently measured electrodes on the same substrate [Supplementary Figure S1]. The series resistance
does not exhibit any clear trends over the same measurement duration [Supplementary Figure S2].

Figure 5 compares the measured $p_{O2}$ dependence of the thin film $VSC$ to that predicted by the p-type, metallic, and empirical thermodynamic models shown in Figure 1. While the empirical model agrees well with the observed capacitance, neither the p-type nor metallic model accurately captures the measured $VSC$’s absolute value and $p_{O2}$ dependence.

Nonlinear impedance.—To account for drift in electrode performance during an NLEIS sweep (lasting ~4 hours), a unique $R_c$ for each perturbation frequency was fit from the linear portion of the thermodynamic model based on the data in Figure 1 would inform the film electrode model detailed in the Theory section. Ideally, a physical thermodynamic model based on the data in Figure 1 would inform the electrode’s predicted response. However, apparent in Eq. 8, deviations between data points are drawn merely to guide the eye.

Nonlinear impedance.—To account for drift in electrode performance during an NLEIS sweep at 600 °C: (top) unscaled and (bottom) scaled and drift-corrected linear impedance. Connecting lines between data points are drawn merely to guide the eye.

Figure 6. EIS spectra for the initial $p_{O2}$ sweep at 600 °C: (top) unscaled and (bottom) scaled and drift-corrected linear impedance. Connecting lines between data points are drawn merely to guide the eye.
Figure 7. NLEIS spectra for the initial pO2 sweep at 600°C: scaled (top) second and (bottom) third dimensionless harmonic voltage response coefficients. Phasor lines intersect U_{jk} at the frequency n = \frac{1}{2}; this corresponds to angular frequencies of 1.5, 5.0, and 6.4 Hz for U_{22} and 1.0, 3.3, and 4.3 Hz for U_{33} for 1%, 10%, and 100% O2, respectively. Connecting lines between data points are drawn merely to guide the eye.

NLEIS response, supporting the use of the empirical thermodynamic model. The linearity of Figure 1 at high pO2 (implying B_2 \ll B_1) and the scarcity of data prevent a unique fit of B_3 from thermogravimetry alone. However, the NLEIS spectra are extremely sensitive to small Log \( B_0 \sim \text{Log} \ p_0 \) nonlinearities—in fact, all modeled scenarios with \( B_2 = 0 \) predict U_{22} and U_{33} to be pO2 independent, and are thus unable to capture the observed U_{22} trends in Figure 6. Conversely, as a result of the aforementioned nonlinear scaling, U_{22} and U_{33} are insensitive to the absolute oxygen nonstoichiometry. Assuming the bulk thermogravimetry, thin film VSC, and thin film NLEIS data all depend on the same thermodynamic behavior—though each with unique sensitivities—we choose to fit the datasets in aggregate. To do so, we maximize the equally-weighted sum of R² for the three datasets by first selecting an empirical rate law (via incremental values of \( B_j \)).

Figures 9 and 10 show the best aggregate fit for a rate law with \( n = 2 \). By allowing \( B_2 > 0 \), the model captures the observed U_{22} pO2 trends for the low-frequency intercept and excursion while still obeying the near-linearity of Figure 1. For \( n < 2 \) (e.g. \( n = 1 \), supplementary Fig. S3), the predicted excursions for U_{22} and U_{33} become much larger than observed in the data. For \( n > 2 \) (e.g. \( n = 3 \), supplementary Fig. S4), calculated values of \( U_{jj} \) agree well with the NLEIS data, but the predicted VSC and Log \( B_0 \sim \text{Log} \ p_0 \) deviate from measurements.

To capture the transient nonlinear behavior in Figure 8 while maintaining a near-constant VSC, we repeated the above procedure for the 100% O2 measurements at \( t = 25 \) and \( t = 49 \) hours, assuming an \( n = 2 \) rate law. Figure 11 shows that very small changes in the electrode reducibility at 100% O2 (well within the observed changes in VSC, as shown by Fig. S5) can reproduce U_{22}’s transition between a circular (\( t = 25 \) hours) and semi-circular (\( t = 49 \) hours) shape. Alternatively, if we assume the electrode’s thermodynamic behavior remains unchanged, this transition in the NLEIS response from \( t = 25 \) to \( t = 49 \) corresponds to a shift in reaction order from \( n = 2 \) to \( n = 2.3 \), respectively, shown in Fig. S6.

Discussion

Thermodynamic behavior.—The magnitude of the VSC, as well as close agreement between the measured thin film capacitance and that predicted based on the measured oxygen nonstoichiometry in bulk (microcrystalline) LSCF suggests that the majority of the measured VSC arises from the oxygen storage capacity of LSCF. Furthermore, the ability for a single thermodynamic model to describe both thin film measurements (VSC and NLEIS) as well as freestanding bulk data implies that thin film LSCF-6428 behaves thermodynamically similarly to its bulk counterpart.

This similarity is somewhat remarkable when compared to LSC, which exhibits substantially modified thermodynamic properties as a thin film vs. bulk LSC.\(^{17,28}\) In the case of LSC, one possible cause of modified properties is maldistribution of the Sr dopant, which has a proportional influence on the enthalpy of oxygen incorporation, and thus an exponential impact on oxygen vacancy concentration.\(^{16,29}\)

A number of workers have reported that the Sr dopant concentration near the surface of as-sintered LSCF is substantially increased, either by stratification or segregation, which might be expected to lead to an overall average increase in oxygen nonstoichiometry that depends on surface area.\(^{20-21}\) Indeed, this possibility is consistent with
published TGA measurements, which reveal an increase in the overall nonstoichiometry in LSCF with decreasing sintering temperature (i.e. increasing surface area).\textsuperscript{4,5} In the case of LSCF-6428, there is also a pronounced qualitative deviation in nonstoichiometry behavior from a spatially-uniform semiconducting point-defect model at high $p_{O_2}$ (where our electrochemical measurements are focused).\textsuperscript{4} Although the origin of this deviation is not currently understood, we speculate that this might be caused either by variations in thermodynamic properties near the surface, or by spatially uniform dispersion in the bulk enthalpy of oxygen incorporation caused by the 20\% cobalt doping.

In order to explore the possibility that thermodynamic properties might be altered near the surface, we considered a two-layer semiconductor point-defect model consisting of a surface layer with enhanced A-site Sr mole fraction $x_s > 0.4$ and volume fraction $\lambda$, and a bulk layer with depleted Sr content $x_b < 0.4$ (see Supplementary Material for details). Figure 12 and 13 show a scenario consistent with our thin film VSC and NLEIS measurements, assuming an 8 vol. \% Sr-rich ($x_s = 0.97$) surface phase and an empirical rate law with $n = 3$. As shown in Figure 13, these thermodynamic assumptions are also consistent with Kuhn et al.’s nonstoichiometry data for a semi-porous pellet at 600° C.\textsuperscript{4}

Comparing the two sample geometries, the specific surface area (SSA) for a 20 nm thick, 200 μm diameter film of LSCF is $\sim 8$ m$^2$/g, while we estimate the SSA of samples measured Kuhn et al. to be somewhere between 2~5 m$^2$/g (based on comparison/extrapolation of BET measurements made by Bishop et al. at higher temperatures).\textsuperscript{4,9} These surface areas are similar enough that it is possible that both the thin film and the “bulk” samples exhibit enhanced nonstoichiometry near the surface. On the other hand, the similarity in surface area makes it hard to eliminate the possibility that at least some of the deviation from a point defect model comes from nonideality in the bulk. Indeed, first-principles calculations suggest increasing surface charge and strain relaxation can only drive Sr segregation across the first several monolayers of LSCF,\textsuperscript{30} and thus it is unclear what forces might cause Sr segregation beyond the space charge zone (to an apparent volume fraction of 8%). On the other hand, non-equilibrium Sr stratification caused by electrode processing conditions and “frozen” in place at 600° C could extend well beyond the Debye length.

**Surface kinetics.**—For the initial $p_{O_2}$ sweep, an empirical rate law $r_{O_2} = k_{O_2}(T) p_{O_2} \delta^8(1 - e^{-\delta})$ with $n = 2$ gives the best agreement with the measured NLEIS response, assuming the thin film obeys the homogeneous empirical thermodynamic model. As mentioned in the theory and reference,\textsuperscript{28} a dissociative adsorption-limited mechanism, neglecting any contribution of the surface electronic structure, corresponds to $n = 2$. However, for a p-type electrode, the concentration of holes depends on $p_{O_2}$, likely affecting the exchange rate. By adopting an empirical description of LSCF’s thermodynamics, we cannot predict this hole-dependence; we must therefore assimilate it into $n$, preventing a deeper mechanistic interpretation of the rate law.

**Transient behavior.**—All microelectrodes studied exhibited large fluctuations in $R_t$, while the VSC remained nearly-constant at each
Figure 11. NLEIS data (circles) and aggregate fits (solid curves) of thermodynamic parameters for an $n = 2$ rate law in 100% O$_2$ at $t = 25$ (black) and $t = 49$ hours (red). $t = 25$ hrs: $B_0 = 5.26$, $B_1 = 0.247$, $B_2 = 0.0028$; $t = 49$ hrs: $B_0 = 5.37$, $B_1 = 0.285$, $B_2 = 0.007$. Phasor lines for both data (dashed) and model (solid) correspond to angular frequencies of 1.5 and 5.0 Hz for $U_{22}$ and 1.0 and 3.3 Hz for $U_{33}$ at $t = 25$ and 49 hours, respectively.

$p_{O_2}$. However, concurrently measured values of $R_c$ of neighboring electrodes were uncorrelated (Fig. S1) suggesting that the changes in performance were not systematic (e.g. effects of time at temperature or sustained electrochemical polarization), but unique to each electrode. Any insulating phases formed at the electrode-electrolyte interface would appear as changes in ohmic resistance, not contributing to $R_c$. Over the final 80 hours of electrochemical testing, the VSC changes only 10%, implying that any changes affecting the film’s oxygen storage capacity are slight. In 100% O$_2$ between $t = 25$ and $t = 97$ hours, $R_c$ increased by a factor of 4.3, while the excursion of $U_{22}$ increased by only a factor of 1.4. Any nonlinear phenomena causing a factor of ε increase in $R_c$ corresponds to $\varepsilon^2$ and $\varepsilon^3$ increases in $U_{22}$ and $U_{33}$, respectively, implying that the phenomena driving the transients in Figure 4 are predominantly, but not entirely confined to the parameters appearing exclusively in the scaling factors defined in Table I. For example, in the case of LSC, Kreller et al. posit that such changes in $R_c$ with little or no change in the higher harmonics is most consistent with drifts in the rate coefficient $k_{O_2}(T)$ due to changes in active surface site concentration. The small, seemingly cyclical changes in $U_{22}$ are harder to explain. The thin film electrode model can reproduce these trends by either assuming slight changes in the film’s reducibility (i.e. $B_i$)—imperceptible from the VSC measurements—or by assuming a change in reaction mechanism (i.e. n). The failure of $U_{22}$ to approach a single shape with time, excludes most single-step phenomena occurring in the bulk.

Figure 12. Two-layer semiconductor point-defect model (solid curves), assuming $n = 3$ rate law, surface layer volume fraction $\lambda_s = 0.08$ and Sr mole fraction $x_s = 0.97$, and the remaining bulk volume with a Sr mole fraction $x_b = 0.3$, compared to measurements of the thin film NLEIS spectra at 60°C and differing $p_{O_2}$ (circles). Phasor lines for both data (dashed) and model (solid) correspond to angular frequencies of 1.5, 5.0, and 6.4 Hz for $U_{22}$ and 1.0, 3.3, and 4.3 Hz for $U_{33}$ for 1%, 10%, and 100% O$_2$, respectively.

Figure 13. Same two-layer semiconductor point-defect model described in Figure 12 (solid curves), compared to measurements of the (top) thin VSC, as well as (bottom) Kuhn et al.’s nonstoichiometry data at 600°C. Dashed lines correspond to the homogeneous p-type thermodynamic model shown in Figure 1.
equilibration processes. Due to the limited observation time, we are unable to distinguish between two competing phenomena or a true oscillatory process.

Conclusions

Impedance measurements of 20 nm thin film LSCF-6428 electrodes reveal a thermodynamic behavior similar to independent thermogravimetry measurements on semi-porous pellets. This differs from LSC thin films, which exhibit capacitive properties deviating from bulk thermodynamic measurements. Both the nonlinear impedance and volume-specific capacitance data fail to obey a heterogeneous semiconductor point-defect model. We found two scenarios consistent with both the presented thin film data and Kuhn et al.’s bulk thermodynamic data. The first assumes a homogeneous film described by an empirical thermodynamic model based on Kuhn et al.’s data at $p_{O_2} > 10^{-3}$ atm. The second assumes strontium-enriched LSCF near the gas-solid interface and strontium-depleted LSCF in the bulk, both obeying a semiconductor point-defect model. While there is growing evidence supporting Sr segregation at the LSCF surface monolayer, the driving force for long-range Sr segregation is uncertain. Long-range, non-equilibrium Sr stratification caused by electrode processing conditions offers another explanation. All thin films exhibited large fluctuations in both linear and nonlinear impedance over the hundred-hour measurement duration, implying that the transient phenomena are predominantly, but not entirely, confined to the parameters appearing exclusively in the scaling factors defined in Table I (e.g. surface rate coefficient). The fluctuations in the scaled nonlinear impedance data are consistent with small changes in either the surface thermodynamics or the vacancy reaction order.

This work highlights the need for further thermodynamic analysis of LSCF in both thin film and porous geometries, with a special emphasis on distinguishing the surface thermodynamics from the bulk.

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References