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Modeling Impedance Response of SOFC Cathodes Prepared by Infiltration

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Abstract
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A mathematical model has been developed to understand the performance of electrodes prepared by infiltration of La$_0.8$Sr$_0.2$FeO$_3$ (LSF) and La$_0.8$Sr$_0.2$MnO$_3$ (LSM) into yttria-stabilized zirconia (YSZ). The model calculates the resistances for the case where perovskite-coated, YSZ fins extend from the electrolyte. Two rate-limiting cases are considered: oxygen ion diffusion through the perovskite film or reactive adsorption of O$_2$ at the perovskite surface. Adsorption is treated as a reaction between gas-phase O$_2$ and oxygen vacancies, using equilibrium data. With the exception of the sticking probability, all parameters in the model are experimentally determined. Resistances and capacitances are calculated for LSF-YSZ and there is good agreement with experimental values at 973 K, assuming adsorption is rate limiting, with a sticking probability between $10^{-3}$ and $10^{-4}$ on vacancy sites. According to the model, perovskite ionic conductivity does not limit performance so long as it is above $10^{-7}$ S/cm. However, the structure of the YSZ scaffold, the ionic conductivity of the scaffold, and the slope of the perovskite redox isoherm significantly impact electrode impedance. Finally, it is shown that characteristic frequencies of the electrode cannot be used to distinguish when diffusion or adsorption is rate-limiting.

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reasonably low impedances at 1073 K,\textsuperscript{14,18} despite the fact that, in the strictest sense, there are no three-phase boundary (TPB) sites available. Because modeling the structure in Fig. 2c is significantly simpler, we will focus on this system and discuss the changes that would be expected if the perovskite phase were more particulate in nature. Although Fig. 2b does not show the perovskite particles touching each other, we assume that they are connected electronically.

Considering the picture in Fig. 2c, it is apparent that oxygen transfer from the cathode to the electrolyte will involve gas-phase diffusion of $O_2$ into the composite, electrochemical oxidation of the perovskite surface, diffusion of the oxygen ions through the perovskite film, and transport of ions down the YSZ fins, all taking place in series. In this paper we assume that gas-phase diffusion is sufficiently fast such that the $O_2$ concentration is independent of position. This is the usual case for all but the thickest electrodes operating at high current densities.\textsuperscript{47}

The step that is most difficult to describe is the oxygen reduction reaction at the perovskite surface. This is most often modeled using the Butler-Volmer equation,\textsuperscript{48} which assumes that local field gradients are strong enough to perturb the energies of species along the reaction coordinate. The equation was derived to describe reactions that take place at metal surfaces in solution, where most of the potential drop occurs across a double layer that is approximately 2 nm in thickness,\textsuperscript{49} so that field gradients on the order of 1 V/nm are common. These are large enough to significantly alter the reaction coordinate that describes the rate constant. The Butler-Volmer equation indicates that the rate constant should have an exponential dependence on overpotential, so that the cell potential should decrease exponentially with current density near open circuit.

It is not surprising that Butler-Volmer behavior is seen in proton exchange membrane fuel cells (PEM-FC). With PEM-FC, the catalytic metals near the electrolyte interface are effectively immersed in water so as to facilitate transfer of ions into the electrolyte. The situation for SOFC electrodes is far less clear. First, there are many examples in the literature for which the electrode impedance is independent of current density and is the same under cathodic and anodic polarization\textsuperscript{14,18,21,25-54} and this current independence has been observed in cells with electrolytes as thin as 15 $\mu$m.\textsuperscript{55} An example of this is shown in Fig. 3, which is the $V$-$i$ polarization curve for a cell operating under fuel-cell and electrolysis conditions at 973 K, with a 50% CO-CO$_2$ mixture on the fuel side and an infiltrated LSF-YSZ electrode on air side. Additional details on this cell are given elsewhere\textsuperscript{56}; here, we simply note that the constant slope demonstrates the impedances for both electrodes are independent of current density and the same under fuel-cell and electrolysis conditions as at open circuit.

While there are also many examples of nonlinear $V$-$i$ curves, it should be noted that the overall shapes of these curve are often significantly different from that predicted by Butler-Volmer.\textsuperscript{47,58}

Table I. Material Properties of Doped LaFeO$_3$ and LaMnO$_3$.

<table>
<thead>
<tr>
<th>Parameter (Units)</th>
<th>Symbol</th>
<th>Value (Ref)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic conductivity of La$<em>{0.8}$Sr$</em>{0.2}$FeO$_3$-d</td>
<td>$\sigma_{\text{amb LSF}}$</td>
<td>$8.3 \times 10^{-4}$ (14)</td>
</tr>
<tr>
<td>Ionic conductivity of La$<em>{0.8}$Ba$</em>{0.2}$FeO$_3$-d</td>
<td>$\sigma_{\text{amb LBF}}$</td>
<td>$3.1 \times 10^{-5}$ (14)</td>
</tr>
<tr>
<td>Ionic conductivity of La$<em>{0.8}$Ca$</em>{0.2}$FeO$_3$-d</td>
<td>$\sigma_{\text{amb LCF}}$</td>
<td>$3.8 \times 10^{-5}$ (14)</td>
</tr>
<tr>
<td>Ionic conductivity of La$<em>{0.8}$Sr$</em>{0.2}$MnO$_3$-d</td>
<td>$\sigma_{\text{amb LSM}}$</td>
<td>$4.0 \times 10^{-8}$ (74)</td>
</tr>
<tr>
<td>Reducibility parameter of La$<em>{0.8}$Sr$</em>{0.2}$FeO$_3$-d</td>
<td>$m_{\text{LSF}}$</td>
<td>$-0.034$ (63)</td>
</tr>
<tr>
<td>Reducibility parameter of La$<em>{0.8}$Sr$</em>{0.2}$MnO$_3$-d</td>
<td>$b_{\text{LSM}}$</td>
<td>$0.037$ (63)</td>
</tr>
</tbody>
</table>

Figure 1. SEM images of (a) the YSZ scaffold used in electrode fabrication, and the 40-wt % LSF-YSZ composites prepared by calcination (b) 1123 K and (c) 1373 K.
Although the LSF-YSZ electrodes that we are modeling show identical rate constants but these are not related to overpotential. Finally, MIEC-air interface that will be important in determining adsorption. Recognize that there may be field gradients due to space-charge at the MIEC-electrode that does not rely on Butler-Volmer kinetics. We recognize that there may be field gradients due to space-charge at the MIEC-air interface that will be important in determining adsorption. For these reasons, we propose an alternative model of cathode performance are proposed.

A glossary of symbols and their definitions is presented at the end of this manuscript. We will first present the steady-state models, then solve for the expected electrode resistances for cases where adsorption of O$_2$ is rate-limiting or diffusion of ions through the perovskite film is rate limiting. We will then estimate the capacitances that would be expected for the electrodes in non-steady-state measurements.

### Steady-State Model

**Structure of the composite electrode.**—The cathode geometry presented in Fig. 2c consists of a series of straight YSZ fins of height, $h$, and width, $w$, stemming from the solid YSZ electrolyte and extending to a distance $Z$ in the $z$-direction. Each fin is separated from the next by a distance, $L$. Although these fins are pictured as straight, we incorporate a tortuosity factor, $t$. This is in recognition of the fact that the YSZ scaffold of the actual cathode through which the ions will be diffusing could have a complex geometry and a length scale greater than $h$. This tortuosity effectively reduces the ionic conductivity of the YSZ fins by a factor of $t$ such that

$$\sigma'_{YSZ} = \frac{\sigma_{YSZ}}{t} \quad [1]$$

where $\sigma'_{YSZ}$ and $\sigma_{YSZ}$ are the effective and bulk ionic conductivities of YSZ, respectively. It is important to note that we are defining $t$ for the conduction of ions in the YSZ, not for diffusion in the gas phase.

The parameters defined here can be related to experimental parameters. For example, the tortuosity can be estimated from four probe conductivity measurements on porous slabs. $^{66}$ The resulting tortuosity value arises from the network of interconnected YSZ fins (the contribution from dead-end fins is not explicitly accounted for). For straight YSZ fins shown in Figs. 2b and 2c, the conductivity would be that of bulk YSZ multiplied by $(1-p)$, where $p$ is the porosity of the YSZ scaffold. The width, $w$, of the fins is the characteristic size of the YSZ scaffold and can be estimated from the SEM in (Fig. 1a). $L$, the characteristic repeat distance in the scaffold, can be related to $w$ and $p$ from Eq. $^{22}$

$$L = \frac{w}{1-p} \quad [2]$$

These parameters can also be related to the specific surface area of the YSZ scaffold, $S_b$, a parameter that can be measured using BET isotherms $^{44}$

$$S_b = \frac{2}{wp_{YSZ}} \quad [3]$$

The perovskite phase is assumed to form a dense film of thickness $\lambda$ on the YSZ fins. This thickness can be calculated from the weight
If we allow \( h \) to go to infinity, the condition in Eq. 7 implies that \( h \) is greater than the thickness of the electrode active region, \( h_{eq} \), that part of the electrode in which essentially all of the oxygen reduction takes place. Previous work has shown the active region of some state-of-the-art cathodes to be as small as 10 \( \mu \)m (Refs. 8 and 67) although the thickness of the active region will be larger in poorer performing electrodes.

**Charge flux through the perovskite film.**—To solve Eq. 5, an expression is needed for \( i_s'' \), the current flux originating from ions coming through the perovskite film. We will consider two limiting cases: (1) The case where the perovskite surface is in equilibrium with the gas phase and oxygen ion diffusion through the perovskite is rate limiting; and (2) the case where diffusion through the perovskite film is relatively fast so that oxidation of the perovskite surface is rate limiting. Throughout this manuscript, we assume that the change in vacancy concentration in the perovskite is small enough that the ionic conductivity can be assumed to be constant, whereas gradients in the vacancy concentration are still large enough to drive an oxygen flux.

**Diffusion limiting.**—The ion diffusion through the perovskite film is given by Eq. 8 [14,63]

\[
J_{O_2} = \frac{R_T \sigma_{amb}}{16F^2 \lambda} \ln \left( \frac{PO_{2surf}}{PO_{2fing}} \right)
\]

Here, \( PO_{2surf} \) and \( PO_{2fing} \) correspond to the oxygen fugacities at the film surface in contact with the atmosphere and with the YSZ fin, respectively. \( \sigma_{amb} \) is the ambipolar conductivity of the perovskite as defined by Eq. 9 (Refs. 14 and 63) and is assumed to be constant

\[
\sigma_{amb} = \left( \frac{\sigma_i \sigma_{el}}{\sigma_i + \sigma_{el}} \right)
\]

For materials with much higher electronic than ionic conductivities, as are the cases for LSF and LSM, the ambipolar conductivity is essentially equal to the ionic conductivity. For the case where diffusion of ions through the perovskite film is rate-limiting, \( PO_{2surf} \) is simply 0.21 atm. We assume equilibrium exists at the perovskite-YSZ interface, so that \( PO_{2fing} \) can be related to the potential within the YSZ fin using the Nernst equation

\[
\Phi = \frac{R_T}{4F} \ln \left( \frac{PO_{2amb}}{PO_{2fing}} \right)
\]

In Eq. 10, we implicitly also assume that there is no material difference between current collector and counter electrode, as well as no difference between the counter electrode potential and that of the electrolyte at the point of contact with the counter electrode. By combining Eqs. 8 and 10, the flux of oxygen ions through the perovskite film at any position can be directly related to the electric potential within the YSZ fin.

Finally, the oxygen flux can be related to \( i_s'' \) through Eq. 11 (Ref. 63)

\[
i_s'' = 4FJ_{O_2}
\]

**Surface reaction limiting.**—Although the dissociative adsorption rate of \( O_2 \) on the perovskite surface could have been written in terms of surface-exchange rates, this formalism would not have allowed the rates to be expressed in terms of the oxidation state of the surface. Therefore, for the surface reaction-limited case, we assume that oxygen incorporation into the perovskite can be treated as a reaction between gas-phase \( O_2 \) and the oxygen vacancies in the perovskite lattice. If the vacancies are identical and independent of each other, the rate per area of surface will be proportional to the
collision frequency between gas molecules and the surface and given by Eq. 12

\[
\dot{r}_{\text{ads}} = \frac{PO_{2,\text{atm}}}{(2\pi MR_gT)^{1/2}} \cdot S
\]  

[12]

Here, \( S \) is the sticking coefficient, the probability that a molecule striking the surface will adsorb. Because a molecule must find a vacancy site in order to react, the sticking coefficient will depend on the vacancy concentration of the perovskite and a vacancy sticking probability, \( S_0 \).

For a perovskite of composition \( \text{ABO}_3 \), it is reasonable to suggest, as a first approximation, that

\[
S = S_0 \left( 1 - \frac{3 - \delta}{3 - \delta_0} \right)
\]  

[13]

where \( S_0 \) is a constant at any given temperature and the term in parenthesis is the fraction of oxygen lattice sites that are vacant in the bulk. We are assuming here that only \( \text{O}_2 \) molecules impinging on unfilled lattice sites will be able to react with the surface. Although \( S \) may depend on the square of the vacancy concentration for dissociative adsorption (i.e. adsorption of an \( \text{O}_2 \) molecule will require two available sites, one for each oxygen atom.), we treat the dependence of \( S \) on the vacancy concentration as linear for simplicity in order to obtain an analytical solution. Furthermore, adsorption of non-dissociative molecular \( \text{O}_2 \) is known to be the rate limiting step for CO oxidation on Pt,\(^6\) so that Eq. 13 may indeed be a better description of the actual kinetics. Although we recognize that oxygen adsorption rates in SOFC are more typically described using an exchange coefficient, \( k^* \), the advantage of using a sticking coefficient is that it allows us to define a rate constant, \( S_0 \), that is not dependent on \( PO_2 \). It is noteworthy that \( k^* \) has been shown to vary with \( PO_2 \) in ways that correlate with bulk oxygen vacancy concentrations in perovskite cathodes, an observation that supports the validity of the assumption made in Eq. 13.\(^7\)

At equilibrium, \( \delta \) will be a function of stoichiometry, temperature, and \( PO_2 \). For most materials of interest for SOFC cathode applications, \( \delta \) varies almost linearly with respect to \( \log(PO_2) \) over the range of interest for SOFC cathodes, \( 1 > PO_2 > 10^{-2} \text{ atm} \), as demonstrated by the thermodynamic data for LSM, LSF, and LSCo presented in Fig. 4.\(^8\),\(^9\),\(^10\) Therefore, we express the concentration of oxygen vacancies at the perovskite surface using Eq. 14

\[
\delta = m \log(P_{O_2}) + b
\]  

[14]

Here, \( m \) and \( b \) are the slope and intercept of a plot of \( \delta \) versus \( \log(PO_2) \). From Fig. 4, it can be seen that \( m \) and \( b \) vary widely with perovskite composition. Upon combining Eqs. 12, 13, and 14, the adsorption rate can be expressed as follows

\[
\dot{r}_{\text{ads}} = \frac{PO_{2,\text{atm}}S_0}{(2\pi MR_gT)^{1/2}} \cdot \frac{m \log(P_{O_2,\text{atm}}) + b}{3}
\]  

[15]

When rates are limited by surface adsorption (i.e. diffusion of ions through the perovskite film is relatively fast), the surface vacancy concentration will be equal to that of the bulk and \( PO_{2,\text{surf}} \) will be equal to \( PO_{2,\text{atm}} \).

In the absence of ion flow (open-circuit conditions for the electrode), there will be an equilibrium vacancy concentration corresponding to the \( PO_{2,\text{atm}} \) of the gas phase within the electrode. Because \( \text{O}_2 \) desorption must balance \( \text{O}_2 \) adsorption in order to establish this equilibrium, we define this equilibrium desorption as the adsorption rate at \( PO_{2,\text{atm}} \). If we assume that lattice oxygen sites are equivalent and that changes in \( \delta \) are small, it is reasonable to assume that the desorption rate, \( r_{\text{des}} \), is constant and given by Eq. 16

\[
\dot{r}_{\text{des}} = \frac{PO_{2,\text{atm}}S_0}{(2\pi MR_gT)^{1/2}} \cdot \frac{m \log(P_{O_2,\text{atm}}) + b}{3}
\]  

[16]

As with the diffusion-limited case, the adsorption rate can then be related to the potential at any position along the YSZ fin and the net rate of adsorption can be related to \( \epsilon_y \) through Eq. 17

\[
\dot{r}_y = 4F(r_{\text{ads}} - r_{\text{des}})
\]  

[17]

Analytical, Steady-State Solutions

Because the net rate of oxygen adsorption at the gas-phase surface of the perovskite film must equal the flux of ions through the film, Eqs. 8 and 15 can be combined to solve for the oxygen fugacity of the perovskite at the gas-phase surface, Eq. 18

\[
\log P_{O_2,\text{surf}} = \frac{A}{2\sqrt{2T}} - \frac{m \log(P_{O_2,\text{surf}})}{\sqrt{2T}} - B
\]  

[18]

In this equation, there is no assumption as to whether the rate is limited by adsorption or diffusion; \( A \) and \( B \) are the prefactors for the diffusive flux and adsorption rate, respectively

\[
A = \frac{R_g T \sigma_{\text{amb}}}{16F^2 \kappa}
\]  

[19]

and

\[
B = \frac{S_0 P_{O_2,\text{surf}}}{3\sqrt{2 \pi M R_g T}}
\]  

[20]

The relative magnitude of \( A \) and \( B \) determines which process is rate limiting. If \( A \) is much larger than \( B \), \( PO_{2,\text{surf}} \) will become equal to \( PO_{2,\text{atm}} \) and surface adsorption is rate limiting. Conversely, if \( B \) is much larger than \( A \), diffusion is the rate limiting process and \( PO_{2,\text{surf}} \) will become equal to \( PO_{2,\text{atm}} \). We consider the analytical solutions for the expected electrode resistances for each of these limiting cases separately.

**Diffusion limited**—By combining Eqs. 8, 10, and 11, the oxygen flux can be related to chemical potential at any given point in the YSZ fin, allowing one to solve for \( \epsilon_y \) at any position along the fin.
providing an expression for the amount of current entering the YSZ fin at a given point

\[ i_y = \frac{\sigma_{amb}}{\lambda} \Phi_y \]  \[21\]

Solving Eq. 5 using the boundary conditions specified in Eqs. 6, 7 (with \( h = \infty \)), and 21 provides expressions for the potential and the total current within the YSZ fin. From these, the DC electrode resistance, \( R \), can be calculated from the ratio between the overpotential and the current. These solutions are shown in Eqs. 22 through 24.

\[ \Phi(y) = \Phi_0 \exp \left( -\frac{y}{\sqrt{\frac{\sigma_{amb}}{3}}} \right) \]  \[22\]

\[ i(y) = (1 - p) \sqrt{\frac{\sigma_{amb} \sigma_{YSZ} \Phi(y)}{\frac{\lambda}{3}}} \]  \[23\]

\[ R = \frac{1}{(1 - p)} \sqrt{\frac{\frac{\lambda}{3}}{\sigma_{amb} \sigma_{YSZ}}} \]  \[24\]

Although these results will be discussed more in depth later, it is worth noting that the dependence of the resistance upon \( \sigma_{amb}^{-1/2} \) is analogous to the result found by Adler and coworkers\(^{13} \) when modeling the impedance of a porous layer of a mixed conducting material on a flat electrolyte.

**Surface adsorption limited.—** The potential gradient within the YSZ fin for the case where surface adsorption is rate limiting can be obtained in the same manner as the diffusion-limited case, and the analytical solution takes a similar form. Combining Eqs. 10, 15, 16, and 17 with large \( \Lambda/B \) (such that \( PO_{2,\text{surf}} \) equals \( PO_{2,\text{fin}} \)) results in the following expression for \( i_y^{\infty} \)

\[ i_y^{\infty} = E \frac{mS_0}{3} \Phi \]  \[25\]

where \( E \) is a simplifying collection of constants:

\[ E = -\frac{16F^2 \rho_{O_2,\text{exc}} \log(e)}{(2\pi M)^{1/2}(R_T)^{3/2}} \]  \[26\]

Substituting this expression into Eq. 5 and again using the boundary conditions specified in Eqs. 6 and 7 (for \( h = \infty \)), we obtain expressions for the potential in the YSZ fin, the total current from each fin, and the overall electrode resistances, Eqs. 27 through 29.

\[ \Phi(y) = \Phi_0 \exp \left( -\frac{y}{\sqrt{\frac{E \cdot mS_0}{3}}} \right) \]  \[27\]

\[ i(y) = (1 - p) \sqrt{\frac{E \cdot mS_0 \sigma_{YSZ} \Phi(y)}{3}} \]  \[28\]

\[ R = \frac{1}{(1 - p)} \sqrt{\frac{3}{E \cdot mS_0 \sigma_{YSZ}}} \]  \[29\]

An important conclusion from this result is that the electrode resistance depends primarily on the slope, \( m \), of the equilibrium, redox isotherm for the perovskite. This suggests that more reducible materials should show lower resistances.

For both the diffusion-limited case, Eq. 24, and the adsorption-limited case, Eq. 29 the electrode impedance depends on structural properties (porosity and fin size) and the dependencies shown are similar to those proposed previously by Tanner, et al.\(^{22} \) Both results also show an inverse square-root dependence of the electrode resistance on the ionic conductivity of the electrolyte scaffold. This suggests that the use of composites with an electrolyte of higher ionic conductivity (i.e., O\( \_d \)-doped ceria) should decrease the impedance regardless of whether adsorption or diffusion is limiting. Finally, it is interesting to consider that the resistances obtained for both cases should not depend on the direction of the currents, so that impedances for electrodes operating cathodically or anodically should be the same, as we have already observed is often the case experimentally, as in Fig. 3.

**Effect of Perovskite Structure**

It is interesting to consider the case where the perovskite particles are more particulate in nature, similar to that shown diagrammatically in Fig. 2b, rather than film-like. Equations 5 through 7 which describe the potential in the YSZ fin would remain unchanged from the film case described above. Only the expression for \( i_y^{\infty} \) would be affected. Coming up with an expression for \( i_y^{\infty} \) in this situation is now more difficult. Considering just an individual perovskite particle on the YSZ surface, the picture is essentially that which is commonly used in modeling TPB sites.\(^{21} \) There will now be sites where the perovskite particle, the YSZ, and the gas phase all come into contact. In principle, \( O_2 \) molecules could adsorb on the perovskite particles at sites far from the TPB sites and then diffuse to the YSZ interface, either through the bulk or along the perovskite surface.

For the case where adsorption of \( O_2 \) is rate limiting, the entire perovskite particle will be at the same chemical potential, determined by the potential of the YSZ at that position along the fin. The solutions given in Eqs. 27–29 would apply to this case, except that there would now be an increased surface area for adsorption. The surface area in the rate expression of Eq. 12 is accounted for only in the perimeter of the YSZ fin. Depending on whether oxygen ions can be transferred between adjacent perovskite particles (Contact is required for electrical conduction.), the available surface area could be that of the particles in contact with the YSZ or could include particles that are only in contact with the YSZ through their interaction with other particles.

For the diffusion-limited case, the question is the relative importance of TPB sites compared to that of the bulk sites at the point of contact between the perovskite particles and the YSZ. For the “bulk” sites, Eqs. 22 through 24 still approximately apply, although the relevant length scale for diffusion, \( \lambda \), would now be the particle size. For both the diffusion-limited and surface-adsorption-limited cases, the electrode impedances are expected to be smaller for the particulate case.

**Non-Steady State Solutions**

The framework developed in the previous sections can also be used to model the time response of the system to sudden changes in the cathode overpotential. Rather than using the steady-state approximation for the permeation flux through a thin perovskite film as specified in Eq. 8, the flux entering the YSZ fin, which is related to \( i_y^{\infty} \) through Eq. 11, can be expressed in terms of the oxygen-ion concentration gradient by the tracer self-diffusion coefficient, \( D \), such that\(^3 \)

\[ J_{O_2} = D \frac{\partial [O_2]}{\partial x} \]  \[30\]

The ionic conductivity can then be expressed in terms of the diffusion coefficient \( D \) and the stoichiometry parameter, \( \delta \), as shown in Eq. 31\(^{63} \)

\[ \sigma_i = D \frac{16F^2}{RTV} \delta \]  \[31\]

where \( V \) is the volume of the perovskite unit cell. Substituting Eq. 14 into 31, we obtain

\[ \sigma_i = D \frac{16F^2}{RTV} (m \log pO_2 + b) \]  \[32\]
It is important to note that the relationship between $\sigma_i$ and $D$ includes a dependence on $m$, the reducibility parameter. The time-dependent, oxygen-ion concentration profile within the film was then modeled using a one-dimensional form of Fick’s second law of diffusion:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{33}$$

$J_o$, can again be expressed in terms of $t'$ through Eq. 11. At the interface between the perovskite and the YSZ fin, a pair of matching conditions was used such that the chemical potential in the film and the fin were equal and that the fluxes of ions leaving the film and entering the fin were equal. At the perovskite surface in contact with the gas phase, net O$_2$ adsorption was again modeled according to Eqs. 15 and 16.

Electrochemical impedance spectroscopy (EIS) is a powerful technique that can provide information for identifying these different processes. These measurements can be performed either through sine wave testing or through current- or potential-step techniques, both of which provide identical information about the system being tested. Sine wave testing typically consists of applying a sinusoidal current perturbation and measuring the phase-shifted potential response of the system. The complex frequency domain impedance, $Z(v) = \Phi(v)i(v)$, is measured across a range of frequencies and presented on a Nyquist plot. Similarly, a potential step can be applied to the system while the current response is measured. Frequency domain data, identical to that which would be measured using sine wave testing, can then be obtained by performing a Fourier Transform of the time-dependent current and voltage profiles, $i(t)$ and $\Phi(t)$, followed by complex division.$^{70-73}$

For the simulations in this work, we modeled the current responses to step changes in the cathode overpotential. For $t < 0$, the system was assumed to be at “open-circuit” voltage, with no overpotential applied to the YSZ fin. Because the system was considered at equilibrium, the vacancy concentration everywhere within the perovskite was set equal to $C_o$, the concentration of oxygen ions at PO$_{2, atm}$, corresponding to an overpotential of 0 V. Beginning at $t = 0$, the overpotential at the base of the YSZ fin was set equal to $\Phi_o$. Following this step change in potential, the current responses were calculated until new steady states were reached. Representative examples of the potential step, with a $\Phi_o = 0.01$ V, and the resulting current response are provided in Fig. 5, as well as the corresponding Nyquist plot, shown in Fig. 6. By integrating the current response of the system over time, the capacitances were obtained. Because this model incorporated both oxygen adsorption at the perovskite surface and diffusion through the perovskite film, it allowed the calculation of resistances and capacitances for co-limited cases as well as the purely diffusion or adsorption limited cases addressed previously. Since these results were obtained numerically, they will be presented in the next section for various ranges of parameters.

Model Implications and Example Calculations

In this section, we examine the implications of this model for typical experimental conditions. Unless otherwise noted, all calculations use the thermodynamic and conductivity parameters presented in Table I and the structural parameters presented in Table III.

Electrodes based on infiltrated LaFeO$_3$.—Figure 1b shows an SEM micrograph of an LSF-YSZ electrode prepared by infiltration of 40-wt % LSF into a YSZ scaffold that was 66% porous, after calcination to 1373 K.$^{14}$ This electrode was prepared as part of a study in which LaFeO$_3$-based electrodes were synthesized with Ca, Sr, and Ba as dopants in order to examine the effect of changes in the ionic conductivities.$^{14}$ A related study of infiltrated LaNi$_{0.9}$Sr$_{0.1}$O$_3$, La$_{0.91}$Sr$_{0.09}$Ni$_{0.6}$Fe$_{0.4}$O$_3$, and La$_2$CoO$_4$ was carried out with the same YSZ scaffold and treatment conditions.$^{15}$ Of particular importance here is the fact that all of the parameters from our calculations, with the exception of $S_o$, have been measured in the characterization of these electrodes.

The impedances of electrodes made with all of the above perovskites, at 973 K in air, depended on current density; but, at open circuit, the impedances of the electrodes calcined at 1373 K were $\sim$3 $\Omega$ cm$^2$. The impedances did not show the logarithmic dependence that would be expected for Butler-Volmer behavior$^{85}$ and the differences in the open-circuit impedances after calcination to 1373 K appear to be within the variability of different measurements.$^{14,18}$

If the electrodes were limited by oxygen-ion diffusion through a dense perovskite film, the resistances can be calculated using Eq. 24. Using the parameters from Table I, the anticipated electrode impedances would vary from 0.06 $\Omega$ cm$^2$ with LSF-YSZ electrodes to 0.3 $\Omega$ cm$^2$ for the LCF-YSZ electrodes as shown in Table IV. Since one would expect this calculation to overestimate the resistance, given that the experimental perovskite films are almost certainly not perfectly dense, the fact that the measured impedances are significantly larger than the values predicted by the diffusion-limited calculation implies that diffusion limitations are likely not important.

Another way of looking at the issue is to calculate what the ionic conductivity would have to be in order for the electrodes to exhibit an impedance of 3 $\Omega$ cm$^2$. Based on Eq. 24, the parameters in Table III, $\sigma_{amb}$, would have to be less than $10^{-7}$ S/cm. Although doped LaFeO$_3$ species have ionic conductivities much greater than this value, studies have shown LSM to have a significantly lower ionic conductivity.$^{74}$ This lower ionic conductivity suggests that LSM-YSZ electrodes may be limited by diffusion. This provides a possible explanation as to why LSM shows higher impedances compared to doped LaFeO$_3$.$^{18,75}$ Figure 7 shows the resistance as a function of perovskite and YSZ ionic conductivity for the diffusion limited case as calculated by Eq. 24.

If one assumes that the adsorption rate is limiting and that the vacancy concentrations at a given PO$_2$ are similar across this set of samples, Eq. 29 can be used to estimate a sticking coefficient for the
vacancy sites, \( S_0 \). As shown in Fig. 8, using an electrode resistance of 3 \( \Omega \) cm\(^2\) and the parameters in Tables I and III, \( S_0 \) is calculated to be \( \sim 10^{-2} \), a reasonable value for a reactive sticking probability. This, along with the fact that the resistances did not change with the addition of this extra term, indicates that the performance of the infiltrated LaFeO\(_3\)-based electrodes was limited by adsorption.

As noted previously, when modeling dissociative adsorption, \( S \) is typically assumed to depend on the square of the vacancy concentration, effectively replacing Eq. 13 with Eq. 34:

\[
S = S_0 \left( 1 - \frac{3}{3} - \frac{S_0}{S_0} \right)^2
\]  

Because the \( \delta \) is of the order \( \sim 0.1 \) for overpotentials between 0.1 and 0.2 V in LSF, the presence of this additional term would require that the value of \( S_0 \) increase by a factor of 30 to obtain resistances of \( \sim 3 \) \( \Omega \) cm\(^2\). It is also worth noting that the use of Eq. 34 will also introduce a non-linearity into the resulting V-I curve. For example, when using a \( S_0 \) of \( 30 \times 10^{-4} \) and the parameters specified in Tables I and III, the calculated resistances are \( \sim 3 \) \( \Omega \) cm\(^2\) at overpotential 0.01 V and \( \sim 2 \) \( \Omega \) cm\(^2\) at overpotential 0.25 V. This suggests that dissociative adsorption may be a cause of the nonlinear V-I curves sometimes seen experimentally.

When calcined at only 1123 K, all of the LaFeO\(_3\)-based electrodes showed perovskite particles that were particulate in nature, rather than film-like, similar to that shown in Fig. 2b. All of these electrodes exhibited a current-independent impedance of 0.2 \( \Omega \) cm\(^2\) at 973 K. As discussed earlier, the particulate nature of the infiltrated perovskites would be expected to affect both the diffusion-limited and the adsorption-limited case, so that this observation cannot be used to infer which process is limiting. However, if diffusion is not limiting for the electrodes calcined at 1373 K, diffusion limitations will certainly not be a factor for 1123-K electrodes, given that the length scale for diffusion will be much smaller.

### Table III. Structural Parameters for Typical Composite Cathode.

<table>
<thead>
<tr>
<th>Parameter (Units)</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fin width (( \mu )m)</td>
<td>w</td>
<td>1</td>
</tr>
<tr>
<td>Electrode porosity</td>
<td>p</td>
<td>0.66</td>
</tr>
<tr>
<td>Perovskite film thickness (( \mu )m)</td>
<td>( \lambda )</td>
<td>0.26</td>
</tr>
<tr>
<td>Electrode thickness (( \mu )m)</td>
<td>h</td>
<td>50</td>
</tr>
<tr>
<td>Tortuosity factor</td>
<td>( \tau )</td>
<td>7</td>
</tr>
<tr>
<td>Ionic conductivity of YSZ at 973 K (S/cm)</td>
<td>( \sigma_{YSZ} )</td>
<td>( 2.0 \times 10^{-4} )</td>
</tr>
<tr>
<td>Effective Ionic conductivity of YSZ at 973 K (S/cm)</td>
<td>( \sigma_{YSZ} )</td>
<td>( 2.9 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

**Comparison of sticking coefficient to alternate rate expressions.** In SOFC, \( O_2 \) adsorption rates are most commonly presented in terms of the exchange coefficient, \( k^* \), or exchange current density, \( i_0 \), rather than a sticking coefficient. Values of \( k^* \) are typically determined from isotope exchange experiments\(^{63} \) and can be related to oxygen adsorption through the relation

\[
r_{ads} = k^* (C_{A0} - C)
\]  

where \( k^* \) has units of cm/s, and \( C_{A0} \) is the oxygen concentration of the surface in equilibrium with the gas. Literature values of \( k^* \) range from \( \sim 5 \times 10^{-5} \) cm/s at 973 K for La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\) \( \text{YSZ} \) \( (\text{Ref. 59}) \) to \( \sim 10^{-6} \) cm/s (Ref. 76) at 973 K for La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\). By substituting Eqs. 13 and 35 into Eqn. 12, and accounting for units, \( S_0 \) can be shown to be approximately 50 times \( k^* \). It is interesting to notice that \( k^* \) values reported in the literature correspond to \( S_0 \) values in the range of \( 10^{-5} - 10^{-7} \), which are in general agreement with the value of \( S_0 = 10^{-4} \) coming out of our calculations.

Exchange current densities are sometimes used as fitting parameters in the Butler-Volmer expression and correspond to the forward and reverse reaction rate at equilibrium. By substituting Eqs. 13 and 14 into Eq. 12 and assuming \( PO_2 = PO_2_{\text{am}} \) at equilibrium, an \( S_0 \) value of the \( 10^{-4} \) can be shown to correspond to an \( i_0 \) of 1.3 mA/cm\(^2\). This value is somewhat lower than the \( i_0 = 300 \text{ mA/cm}^2\) reported in the literature for LSF at 973 K.\(^{77} \)

**Thickness of the electrochemically active region.** The analytical solutions for the adsorption- and diffusion-limited cases were derived assuming the electrodes were infinitely thick. It is therefore of interest to relax the assumption of an infinitely thick electrode
and determine the thickness of the active region, where the majority of the electrochemical reaction takes place. Equations 22 and 27 indicate that electrical potential within the YSZ fins decreases exponentially; when the electrical potential in the YSZ is zero, there is no potential driving force for oxygen transport through the perovskite. Defining \( h_{AR} \) as the distance into the electrode at which the potential is 10% of the total electrode overpotential, it can be shown through manipulation of Eqs. 22 and 24 or 27 and 29 that

\[
h_{AR} = -\ln(0.1)\sigma_{YSZ} R(1 - p)
\]

For a measured impedance of 0.3 \( \Omega \text{ cm}^2 \) using porosity values provided in Table III, this equation predicts that the active region will be \( \sim 7 \mu \text{m} \) thick. This is in good agreement with literature reports that have determined the active region to be on the order of 10 \( \mu \text{m} \) thick.8,67

When the electrode thickness is less than \( h_{AR} \), the electrode impedance will be greater than that calculated from Eqs. 24 or 29, and Eq. 5 must be solved with the appropriate value of \( h \) for the boundary condition in Eq. 7. To demonstrate the effect that thinner electrodes can have, we present results from a calculation in which adsorption is assumed to be rate limiting, with \( S_0 \) equal to 10\(^{-5} \). Using the physical parameters listed in Table III, the electrode impedance for an infinitely thick electrode is determined to 3.1 \( \Omega \text{ cm}^2 \) and \( h_{AR} \) is found to be \( \sim 65 \mu \text{m} \) from Eq. 36. Figure 9 shows numerically calculated results for the potential within the YSZ fins for electrodes having thicknesses of 20, 50, and 100 \( \mu \text{m} \), assuming an overpotential of 0.2 V. For an electrode that is 100 \( \mu \text{m} \) thick, the potential profile is very similar to that which would be observed for an infinitely thick electrode and the electrical potential at the tip of the YSZ fin is approximately 0.02 V. The calculated impedance is identical to that obtained from Eq. 29, 3.1 \( \Omega \text{ cm}^2 \). For the 20- and 50-\( \mu \text{m} \) electrodes, the potentials within the electrode deviate from that of Eq. 27 but the calculated resistances, 3.33 and 5.42 \( \Omega \text{ cm}^2 \), were significantly different only for the 20-\( \mu \text{m} \) electrode.

**Non-Steady State Solutions**

In the following sections, we used the time-dependent equations to examine the effects of \( D \) and \( S_0 \) on the electrode resistances and capacitances. The work in this section assumes an electrode thickness of \( h = 50 \mu \text{m} \).

**Diffusion and adsorption co-limited resistances.**—To determine what the effect would be of having diffusion and adsorption be co-limited, we calculated electrode resistances from the solution to the non-steady-state equations after long times. The results for typical experimental parameters from Table III are shown in Fig. 10 as a function of the diffusion coefficients and sticking coefficients. As expected, for a given value of \( D \), the diffusion-limited case gives the lowest possible impedance and this minimum value decreases as \( D \) increases. Figure 10 also illustrates that for a given sticking coefficient, once the diffusion coefficient is sufficiently large and diffusion is no longer limiting, the impedance becomes independent of \( D \).

**Calculated capacitances.**—Characterization of electrode performance by impedance spectroscopy measures the time response of the electrode to changes in the input. The capacitance of the electrode is measured in addition to the electrode impedance. To determine expected electrode capacitances for our model, we numerically calculated the current response to step changes in the overpotential from \( \Phi = 0 \) to 0.01 V. This step change caused spikes in current density, which then relaxed to the steady-state currents expected for the steady-state electrode resistances. The area under the plot of current-versus-time was used to calculate the capacitance, similar to what would be done experimentally in current-interrupt measurements. It should be noted that we have ignored double-layer capacitances that can be found at rate-limiting air-MIEC interfaces.

Figure 11 shows the calculated capacitances as a function of both \( D \) and \( S_0 \) again using physical parameters from Table III. As with the calculated resistances in Fig. 10, the purely diffusion-limited case provides the minimum capacitance value for a given \( D \). For the cases where the adsorption rate becomes limiting, the calculated capacitance decreases as the sticking coefficient decreases. For a given \( S_0 \), the capacitance values are fairly constant and the adsorption and diffusion co-limited regions are not as easily identifiable as they were from Fig. 10.

**Analysis of non-steady state solutions.**—From the results in Figs. 10 and 11, it is possible to calculate the characteristic frequency for the electrode. Often, electrode impedances are modeled using equivalent RC circuits such that the characteristic frequency, \( f_c \), can be related to the low-frequency intercept, \( R \), and the electrode capacitance, \( C_{pe} \), by

\[
f_c = \frac{1}{2\pi R C_{pe}}
\]
This characteristic frequency has been used to identify the process contributing to the impedance, with the assumption that larger frequencies correspond to electrochemical reactions and lower frequencies to diffusion processes. Figure 12 combines the data of Figs. 10 and 11, showing impedance as a function of frequency. The uppermost curve, off of which the different branches emanate, corresponds to the purely diffusion limited case. Each of the branches from the main curve represents a particular value of $S_0$; these branches deviate from the main curve at the point where adsorption becomes limiting for that particular $S_0$.

The characteristic frequencies in Fig. 12 agree very well with the range of frequencies observed experimentally for infiltrated LSF-YSZ (Ref. 45) and LSM-YSZ (Ref. 44) electrodes. For calcination at 1123 K, the infiltrated LSF-YSZ electrodes exhibited an impedance of 0.2 $\Omega \cdot \text{cm}^2$ and a characteristic frequency of 400 Hz, which changed to 3 $\Omega \cdot \text{cm}^2$ and 4 Hz after calcination to 1373 K. A selection of experimentally measured frequencies and impedances are presented for comparison as individual data points in Fig. 12.

However, one very interesting result from Fig. 12 is that the characteristic electrode frequencies are very similar for the diffusion-limited and the adsorption-limited cases. In general, the
frequencies for a given impedance differed by a factor of only two for the two different limiting cases. Closer inspection shows that this result should have been expected. For both diffusion and adsorption limits, the electrode capacitance results from diffusion of ions out of the perovskite film. In both cases, a step change in the overpotential requires diffusion of ions from that part of the perovskite that is in contact with the YSZ. The only difference between the two cases is that perovskite surface in contact with the gas phase remains unaffected in the diffusion-limited case but decreases over time in the adsorption-limited case. Therefore, an important consequence of the model is that the characteristic frequency does not allow one to argue which of these two processes is rate limiting.

**Effect of thermodynamics on electrode performance.**—It was shown in Eq. 29 that the electrode impedance for the adsorption limited case depends on the slope, m, of the equilibrium, redox isotherm for the perovskite. Using the non-steady-state model, the effect of varying m was examined for an adsorption limited, a diffusion limited, and a co-limited case. As shown in Fig. 13, increasing values of m lead to decreasing electrode resistances regardless of the limiting mechanism. This agrees with expectations from the steady-state solutions, since the substitution of Eq. 32 into Eq. 24 for the diffusion-limited case illustrates a dependence on m similar to that seen in Eq. 29 for the adsorption-limited case. This result suggests that highly reducible materials (i.e., LSCF) should provide superior performance for both the adsorption- and diffusion-limited cases. It is worth noting, however, that large values of m and high ionic conductivities are often related.

**Conclusions**

In this paper, we have modeled the electrode properties of electrodes formed by infiltration of perovskites into a porous layer of the electrolyte, followed by calcination to temperatures high enough for the perovskite to form a dense film of the electrolyte scaffold. Although the model is very simple, it captures the essential features that O₂ must adsorb onto the perovskite and then diffuse through the perovskite. By comparison with experimental data, the model shows that adsorption of O₂ onto the perovskite surface is likely rate limiting for perovskites with high ionic conductivities greater than 10⁻² S/cm. According to the model, electrode impedances depend strongly on the ionic conductivity of the electrolyte scaffold, the structure of the scaffold, and the slope of the perovskite oxidation isotherm. Finally, the characteristic frequency of the electrode cannot be used to determine whether diffusion or adsorption are rate limiting.

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**List of Symbols**

- L length of repeating modeled unit
- m reducibility parameter
- M molecular weight of O₂
- p porosity
- Pₒ₂,N₂ atmospheric O₂, N₂ partial pressure
- Pₒ₂,surf O₂ fugacity at the perovskite surface
- R zero-frequencyimpedance
- θ ideal gas constant
- ρ density of perovskite
- ρₚₓₛ density of YSZ
- S sticking coefficient
- Sₑ specific surface area
- Sₚ sticking coefficient constant
- T temperature
- V volume of perovskite lattice
- w fin width
- Z characteristic length scale in z-dimension

**Greek**

- δ nonstoichiometry parameter
- θ percent weight loading of perovskite
- λ thickness of perovskite film
- μ density of perovskite
- ρₚₓₛ density of YSZ
- ρₚₓₛ,mallohmic conductivity of the perovskite
- ρₑ ionic conductivity of the perovskite
- σₑ electronic conductivity of the perovskite
- σₑ,YSZ effective ionic conductivity of YSZ
- µ tortuosity
- Φ electrical potential
- Ψ₀ applied overpotential

**References**
