Component potential modelling based on solid-oxide electrochemistry is used to study a single-particle configuration where a hemispherical LSM particle sits on a YSZ electrolyte half-space. The primary comparison is between two pathways: one where oxide ions travel on the particle surface; the other where these ions travel through the bulk particle interior. The systems that model each of the pathways are analyzed both mathematically and numerically, yielding insights into diffusion-reaction-conduction processes for this single-particle model. A broad range of parameter values are considered, particularly in regarding the least well established value, the surface conductance for the surface pathway. This work includes a number of case studies that indicate which pathway dominates for a variety of parameter choices.

*The support of the National Science Foundation under grant DMS-0707692 is gratefully acknowledged.
1 Introduction

A triple phase boundary (TPB) is, generically, a point in two dimensions or a curve in three dimensions where three phases (here, gas, solid electrode and electrolyte) come together simultaneously. TPBs are frequently cited in the fuel cell literature (cf. citations below), and they play a central role in a number of other electrochemical systems involving coupled diffusion-reaction-conduction processes where the simultaneous occurrence of three separate phases is essential, i.e., where gaseous, electronic, and ionic species are simultaneously necessary for a reaction to proceed.

Figure 1 provides a simplified illustration of the TPB concept for a solid-oxide fuel cell (SOFC) cathode. SOFC cathodes are designed to provide a high reaction rate for the multi-step oxygen reduction reaction (ORR):

\[
\frac{1}{2} \text{O}_2^{\text{gas}} + 2e^{\text{electrode}} \rightleftharpoons O_2^{\text{electrolyte}}
\]

This multi-step reaction involves all three phases and several processes, including diffusion, adsorption, electronic conduction, charge transfer reaction, and ionic conduction. In most instances, this entire reaction occurs almost exclusively in the immediate vicinity of TPBs via one of several possible reaction pathways. For the most common SOFC cathode materials (electron-conducting perovskite-type materials such as doped LaMnO$_3$, LaCoO$_3$, SmCoO$_3$, or LaFeO$_3$), three possible reaction pathways are typically considered (following Fleig [9]):

Figure 1: Possible reaction pathways in SOFC cathodes (adapted from Fleig [9]).
1. The electrode surface pathway. The electrode surface pathway (Figure 1a) considers adsorption of oxygen species on the cathode electrode surface and their migration along the electrode surface toward the TPB (where the electrolyte, electrode, and gas phase meet), followed by complete ionization and ionic transfer into the electrolyte.

2. The electrode bulk pathway. The electrode bulk pathway (Figure 1b), like the electrode surface pathway, begins by considering adsorption of oxygen species on the cathode surface. However in this case, the oxygen species are locally dissociated, ionized, and incorporated into the solid electrode. Oxide ion transport then proceeds through the electrode bulk, followed by ionic transfer into the electrolyte.

3. The electrolyte surface pathway. The electrolyte surface pathway (Figure 1c) considers adsorption of oxygen species on the electrolyte surface and their migration along the electrolyte surface toward the TPB. Unless partial ionization (via electron donation) can be accomplished by the electrolyte, this pathway is geometrically similar to the electrode surface pathway. Frequently, this pathway is ignored in favor of the electrode surface pathway due to the smaller total surface area and extremely low electronic conductivity of most relevant electrolyte surfaces, and we will ignore it here.

To study these three pathways, let us fix a representative geometry. Consider a hemispherical solid electrode particle (cf. Figure 2) sitting on top of a half-space of electrolyte ($z < 0$). Let the region above the electrolyte and outside the particle be the gas phase. The particle is nominally La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) and is assumed to be electrically connected to complete a circuit, though this connection is not shown in the diagram. The electrolyte is nominally yttria-stabilized zirconia (YSZ) and is also assumed to be electrically connected. The gas phase is simply air at 1 atm.

![Figure 2: Schematic geometry for our problem. The hemispherical LSM solid electrode particle is in red. This particle sits on top of the surface of the YSZ electrolyte (in blue at $z = 0$). The outside of the particle is air for $z > 0$ and YSZ for $z < 0$.](image)
A detailed understanding of the dominant ORR pathways associated with SOFC cathode structures can predict cathode performance and guide future electrode designs. Considering the general reaction schemes presented above, several important questions arise:

- What is the typical size of the TPB reaction region? In other words, how far does the electrochemically active region extend beyond the actual contact curve or point of the TPB?

- What determines the size of the TPB reaction region and how does this change with cathode properties or with operating conditions?

- What determines the relative importance of the surface reaction pathway versus the bulk pathway?

- Does the relative importance of the surface versus bulk pathway change depending on the scale (size) of the electrode particle?

It is important to understand TPB behavior in SOFC cathodes because the density and properties of the TPBs often determine the overall cathode performance. Because real SOFC cathodes are composite porous structures that exhibit relatively complex geometry/morphology, however, TPB properties have proven exceptionally difficult to determine experimentally. In order to eliminate this complexity, geometrically well-defined patterned microelectrodes have recently been used to enable quantitative correlation between TPB geometry and the ORR kinetics. These microelectrode studies allow ORR processes to be experimentally studied in the context of simple single-particle electrode/electrolyte contact geometries. Among notable SOFC cathode microelectrode studies, Horita et al. [12] constructed geometrically well-defined mesh-like LSM electrode structures on yttria-stabilized zirconia (YSZ) electrolyte. Based on oxygen isotope exchange measurements, they were able to show that electrochemical reactivity was strongly localized near the LSM/YSZ TPBs. They concluded that either the electrode surface pathway or a “localized” bulk pathway near the edges of the LSM mesh-stripes dominated the ORR response. Brichzin et al. [4, 3] employed circular microelectrodes (dense LSM microelectrodes with diameters from 20-200µm and thickness values of 100 and 250 nm supported on YSZ electrolyte) to study the SOFC ORR kinetics. They showed LSM/YSZ polarization response to be proportional to microelectrode area and thickness, thereby supporting the dominance of the bulk oxygen ion transport pathway (Figure 1b) in LSM. Similarly, Koep et al. [13] have recently examined the impedance of dense LSM microelectrodes on YSZ as a function of LSM thickness, determining that bulk oxygen ion pathway dominates for electrodes less than 360nm thick at 700 C. In contrast, R. Radhakrishnan et al. [20] also investigated the ORR process on patterned LSM electrodes, showing that the charge-transfer resistance was inversely proportional to TPB length. Their findings were consistent with a TPB, rather than bulk-dominated reaction pathway. At higher temperatures (>800 C), however, some bulk transport through LSM also appeared to occur. Most recently, G. J. la O’ et al. [14] investigated well-defined LSM microelectrodes on YSZ over a wide range of temperatures. Their results suggest that the overall ORR rate may be limited.
by mixed bulk/TPB charge transfer processes below 700 C and surface chemical
reactions above 700 C. Their detailed analysis furthermore suggests that the ma-
jority of ORR current passes through the TPB below 600 C, while above 600 C, a
significant fraction of current passes through the bulk of the LSM microelectrodes.
While these various experimental studies have, in many circumstances, presented
conflicting observations, a broad trend is beginning to emerge. In general, the bulk
ORR appears to be favored for thinner LSM microelectrode features and/or higher
temperatures, while the surface electrode ORR pathway appears to be favored with
larger (particularly thicker) LSM microelectrodes and/or lower temperatures.
In addition to experimental investigations of ORR TPB kinetics in SOFC cath-
odes, there have also been several attempts to model TPB processes. Because of
the large variation in experimental conclusions, single-particle models focusing on
the properties of the TPB can yield valuable insights. Single-particle modeling ap-
proaches prove especially helpful because the scale of these models is commensurate
with the scale of the triple-phase contact. Unlike many particle cathode models
(which neglect current inhomogeneities within individual particles and focus instead
on connectivity and percolation issues), single-particle models are able to examine
local current distributions in cathode particles and in the electrolyte adjacent to the
electrochemically active cathode regions. In other words, single-particle models are
well suited to examine current inhomogeneities close to TPBs. Fleig has examined
local current distributions in electrochemically active cathode/electrolyte contact
regions using finite element modeling approaches. His studies indicate that for both
surface and bulk pathways, considerable current inhomogeneities can occur, with re-
action zones strongly localized close to TPBs [10] [11]. Calculations indicate that the
effective width of this TPB active zone is likely on the order of tens of nanometers [8].
Tanner et al. [23] modeled the polarization response of porous SOFC cathodes by
considering a reaction pathway dominated exclusively by the TPB. The macroscopic
properties of the porous electrode were then related to this TPB pathway through
the calculation of an effective TPB resistance. In contrast, Adler et al. [2, 1] de-
veloped a theoretical model focusing on the AC impedance response of the bulk
pathway but did not include a treatment of the surface/TPB pathway. Liu [15] used
a resistor network/equivalent circuit approach to analyze ORR processes in mixed
ionic-electronic conducting cathodes, concluding that as the ionic conductivity of
the electrode decreases, the ORR becomes strongly restricted to the vicinity of the
TPB. Svensson et al. [21, 22] introduced a theoretical model that separately consid-
ered both the surface and bulk reaction pathways. However, their choice to define
the current at the electrode/electrolyte interface as a boundary condition in their
model made it difficult to quantitatively compare the surface versus bulk reaction
pathways. Coffey et al. [5] subsequently introduced a model addressing this limita-
tion by simultaneously considering the bulk and surface reaction pathways. They
show that depending on the conditions and/or cell overpotential one pathway may
dominate over the other pathway but their model lacks a Laplace condition required
to impose net charge neutrality.
The modeling approach used here to describe reaction-diffusion-conduction pro-
cesses for single particle SOFC cathode/electrolyte contacts is based on the compo-
nent potential approach first introduced by Fehribach et al. [7, 6] in the context of
electrolyte wedge triple junctions in molten-carbonate fuel cells. The major benefit of the component potential approach is that it greatly simplifies the treatment of reaction-diffusion-conduction problems compared to traditional concentration-based approaches. This reduction in complexity facilitates both numerical and theoretical treatment, and in some cases enables the formulation of exact solutions. In addition, this model uses a voltage (overpotential) rather than current boundary condition at the electrode/electrolyte interface, thereby enabling quantitative comparison of the bulk and surface reaction pathways. Finally, this approach inherently incorporates the Laplace condition, ensuring net charge neutrality and therefore physically realistic behavior at the TPB interface.

In the sections that follow, we apply the component potential model to the SOFC single particle TPB problem illustrated schematically in Figure 2. In particular, we provide component potential formulations for the two pathways most often discussed in the SOFC literature: (1) the electrode surface pathway (cf. (14) and (15)), and (2) the electrode bulk pathway (cf. (26), (27) and (28)). We will not consider the electrolyte surface pathway, because as has been previously pointed out, this pathway is geometrically similar to the electrode surface pathway and can be ignored in favor of the electrode surface pathway due to the smaller total surface area and extremely low electronic conductivity of most relevant electrolyte surfaces. We will show that the results obtained from these models are reasonable and consistent with previous experimental and modeling efforts based on LSM/YSZ SOFC cathodes. Finally, we use our two model formulations to examine various particle geometry scaling effects for LSM/YSZ single-particle contacts. In particular, we examine the relative dominance of the surface versus bulk pathway for different transport parameters and electrode particle sizes.

2 Electrochemistry and Component Potentials

2.1 The Surface Pathway

For the surface pathway, the ORR is achieved by the following three reaction steps:

\[
\begin{align*}
\frac{1}{2} \text{O}_2 & \rightleftharpoons \text{O}_s \\
\text{O}_s + 2\text{e}^- & \rightleftharpoons \text{O}_s^- \\
\text{O}_s^- & \rightleftharpoons \text{O}_e^-
\end{align*}
\]

In these steps, the subscript \(s\) indicates that the species is adsorbed (attached) to electrode surface, while the subscript \(e\) indicates that the species is inside the electrolyte. The first step (2) is the adsorption of molecular oxygen from the gas phase to atomic oxygen on the electrode surface. The second step (3) is the ionization of the surface atomic oxygen to form surface oxide ions. This charge transfer process likely proceeds through a sequence of more elementary steps. These first two steps occur anywhere (and everywhere) on the electrode surface. The final step (4) occurs at the TPB (the curve where the electrode surface meets the electrolyte). Here the oxide ions move off the surface and into the electrolyte.
Mathematically, one can treat any (or all) of the three steps above as slow (or rate determining). Electrochemically, however, it is generally assumed that the second step (3) is rate determining, and therefore that the other two remain in equilibrium throughout the ORR. Let $\mu_X$ be the electrochemical potential (defined e.g. in Mills [16] or Newman [18]) of species X. Assuming that the first and third steps are fast and in equilibrium throughout the process, one then has that

$$\frac{1}{2} \mu_{O_2} = \mu_s$$

$$\mu_{O_2} = \mu_{O_2}^-.$$  

(5)

(6)

Based on the electrochemistry above, define two component potentials, the oxidant potential $u$ and the current potential $v$:

$$u := \begin{cases} \frac{1}{2} \mu_{O_2} & \text{(gas phase)} \\ \mu_s & \text{(electrode surface)} \end{cases},$$

$$v := \begin{cases} \mu_{O_2}^- & \text{(electrode surface)} \\ \mu_{O_2}^- & \text{(electrolyte)} \end{cases}.$$  

(7)

(8)

The rate determining nature of the second step, on the other hand, means that the difference between the electrochemical potentials on each side of this step (the affinity of this step) is related to the Faradaic current density by the Butler-Volmer equation:

$$i_F = i_0 \frac{\exp (\alpha_a F \frac{\eta_s}{R_g T}) - \exp (-\alpha_c F \frac{\eta_s}{R_g T})}{2}$$

(9)

where $\eta_s := (u - v)/F$ is the surface overpotential. Throughout what follows, assume that $\alpha_a$ and $\alpha_c$ (the anodic and cathodic transfer coefficients) are both identically equal to 1; this assumption implies perfect reaction symmetry and a two electron charge transfer. The constants $F$, $R_g$ and $T$ are, respectively, the Faraday constant, the gas constant and the temperature. Finally $i_0$ is the exchange current density.

With this assumption (9) simplifies to

$$i_F = i_0 \sinh \left(\frac{u - v}{R_g T}\right)$$

(10)

This represents a source term on the surface of the electrode.

For this pathway, let $\Omega$ be the hemispherical surface of the solid electrode particle in Figure 2 (the gas-solid interface). Since transport in the gas phase is relatively fast, and since the solid electrode is a very good (though not perfect) electronic conductor, the major transport concern for this pathway is ionic transport on the surface. Since the oxide ions are present in excess on the surface, their concentration is essentially constant, and the definition of the electrochemical potential for the oxide ions implies

$$\nabla \mu_{O_2}^- = \nabla (\mu_{O_2}^- + nF\phi) = nF \nabla \phi$$

(11)

where $\mu_{O_2}^-$ is the chemical potential for the oxide ions, $\phi$ is the electrical potential, and $n$ is the ionic valence (here $n = -2$). The standard relation between electrical potential and current density is

$$\nabla (\sigma_s \nabla \phi) = i_F$$

(12)
where $\sigma_s$ is the surface electrical conductance (indeed (12) is the definition of $\sigma_s$). Therefore

$$-\nabla(\kappa_s \nabla v) = i_F$$

(13)

provided that the electrochemical conductance is $\kappa_s := \sigma_s/2F$. Thus the current production for the surface pathway for a single particle can be expressed as a single relatively simple equation and its boundary condition:

$$-\nabla(\kappa_s \nabla v) = i_0 \sinh((u - v)/R_g T) \quad x \in \Omega$$

(14)

$$v = v_0 \quad x \in \partial \Omega$$

(15)

Clearly this system is mathematically well-posed (has a unique solution). The PDE (14) is based on the Butler-Volmer equation. Because (on the scale of this problem) diffusion in the gas phase is fast, the oxidant potential $u$ is constant, and since one of the potentials can be set to a reference value, set $u \equiv 0$. In addition suppose that transport in the electrolyte is fast, meaning that $v = v_0$ is constant in the electrolyte. This is probably the most problematic assumption and it will need to be relaxed in future discussions. But with this assumption, the boundary value $v_0$ is determined by the electrical potential difference between the electrode and the electrolyte.

To find an expression for $v_0$, one needs to examine how $u$ and $v$ are related to concentrations and electrical potentials. Using the ideal gas law, one has

$$u = \frac{1}{2} \mu_{O_2} = \frac{1}{2} \mu_{O_2}^{eq} + \frac{1}{2} R_g T \ln \left( \frac{P_{O_2}}{P_{eq O_2}} \right)$$

(16)

and

$$v = \mu_{O^=} = \mu_{O^=}^{eq} + R_g T \ln \left( \frac{C_{O^=}}{C_{eq O^=}} \right) - 2F \phi_b$$

(17)

where $C$ denotes the concentration (in any convenient units), $P$ denotes the oxygen pressure and $eq$ indicates an equilibrium reference value. The difference between the two equilibrium (reference) potentials can be related to the equilibrium half cell potential $\Delta \phi_{Half}^{eq}$ for the system:

$$\frac{1}{2} \mu_{O_2}^{eq} - \mu_{O^=}^{eq} = -2F \Delta \phi_{Half}^{eq}$$

(18)

This half cell potential is not known, however, one can express the difference between the equilibrium half cell potential and the electrical potential difference across the half cell surface-electrolyte interface (as represented by $\phi_b - \phi_s \equiv \phi_b$ since $\phi_s \equiv 0$ is the reference potential) as an overpotential, $\eta$:

$$\eta := \phi_b - \Delta \phi_{Half}^{eq}$$

(19)

Thus the component potential difference at the surface-electrolyte interface is

$$u - v = \frac{1}{2} R_g T \ln \left( \frac{P_{O_2}}{P_{eq O_2}} \right) - R_g T \ln \left( \frac{C_{O^=}}{C_{eq O^=}} \right) + 2F \eta$$

(20)
At equilibrium, \( P_{O_2} = P_{O_2}^{\text{eq}} \), \( C_{O^=} = C_{O^=}^{\text{eq}} \), \( \phi_b = \Delta \phi_H^{\text{eq}} \), and thus \( \eta = 0 \) and \( u = v \) throughout the system. The overpotential \( \eta \) can then be used to drive the system away from equilibrium while keeping \( P_{O_2} = P_{O_2}^{\text{eq}} \) and \( C_{O^=} = C_{O^=}^{\text{eq}} \). Since \( u = 0 \) was established as a reference value, the boundary condition at the surface-electrolyte interface becomes \( v_0 = -2F\eta \).

### 2.2 The Bulk Pathway

For the bulk pathway, the ORR is achieved by the following three reaction steps:

\[
\begin{align*}
\frac{1}{2} O_2 & \rightleftharpoons O_s \quad (21) \\
O_s + 2e^- & \rightleftharpoons O_b^= \quad (22) \\
O_b^= & \rightleftharpoons O_e^= \quad (23)
\end{align*}
\]

These are of course essentially the same steps as in the surface pathway, but here the subscript \( b \) indicates that the oxide ions exist inside the electrode particle (in the bulk solid electrode phase) rather than on its surface. As with the surface reaction pathway, the first step for the bulk pathway (21) is the adsorption of molecular oxygen from the gas phase to atomic oxygen on the electrode surface. But the second step (22) is now an ionization/incorporation step, whereby the surface atomic oxygen is ionized to oxide ions and incorporated into the bulk electrode. As with the previous pathway, these first two steps occur anywhere (and everywhere) on the electrode surface. In contrast to the surface pathway, however, the final step (23) can now occur anywhere along the two-dimensional interface between the electrode particle and the electrolyte (i.e., anywhere along the base of the hemisphere in Figure 2 where \( z = 0 \)). Here the oxide ions move from the electrode bulk into the electrolyte, and so this process is not necessarily restricted to near the TPB as it is in the surface pathway. In the SOFC literature, this condition is sometimes referred to as a “two-phase” boundary in order to distinguish it from the triple-phase boundary.

As with the surface reaction pathway, it is generally assumed that the second step (22) is rate determining for the bulk pathway, and therefore that the other two remain in equilibrium throughout the ORR. In analogy with the surface pathway, one can again define two component potentials, the oxidant potential \( u \) and the current potential \( v \):

\[
\begin{align*}
u & := \begin{cases}
\frac{1}{2} \mu_{O_2} & \text{(gas phase)} \\
\mu_{O_s} & \text{(electrode surface)}
\end{cases}, \\
v & := \begin{cases}
\mu_{O_b^=} & \text{(electrode bulk)} \\
\mu_{O_e^=} & \text{(electrolyte)}
\end{cases}
\end{align*}
\]

The derivation of the PDE and BC for this pathway then proceeds in much the same way as for the previous pathway. The source term corresponding to the slow reaction step again sits on the solid-gas interface (the upper hemispherical surface). The two major differences for this pathway are that ion conduction now occurs through the solid electrode and that the value of ionic conductivity is therefore rather different from the value of ionic conductance for the surface pathway (indeed the units are
different). Ionic transport through the bulk solid is by vacancy conduction in the opposite direction to the net oxide ion flow. So for this pathway, $\Omega$ is the interior of the particle. Again assuming that conduction through the electrolyte is fast, the BC at the base of the solid particle is the same as at the TPB in the surface pathway.

$$-\nabla (\kappa_b \nabla v) = 0 \quad x \in \Omega$$

$$v = v_0 \quad x \in \partial_{eb} \Omega$$

$$\kappa_b \nabla v \cdot n = i_0 \sinh((u - v)/R_g T) \quad x \in \partial_{bg} \Omega$$

The system (26–28) for this pathway is depicted schematically in Figure 3.

![Schematic geometry for the bulk path.](image)

Figure 3: Schematic geometry for the bulk path. The LSM solid electrode particle is in red. The blue lines are the electrolyte-gas interface at $z = 0$.

### 3 Analysis and Computations

#### 3.1 Parameter values:

To compute meaningful solutions for either pathway, one needs to have accurate values of the various coefficient parameters both for surface pathway (14) and (15) and for the bulk pathway (26), (27) and (28).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Faraday constant</td>
<td>$F = 96490$ Coulomb/mole</td>
</tr>
<tr>
<td>gas constant</td>
<td>$R_g = 8.314$ Joule/(mole K)</td>
</tr>
<tr>
<td>temperature</td>
<td>$T = 950$ C = 1223 K</td>
</tr>
<tr>
<td>oxygen partial pressure</td>
<td>$P_{eq}^{O_2} = 0.21$ atm</td>
</tr>
<tr>
<td>bulk ionic conductivity</td>
<td>$\sigma_b = 2 \times 10^{-7}$ S/cm [17]</td>
</tr>
</tbody>
</table>

Other values can only be limited to certain ranges:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>exchange current density</td>
<td>$10 \leq i_0 \leq 100$ (mA/cm$^2$) [24]</td>
</tr>
<tr>
<td>oxide concentration</td>
<td>$0.001 \leq C_{O_x}^{eq} \leq 0.01$ (mole/cm$^3$)</td>
</tr>
<tr>
<td>particle radius</td>
<td>$0.1 \leq R \leq 100$ ($\mu$m)</td>
</tr>
<tr>
<td>overpotential</td>
<td>$0.1 \leq \eta \leq 0.9$ (V)</td>
</tr>
<tr>
<td>surface ionic conductance</td>
<td>$10^{-17} \leq \sigma_s \leq 10^{-3}$ (S)</td>
</tr>
</tbody>
</table>
For the computations in this section, representative values in these ranges for \( i_0 \) and \( \eta \) have been chosen, while several differing illustrative values of \( R \) and \( \sigma_s \) are used.

\[
\begin{align*}
\text{exchange current density} & : \quad i_0 = 50 \text{ mA/cm}^2 \\
\text{overpotential} & : \quad \eta = 0.5 \text{ V} 
\end{align*}
\]

(31)

The effects of varying all of these parameters across their ranges will be considered in the following case studies section. Because the value of \( \sigma_s \) is not well established, the range of values considered for it is particularly wide. Because it appears only in the reference potential, the exact value of \( C_{\text{eq}}^{\text{red,e}} \) is not needed in these computations. The units for the component potentials \( u \) and \( v \) are in Joule/mole; the exchange current density is in area-based units (A/cm\(^2\) or mA/cm\(^2\)).

### 3.2 Surface Pathway

The system of equations describing the potential and current density on the surface, (14) and (15) is mathematically well posed, but it is not simple enough to easily derive explicit solutions for the potentials or the current density (because of the nonlinearity of the sinh term, and complications of having the Laplacian on the hemispherical surface). Still the symmetry of the system does reduce the problem to a boundary value problem for an ODE, making it simple enough to draw several important mathematical conclusions. These conclusions do not depend strongly on the specific hemispherical geometry; they would be the same for any similar cathode geometry.

First the PDE and BC together imply a characteristic length scale for the width of the reaction region on the surface next to the TPB. This width is

\[
w := \sqrt{\frac{\kappa_s v_0}{i_0}}
\]

(32)

Let \( R \) be the radius of the hemispherical solid electrode. Then for \( R \ll w \), the entire surface of a solid electrode will be “inside” the reaction region, and the potential and current density will be essentially uniform. If on the other hand \( w \ll R \), then there will be a sharp boundary layer of width \( w \) next to the TPB. The reaction region will be inside this boundary layer, and the surface outside this layer (the majority of the entire surface) will be nonreactive. Finally if \( R \) and \( w \) are of similar size (within roughly a factor of ten) the entire surface will be active, but the current component potential and current density will not be uniform. Rather they will decrease as one moves away from the TPB, but there will be no sharp boundary layer and \( v \) and \( i_F \) will not be close to zero in the middle of the surface. These results are illustrated numerically in Figure 4 below.

A second issue that can be dealt with analytically is the nature of the solution when one can linearize the source term on the righthand side of the PDE (14). Linearization is valid when \( |u-v|/R_gT \ll 1 \), and this inequality is satisfied away from the boundary layer. In this case, the righthand side becomes in effect \( \alpha i_0 (u-v)/R_gT \), and one can obtain an explicit solution for the current component potential:

\[
v(y) = v_0 \exp \left( -\sqrt{\frac{\alpha i_0}{\kappa_s R_g T}} y \right)
\]

(33)
Thus both this potential and the corresponding current density will have log-linear profiles away from the TPB with a slope $-\sqrt{\alpha i_0/\kappa_s R_0 T}$. This sort of profile can be seen in Figure 5 and in Fleig [9, p. 387], Figure 29.

Using the parameter values discussed above, one can compute the potential $v$ and the corresponding current density $i_F$ for various cathode particle radii and/or surface or bulk transport parameters. These computations are depicted in several plots below. All of the numerical computations were carried out using Femlab, a.k.a COMSOL Multiphysics.

Figure 4: Current potential on the surface of a hemispherical cathode cap with radius $R = 1.0 \, \mu m$ and $\kappa_s = 10^{-12} \, S \, mole/Coulomb$. For the given set of parameter values, the reaction region width is $w = 13.9 \, \mu m$. The PDE and BC together guarantee that this potential and the associated current density are radially symmetric.

The first image, Figure 4, is a view of the current potential on the upper particle surface (the gas-solid cathode interface) looking down from above. The computations are two dimensional, but the derivatives are corrected to account for the curvature of the surface of the hemisphere. The surface electrochemical conductance $\kappa_s = 10^{-12} \, S \, mole/Coulomb$ is chosen to illustrate cases where the reaction region width, $w$, and the particle size, $R$, are comparable. This value is in the middle of the range considered in the conductance case study in Section 4 below. The radius ($R = 1.0 \, \mu m$) is somewhat smaller than the width of the reaction region corresponding to these parameter values (here $w = 13.9 \, \mu m$). As a result, there is no sharp boundary layer and the entire surface is active. Indeed the minimum jump at
the surface between the reference oxygen component potential $u = 0$ and the current component potential $v$ is approximately $4 \times 10^4$ Joule/mole, which implies that there is a significant Faradaic current density $i_F$ on the entire surface. For smaller radii or larger surface conductance, the current potential current density would become essentially uniform. For larger radii or smaller surface conductance, on the other hand, current density production quickly becomes confined to a reaction region near the TPB and the vast majority of the surface produces little current. Thus the magnitude of the surface conductance strongly influences how much of the particle effectively participates in the reaction process. The total current produced by the surface pathway for the particle surface depicted in Figure 4, the integral of current density over the entire particle surface, is $1.6 \times 10^{-6}$ A.

![Figure 5: Current density on a hemispherical cathode cap with $R = 100 \mu$m. Only the first five microns from the TPB are shown. The PDE and BC together guarantee that the current density is radially symmetric. Here $\kappa_s = 10^{-14}$ S mole/Coulomb.](image)

The second plot is a log-linear profile of the current density for a much larger cathode radius and smaller ionic surface conductance. Here $R = 100 \mu$m and $\kappa_s = 10^{-14}$ S mole/Coulomb. The main observations in this case are again that the current density rapidly drops off as one moves away from the TPB and that the current density profile is linear (on a log scale) far away from the TPB with slope given in (33). Again far away from the TPB the current density is low and the linearization of the full solution is valid.

3.3 Bulk Pathway

The system describing the bulk current potential and current density on the surface, (14) and (15) is also well posed. A cross sectional plot of the bulk current component potential is shown in Figure 6. The most important difference between the two pathways that can be seen by comparing this plot with the previous surface plot in Figure 4 is that very little oxygen is crossing the surface in the bulk pathway compared to the amount that is adsorbed onto the surface in the surface pathway.
Figure 6: Current potential in a bulk hemispherical cathode cap with radius $R = 1 \ \mu m$. Here $\kappa_b = 10^{-12}$ S mole/(Coulomb cm) which corresponds to $\sigma_b = 2 \times 10^{-7}$ S/cm [17], a typical experimentally-measured ionic conductivity for LSM at $T = 950$ C. Also on the upper surface, $\nu \simeq 130$ Joule/mole, which is essentially zero since $\nu_0 = 96490$ Joule/mole.

Indeed the potential difference $u - v$ is nearly zero on almost the entire surface in Figure 6. The only exception is very close to the TPB. Thus in the bulk case there is very little Faradaic current associated with almost the entire solid cathode surface, whereas for the surface pathway, there is a significant Faradaic current associated with the entire solid cathode surface for $\kappa_b$ near $10^{-12}$ S mole/Coulomb. Mathematically this result follows from the fact that the Butler-Volmer term is a source term for the entire domain for the surface pathway, while this source is confined to the boundary for the bulk pathway. In terms of the electrochemistry, the result comes from the fact that the surface is everywhere well-supplied with oxygen, while the bulk is almost everywhere separated from the oxygen source by a layer of slow-transport solid cathode. The total current produced by this cathode particle through the bulk pathway (now the integral of the current density over the circular base of the hemispherical cathode particle) is $3.5 \times 10^{-10}$ A which is roughly 5000 times smaller than the total current through the surface pathway. Note well that these results very much depend on the surface conductance and bulk conductivity having similar numerical value; other possibilities will be considered in the next section.
Finally, it is worth noting that there is never a boundary layer in the current potential $v$ for the the bulk pathway as there can be in the surface pathway. For very large values of $\kappa_b$ or very small values for $R$ (well out of the physically meaningful range), the current potential will be uniform. For more physically meaningful, smaller values of $\kappa_b$ or larger values for $R$, the current potential will be nearly zero on almost all of the surface, while the interface condition fixes $v = v_0$ on the particle-electrolyte interface. Again this is illustrated in Figure 6. Near the TPB, the contours for $v$ emanate almost radially from the TPB. Since the spacing is essentially constant, the angular partial derivative $v_\phi$ is also essentially constant. Since in the bulk $i_F = \kappa_b \nabla v = \kappa_b v_\phi/r$, the current density is directly proportional to the bulk conductivity and inversely proportional to the distance from the TPB. Thus for physically meaningful parameter values, there will be a boundary layer in the current density even though there is not one in the current potential.

Because of the small value of $(u - v)/RT$ for the bulk pathway over the surface where the Butler-Volmer term controls the dynamics, it is possible to linearize the Butler-Volmer term and study the bulk pathway problem near the TPB, at least for sufficiently small driving overpotentials $\eta$ or $v_0$. This approach is the same as the one taken by Fehribach [6] for a molten carbonate fuel cell (MCFC) electrode. The main result from this approach is that the total current produced through the bulk pathway depends primarily on the contact angle between the particle upper surface (gas-particle interface) and the particle base (particle-electrolyte interface). This angle has been fixed at $\pi/2$ in our work so far, but will be varied in our final case study below.

4 Case Studies

This section considers the total current response behavior and the relative dominance of the surface and bulk pathways for a variety of different scenarios. Starting from a set of base-case parameter values, we examine how changes in surface conductance (as determined by $\kappa_s$), particle size ($R$), overpotential ($\eta$) and contact angle ($\theta$) affect the total current produced for the solid particle through each of the two pathways. The base parameter values are chosen to be representative of typical experimental values to the extent such values are available. The values used here are the same as those used in the previous section, except that $\kappa_s$ is seven orders of magnitude lower. This value may be more physically realistic, though this is difficult to say with certainty. While the value of $\sigma_b$ (and hence $\kappa_b$) is reasonably well known for LSM, the value of $\sigma_s$ (and hence $\kappa_s$) is not well established. In the absence of an experimentally established value for $\sigma_s$, a reasonable approach for estimating its value is to choose a value that is consistent with the bulk conduction properties of LSM. From this approach, the surface conductance, $\sigma_s$ (units of S) might be estimated from the bulk conductivity, $\sigma_b$ (units of S/cm) by multiplying by the thickness of the surface layer through which surface conduction proceeds. For a truly surface-based conduction process, this thickness should correspond to at most a couple atomic layers, or about $1 \times 10^{-8}$ cm. This exercise yields an estimate for $\sigma_s \approx 2 \times 10^{-14}$ S for $\sigma_b = 2 \times 10^{-7}$ S/cm. The resulting estimate for $\kappa_s = \sigma_s/2F$ is
therefore \( \kappa_s \simeq 1 \times 10^{-19} \text{ S mole/Coulomb} \). This value for \( \kappa_s \) is consistent with the limited knowledge of the boundary-layer width when it is computed using (32).

Although varying these four parameters \((\kappa_s, R, \eta \text{ and } \theta)\) does not exhaust all possible cases, it does cover many of the most interesting ones. For example, varying \( \kappa_s \) is equivalent to varying \( i_0 \) for the surface pathway, thus we hold \( i_0 \) fixed. Because our model incorporates an overpotential (rather than current) boundary condition, we can directly compare how much current is generated by each pathway at the same overpotential (driving force) to determine which pathway is dominant for a given set of conditions. For each pathway, the total current is calculated by integrating the current density over the entire gas-solid interface (the hemispherical particle surface).

The following subsections explore the roles of the four parameters mentioned above on both pathways (surface and bulk). First the role of surface conductance is considered by varying \( \kappa_s \) through many orders of magnitude while holding all other parameters constant at their base values. Next the role of particle size is considered by varying \( R \) through the range of physically meaningful values, followed by consideration of the role of overpotential by varying \( \eta \). Finally the role of contact angle is considered by varying it across its entire meaningful range. The specific parameter variations examined in these case studies are summarized in Table 1.

<table>
<thead>
<tr>
<th>Study</th>
<th>Base Values</th>
<th>Surface Conductivity</th>
<th>Particle Size</th>
<th>Over Potential</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log(\kappa_s) )</td>
<td>-19</td>
<td>(-22 &lt; \log(\kappa_s) &lt; +\infty)</td>
<td>Base Value</td>
<td>Base Value</td>
<td>Base Value</td>
</tr>
<tr>
<td>( R )</td>
<td>1.0 ( \mu \text{m} )</td>
<td>Base Value</td>
<td>Base Value</td>
<td>Base Value</td>
<td>Base Value</td>
</tr>
<tr>
<td>( \eta )</td>
<td>0.5 V</td>
<td>Base Value</td>
<td>Base Value</td>
<td>Base Value</td>
<td>Base Value</td>
</tr>
<tr>
<td>( \theta )</td>
<td>( \pi/2 )</td>
<td>Base Value</td>
<td>Base Value</td>
<td>Base Value</td>
<td>( \pi/32 &lt; \theta &lt; \pi/2 )</td>
</tr>
</tbody>
</table>

Table 1: The Case Studies: The base values and parameter ranges for our case studies. The units for \( \kappa_s \) in the common logarithm are S mole/Coulomb.

other parameters and constants, unless specifically noted, are held constant at their values in the previous section (cf. (29)).

### 4.1 Surface conductance study

The effect of varying \( \kappa_s \) on the absolute current produced by the surface pathway is illustrated in Figure 7. As \( \kappa_s \) increases above approximately \( 10^{-10} \text{ S mole/Coulomb} \), the total current \( I_s \) approaches its maximum value (roughly \( 2 \times 10^{-5} \text{ A} \)) which corresponds to perfect surface conductance. The perfect-conductance value for total current is essentially reached when \( \kappa_s \) reaches roughly \( 10^{-8} \text{ S mole/Coulomb} \). As \( \kappa_s \) decreases below \( 10^{-10} \text{ S mole/Coulomb} \), on the other hand, the total current \( I_s \) produced by the surface pathway also decreases becoming essentially linear for \( \kappa_s \) below approximately \( 10^{-11} \text{ S mole/Coulomb} \). This linearity follows from the linear scaling in \( \kappa_s \) of the entire system for very small values of \( \kappa_s \) because the current density (and therefore the domain for the entire system) becomes restricted to a thin-strip boundary layer on the surface near the TPB. The total current produced by the bulk pathway is of course independent of \( \kappa_s \); it is indicated by the dark solid line in Figure 7 (assuming \( \sigma_b = 2 \times 10^{-7} \text{ S/cm} \)).
Figure 7: Dependence of total surface current $I_s$ on surface electrochemical conductance $\kappa_s$. The maximum value of $I_s$ corresponding to $\kappa_s = \infty$ (perfect surface conductance) is $2.08 \times 10^{-5}$ A and is depicted by the horizontal dotted upper line. The lower horizontal line indicates the total bulk current $I_b = 3.5 \times 10^{-10}$ A, independent of $\kappa_s$.

4.2 Particle size study

The effect of varying $R$ on the total current produced by both the surface and bulk pathways is illustrated in Figure 8. As the particle radius $R$ increases, all total-current curves also increase. This trend simply reflects the greater surface area and volume available for reaction as $R$ increases. The total bulk current $I_b$ increases faster, however, than the total surface current $I_s$, indicating that the bulk pathway is favored for larger particles, while the surface pathway is favored for smaller particles. Strikingly, the relative dominance of the surface or bulk pathways depends very sensitively on the relative size of $\kappa_s$ and $\kappa_b$. For fixed $\kappa_b$, a change in $\kappa_s$ by only one order of magnitude is sufficient to completely switch from surface to bulk pathway dominance over nearly the entire range of realistic particle sizes. In addition, if surface conductance is between approximately $10^{-19}$ and $10^{-20}$ S mole/Coulomb, the two pathways are roughly equally effective across the entire range of particle sizes.

Normalized by particle surface area (or volume), the current density for either pathway (A/cm$^2$ or A/cm$^3$) actually increases as the particle size decreases, indicating that smaller particles are more fully utilized because the region near the TPB becomes a larger fraction of the total particle volume. Interestingly, on a perimeter normalized basis, the current produced by surface pathway is essentially independent of particle size, while the current produced by the bulk pathway increases on a perimeter normalized basis as the particle size increases. This scaling behavior is consistent with the strong localization of the surface pathway current to a reaction
Figure 8: Dependence of total current $I_b$ and $I_s$ on particle radius $R$. As $R$ increases, the total current produced by both pathways also increases linearly on this log-log scale, though the total bulk current increases more rapidly.

region near the TPB, while indicating that the bulk pathway benefits to some extent from its ability to utilize a somewhat larger portion of the entire particle-electrolyte contact area for larger particle sizes.

4.3 Overpotential study

The effect of varying $\eta$ on the total current produced by both pathways is illustrated in Figure 9. As $\eta$ increases, the total current produced through both pathways also increases. This behavior simply reflects that there is more driving force for the electrochemical reaction as the overpotential increases (as governed by the Butler Volmer relation expressed either in (9) or (10)).

Analogous to the particle size study, this overpotential study also indicates a shift in the relative dominance of the two pathways. As the particle overpotential increases, the total current generated by the surface pathway increases faster than the total current generated by the bulk pathway, indicating that the surface pathway is favored at higher overpotentials, while the bulk pathway may be favored at lower overpotentials. As the overpotential increases, an increasingly sharp reaction region near the TPB carries an increasingly greater fraction of the total current produced by the particle. This increasing dominance of the TPB with increasing overpotential has also been observed in previous studies of both SOFC and PEMFC systems [19] (cf. also [12]).
Figure 9: Dependence of total current $I_b$ and $I_s$ on overpotential $\eta$. Total current increases with overpotential for both pathways, but the surface total current increases exponentially (the curve is linear on this log scale), while the bulk total current increases somewhat more slowly. The critical crossover potential is approximately 0.45 V (given all of the other base parameter values).

4.4 Contact angle study

The effect of varying the contact angle $\theta$ on the total current produced by both the surface and bulk pathways is illustrated in Figure 11. In this study, the particle radius is held constant; therefore the cap surface area and base contact area both decrease with decreasing contact angle. Typical particle geometries for several contact angles are shown schematically in Figure 10. As shown in Figure 11, as $\theta$ decreases, the total current $I_s$ produced through the surface pathway also decreases, but total current $I_b$ produced through the bulk pathway increases until a maximum value is reached when $\theta$ is near $\pi/4$. For contact angles smaller than roughly $\pi/4$, the bulk-pathway total current also decreases. For very small contact angles, this decrease is simply due to the reduction in cap volume, surface area and perimeter. Importantly, though, the surface-pathway total current decreases faster than the bulk-pathway total current. The surface pathway current, which is tied directly to the TPB length, decreases linearly with decreasing cap perimeter for the same reason that it decreases linearly with decreasing radius in the previous study. The bulk pathway current decreases more slowly, however, because the transport distance across the particle bulk is significantly less, broadening the bulk reaction near the TPB. The total current due to either pathway is approximately the same when the contact angle is roughly $\pi/3$.

For much larger values of $\kappa_s$ (say $\kappa_s = 10^{-14}$ S mole/Coulomb), the bulk pathway still becomes the dominant pathway for sufficiently small contact angles. But depending on the exact value of $\kappa_s$, the contact angle where this crossover takes
place may be extremely small. For $\kappa_s = 10^{-14}$ S mole/Coulomb, the crossover takes place at roughly $\theta = \pi/400$, at which point the particle has more-or-less become a thin film. For this thin-film configuration, the geometric transport advantage provided by the bulk pathway overcomes the resupply advantage provided by the surface pathway even for relatively large values of $\kappa_s$. This increasing contribution from the bulk pathway for thin-film type LSM electrode geometries has been noted experimentally (cf. the introduction, [4] [3] [13]).
5 Conclusion

This paper has detailed the application of the component potential formulation to the TPB problem for a single-particle, SOFC electrode/electrolyte system. The single-particle TPB model represents just one of several different levels of scale used in SOFC electrode modeling. Observations gleaned from this analysis must be considered within the context of both larger and smaller scale processes. For example, our single-particle analysis shows that smaller electrode particles are more effective (more fully utilized) because the TPB becomes a larger fraction of the total particle volume. However, when this result is extrapolated into a multi-particulate model of an entire SOFC cathode (which considers, for example, percolative electrical and gas transport through assemblies of particles), the utilization advantage of increasingly smaller particles may be offset by a transport disadvantage. At the molecular scale, on the other hand, additional details of the ORR reaction (such as oxygen surface adsorption, coverage, dissociation, and the elementary-step details of the two-electron transfer reaction), which are not considered in this continuum treatment, may become important under certain conditions or under certain particle geometries.

The scaling trends observed in this model study generally support the emerging experimental consensus concerning the behavior of the TPB for LSM/YSZ systems. Our case studies suggest that the bulk pathway is favored for larger particles, lower overpotentials and/or smaller contact angles, while the surface pathway is favored for smaller particles, higher overpotentials and/or larger contact angles. The approximate equality between the total currents for each pathway is achieved as a balance between the poor surface transport due to the very small surface conductance used in our case studies and the near perfect resupply of oxygen to the surface from the gas phase (there is no similar mechanism to supply oxygen directly into the bulk).

Importantly, our model demonstrates that even in situations where the bulk pathway is dominant, considerable current density inhomogeneities occur, with a significant fraction of the total reaction current often still strongly localized close to TPBs. In other words, even the bulk pathway is mostly restricted to regions very close to the TPB. This behavior (which is consistent with prior observations from Fleig [9], Horita [12], and others) is largely due to the fact that LSM is an extremely poor ionic conductor ($\kappa_b$ is small). A considerably broader reaction region can be created if a true mixed ionic-electronic conductor (MIEC) is used (thereby effectively increasing $\kappa_b$ by several orders of magnitude). Alternatively, the ionic conductivity of LSM can be improved by increasing the temperature. This may help explain why experimental observations show that the bulk pathway is increasingly favored at higher temperatures.

For the surface pathway, the scaling in our model suggests that the width $w$ of the reaction region associated with the TPB can be defined by (32). Although surface conduction $\kappa_s$ values are extremely hard to determine or estimate, our assumed value of $\kappa_s = 10^{-19}$ S mole/Coulomb (along with other base values) yields a TPB width of approximately 4.4 nm. This value is consistent with estimates from Fleig [8] and others, providing further confirmation that our assumed base value for $\kappa_s$ is at least reasonable. Such a magnitude for $\kappa_s$ also appears to be consistent with best-guess
estimates for oxygen surface diffusivity on LSM at 900–1000°C [14].

Most importantly, however, these estimates highlight that reaction processes in LSM/YSZ cathodes are highly localized to a narrow reaction region near the TPB if $\kappa_s = 10^{-19}$ S mole/Coulomb. Our computations also demonstrate that if $\kappa_s$ is larger (say $10^{-14}$ S mole/Coulomb or bigger), much or all of the particle surface will be in the reaction region, and the surface pathway will dominate for almost all choices of the other parameters. The only exception occurs when a very small contact angle makes the particle effectively a thin film.

In future work, several limitations of the current component potential model must be addressed. In particular, the present treatment assumes that transport in the electrolyte is fast, meaning that $v = v_0$ is constant in the electrolyte. This is a problematic assumption for either pathway and likely unrealistic, particularly at large overpotential. Incorporating the finite ionic conductivity of the electrolyte would lead to a decrease in computed current densities for all scenarios. Another issue to consider is the particle geometry. The present work assumed a hemispherical particle (modified in the contact angle study) which does not extend into the electrolyte half space. One could also consider, for example, a spherical (or near spherical) particle half embedded into the electrolyte. In particular, having a significant portion of the particle embedded would dramatically change the contact-angle results. One could also consider complex particle-electrolyte geometries which would be physically more realistic.

References


[20] R. Radhakrishnan, A. V. Virkar, and S. C. Singhal, *Estimation of charge-transfer resistivity of La$_{0.8}$Sr$_{0.2}$MnO$_{3}$ cathode on Y$_{0.16}$Zr$_{0.84}$O$_{2}$ electrolyte using patterned electrodes*, J. Electrochem. Soc. 152 (2005), A210–218.

