A Nonlinear Elliptical Problem for Solid Oxide Fuel Cell Cathodes

A Major Qualifying Project
Submitted to the Faculty of the
WORCESTER POLYTECHNIC INSTITUTE
in partial fulfillment of the requirements for the
Degree of Bachelor of Science in Mathematical Sciences
and Degree of Bachelor of Science in Physics

By Xiaojing Wang

Date: April 23, 2013

Advisors:

--	--
Dr. Joseph D. Fehribach	Dr. Germano Iannacchione
Department of Mathematical Sciences	Department of Physics

Key Words: fuel cell, triple phase boundary (TPB), non-linear elliptical partial differential equations

Abstract

This Major Qualifying Project considers a nonlinear elliptical steady-state reaction-diffusion-conduction problem for solid oxide fuel cells (SOFCs). The existence of a solution is proven by showing the existence of a minimum of an appropriate energy functional, then using the Dirichlet principle to show that the minimum is a solution to the original problem. The uniqueness of the solution can be proven by application of Green's first identity. Numerical computations of the solution are performed, and comparisons are made to decide on a range for the surface exchange current density parameter.

Acknowledgements

I would like to express sincere appreciation to the following individuals and/or groups.

- My advisors, Professor Joseph Fehribach and Professor Germano Iannacchione, for the great inspiration and guidance they have given me throughout the project
- Professor Ryan O'Hayre, especially for his help in finding one specific parameter value
- Miss Rebecca Gaddis, for providing this Latex template and helping me with many physical concepts
- Miss Sarah Bober and Miss Chuqiao Yang, for helping me adjusting and editing the project report
- Last but not least, I appreciate all the support from faculty and staff members of the Department of Mathematical Sciences and the Department of Physics at WPI

Contents

I Introduction

A fuel cell generates electricity through oxidizing a fuel with an oxidizing agent. It is similar to a battery, as they both convert chemical potential to electrical energy by creating an electrical current. But unlike a battery, a fuel cell's reactants are from an external supply. A fuel cell has three essential components: the positive electrode (cathode), the negative electrode (anode), and the electrolyte. At each electrode, an oxidation-reduction reaction occurs. One of these reactions generates ions, which are transferred to the other electrode through the electrolyte. They act as a reactant for the other half-cell reaction. It is important that only these ions pass through the electrolyte, and that the electrolyte not be a conductor of electrons. This is because that free electrons are produced in the anode reaction, and these the free electrons must flow through the external load, not through the electrolyte [1].

A solid oxide fuel cell (SOFC) is a fuel cell whose electrolyte is made of solid state materials, and an oxide reacts at its cathode. In this case, oxygen ions are produced from the reaction at the cathode, and the electrolyte carries them to the anode. In the overall reaction, the oxide is the oxidizing agent, which ensures the occurrence of the reaction and the functionality of the fuel cell [1].

A triple phase boundary (TPB) is a boundary where three distinct phases are in contact. In this project, TPB refers to the boundary where the oxygen gas, the solid cathode, and the electrolyte are all in contact with one another [2]. As shown in Figure I.1, typically there are three possible reaction pathways near the TPB. The first pathway is the electrode surface pathway. In this pathway, the oxygen gas is adsorbed onto the cathode surface first, and then diffuses along the electrode surface while ionizing and transferring into the electrolyte. Complete ionization is reached at the TPB. The second pathway is the electrode bulk pathway. This pathway is very similar to the electrode surface pathway, except that the adsorbed oxygen species move inside of the electrode particle instead of moving along its surface. Complete

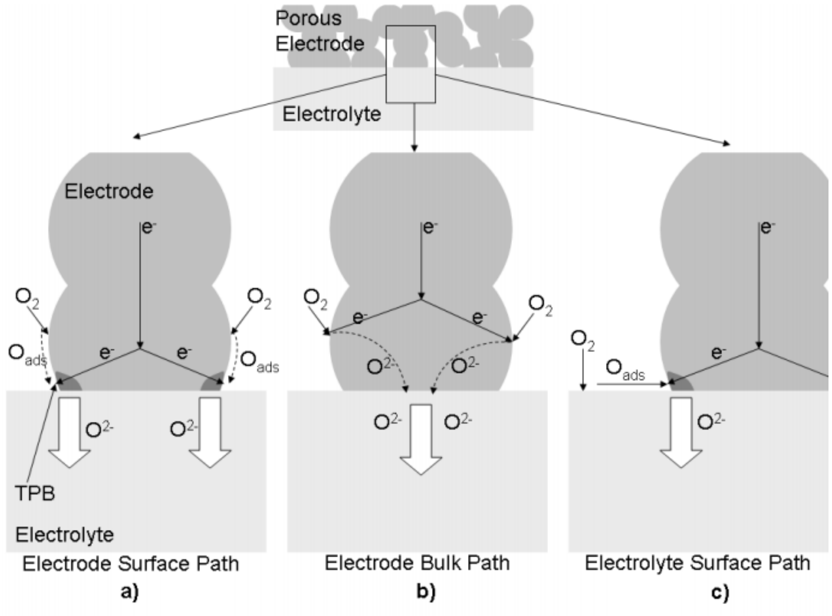

Figure I.1: The three typical pathways of cathode reactions in SOFCs taken from Ref. 2

ionization is reached at the electrode-electrolyte interface. The third pathway is the electrolyte surface pathway. Oxygen molecules adsorb onto the electrolyte surface first, then they move along this surface to the TPB, where they get ionized [3].

In Fehribach & O'Hayre [2], the electrode surface pathway and the electrode bulk pathway are considered in detail; the electrolyte surface pathway, on the other hand, is only briefly mentioned because it was considered less significant. The major goal of this project is to study the electrolyte surface pathway in comparison with the electrode surface pathway.

In this project, we assume the material of the cathode is lanthanum strontium manganite (LSM), which is lanthanum manganite doped with strontium oxide. We also assume that the material of the electrolyte is yttria-stabilized zirconia (YSZ), which is zirconia doped with yttria. These materials are both nominal for their respective applications in SOFCs, and they were also assumed in the previous study [2].

In this project, we consider a nonlinear steady-state reaction-diffusion-conduction problem in solid oxide fuel cells cathodes. The equations are formulated in terms of electrochemical potentials of the reactants and the products of each reaction using the Butler-Volmer equation [4]. We then prove the existence and uniqueness of the solution. Existence is established by first showing the existence of a minimizer of an appropriate energy functional, then using the Dirichlet principle, to show that the minimizer is a solution to the original problem. Uniqueness is proven by applying Green's first identity. Afterwards, we generated numerical computations of the solution for reasonable parameter values. Due to lack of information on the exchange surface current density for the adsorption number,a series of computations are performed to determine its range. Finally, a counter example for the maximum principle is also presented.

II The Mathematical Model

In the electrolyte surface pathway, the first step of reaction is for oxygen gas molecules to attach to the surface of the electrolyte through adsorption. Then they diffuse along the electrolyte surface until they reach the TPB. During this process, the bond between the oxygen atoms breaks. But none of these free oxygen atoms can gain electrons, because free electrons only exist in or on the solid electrode. Once the oxygen atoms reach the TPB, an oxidation-reduction reaction occurs, which turns the oxygen atoms into oxygen ions with the charge of $-2e$. After this reaction, the oxygen ions move from the electrolyte surface to its interior.

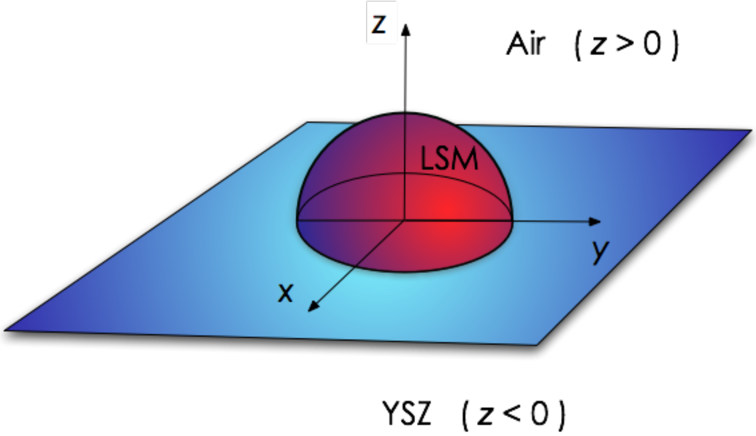

Figure II.1: The red hemisphere represents the solid electrode, and the blue plane represents the electrolyte surface [2].

Figure II.1 is a geometric configuration for the process described above. The hemispherical structure represents a particle of the solid electrode sitting on the electrolyte surface (the x-y plane). The electrolyte extends in the $-z$ direction, filling the half-space under the electrolyte surface. The air, and especially oxygen gas, exists in the region that is above the electrolyte surface and outside of the electrode particle. The shape of the electrode particle is arbitrary; it does not need to be hemispherical, or even convex.

In this pathway, since all concentrations would remain constant except on the

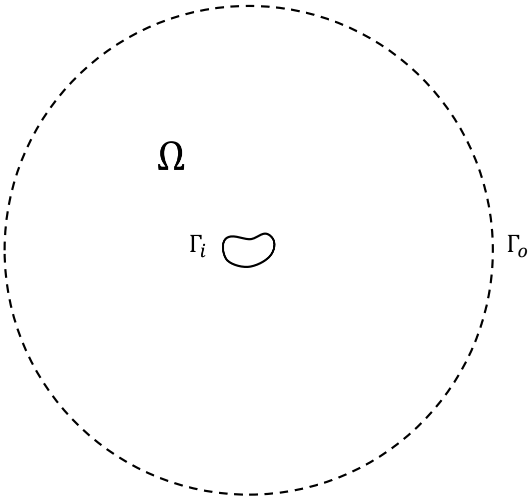

Figure II.2: A top view of the domain Ω, the far field boundary Γ_o, and the cathode boundar Γ_i

electrolyte surface, we are only interested in analyzing the physical and chemical processes happening on this surface. Here, the intersection of the electrode and the electrolyte is the TPB. Let Ω be the domain of our problem, which is the surface with the outer boundary (dashed curve) being the far field with radius r_f, and the inner boundary (perimeter of the kidney-shaped object) being the intersection of the electrode and electrolyte surfaces. Let Γ_o be the outer boundary, and Γ_i be inner boundary. Γ_o would not necessarily have to be circular, but it has to be far enough from the particle so that there is no oxygen flux passing through it. Figure II.2 gives a top view of the domain. Notice that this process is in steady-state.

Looking at this process from a chemistry perspective, it can be broken down to the following reaction steps:

$$\begin{aligned} \frac{1}{2}\mathrm{O}_2 &\rightleftharpoons \mathrm{O}, \\ \mathrm{O} + 2\mathrm{e}^- &\rightleftharpoons \mathrm{O}^=. \end{aligned}$$

In order to analyze this process in greater detail, it is necessary to assume that certain steps are rate determining. In this specific project, two cases are discussed, with the first serving as a limiting case of the second. The first case is relatively straightforward: the second reaction is assumed to be rate determining, and a mathematical model is built based on that. Being parameterized, the second case is more complicated.

II.1 Fast Surface Transport

In this case, the second reaction is assumed to be rate determining. The first reaction could occur anywhere in Ω, as it is simply the adsorption process of oxygen. The second reaction cannot occur until the oxygen atoms reach the TPB, because the electrode is the only source of electrons in this system. In this reaction, each oxygen atom receives two electrons and becomes an oxygen ion. Notice that since this is the rate determining step, the chemical potential of the reactants and the product may be different. The oxygen current due to this potential difference can be modeled as an analogy of the Butler-Volmer equation. This classical equation gives an expression of current density as a function of the electrochemical potentials of reactants and products. After the second reaction, the oxygen ions move from the surface of the electrolyte to the interior of the electrolyte.

Let μ_X denote the electrochemical potential of substance X. Since the first and the third reactions are in equilibrium, it is safe to assume

$$\frac{1}{2}\mu_{\mathrm{O}_2} = \mu_{\mathrm{O}}.$$

Based on this assumption, the electrochemical potentials of the reactants (u) and the electrochemical potential product (v) for the second reaction could be defined:

$$\begin{aligned} u &:= \begin{cases} \frac{1}{2}\mu_{\mathrm{O}_2} & \text{(gas phase)} \\ \mu_{\mathrm{O}} & \text{(electrolyte surface)} \end{cases}, \\ v &:= \mu_{\mathrm{O}^=} \quad \text{(electrolyte surface/electrolyte interior).} \end{aligned}$$

As discussed earlier, the relationship between u and v is then modeled by the Butler-Volmer equation:

$$j_F = \frac{j_0}{2}\left[\exp\left(\frac{\alpha_a F}{R_g T}\eta\right) - \exp\left(-\frac{\alpha_c F}{R_g T}\eta\right)\right], \tag{1}$$

where j_F is the oxygen current density, and j_0 is the exchange current density on Ω. α_a and α_c are the transfer coefficients of this reaction, whose values usually range between 0.2 and 2. They are kinetic parameters that help describe the process. As we assume this process is ideal, they are taken to be 1 throughout this project. R_g is the ideal gas constant. $\eta := (u - v)/F$ is the surface overpotential, a parameter that accounts for the potential difference of the reactants and the product [4].

Notice that equation (1) can be simplified into the following form:

$$j_F = j_0 \sinh\left(\frac{u - v}{R_g T}\right). \tag{2}$$

Also, since the second reaction is rate determining, it is safe to assume that the oxygen atoms exist in excess on the electrolyte surface. In Fehribach & O'Hayre [2], the current density is also expressed using the potential of the oxygen species on the surface:

$$-\nabla \cdot (\kappa_s \nabla v) = i_F, \tag{3}$$

where κ_s is the surface electrochemical conductance. However, the current density modeled in Ref. [2] is an electric current density. To find an expression for the oxygen current density, we need to convert κ_s into a quantity with an appropriate physical meaning. By applying an electrochemistry analysis, we have obtained the following equation for our specific problem.

$$-\nabla \cdot (\kappa \nabla v) = j_F, \tag{4}$$

where $\kappa := \kappa_s/2F$, and F represents the Faraday constant. In Fehribach & O'Hayre [2], $\kappa_s := \sigma_s/2F$, where σ_s is the surface electrical conductance. Therefore, in our case, $\kappa := \sigma_s/4F^2$.

Thus, the following partial differential equation (PDE) system could be formulated:

$$-\nabla \cdot (\kappa \nabla v) = j_0 \sinh\left(\frac{u-v}{R_g T}\right),\ \mathbf{x} \in \Omega, \tag{5}$$

$$u = u_0,\ \mathbf{x} \in \Gamma_o, \tag{6}$$

$$v = v_0,\ \mathbf{x} \in \Gamma_i. \tag{7}$$

This model reflects the physical situation well, as the PDE describes the oxygen flux in the domain, while the boundary conditions matching with the corresponding potentials indicates that the system is in equilibrium. This case is less interesting and is not considered in detail in this study.

II.2 Parameterized Surface Transport

The problem becomes more interesting without assuming fast transportation. Thus, there may or may not be a sufficient amount of oxygen atoms on the surface of the electrolyte. The analysis is based on the first case, with the electrochemical potential of oxygen in different phases as parameters.

Define the following electrochemical potentials:

$$\begin{aligned} u &:= \tfrac{1}{2}\mu_{\mathrm{O}_2} \quad \text{(gas phase)} \ , \\ w &:= \mu_{\mathrm{O}} \quad \text{(electrolyte surface)} \ , \\ v &:= \begin{cases} \mu_{\mathrm{O}^=} & \text{(electrolyte surface)} \\ \mu_{\mathrm{O}^=} & \text{(electrolyte)} \end{cases} \ . \end{aligned}$$

In this model, we assume that the distribution of oxygen molecules in gas phase is uniform. The electrochemical potential of the oxygen molecules would then be a constant everywhere in the gas. So, $u = u_0$, while u_0 is an arbitrary constant. Similarly, after the second reaction, the oxygen ions would move into the electrolyte directly. The electrochemical potential of $\mathrm{O}^=$ ions would then be some constant v_0 in the electrolyte.

Using the derivation in the first case, the following Poisson Equation can be constructed:

$$-\nabla \cdot (\kappa \nabla w) = j_0 \sinh\left(\frac{u_0 - w}{R_g T}\right), \ \mathbf{x} \in \Omega, \tag{8}$$

where the function on the right is a source term that reflects the flow of oxygen. As shown in the equation, it is a function of the potential difference between the oxygen gas and the oxygen on the surface. For this equation to be physically meaningful, j_0 is non-negative.

Physically, this difference should vanish when arbitrarily far from the origin. Since Γ_o is the far field where there is no flux of oxygen atoms,

$$\partial_n w = 0, \ \mathbf{x} \in \Gamma_o. \tag{9}$$

On Γ_i, the second reaction occurs. Similar to the fast surface transport case, the curreny desity, or the oxygen flux pointing out from Ω, can be expressed using the

Butler-Volmer equation. Thus, the corresponding boundary condition is

$$\kappa \partial_n w = -i_0 \sinh\left(\frac{w - v_0}{R_g T}\right), \ \mathbf{x} \in \Gamma_i, \tag{10}$$

where i_0 is the oxygen current density on the boundary. Similarly, i_0 is non-negative. Figure II.3 gives a visualization of the problem set-up.

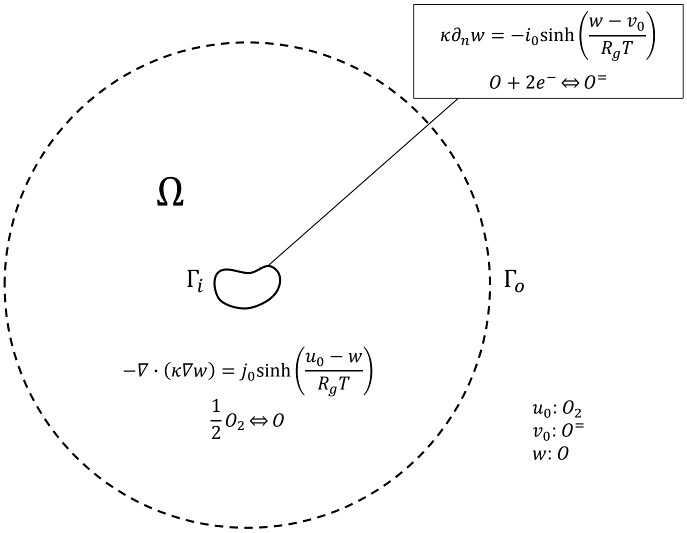

Figure II.3: Correspondence of equations (11)-(13) to the model domain of this problem

Notice that, when the j_0 is large enough in comparison to i_0, this model should give the same solution as the Fast Transport model. This model is more interesting not only because of the more general approach, but also due to the fact that, at first glance, it is unclear whether this PDE system has a solution. Therefore, we decided to examine the existence and uniqueness of the solution in the next section.

III Existence and Uniqueness of the Solution

Before attempting to solve the PDE system in the parameterized surface transport case, it is necessary to discuss the existence and uniqueness of the solution to the most generic form of the problem. This problem has a unique solution. To show existence of a solution, we first prove that the energy functional corresponding to this problem has a minimizer. Then, using the Dirichlet principle, it can be shown that any minimizer of the energy function is a solution to the proposed problem. The uniqueness of the solution can be proved using Green's identities. To make the discussion as simple as possible, the problem can be non-dimensionalized. Let $x = lX$, $y = lY$, $w = R_gTW$, and $u_0 = R_gTU_0$; then the non-dimensionalized form of the problem is:

$$-\triangle W = J_0 \sinh(U_0 - W), \mathbf{x} \in \Omega, \tag{11}$$

$$\partial_n W = 0, \mathbf{x} \in \Gamma_o, \tag{12}$$

$$\partial_n W = -I_0 \sinh(W - V_0), \mathbf{x} \in \Gamma_i, \tag{13}$$

where $J_0 = \frac{j_0 l^2}{\kappa R_g T}$ and $I_0 = \frac{i_0}{\kappa R_g T}$. For simplicity, lower case letters are used in the following analysis.

III.1 Existence of Energy Minimizer

Consider a functional $I[w] = \int_\Omega L(D(w(x)), w(x), x)dx$. Then the expression L in the integral can be parameterized as $L(p, z, x)$. One way to show that it has a minimizer is to apply the following theorem.

Theorem III.1 (Existence of Minimizer [5])**.** *Assume that L satisfies the coercivity condition and is convex in the variable p. Suppose also the set of admissible functions*

A is nonempty. Then there exists at least one function $u \in A$ solving

$$I[u] = \min_{w \in A} I[w]. \tag{14}$$

Notice that this theorem requires $I[\cdot]$ to be coercive and $L(p, z, x)$ to be convex with respect to p. Therefore, we will now introduce coercivity and convexity.

Suppose $q \in (1, \infty)$ is fixed, and there exist constants $\alpha > 0, \beta \geq 0$ such that $L(p, z, x) \geq \alpha |p|^q - \beta$ for all $p \in \mathbb{R}^n, z \in \mathbb{R}, x \in U$. Then, $I[w] \geq \alpha ||Dw||^q{}_{L^q(U)} - \gamma$ for $L(Dw, w, x)$. This is called the *coercivity* condition on $I[\cdot]$[5]. It is clear that functionals that satisfy the coercivity condition are bounded below.

Another important property is the convexity of $L(p, z, x)$ with respect to p. A function $f : D \to (-\infty, \infty)$ is *convex* if given $a \in [0, 1]$, $f[au + (1 - a)v] \leq af(u) + (1 - a)f(v)$ for all $u, v \in D$. According to Evans [5], if the mapping $p \to L(p, z, x)$ is convex for any $z \in \mathbb{R}^n$ and $x \in \Omega$, then $I[\cdot]$ is weakly lower semicontinuous on $W^{1,q}(\Omega)$. The lower semicontinuity ensures that I attains its infimum, given that it is bounded below.

Define $f(w) := j_0 \sinh(u_0 - w)$ and $g(w) := -i_0 \sinh(w - v_0)$. Accordingly, let $F(w) := \int_0^w f(\tilde{w}) d\tilde{w} = -j_0 \cosh(u_0 - w) + j_0$, and $G(w) := \int_0^w g(\tilde{w}) d\tilde{w} = -I_0 \cosh(w - v_0) + i_0$. Then, the energy functional for our problem is

$$I[w] = \frac{1}{2} \int_\Omega |\nabla w|^2 - \int_\Omega F(w) - \int_{\Gamma_i} G(w).$$

Notice that $I[w]$ could only be applied to functions that satisfy the boundary condition equations (12)-(13). To get the corresponding $L(Dw, w, x)$, we need to find an equivalent functional over the domain. Especially, it is necessary to express the last term in the energy functional as an integral over an area instead of a line integral.

Consider extending the domain inward. In the modeling section, Γ_i is defined to an arbitrary shape; it needs to be a closed smooth curve of finite length and a curvature bounded above. Define the extended inner boundary, Γ_ϵ, as a closed curve bounded by Γ_i, such that $dist(x, \Gamma_\epsilon) = \epsilon$ for some $\epsilon > 0$ and all $x \in \Gamma_i$, where ϵ is less than the radius of curvature at any $x \in \Gamma_i$, and there is no oxygen flux on Γ_ϵ. Notice that we can form an one-to-one correspondence of the points on Γ_i and Γ_ϵ based on this definition. Denote the extended part of the domain as Ω_ϵ. For this system to be stationary, we get the following using the divergence theorem:

$$\int_{\Omega_\epsilon} \triangle w_\epsilon = \int_{\Gamma_i} -g(w),$$

where w_ϵ is the oxygen electrochemical potential in the extended domain. Specifically, $w_\epsilon = w$ on Γ_i. Therefore, this extended problem is equivalent to the original problem we were considering in the original domain.

Define the one-to-one correspondence such that for any two corresponding points $x \in \Gamma_i$ and $y \in \Gamma_\epsilon$, $dist(x, y) = \epsilon$. Then, the integral of $\triangle w_\epsilon$ over the line segment between x and y equals to $g(w(x))$. Using w^* to express the oxygen electrochemical potential in $\Omega \bigcup \Omega_\epsilon$, the corresponding energy functional for the extended problem is

$$\begin{aligned} I[w^*] &= \frac{1}{2} \int_{\Omega \bigcup \Omega_\epsilon} |\nabla w^*|^2 - \int_{\Omega \bigcup \Omega_\epsilon} F^*(w^*) \\ &= \frac{1}{2} \int_{\Omega \bigcup \Omega_\epsilon} |\nabla w^*|^2 - \int_{\Omega} F(w) - \int_{\Omega_\epsilon} F^*(w_\epsilon), \end{aligned}$$

where $F^*(w^*)$ is the integral of the source term over $\Omega \bigcup \Omega_\epsilon$. Since f^* is bounded and Ω_ϵ is bounded, $\int_{\Omega_\epsilon} F^*(w_\epsilon)$ is finite. Therefore, $I[w^*]$ is coercive. Since it is also convex with respect to ∇w^*, $I[w^*]$ has a minimizer.

III.2 Existence of A Solution

By the Dirichlet principle, among all the functions that satisfy the given boundary conditions, the minimum of the energy functional is attained by the solutions of the given PDE system [6].

To see this more clearly, suppose w_1 is a solution of equations (11)-(13), and w_2 is any function that satisfies the boundary conditions of the PDE system. In other words,

$$\begin{aligned}
-\triangle w_1 = J_0 \sinh(u_0 - w_1), &\qquad \mathbf{x} \in \Omega, \\
\partial_n w_1 = 0, &\qquad \mathbf{x} \in \Gamma_o, \\
\partial_n w_1 = -I_0 \sinh(w_1 - v_0), &\qquad \mathbf{x} \in \Gamma_i,
\end{aligned}$$

$$\begin{aligned}
\partial_n w_2 = 0, &\qquad \mathbf{x} \in \Gamma_o, \\
\partial_n w_2 = -I_0 \sinh(w_2 - v_0), &\qquad \mathbf{x} \in \Gamma_i.
\end{aligned}$$

Let $\omega := w_1 - w_2$, then

$$\begin{aligned}
I[w_2] &= \frac{1}{2}\int_\Omega |\nabla w_2|^2 - \int_\Omega F(w_2) - \int_{\Gamma_i} G(w_2), \\
&= \frac{1}{2}\int_\Omega |\nabla w_1|^2 + \frac{1}{2}\int_\Omega |\nabla \omega|^2 - \int_\Omega \nabla w_1 \cdot \nabla \omega \\
&\qquad - \int_\Omega F(w_1 - \omega) - \int_{\Gamma_i} G(w_1 - \omega).
\end{aligned}$$

By Green's first identity,

$$\begin{aligned}
= I[w_1] + \frac{1}{2}\int_\Omega |\nabla \omega|^2 + \int_\Omega (F(w_1) - F(w_1 - \omega)) + \int_{\Gamma_i} (G(w_1) - G(w_1 - \omega)) \\
- \int_\Omega \omega f(w_1) - \int_{\Gamma_i} \omega g(w_1).
\end{aligned}$$

By mean value theorem, for any point in the domain, there exist constants $c_1 \in (min(w_1 - \omega, w_1), max(w_1 - \omega, w_1))$, $c_2 \in (min(w_1 - \omega, w_1), max(w_1 - \omega, w_1))$ such that $F(w_1) - F(w_1 - \omega) = \omega f(c_1)$ and $G(w_1) - G(w_1 - \omega) = \omega g(c_2)$, so

$$= I[w_1] + \frac{1}{2}\int_\Omega |\nabla\omega|^2 + \int_\Omega \omega(f(c_1) - f(w_1)) + \int_{\Gamma_i} \omega(g(c_2) - g(w_1)).$$

When $\omega = 0$, it is clear that $I[w_2] = I[w_1]$.

When $\omega > 0$, we get $c_1, c_2 \leq w_1$. Since $i_0, j_0 \geq 0$, then $f(c_1) < f(w_1)$ and $g(c_2) < g(w_1)$.

When $\omega < 0$, we get $c_1, c_2 \geq w_1$. Since $i_0, j_0 \geq 0$, then $f(c_1) > f(w_1)$ and $g(c_2) > g(w_1)$.

In all these cases, we can conclude that $\int_\Omega \omega(f(c_1) - f(w_1)) \geq 0$ and $\int_{\Gamma_i} \omega(g(c_2) - G(w_1)) \geq 0$. Thus, $I[w_2] \geq I[w_1]$. Therefore, minimizers of the energy functional can only be solutions of equations (11)-(13).

III.3 Uniqueness of The Solution

As the existence of a solution is proven, we now explore whether the PDE system has a unique solution.

Suppose w_1, w_2 are solutions of the PDE system given in equations (11)-(13). By Green's First Identity, for any function $p \in C^1$,

$$\int_{\Gamma_i} p\nabla_n w_1 = \int_\Omega \nabla p \cdot \nabla w_1 + \int_\Omega p\triangle w_1, \tag{15}$$

$$\int_{\Gamma_i} p\nabla_n w_2 = \int_\Omega \nabla p \cdot \nabla w_2 + \int_\Omega p\triangle w_2. \tag{16}$$

Subtracting equation (16) from (15) and using the $f(w)$ and $g(w)$ defined in the last section, we get

$$\int_{\Gamma_i} p(g(w_1) - g(w_2)) - \int_\Omega p(f(w_2) - f(w_1)) = \int_\Omega \nabla p \cdot (\nabla w_1 - \nabla w_2).$$

Now, choose $p = w_1 - w_2$. The equation above becomes

$$\int_{\Gamma_i} (w_1 - w_2)(g(w_1) - g(w_2)) + \int_{\Omega} (w_1 - w_2)(f(w_1) - f(w_2)) = \int_{\Omega} |\nabla w_1 - \nabla w_2|^2.$$

It is clear that the right hand side of the equation is non-negative. Meanwhile, by definition, $f(w)$ and $g(w)$ are strictly decreasing, so both integrals on the left hand side are non-positive. So this equation holds if and only if both sides of the equation equal zero. To make the left hand side equal to zero, $w_1 = w_2$. Therefore, the solution to the PDE system is unique.

IV Computations

As mentioned before, this project is a continuation of a previous study [2]. One thing we are highly interested in is to compare the electrolyte pathway with the electrode surface pathway and electrode bulk pathway. To quantify the comparison, we would like to find the solution to the PDE system and compute the total current produced by the electrolyte surface pathway accordingly. The numerical computations for this project are completed using COMSOL Multiphysics, version 4.3.

IV.1 Parameters

Before attempting to find a solution, it is necessary to know the parameters as accurately as possible. For computation purposes, the following parameters are chosen.

Gas constant : $R_g = 8.314$ J/(mol·K)
Temperature : $T = 1223$ K
Faraday constant : $F = 96490$ C/mol
Surface electric conductance : $\sigma = 10^{-11}$ S
Surface overpotential : $\eta = 0.5$ V
Current density : $i_0 = 5 \times 10^{-4}$ A/m

Also, choose $u_0 = 0$ J/mol, then $v_0 = -2F\eta = -96490$ J/mol. As discussed in a previous section, $\kappa = \sigma/4F^2 = 2.69 \times 10^{-22}\ \mathrm{mol}^2/(\mathrm{J} \cdot \mathrm{s})$ [2].

All of the parameters above are either constants or typical values used for this reaction, except for σ. σ is obtained by taking a typical representative value of ionic conductivity for solid state electrolytes, which is 10^{-4} S/cm, and multiply it by a thickness representative of a surface pathway, which is about 1 nm. Therefore, we take $\sigma = 10^{-11}$ S.

Notice that the parameter j_0 is still yet to be determined. Unfortunately, there is no experimental data available for this. The following section discusses how a range for j_0 is found.

IV.2 Range for j_0

As mentioned before, this study is based on a previous research about two different reaction pathways, the electrode surface pathway and the bulk pathway [2]. To make the electrolyte surface pathway not negligible yet not dominant, the total resulting current from this pathway should be within, say, two orders of magnitude of the total current in either of the other two pathways. For the computation, an elliptical particle with major axis length 2.5 microns and minor axis length 1.32 microns to demonstrate versatility of the model. The choice of ellipse dimensions allows the perimeter of the ellipse to match the perimeter of the circular particle in the previous study [2]. The particle is chosen to not be particle to demonstrate the compatibility of the model with no annular symmetry.

In Fehribach & O'Hayre [2], it was computed that the nominal value of the total currents in the electrode surface pathway has an order of magnitude of 10^{-10} A. Also, the total current in the electrode bulk pathway is a constant, 3.5×10^{-10} A. For the electrolyte surface pathway, different j_0 values give very different computation results, and therefore the total current varies by j_0 greatly. For example, Figure IV.2.1 demonstrates the computed values of w, the solution to the PDE system (11)-(13), when $j_0 = 5 \times 10^{-8}\ \mathrm{mol/(s \cdot m^2)}$.

As shown in Figure IV.2.1, the outer circle represents the far field, Γ_o; and the inner ellipse represents the cathode particle, whose boundary is Γ_i. The electrochemical potential of oxygen species drops rapidly within about 5 microns of the electrode particle. To understand this solution better, notice that the oxygen atoms come from the source term of equation (8). The value of j_0 is proportional to the value of the source term. Therefore, when a relatively small j_0 value is chosen, less oxygen atoms

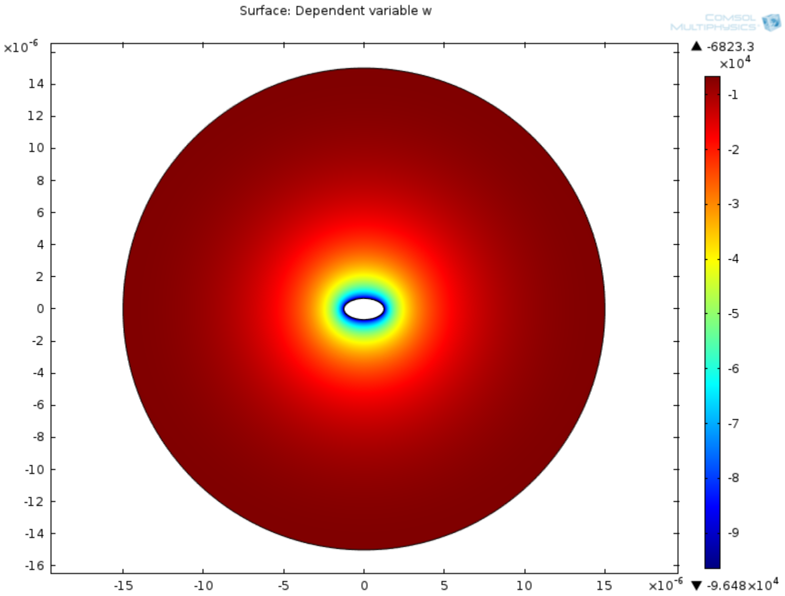

Figure IV.2.1: Solution with $j_0 = 5 \times 10^{-8}$ mol/(s $\cdot$ m^2). The corresponding total current is $I = 5.65 \times 10^{-11}$ A.

come into the domain. To ensure the continuation of the reaction at Γ_i, oxygen atoms are drawn from the area nearby the particle. If j_0 is small enough, such an effect would cause a rapid decrease in electrochemical potential around the electrode particle. The total oxygen current for $j_0 = 5 \times 10^{-8}$ mol/(s $\cdot$ m^2) is 2.93×10^{-16} mol/s; multiplying it by $2F$, we can obtain that the total electrical current is 5.65×10^{-11} A.

On the contrary, if the j_0 value is relatively large, as demonstrated in the following Figure IV.2.2, the solution to our problem is almost uniform, except for a small area right around Γ_i. The total current in this case is 2.95×10^{-6} A.

As mentioned before, we are looking for a range for j_0 such that the total current in the electrolyte surface pathway is within two orders of magnitude of the other two pathways. Since the total current of the other two pathways are both $\sim 10^{-10}$ A, the total current of the electrolyte surface pathway should have an order of magnitude between 10^{-12} and 10^{-8}. We found the corresponding j_0 range to be 5×10^{-12} to 5×10^{-2} mol/(s $\cdot$ m^2).

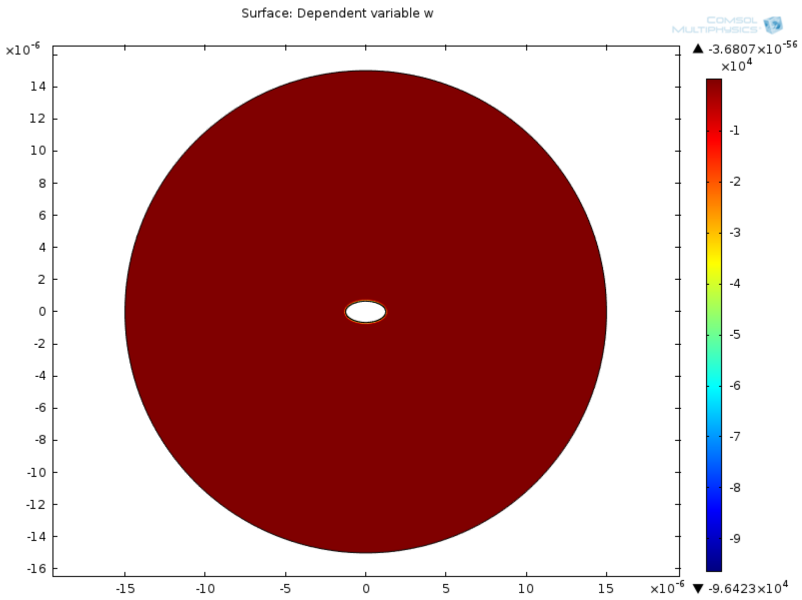

Figure IV.2.2: Solution with $j_0 = 5$ mol/(s $\cdot$ m^2). The corresponding total current is $I = 2.95 \times 10^{-6}$ A.

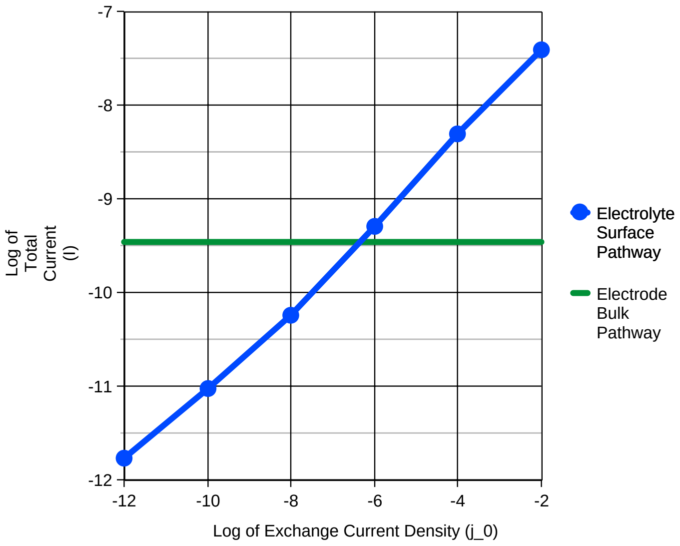

Figure IV.2.3: Log-log plot of j_0 versus I for the electrolyte surface pathway. The total current for the electrode bulk pathway is given as a comparison.

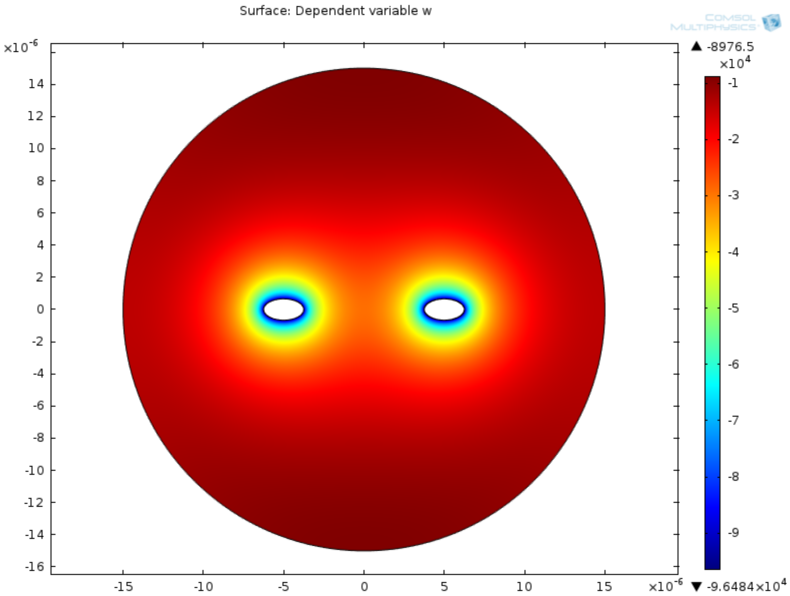

Figure IV.2.4: Solution for two particles with $j_0 = 5 \times 10^{-8}$ mol/(s · m^2). The corresponding total current is $I = 1.13 \times 10^{-10}$ A.

Figure IV.2.3 gives a plot of the surface exchange current density j_0 versus the total current I for the electrolyte surface pathway and the electrode bulk pathway over the range of j_0 we have chosen. For demonstration purposes, the x-axis is shifted to the left by $log_{10}5$. Notice that for the electrolyte surface pathway, j_0 and I seem to have a log-log linear relationship when j_0 is between 10^{-8} to 10^{-2} mol/(s · m^2). Since the I for the electrode bulk pathway is a constant, it is plotted as a reference value in this figure. As this has shown, give a specific j_0 value, we are able to determine whether the electrolyte surface pathway is dominant.

Meanwhile, we would like to point out that our model works for multiple particles as well. Figure IV.2.4 is a computation result for two elliptical particles, with their centers apart by 10 microns, and symmetrically located in the domain. The j_0 value is 10^{-8} mol/(s · m^2), and the corresponding total current is 1.13×10^{-10} A. Therefore, effects of various particle positions could be potentially studied.

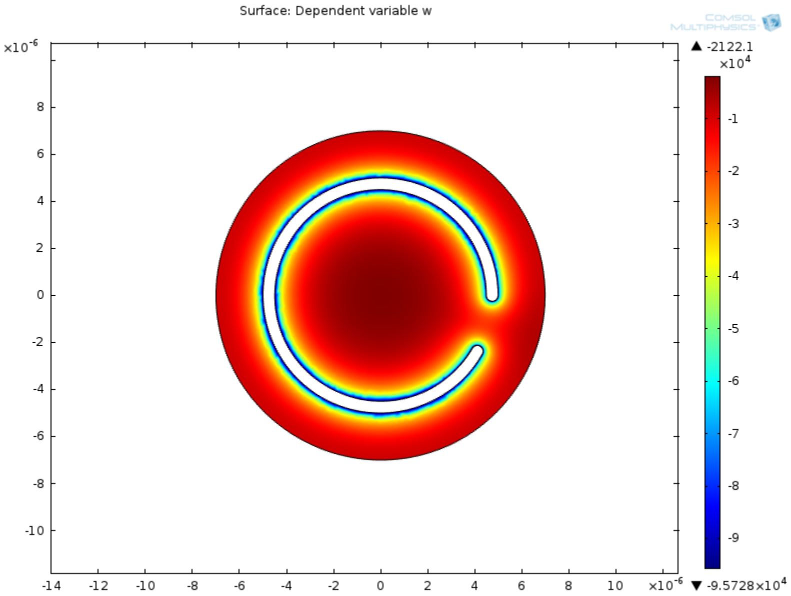

Figure IV.3.1: An counter example to the maximum principle. Notice that the maximum of the solution occurs as the center of the domain.

IV.3 Maximum Principle

The maximum principle states that the solution of a given PDE system always attain its maximum value on the boundary of the domain [6]. No maximum principle exists for this problem, as the following counter example shows. As shown in Figure IV.3.1, we have a thin, “C”-shaped particle. As discussed, the particle we are interested in is of an arbitrary shape that is not necessarily convex. This counter example makes use of this fact. In this case, the maximum for this specific geometry occurs at the center of the domain. This is because the area of the domain in the center is large enough so that an excess of oxygen atoms is adsorbed. In comparison, the domain on the side is relatively thin so that less oxygen atoms are available for the boundary reaction.

V Conclusion

In this project, we set up a model for the electrolyte surface pathway of the cathode reaction for SOFCs. Next, we examined two main aspects of the model: the existence and uniqueness of a solution, and a range for the surface exchange current density of YSZ. We proved the existence and uniqueness of a solution mathematically and we estimated a range of the unknown parameter with computational aids. With these analyses, we compared our results with a previous study, where this project emerged from.

There are several directions for future works on this topic. One topic could be a discussion of how realistic the determined range for j_0 is. This range is determined purely based on the comparison with the other two pathways, but no experimental data can be found to support this result. One could consider arguing physically to justify this range. Another topic for future work could be the analysis of the case with multiple particles in the domain. As the configuration differ, the total current is expected to change. It may be practical to examine how to maximize the total current.

References

[1] R. O'Hayre, S.-W. Cha, W. Colella, and F. B. Prinz. *Fuel Cell Fundamentals*. Wiley, New York, 2^{nd} edition, 2009.

[2] J. D. Fehribach and R. O'Hayre. Triple phase boundaries in solid-oxide cathodes. *SIAM J. Appl. Math.*, 70:510–530, 2009.

[3] J.Fleig. Solid oxide fuel cell cathodes: Polarization mechanisms and modeling of the electrochemical performance. *Annu. Rev. Mater. Res..*, 33:361–382, 2003.

[4] J. S. Newman and K. E. Thomas-Alyea. *Electrochemical Systems*. Wiley, Hoboken, NJ, 3^{rd} edition, 2004.

[5] L. Evans. *Partial Differential Equations*, volume 19 of *Graduate Studies in Mathematics*. AMS, Providence, RI, 1998.

[6] Walter A. Strauss. *Partial Differential Equations*. Wiley, 2nd edition, December 2007.