April 2006

The Second Electrolyte Wedge Problem

Kimberly M. Ware
Worcester Polytechnic Institute

Project Number: MA-JDF-0511

THE SECOND ELECTROLYTE WEDGE PROBLEM

A Major Qualifying Project Report:

submitted to the Faculty

of the

WORCESTER POLYTECHNIC INSTITUTE

in partial fulfillment of the requirements for the

Degree of Bachelor of Science

by

Kimberly M. Ware

Date: April 25, 2006

Approved:

Professor Joseph D. Fehribach, Major Advisor

Abstract

The Second Electrolyte Wedge problem studies diffusion-reaction-conduction processes associated with current production in a porous electrode. Two rate-determining reaction steps occur in this formulation - one in the electrolyte wedge and one at the electrolyte-solid interface. Existence and uniqueness of solutions to this problem are proven, and thus current density is proven to be finite. Numerical and asymptotic analysis are completed and expressions for the current density and total current produced by the electrolyte are given.

Executive Summary

The linear system depicted in the figure below describes diffusion, reaction, and conduction processes in three regions (gas, electrolyte, and solid) of a porous electrode. In two dimensions, a meniscus corner is formed by the joining of the three regions mentioned above at a single point. This corner forms a wedge of electrolyte, a structure found in many porous electrodes. One might suspect that a singularity in the current density occurs at the tip of the electrolyte wedge, but our analysis here will show that this is not the case. This system is motivated specifically by the Molten Carbonate Fuel Cell (MCFC), but it could apply to any electrode in which the gas, electrolyte, and solid regions form a wedge. When they are present, it is within such wedges that a large majority of the current of an electrode is produced, making the wedge an interesting portion on which to focus.

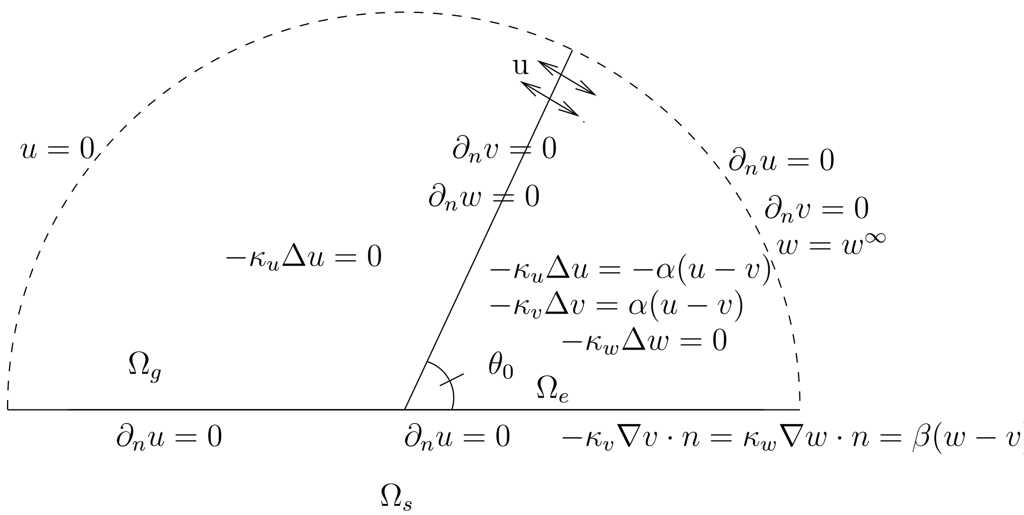

Figure 1: Domain for the EWP2 with the differential equations and boundary conditions describing it. On $\partial\Omega_{ge}$, the double arrows represent the conditions $u_g = u_e$ and $\kappa_u \nabla u \cdot n|_g = \kappa_u \nabla u \cdot n|_e$, i.e. both u and the flux in u are continuous across this interface.

In this system, let Ω_g denote the gas phase, Ω_e, the electrolyte phase, Ω_s, the solid phase, and $\Omega := \Omega_g \cup \Omega_e \cup \partial\Omega_{ge}$, the domain for the problem (all values are constant in Ω_s, so it is not part of the domain). The electrolyte wedge is represented by Ω_e. The angle between $\partial\Omega_{ge}$ and $\partial\Omega_{es}$, which represents the contact angle for this electrolyte meniscus, will be denoted by θ_0.

The system describes in terms of the component potentials u, v, and w a steady-state diffusion-reaction-conduction process associated with current production in the porous electrode. Oxidant (O_2 and CO_2) diffuses across the gas phase and into the electrolyte phase. In Ω_e, the oxidant continues to diffuse until the first of two rate-determining reaction steps occurs, and the oxidant component is transformed into the reactant component. The second of the rate-determining reaction steps occurs on the electrolyte-solid interface where the reactant is transformed into the current component (electrons and $CO_3^=$) which flows by conduction from the solid back through the electrolyte. The amounts of each of these components are goverened by their respective potentials.

In this problem, u, v, and w are defined below as linear combinations of electrochemical potentials. The oxidant component potential u and the flux in u are continuous across $\partial\Omega_{ge}$. The reactant potential, v, and the current potential, w, are defined only in Ω_e. The definitions used in this system describe all transport (diffusion and conduction) in terms of a generalized conduction. κ_u, κ_v, and κ_w denote the component conductivities for the oxidant, reactant, and current component potentials, respectively. α is the inverse charge-transfer resistance for the rate-limiting reaction in Ω_e, and β represents the same resistance for the rate-limiting reaction on $\partial\Omega_{es}$. Finally, w^∞ is the constant value of the current potential on $\partial\Omega_e$.

This system is an extension of the original Electrolyte Wedge Problem (EWP) discussed by Fehribach [4], and therefore it will be referred to as the *Second Electrolyte Wedge Problem* (EWP2). In the original problem, there was only one rate-determining step occurring on $\partial\Omega_{es}$, causing the oxidant and reactant component potentials to be equal. The asymptotics and numerics completed are similar to those in Fehribach [4], but proving existence and uniqueness and thus showing that the current density is finite require significantly more effort.

To establish existence and uniqueness of solutions for the system, it is helpful to first reformulate the problem in a way that is different from, but nonetheless equivalent to, the original problem. This will be completed in three steps. After this has been done, existence and uniqueness of solutions for the modified problem can be proven using variational techniques. For these purposes, the following definition for the energy associated with the modified problem is used:

$$E[\eta] := \int_\Omega \kappa_\eta |\nabla \eta|^2 + \alpha\eta^2 \; dx. \tag{1}$$

Then, the existence of a minimizer of (1) can be established by noting the *coercivity*, *convexivity*, and *weakly lower semicontinuity* of this energy. The existence of this minimizer in turn gives the existence of a solution to the problem. Uniqueness can similarly be proven using a classical technique. Finally, the solutions to the problem are explored using numerical approximations and matched asymptotics. Behavior of the component potentials is analyzed, and the following expression for the total current produced in the wedge is found based on the smallness of the contact angle and transport in the electrolyte region:

$$\begin{aligned} i_F &= \beta(w-v)/F \\ &= \frac{\beta w^\infty}{F\theta_0}\left[\theta_0 - \tan^{-1}\left(\frac{\tan(\theta_0)}{1+\epsilon/(\theta_0\beta r)}\right)\right] + O(\epsilon, \theta_0^2). \end{aligned} \tag{2}$$

This can be integrated to give the total current produced in the wedge,

$$\int_0^{r^\infty} i_F dr = \frac{\varepsilon w^\infty}{F\theta_0}\Bigg[R^\infty\left(\theta_0 - \tan^{-1}\left(\frac{\tan\theta_0}{1+1/(\theta_0 R^\infty)}\right)\right) + \frac{X_0 \sin\theta_0}{2}\ln\left(\left(\frac{R^\infty}{X_0}\right)^2 + 2R^\infty\theta_0 + 1\right) - X_0\cos\theta_0\left(\theta_0 - \tan^{-1}\left(\frac{\tan\theta_0}{1+R^\infty/(X_0\cos\theta_0)}\right)\right)\Bigg] + O(\epsilon^2, \theta_0^2), \tag{3}$$

where $R^\infty := r^\infty\beta/\varepsilon$. If one were to approximate the distribution in the electrode of the electrolyte wedges studied in this problem, then use that information along with the expression for the total current obtained, one could in principle approximate the total current produced by the entire electrode.

1 Introduction

Fuel cells are an important means of energy conversion, typically relying on a constant supply of fuel (hydrogen) and air (oxygen). As long as these supplies are maintained, a fuel cell can continue to produce energy almost indefinitely, making it an interesting device to study. Inside many fuel cell electrodes, a feature called a meniscus corner can form where the gas, electrolyte, and solid regions join along a single curve in three-space. Viewed in two dimensions, this corner forms a wedge of electrolyte. Since the diffusion pathways in this corner are arbitrarily short, one might suspect that the current density would be singular at the tip of the electrolyte wedge, but further analysis will show that this is not the case. This system is motivated specifically by the Molten Carbonate Fuel Cells (MCFC), but it could apply to any electrode in which the gas, electrolyte, and solid regions form a wedge. When they are present, it is within such wedges that a large majority of the current of an electrode is produced, making the wedge an interesting portion on which to focus.

The following linear system describes diffusion, reaction, and conduction processes in the three regions (gas, electrolyte, and solid) of a porous electrode.

$$
\begin{array}{lrcll}
(a) & -\kappa_u \triangle u & = & 0 & \text{in } \Omega_g\,, \\
(b) & -\kappa_u \triangle u & = & -\alpha(u-v) & \text{in } \Omega_e\,, \\
(c) & -\kappa_v \triangle v & = & \alpha(u-v) & \text{in } \Omega_e\,, \\
(d) & -\kappa_w \triangle w & = & 0 & \text{in } \Omega_e\,, \\
\\
(e) & \partial_n u & = & 0 & \text{on } \partial\Omega_{gs} \cup \partial\Omega_{es} \cup \partial\Omega_e,\,, \\
(f) & \partial_n v & = & 0 & \text{on } \partial\Omega_{ge} \cup \partial\Omega_e\,, \\
(g) & \partial_n w & = & 0 & \text{on } \partial\Omega_{ge}\,, \\
(h) & u & = & 0 & \text{on } \partial\Omega_g\,, \\
(i) & w & = & w^\infty & \text{on } \partial\Omega_e\,, \\
(j) & \multicolumn{3}{c}{-\kappa_v \nabla v \cdot n = \kappa_w \nabla w \cdot n = \beta(w-v)} & \text{on } \partial\Omega_{es}\,,
\end{array}
\qquad (1)
$$

In this system, let Ω_g denote the gas phase, Ω_e, the electrolyte phase, Ω_s, the solid phase, and $\Omega := \Omega_g \cup \Omega_e \cup \partial\Omega_{ge}$, the domain for the problem (all values are constant in Ω_s, so it is not part of the domain). The electrolyte wedge is represented by Ω_e. In this problem, the gas and electrolyte phases will be depicted side-by-side with the solid phase underneath them. The angle between $\partial\Omega_{ge}$ and $\partial\Omega_{es}$, which represents the contact angle for this electrolyte meniscus, will be denoted by θ_0.

This system is perhaps best understood in terms of the diagram in Figure 1. It describes in terms of the component potentials u, v, and w a steady-state diffusion-reaction-conduction process associated with current production in the porous electrode. Oxidant (O_2 and CO_2) diffuses across the gas phase and into the electrolyte phase. In Ω_e, the oxidant continues to diffuse until the first of two rate-determining reaction steps occurs, and the oxidant component is transformed into the reactant component. The second of the rate-determining reaction steps occurs on the electrolyte-solid interface where the reactant is transformed into the current component (electrons and $CO_3^{=}$) which flows by conduction from the solid back through the electrolyte. The amounts of each of these components are goverened by their respective potentials.

In this problem, u, v, and w are defined below as linear combinations of electrochemical potentials. The oxidant component potential u and the flux in u are continuous across $\partial\Omega_{ge}$. The reactant potential, v, and the current potential, w, are defined only in Ω_e. The definitions used in this system describe all transport (diffusion and conduction) in terms of a generalized conduction. κ_u, κ_v, and κ_w denote the component conductivities for the oxidant, reactant, and current component potentials, respectively. α is the inverse charge-transfer resistance for the rate-limiting reaction in Ω_e, and β represents the same resistance for the rate-limiting reaction on $\partial\Omega_{es}$. Finally, w^∞ is the constant value of the current potential on $\partial\Omega_e$. All of these quantities are more completely defined below.

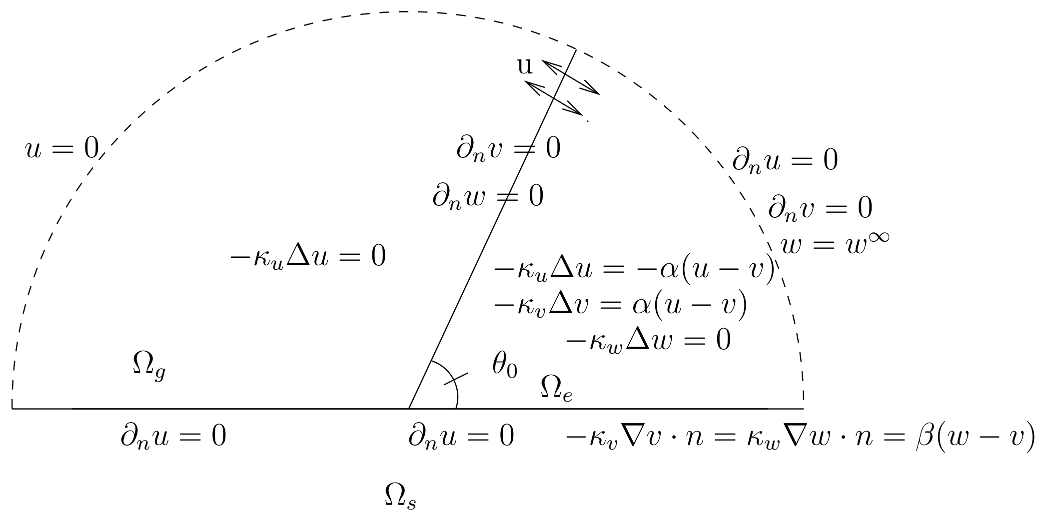

Figure 1: Domain for the EWP2 with the differential equations and boundary conditions describing it. On $\partial\Omega_{ge}$, the double arrows represent the conditions $u_g = u_e$ and $\kappa_u \nabla u \cdot n|_g = \kappa_u \nabla u \cdot n|_e$, i.e. both u and the flux in u are continuous across this interface.

System (1) is an extension of the original Electrolyte Wedge Problem (EWP) discussed by Fehribach [4], and therefore (1) will be referred to as the *Second Electrolyte Wedge Problem* (EWP2). In the original problem, there was only one rate-determining step occurring on $\partial\Omega_{es}$, causing the oxidant and reactant component potentials to be equal. The asymptotics and numerics present here are similar to those in Fehribach [4], but proving existence and uniqueness and thus showing that the current density is finite require significantly more effort.

The next section of this paper describes in detail the reactions considered in this study and uses them to define the three component potentials. Related parameters are also defined in this section. Particularly, specific definitions for the conductivites and the charge-transfer resistances are given. Section 3 describes two modifications to the EWP2 and establishes their equivalence to (1). These modifications make easier the proof of existence and uniqueness of solutions to (1). The fourth section begins with a theorem which asserts the existence and uniqueness of the problem described in Section 3. To prove this theorem, an auxilary problem is defined, and several lemmas are introduced. Section 5 presents numerical computations completed using Femlab, and section 6 uses the technique of matched asymptotics to approximate a solution to the system. An outer and inner solution are found, which are then matched to yield a uniform solution to the problem. Finally, an expression for the current density within the wedge is obtained.

2 Component Potentials and Related Parameters

The component potentials, u, v, and w, used in the EWP2 can be defined using any one of the reaction mechanisms found in Molten Carbonate Fuel-Cell (MCFC) cathodes. For instance, Fehribach, *et al.* [5] use definitions based on superoxide and superoxide-peroxide mechanisms. Makkus, *et al.* [7] give another example of a formulation using the superoxide-peroxide mechanism. Here our component potential definitions are based solely on the peroxide mechanism.

In MCFC cathodes, the overall half reaction is $\mathrm{O_2} + 2\mathrm{CO_2} + 4e^- \rightleftharpoons 2\mathrm{CO_3^=}$. In the peroxide mechanism, this half reaction is accomplished in 5 steps:

$$\begin{array}{llcl} (a) & \mathrm{CO_2}(g) & \rightleftharpoons & \mathrm{CO_2}(e) \\ (b) & \mathrm{O_2} + 2\mathrm{CO_3^=} & \rightleftharpoons & 2\mathrm{O_2^=} + 2\mathrm{CO_2}(e) \\ (c) & \mathrm{O^=} + \mathrm{CO_2}(e) & \rightleftharpoons & \mathrm{CO_3^=} \\ (d) & \mathrm{O_2^=} + e^- & \rightleftharpoons & \mathrm{O^=} + \mathrm{O^-} \\ (e) & \mathrm{O^-} + e^- & \rightleftharpoons & \mathrm{O^=} \end{array} \qquad (2)$$

(2b-e) are electrochemical reactions, while (a) is a physical transition, where carbon dioxide crosses the boundary between the gas and electrolyte phases. Figure 2 shows the steps described in (2). In this figure, dots represent reactions, arrows give the direction of the mechanism, and dashed lines represent boundaries between the three phases. The current-carriers of the mechanism are boxed and the carbonate ions that continue to the next cycle are circled.

Some of these steps occur very quickly, so that the reactions are in equilibrium. Steps (2c) and (2d), however, are the slow, rate-determining reaction steps. When (2) is in equilibrium, a series of equations representing the reaction steps and using electrochemical potentials can be written as follows:

$$\begin{array}{rcl} \mu_{\mathrm{O_2}} + 2\mu_{\mathrm{CO_2}(g)} & = & \mu_{\mathrm{O_2}} + 2\mu_{\mathrm{CO_2}(e)} \\ & = & 2\mu_{\mathrm{O_2^=}} - 2\mu_{\mathrm{CO_3^=}} + 4\mu_{\mathrm{CO_2}(e)} \\ \hline & = & 2\mu_{\mathrm{O_2^=}} - 4\mu_{\mathrm{O^=}} + 2\mu_{\mathrm{CO_3^=}} \\ \hline & = & -2\mu_{\mathrm{O^=}} + 2\mu_{\mathrm{O^-}} - 2\mu_{e^-} + 2\mu_{\mathrm{CO_3^=}} \\ & = & -4\mu_{e^-} + 2\mu_{\mathrm{CO_3^=}} \end{array} \qquad (3)$$

These equations can be traced on the diagram in Figure 2 by moving from the oxidant side on the left to the current side on the right. In this series, each equal sign represents

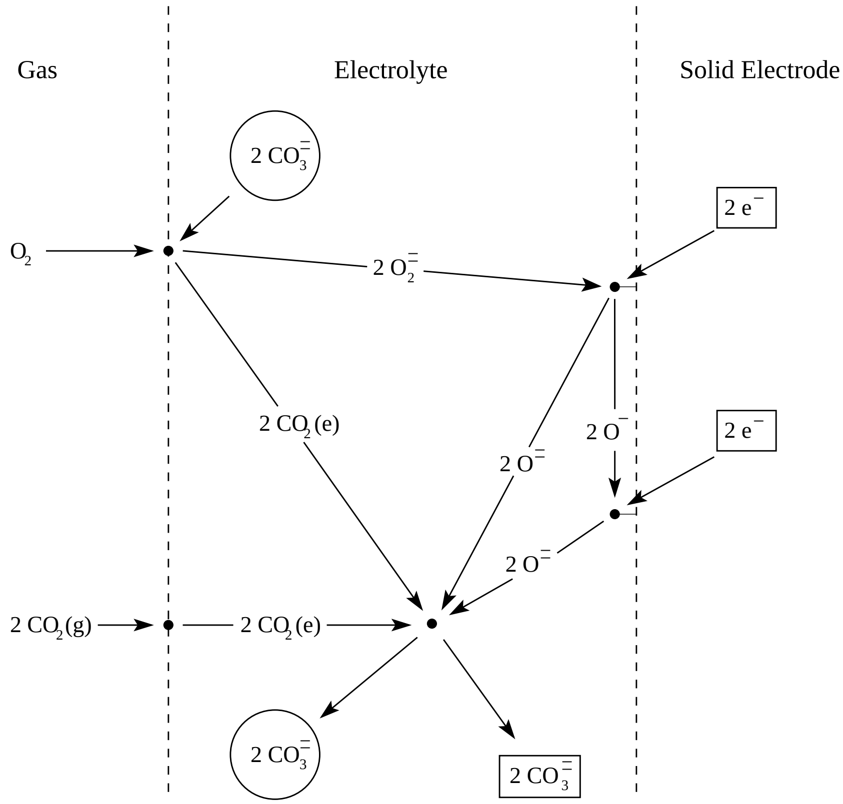

Figure 2: Net cycle diagram for the peroxide mechanism from Fehribach [4]

one reaction step. The lines represent the divisions between the three sides of the rate-determining reaction steps, (2c) and (2d). Everything above the first line, in between the two lines, and below the third line is always in equilibrium. However, it is only when the entire mechanism is in equilibrium that the three sections are equivalent. In nonequilibrium, one can define the three component potentials.

$$\begin{array}{rcccl} u & := & \mu_{ox} & := & \mu_{O_2} + 2\mu_{CO_2(g)} = 2\mu_{O_2^=} - 2\mu_{CO_3^=} + 4\mu_{CO_2(e)} \\ v & := & \mu_r & := & 2\mu_{O_2^=} - 4\mu_{O^=} + 2\mu_{CO_3^=} \\ w & := & \mu_c & := & -4\mu_{e^-} + 2\mu_{CO_3^=} \end{array} \qquad (4)$$

The oxidant potential, u, is the component above the first horizontal line in (3). The reactant potential, v, is the component in between the two lines, and the current potential, w, is the component below the second line. Note that u is defined separately in the gas and electrolyte phases, but these two combinations are always in equilibrium on $\partial\Omega_{ge}$. The *Second Electrolyte Wedge Problem* describes what happens when the mechanism is not in equilibrium and the rate-determining steps result in jumps between u, v, and w.

This formulation of component potentials is equivalent to the more traditional concentration formulation, as proven in Fehribach [4]. However, it was chosen because it is more appropriate for studying the production of current in an electrolyte wedge since it results in only the essential dependent variables.

The current density produced at the electrolyte-solid interface is given by the Butler-Volmer equation, as is shown in [9]:

$$i_F = i_0 \left[\exp\left(\frac{\beta_a F}{R_g T}\eta_s\right) - \exp\left(-\frac{\beta_c F}{R_g T}\eta_s\right) \right], \tag{5}$$

where $\eta_s := (w - v)/F$ is the surface overpotential, R_g is the gas constant, T is temperature, and β_a and β_c are the anodic and cathodic transfer coefficients on $\partial\Omega_{es}$. For this discussion, however, the linear form of the equation will be used:

$$i_F = \frac{i_0(\beta_a + \beta_c)}{R_g T}(w - v). \tag{6}$$

Defining $\beta := i_0(\beta_a + \beta_c)F/R_g T$, one has $i_F F = \beta(w - v)$. A similar derivation for α can be completed using α_a and α_c, the anodic and cathodic transfer coefficients in Ω_e, which results in the definition:

$$\alpha := i_0(\alpha_a + \alpha_c)F/R_g T. \tag{7}$$

The component conductivities κ_u and κ_v in Ω_e are defined to be

$$\kappa_u = \kappa_v := nF^2\rho \left(\sum_k \frac{(s_k)^2}{\kappa_k} \right)^{-1}, \tag{8}$$

where $k = \mu_{O_2^=}$, $\mu_{CO_3^=}$, and $\mu_{CO_2(e)}$ in the case of κ_u, and $k = \mu_{O_2^=}$, $\mu_{O^=}$, and $\mu_{CO_3^=}$ in the definition of κ_v. Also, ρ is the density, s_k is a stoichiometric constant associated with species k, and κ_k is the conductivity associated with species k (which can be written in terms of the diffusivity of species k where appropriate). A more thorough discussion and motivations for these definitions are given in Fehribach [4].

3 Equivalent Problem

To establish existence and uniqueness of solutions for (1), which will be addressed in the next section, it is helpful to first reformulate the problem in a way that is different from, but nonetheless equivalent to, the original problem. This will be completed in two steps. Consider first the problem shown in Figure 3. This is the same as the original diagram in Figure 1, except Ω_e has been separated into two regions, one denoted by Ω_2 in which u and v are defined and the other by Ω_4 in which w is defined. These two regions are now connected by a rectangular strip, denoted by Ω_3 and with width δ, which corresponds to $\partial\Omega_{es}$. The equation within this region is defined based on the boundary condition for the reaction between the reactant and current potentials given by (1j), and their equivalence is explained by the following heuristic argument.

The technique used here for expanding an interface into a region, a well-known tool in numerical analysis, yields a problem equivalent to (1). Note that because of the narrowness of the strip, $-\beta\delta\triangle w = 0$ implies $w_{yy} \simeq 0$ in Ω_3. Thus w can approximately be written

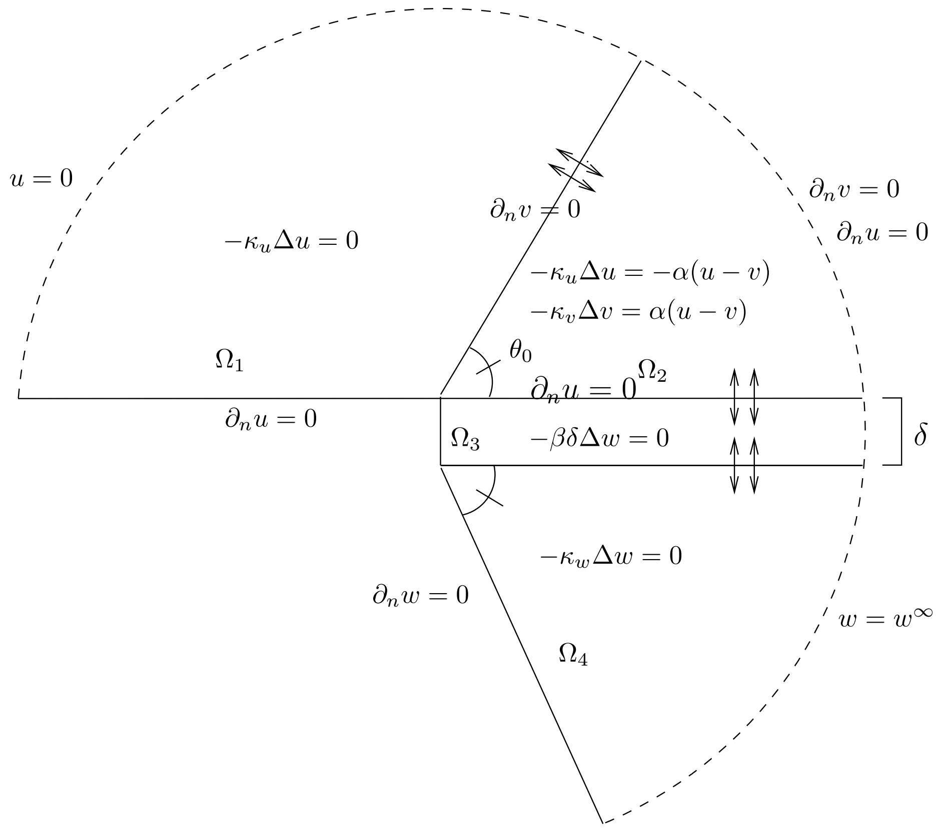

Figure 3: Domain for the intermediate unfolded problem with the differential equations and boundary conditions describing it.

as $w \simeq \gamma y + w_0$. Then, since the flux in w is continuous across $\partial\Omega_{23}$, $-\kappa_w \nabla w \cdot n|_2 = \beta\delta\nabla w \cdot n|_3 \simeq \beta\delta\gamma$. This gives the expression $\gamma \simeq \frac{-\kappa_w \nabla w \cdot n}{\beta\delta}$. Thus, $w \simeq \frac{-\kappa_w \nabla w \cdot n}{\beta\delta} y + w_0$. When $y = \delta$, $w_\delta \simeq \frac{-\kappa_w \nabla w \cdot n}{\beta} + w_0$, which gives us $-\kappa_w \nabla w \cdot n \simeq \beta(w_\delta - w_0)$. Also, in the limit as $\delta \to 0$, $-\kappa_v \nabla v \cdot n|_e = \kappa_w \nabla w \cdot n|_e$. Therefore, $-\kappa_v \nabla v \cdot n = \kappa_w \nabla w \cdot n \simeq \beta(w - w_0)$, and since $w_0 = v$ the original condition on $\partial\Omega_{es}$, given by (1j) is obtained. Thus, this formulation of the problem is equivalent to problem (1).

The second step is another reformulation of the problem which provides more consistency among the regions. Consider the problem given by (9) and shown graphically in Figure 4. In this system, u and v have been extended so that they are defined in all regions. This is helpful for further analysis of the problem as well as for numerical approximations. To correspond to the original system (1), let $\alpha := 0$ in Ω_1, Ω_3, and Ω_4, and $\kappa_v := \kappa_w$ in Ω_4. To simplify notation, let us now rename w in Ω_4 as v so that the new equation $-\kappa_v \triangle v = \alpha(u - v)$ is the same as the previous equation in w (1d). Furthermore, a small diffusivity of ϵ has been employed to allow u to be extended into Ω_3 and Ω_4 and v to be extended into Ω_1. This use of ϵ is justified below. All of the changes result in the following system:

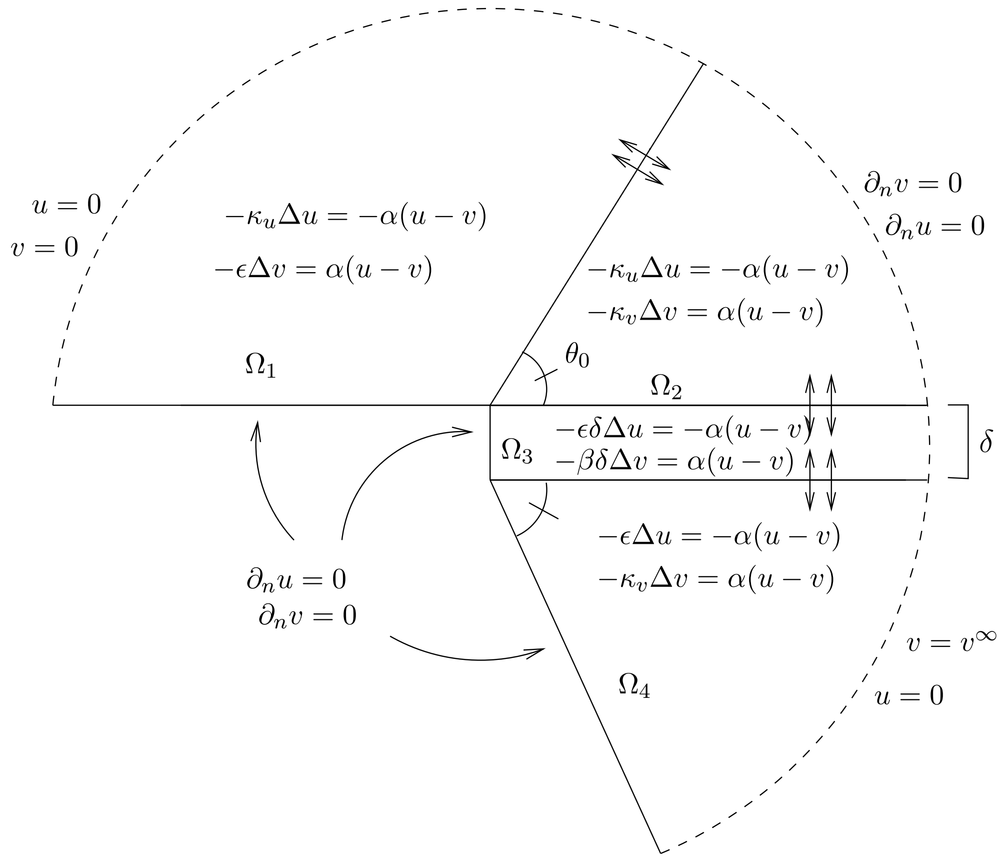

Figure 4: Domain for the unfolded problem with the differential equations and boundary conditions describing it.

$$
\begin{array}{lrcll}
(a) & -\kappa_u \triangle u & = & -\alpha(u-v) & \text{in } \Omega_1 \cup \Omega_2\,, \\
(b) & -\kappa_v \triangle v & = & \alpha(u-v) & \text{in } \Omega_2 \cup \Omega_4\,, \\
(c) & -\epsilon \triangle u & = & -\alpha(u-v) & \text{in } \Omega_4\,, \\
(d) & -\epsilon \triangle v & = & \alpha(u-v) & \text{in } \Omega_1\,, \\
(e) & -\epsilon\delta \triangle u & = & -\alpha(u-v) & \text{in } \Omega_3\,, \\
(f) & -\beta\delta \triangle v & = & \alpha(u-v) & \text{in } \Omega_3\,, \\
 & & & & \\
(g) & u & = & 0 & \text{on } \partial\Omega_1 \cup \partial\Omega_4, \\
(h) & \partial_n u & = & 0 & \text{on } \partial\Omega_2 \cup \partial\Omega_{14} \cup \partial\Omega_3\,, \\
(i) & \partial_n v & = & 0 & \text{on } \partial\Omega_2 \cup \partial\Omega_{14} \cup \partial\Omega_3\,, \\
(j) & v & = & v^\infty & \text{on } \partial\Omega_4\,, \\
(k) & v & = & 0 & \text{on } \partial\Omega_1\ .
\end{array}
\tag{9}
$$

Regarding the introduction of ϵ, notice that, on $\partial\Omega_{12}$, $-\epsilon\nabla v \cdot n|_g = -\kappa_v \nabla v \cdot n|_e$. Taking the limit as $\epsilon \to 0$ forces $\kappa_v \nabla v \cdot n = 0$ on $\partial\Omega_{12}$. Since $\kappa_v \neq 0$, $\nabla v \cdot n = 0$ on this boundary, and v in Ω_1 becomes irrelevant to v in Ω_2. Similarly, noting the boundary condition

$-\kappa_u \nabla u \cdot n|_e = -\epsilon\delta \nabla u \cdot n|_s$ on $\partial\Omega_{23}$, and taking the limit as $\epsilon \to 0$, gives $-\kappa_u \nabla u \cdot n = 0$ on $\partial\Omega_{23}$. Thus, $\nabla u \cdot n = 0$ on this boundary and u in Ω_3 and Ω_4 becomes irrelevant to u in Ω_2. Finally, noting that v in Ω_3 and Ω_4 has been used to denote the original variable w and α is defined to be zero in those regions, (9) is equivalent to the previously discussed formulation, and, therefore, to (1).

4 Existence and Uniqueness of Solutions

Now that the equivalence of systems (1) and (9) has been established, it follows that proving the existence and uniqueness of solutions to (9) implies the same for solutions of (1).

Theorem 4.1 *There exists a unique solution to problem (9). Moreover, the corresponding current densities (potential gradients) are bounded.*

In order to prove this theorem, it is first helpful to construct an auxilary problem in terms of $\eta := v - u$. This construction allows the system of equations in (9) to be reduced to a single equation, for which variational and classical techniques can be used to prove existance and uniqueness. Once these are established for this auxilary problem, the definition of η will allow us to view (9) as a system of Poisson equations, and ultimately prove Theorem 4.1.

If $\eta := v - u$, then η satisfies (10) as shown in Figure 5,

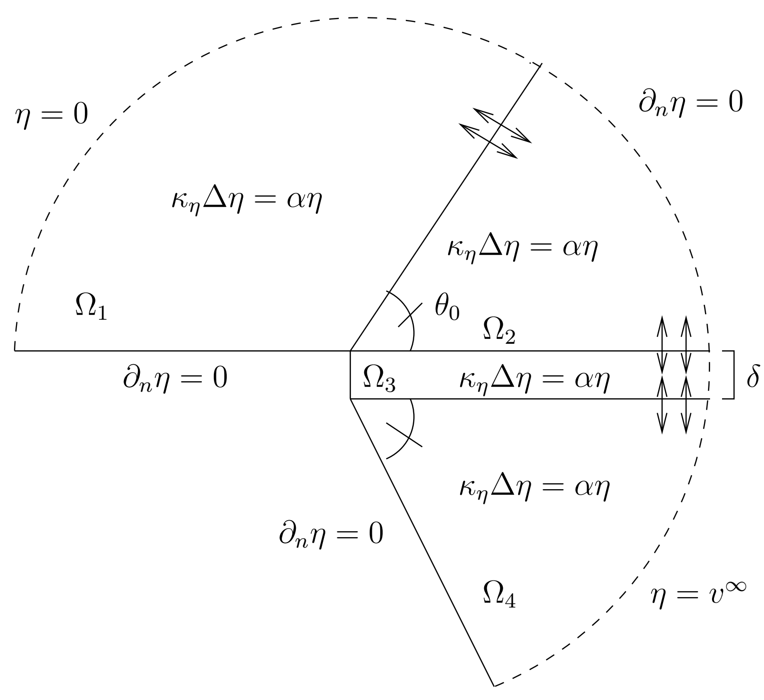

Figure 5: Domain, equations, and boundary conditions for the auxilary problem in terms of η.

$$
\begin{array}{llll}
(a) & \kappa_\eta \triangle \eta & = \alpha\eta & \text{in } \Omega_1 \cup \Omega_2 \cup \Omega_3 \cup \Omega_4\,, \\
(b) & \eta & = 0 & \text{on } \partial\Omega_1\,, \\
(c) & \eta & = v^\infty & \text{on } \partial\Omega_4\,, \\
(d) & \partial_n \eta & = 0 & \text{on } \partial\Omega_2 \cup \partial\Omega_{14}
\end{array}
\tag{10}
$$

where

$$
\kappa_\eta := \begin{cases} \dfrac{\kappa_u \epsilon}{\kappa_u + \epsilon} & \text{in } \Omega_1 \\[2ex] \dfrac{\kappa_u \kappa_v}{\kappa_u + \kappa_v} & \text{in } \Omega_2 \\[2ex] \beta\delta & \text{in } \Omega_3 \\[2ex] \dfrac{\kappa_v \epsilon}{\kappa_v + \epsilon} & \text{in } \Omega_4\ . \end{cases}
\tag{11}
$$

Theorem 4.2 *There exists a unique solution to problem (10).*

PROOF. Consider the following definition for the energy associated with (10):

$$
E[\eta] := \int_\Omega \kappa_\eta |\nabla \eta|^2 + \alpha \eta^2 \; dx. \tag{12}
$$

Note that $E'[\eta] = P[\eta]$, where $P[\eta] = 0$ is the problem in (10), and E' is a variational derivative. Since $E'[\eta] = 0$ at a minimum, the existence of a minimizer to (12) gives the existence of a solution to (10). A proof of the existence of such minimizers for elliptic PDE in general is discussed by Evans [3, pp. 443-449] and, the corresponding argument for this problem is given here.

Let $L(\nabla\eta, \eta, x) := \kappa_\eta |\nabla\eta|^2 + \alpha\eta^2$ so that $E[\eta] = \int_\Omega L \; dx$. Notice that $L(p, \eta, x) \geq \lambda |p|^2 - \mu$ for any $\lambda \leq \kappa_\eta$ and $\mu \geq 0$. Therefore, $E[\eta] \geq \lambda |p|^2_{L^2(\Omega)} - \mu|\Omega|$. This is a *coercivity* condition for $E[\eta]$. Define $A := \{\eta \in W^{1,2}(\Omega) \mid \eta = g \text{ on } \partial\Omega \text{ in the trace sense}\}$. This is the set of *admissible* functions η, and it is nonempty. Let $m := \inf_{\eta \in A} \; E[\eta]$. Let $u_k \in A$ such that $E[u_k] \to m$ as $k \to \infty$. Then $\{u_k\}_{k=1}^\infty$ is a minimizing sequence.

Lemma 1 *There exists a subsequence, u_{k_j}, such that $u_{k_j} \rightharpoonup u$ weakly in $W^{1,2}(\Omega)$.*

PROOF. Let $\mu = 0$ and $\lambda = \kappa_w$ so that $L \geq \lambda |p|^2$, and

$$
E[\eta] \geq \lambda \int_\Omega |\nabla \eta|^2 \; dx. \tag{13}
$$

Since m is finite (because $A \neq \emptyset$),

$$
\sup_k |\nabla u_k|_{L^2(\Omega)} < \infty. \tag{14}
$$

Now, fix $\eta \in A$. Then, $u_k - \eta \in W_0^{1,2}(\Omega)$. Therefore, by Poincare's inequality [1],

$$\begin{aligned} |u_k|_{L^2(\Omega)} &\leq |u_k - \eta|_{L^2(\Omega)} + |\eta|_{L^2(\Omega)} \\ &\leq C|\nabla u_k - \nabla \eta|_{L^2(\Omega)} + C \leq C, \end{aligned} \tag{15}$$

and this uniform bound implies that

$$\sup_k |u_k|_{L^2(\Omega)} < \infty, \tag{16}$$

and hence $\{u_k\}_{k=1}^{\infty}$ is bounded in $W^{1,2}(\Omega)$. Since $W^{1,2}(\Omega)$ is *reflexive*, there exists a subsequence $\{u_{k_j}\}_{j=1}^{\infty} \subset \{u_k\}_{k=1}^{\infty}$ such that $u_{k_j} \rightharpoonup u$ weakly in $W^{1,2}(\Omega)$ [3, p.639, weak compactness theorem]. Note that $W_0^{1,2}(\Omega)$ is weakly closed, and so $u - \eta \in W_0^{1,2}(\Omega)$. This implies that the trace of u is g on $\partial\Omega$, and thus $u \in A$. □

It is now necessary to show that $E[u] \leq \liminf_{j\to\infty} E[u_{k_j}]$, i.e., that E is *weakly lower semicontinuous*. If this can be shown, then $E[u] \leq m$, and since it is already known that $m \leq E[u]$, then u would be the desired minimizer. Notice that $L((p_1, p_2), \eta, x) = \kappa_w(p_1^2 + p_2^2) + \alpha\eta^2$, where $\nabla\eta = (p_1, p_2)$. Then

$$\sum L_{p_i p_j}(\nabla u(x), u(x), x)\xi_i\xi_j = 2k\xi_1^2 + 0 + 0 + 2k\xi_2^2 \geq 0. \tag{17}$$

This inequality shows that L is *convex* in its first argument. Now let us show that this convexivity gives weakly lower semicontinuity:

Lemma 2 *$E[u]$ is weakly lower semicontinuous, and u is the desired minimizer of $E[\eta]$.*

Proof. Note that because $u_k \rightharpoonup u$ weakly, $\sup_k |u_k|_{W^{1,2}(\Omega)} < \infty$. Using a subsequence if necessary, one can suppose $m = \lim_{k\to\infty} E[u_k]$. Using the *compactness* of Ω ([3, p. 272, Rellich-Kondrachov compactness theorem]), $u_k \to u$ strongly in $L^2(\Omega)$, and, therefore,

$$u_k \to u \text{ a.e. in } \Omega. \tag{18}$$

The Egoroff theorem [6, p. 175] then implies that there exists a measurable set E_ϵ such that $|\Omega - E_\epsilon| \leq \epsilon$ and

$$u_k \to u \text{ uniformly on } E_\epsilon \tag{19}$$

for $\epsilon > 0$. Now let

$$F_\epsilon := \left\{ x \in \Omega \mid |u(x)| + |\nabla u(x)| \leq \frac{1}{\epsilon} \right\}. \tag{20}$$

Then $|\Omega - F_\epsilon| \to 0$ as $\epsilon \to 0$. Let

$$G_\epsilon := E_\epsilon \cap F_\epsilon. \tag{21}$$

Then $|\Omega - G_\epsilon| \to 0$ as $\epsilon \to 0$. Now since L is bounded below, assume $L \geq 0$. Otherwise, let $L' = L + \tau \geq 0$, where τ is a positive constant, and continue the following argument for L'. Therefore,

$$\begin{aligned} E[u_k] &= \int_\Omega L(\nabla u_k, u_k, x)\ dx \geq \int_{G_\epsilon} L(\nabla u_k, u_k, x)\ dx \\ &\geq \int_{G_\epsilon} L(\nabla u, u_k, x)\ dx + \int_{G_\epsilon} D_p L(\nabla u, u_k, x) \cdot (\nabla u_k - \nabla u)\ dx, \end{aligned} \tag{22}$$

where the last inequality comes from the convexity of L. Then, from (19), (20) and (21), $u_k \to u$ uniformly on G_ϵ, and

$$\lim_{k\to\infty} \int_{G_\epsilon} L(\nabla u, u_k, x)\ dx = \int_{G_\epsilon} L(\nabla u, u, x)\ dx. \tag{23}$$

Similarly, since $D_pL(\nabla u, u_k, x) \to D_pL(\nabla u, u, x)$ uniformly on G_ϵ and $\nabla u_k \rightharpoonup \nabla u$ weakly in $L^2(\Omega)$,

$$\lim_{k\to\infty} \int_{G_\epsilon} D_pL(\nabla u, u_k, x) \cdot (\nabla u_k - \nabla u)\ dx = 0. \tag{24}$$

Now,

$$m = \lim_{k\to\infty} E[u_k] \geq \int_{G_\epsilon} L(\nabla u, u, x)\ dx. \tag{25}$$

As $\epsilon \to 0$,

$$m \geq \int_\Omega L(\nabla u, u, x)\ dx = E[u]. \tag{26}$$

Thus $E[u]$ is weakly lower semicontinuous. Finally, $E[u] \leq \liminf_{j\to\infty} E[u_{k_j}] = m$, and since $u \in A$,

$$E[u] = m = \min_{\eta\in A} E[\eta]. \tag{27}$$

This proves the existence of a minimizer for $E[\eta]$. □
As discussed previously, the existence of a minimizer of $E[\eta]$ gives the existence of a solution. Since u is a minimizer of $E[\eta]$, $E'[u] = 0$, and $P[u] = 0$. Thus, u is a solution to (10). △

Now, turning our attention to the uniqueness of solutions, assume η_1 and η_2 are two solutions to this problem. Let $\omega := \eta_1 - \eta_2$. Then $\kappa_\eta \triangle\omega = \alpha\omega$ in Ω, and $\frac{\partial\omega}{\partial n} = 0$ or $\omega = 0$ everywhere on $\partial\Omega$. Using Green's first identity and (10a), one has

$$\int_{\partial\Omega} \omega \frac{\partial\omega}{\partial n}\ dS = \int_\Omega |\nabla\omega|^2\ dx + \int_\Omega \alpha\omega^2\ dx\ . \tag{28}$$

Then, using the boundary conditions for ω, one obtains

$$\int_\Omega |\nabla\omega|^2\ dx + \int_\Omega \alpha\omega^2\ dx = 0\ , \tag{29}$$

which can be combined as

$$\int_\Omega |\nabla\omega|^2 + \alpha\omega^2\ dx = 0\ . \tag{30}$$

Given that $\alpha \geq 0$, the integrand is nonnegative, and thus, $|\nabla\omega|^2 + \alpha\omega^2 = 0$ a.e. Since ω is continuous, this implies $\omega \equiv 0$. Thus, the solution to (10) is unique. □

Remark. The existence of a solution to this problem, sometimes referred to as a modified Laplace equation, is also discussed by Carrier & Pearson [2, pp. 152-154]. They attempt to give a Green's Function solution to the problem. The existence of the Green's Function, however, is dependent upon the existence of another unknown function, which also must satisfy the modified Laplace equation. While Miranda [8] shows that this technique can be used, the argument given by Carrier & Pearson is circular. Nonetheless, it does give the partial form of a solution. Let us consider the Carrier & Pearson approach in detail.

Define a Green's function $G(x, x_0)$ by:

$$\triangle G - \alpha G = \delta(x - x_0) \tag{31}$$

$$G = 0 \quad \forall x \, \epsilon \, \partial\Omega \ , \tag{32}$$

where x_0 is a fixed point in Ω and $\delta(x)$ is the Dirac delta function, with $\delta(x - x_0) = 0$ for all $x \neq x_0$. Then, multiplying (10a) by G and (31) by η and subtracting, one obtains

$$G\triangle\eta - \eta\triangle G = -\eta\delta(x - x_0) \ . \tag{33}$$

Integrating over Ω and using Green's second identity gives

$$\int_{\partial\Omega} \left(G\frac{\partial\eta}{\partial n} - \eta\frac{\partial G}{\partial n} \right) \, dS = -\eta(x_0) \ . \tag{34}$$

Because of the boundary conditions for G and rearranging, this simplifies to

$$\eta(x_0) = \int_{\partial\Omega} \eta\frac{\partial G}{\partial n} \, dS \ . \tag{35}$$

The integral (35) will give a solution for η if G can be constructed. First, consider the fundamental solution G_1 which has the correct singularity at x_0. Then $G_1(x, x_0)$ depends only on the radial distance r. Thus,

$$\begin{aligned} \triangle G_1 - \alpha G_1 = \left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} - \alpha \right) G_1 = 0, \qquad & r > 0 \\ G_1 \to 0 \text{ as } \quad & r \to \infty \end{aligned} \tag{36}$$

This ODE has a solution in terms of Bessel functions I_0 and K_0 with

$$G_1 = AK_0(\sqrt{\alpha}r) + BI_0(\sqrt{\alpha}r) \ . \tag{37}$$

Since $K_0 \to 0$ and $I_0 \to \infty$ as $\sqrt{\alpha}r \to \infty$, B must equal 0, giving

$$G_1 = AK_0(\sqrt{\alpha}r) \ . \tag{38}$$

Now, in order to construct G, the appropriate A must be chosen. Consider the following argument for calculating the value of A. Let $\varphi \in C_0^\infty(\Omega)$. Construct a ball of radius $\epsilon > 0$ centered at the origin, $B_\epsilon(0)$, and define $\varphi \equiv 1$ within the ball. Then,

$$1 = \varphi(0) = (\delta, \varphi) = (\triangle G - \alpha G, \varphi) \tag{39}$$

by (31). Linearity allows the righthand side to be split up as

$$(\triangle G, \varphi) - \alpha(G, \varphi), \tag{40}$$

which, after applying the definition of distributional derivatives twice, yields

$$(G, \triangle\varphi) - \alpha(G, \varphi) = 1. \tag{41}$$

Recombining gives

$$(G, \triangle\varphi - \alpha\varphi) = 1, \tag{42}$$

which can be rewritten as

$$\int_\Omega G(\triangle\varphi - \alpha\varphi) = 1. \tag{43}$$

This integral can be divided into two:

$$\int_{\Omega - B_\epsilon} G(\triangle\varphi - \alpha\varphi) + \int_{B_\epsilon} G(\triangle\varphi - \alpha\varphi) = 1 \tag{44}$$

Notice that $\triangle\varphi - \alpha\varphi = O(\epsilon)$ and the second of the two integrals vanishes as $\epsilon \to 0$, and the first integral can be divided again, giving

$$\int_{\Omega - B_\epsilon} G\triangle\varphi - \alpha \int_{\Omega - B_\epsilon} G\varphi = 1. \tag{45}$$

Then, by applying Green's second identity to the first term, it can be seen that

$$\int_{\partial\Omega - B_\epsilon} G\frac{\partial\varphi}{\partial n} - \varphi\frac{\partial G}{\partial n} - \int_{\Omega - B_\epsilon} \varphi\triangle G - \alpha\int_{\Omega - B_\epsilon} G\varphi = 1. \tag{46}$$

Splitting the first integral once again and combining the next two terms yields

$$\int_{\partial\Omega} G\frac{\partial\varphi}{\partial n} - \varphi\frac{\partial G}{\partial n} - \int_{\partial B_\epsilon} G\frac{\partial\varphi}{\partial n} - \varphi\frac{\partial G}{\partial n} + \int_{\Omega - B_\epsilon} \varphi(\triangle G - \alpha G) = 1. \tag{47}$$

Substituting the values of G, φ, and $\triangle G - \alpha G$ simplifies this to

$$\int_{\partial B_\epsilon} \frac{\partial G}{\partial n} = 1 \tag{48}$$

Then, one can evaluate this integral directly using polar coordinates by substituting in the approximation of G:

$$\begin{aligned} 1 &= \int_0^{2\pi} \frac{\partial G}{\partial r}\ r d\theta \\ &= \int_0^{2\pi} \frac{-A}{r}\ r d\theta \\ &= -A(2\pi). \end{aligned} \tag{49}$$

Thus, $A = -1/(2\pi)$ and G can be defined as follows

$$G = -(1/2\pi)K_0(\sqrt{\alpha}r) + M\ , \tag{50}$$

where M must satisfy $\triangle M - \alpha M = 0$ in Ω, and $M = (1/2\pi)K_0(\sqrt{\alpha}r)$ on $\partial\Omega$. Notice, however, M must essentially satisfy the original problem, so its existence is not proven and this argument is circular. If G could be constructed, (35) would be a solution to (10).

Proof of Theorem 4.1. After making the substitution $v - u = \eta$ in the righthand side of (9), system (9) can be viewed as two separate Poisson problems in u and v. Since it has already been proven that η exists, the Poisson equations for u and v give that a solution to (9) also exists. Then, using the same technique as in the proof of Lemma 1 above, it can be proven that the solutions u and v are both unique. The existence and uniqueness of solutions gives that there exists a unique potential discontinuity across $\partial\Omega_{es}$, and thus because of the original boundary condition (1j), a unique bounded potential flux. Therefore, there is no singularity at the tip of the electrolyte wedge, and the current densities are shown to be bounded. □

5 Numerical Approximations

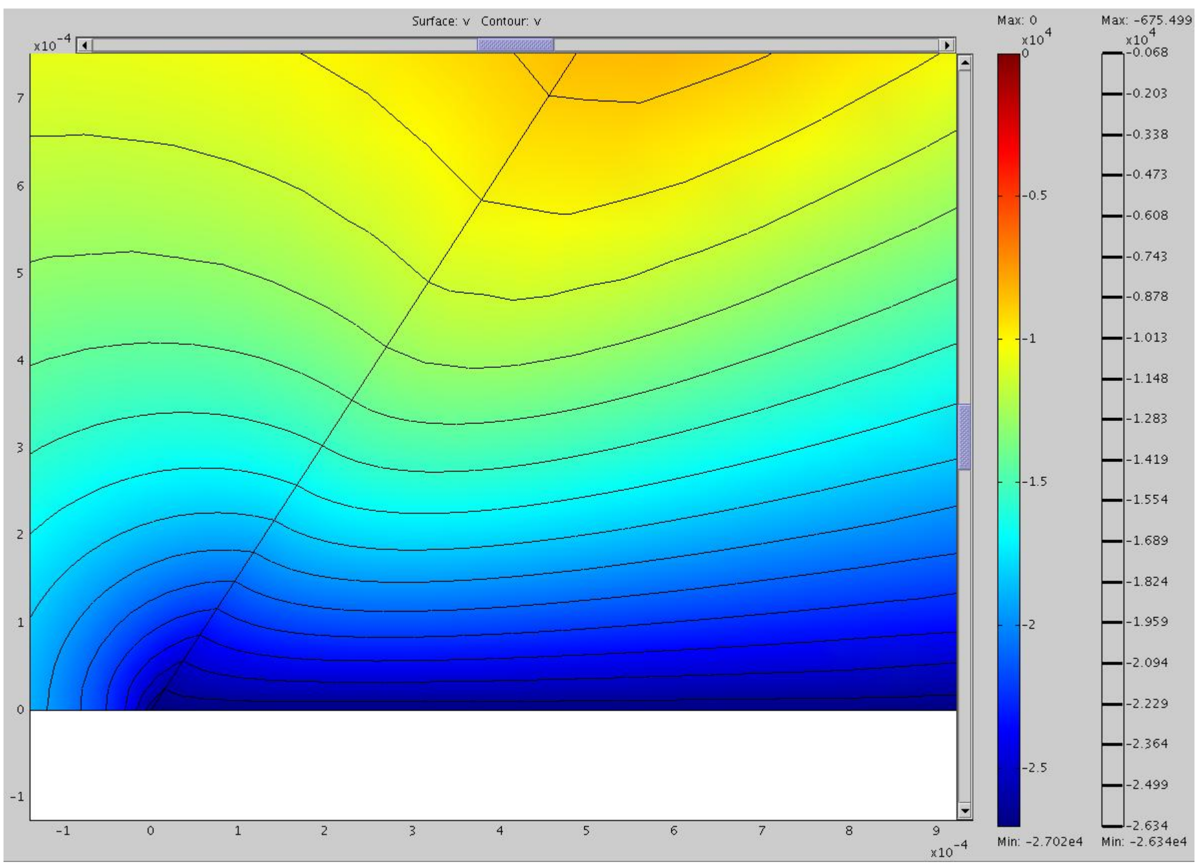

Figure 6: Contour plot of v

This section gives examples of results found for the EWP2 using Femlab. Femlab is a program that allows the user to specify PDEs and boundary conditions of a system and

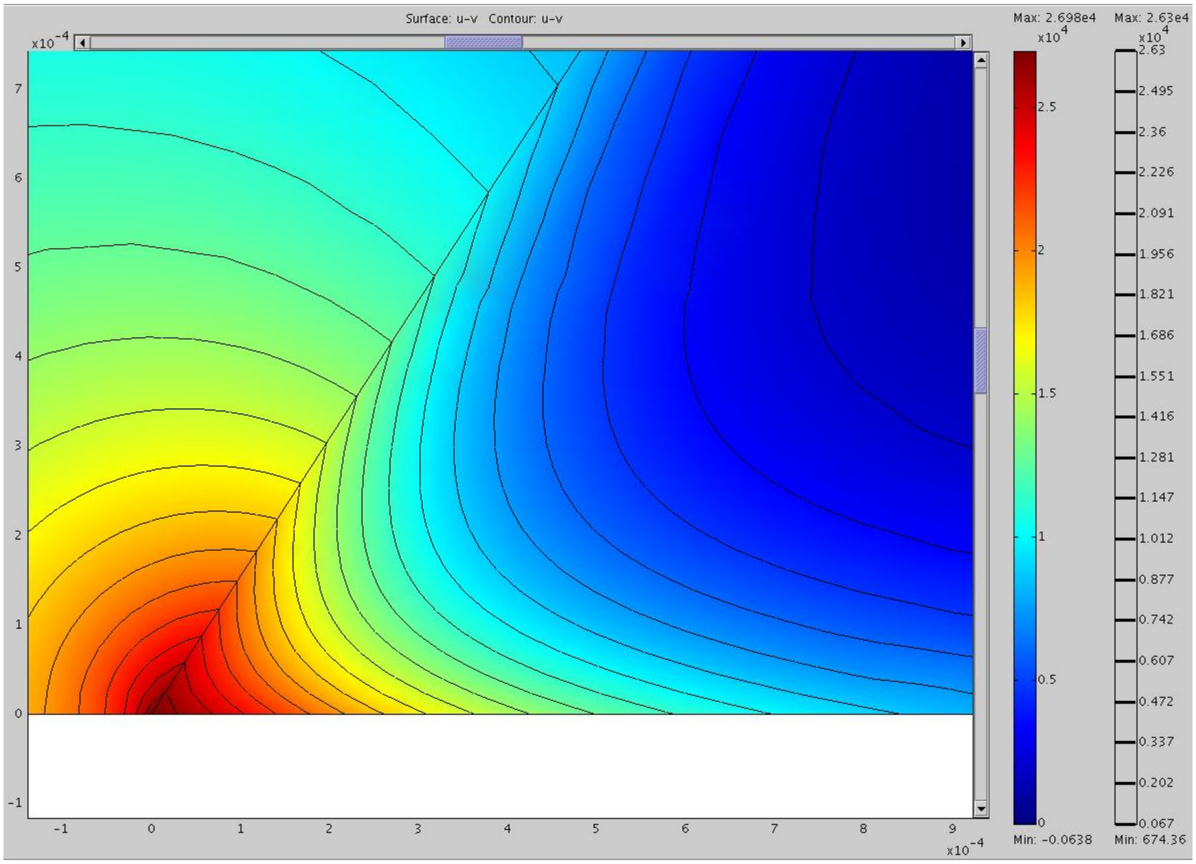

Figure 7: Contour plot of $u - v$

then solves the problem numerically. The results below show the connections between the system found in (1) and the behaviors of the component potentials.

The following numerical values were used to define the constants in the system: $w^{\infty} = -27020$, $\kappa_u = .15$ in $\partial\Omega_g$, $\kappa_u = 6.9e^{-7}$ in $\partial\Omega_e$, $\kappa_v = 6.9e^{-7}$, $\kappa_w = .350$, $\beta = 1.38$, and $\alpha = 10$. These values were all taken from experimental data and are as realistic as possible. The choice of α allows the first rate-determining reaction to be somewhat faster than the second (involving β) without being so fast as to become irrelevant.

In order to find a numerical solution for v in Femlab, it needed to be defined in Ω_g as well. Recall that this was done by using an infintesimally small diffusivity constant for v in this region. Figure 6 shows the results obtained. v is negative throughout Ω_e and obtains its lowest value along the bottom edge of the figure, which represents $\partial\Omega_{es}$. Notice the contour lines for v are perpendicular to $\partial\Omega_{ge}$. This is due to the zero flux boundary condition on this interface.

Figure 7 shows the relationship between u and v in Ω_e. Notice that the values of u and v vary the most near the meniscus corner and along the boundaries. As one moves out toward $\partial\Omega_e$, u and v become nearly equal in value. Their difference is positive in a large marjority of Ω_e until near $\partial\Omega_e$.

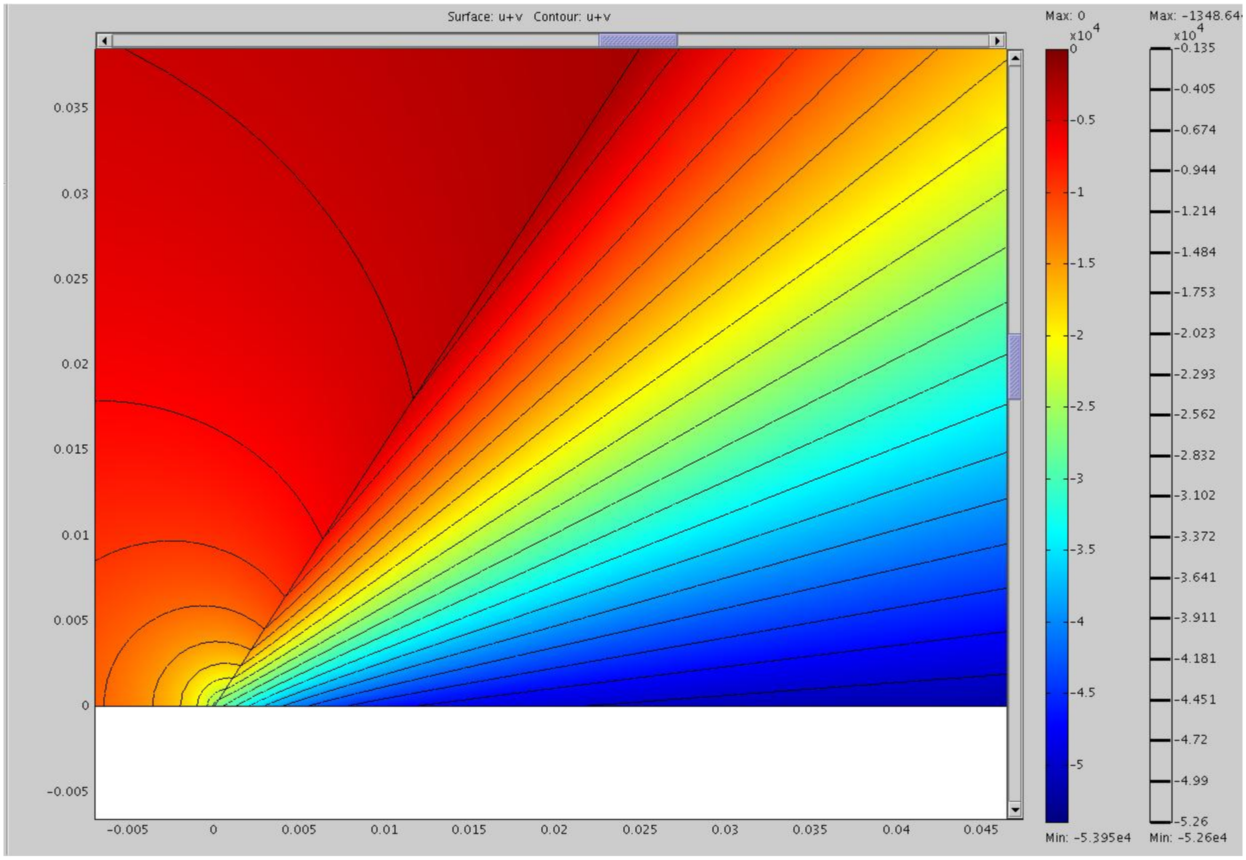

Figure 8: Contour plot of $u + v$

Figure 8 shows the contour lines of the sum of the component potentials u and v. Notice that the contour lines are approximately equally spaced and seem to be radiating from an origin just outside of the region. This suggests that a change of coordinate system could be used in further analysis. This idea will be discussed in the next section using the technique of matched asymptotics.

6 Matched Asymptotics

Now that it has been proven that a unique solution to (1) exists, the technique of matched asymptotics can be used to approximate this solution. Let ϵ_2 denote the conductivity for u and v in Ω_e, and notice that $\epsilon_2 << 1$ (its value was $6.9e^{-7}$ in the previous section). To find uniform zeroth order solutions for the system, it is helpful to first examine the problem in terms of $(u + v)$ and w. The unique behavior of $(u + v)$ that is used here is implied by the numerics discussed previously. Both inner and outer solutions will be found and matched. Then, an expression for v will be obtained, giving a uniform solution to the original problem. Finally, this can be used to find an expression for the current density within the wedge. Consider the outer solutions:

$$\begin{aligned} (u+v)(r,\theta,\epsilon_2) &= (u+v)_0(r,\theta) + \epsilon_2(u+v)_1(r,\theta) + O(\epsilon_2^2) \\ w(r,\theta,\epsilon_2) &= w_0(r,\theta) + \epsilon_2 w_1(r,\theta) + O(\epsilon_2^2), \end{aligned} \tag{51}$$

. By substituting back into the original problem,

$$\begin{aligned} &\kappa_u \triangle u = 0 \text{ in } \Omega_g \\ &\Rightarrow \kappa_u(\triangle u_0 + \epsilon_2 \triangle u_1 + O(\epsilon_2^2)) = 0 \\ &\Rightarrow \kappa_u \triangle u_0 = 0. \end{aligned} \tag{52}$$

Also,

$$\begin{aligned} &u = 0 \text{ on } \partial\Omega_g \\ &\Rightarrow u_0 + \epsilon_2 u_1 + O(\epsilon_2^2) = 0 \\ &\Rightarrow u_0 = 0. \end{aligned} \tag{53}$$

Then, by observing that the flux from the gas side of $\partial\Omega_{ge}$ must equal the flux from the electrolyte side,

$$\kappa_u \partial_n u|_g = \epsilon_2 \partial_n (u+v)|_2. \tag{54}$$

By ensuring that the orders of ϵ_2 match on both sides of the equation, one sees that

$$\partial_n u_0|_g = 0 \text{ on } \partial\Omega_{ge}. \tag{55}$$

Thus, a solution for u_0 in Ω_g can be obtained — namely, $u_0 = 0$.

Similarly,

$$\begin{aligned} &\kappa_w \triangle w = 0 \text{ in } \Omega_e \\ &\Rightarrow \kappa_w(\triangle w_0 + \epsilon_2 \triangle w_1 + O(\epsilon_2^2)) = 0 \\ &\Rightarrow \kappa_w \triangle w_0 = 0. \end{aligned} \tag{56}$$

Also,

$$\begin{aligned} &w = w^\infty \\ &\Rightarrow w_0 + \epsilon_2 w_1 + (O(\epsilon_2^2))) = w^\infty \\ &\Rightarrow w_0 = w^\infty, \end{aligned} \tag{57}$$

and, by observing that the flux into $\partial\Omega_{es}$ is equal to the flux out of the boundary,

$$\begin{aligned} &\epsilon_2 \partial_n (u+v)|_e = -\kappa_w \partial_n w|_e \\ &\Rightarrow \partial_n w_0|_e = 0. \end{aligned} \tag{58}$$

Thus, the solution for w_0 in Ω_e can be given: $w_0 = w^\infty$.

Next, one must solve for $(u+v)_0$ in Ω_e. Notice that, by plugging in the expansions for $u+v$ and w and using the smallness of ϵ_2, $\epsilon_2 \partial_n (u+v)|_e = \beta(v-w)|_e$ on $\partial\Omega_{es}$ simplifies to

$\beta v_0|_e - \beta w_0|_e = 0$. Thus, $v_0|_e = w_0|_e$ on $\partial\Omega_{es}$. Note that $\epsilon_2 \triangle(u-v) = -2\alpha(u-v)$ in Ω_e implies that $2\alpha(u-v)_0 = 0$, and, therefore, $u_0 = v_0$ in Ω_e. Using this, along with $(u+v)_0 = u_0$ on $\partial\Omega_{ge}$, $(u+v)_0 = 0$ on $\partial\Omega_{ge}$ and $(u+v)_0 = 2w^\infty$ on $\partial\Omega_{ge}$. Also, $\partial_n(u+v)_0 = \partial_n u_0 + \partial_n v_0 = 0$ on $\partial\Omega_e$. This suggests $(u+v)_0$ cannot be a function of r and must depend only upon θ. Thus, there must be only one solution for $(u+v)_0$, which must satisfy the conditions $(u+v)_0 0$ when $\theta = \theta_0$ and $(u+v)_0 = 2w^\infty$ when $\theta 0$. This solution is $(u+v)_0 = 2w^\infty(\theta_0 - \theta)/\theta_0$.

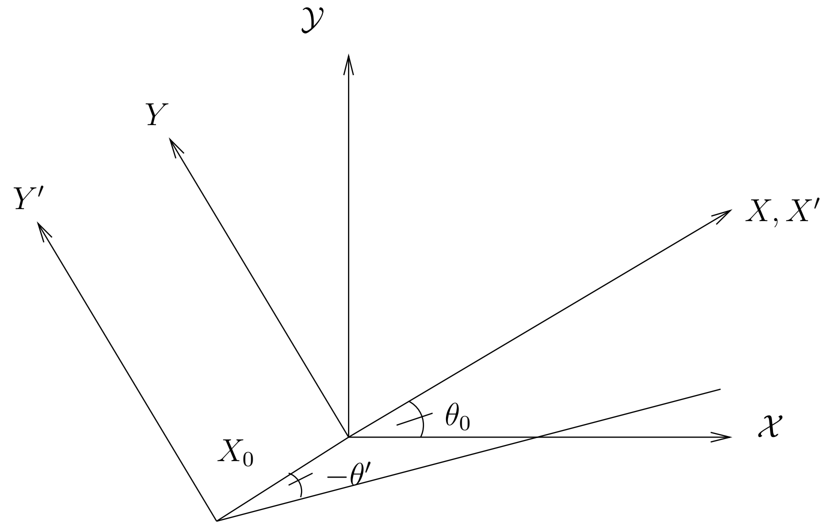

Figure 9: (X, Y) has been rotated by θ_0 and (X', Y') has been rotated and then shifted by X_0

Now, we continue by looking at the inner solution. We first change variables as follows: $\mathcal{X} := x/\epsilon$, $\mathcal{Y} : y/\epsilon$, and $R := r/\epsilon$, where $\epsilon := \epsilon_2/\beta$. Then, let X and Y be variables in a second coordinate system which has been rotated first by θ_0 and rescaled as well (i.e. $X = R\cos\theta$ and $Y = R\sin\theta$, where θ is measured relative to the rotated coordinate system). Finally, let the primed coordinate system also be rescaled and rotated by θ_0 and then shifted by a distance of X_0, where $X' = X + X_0$ and $Y' = Y$. Because we wish to find a representation for the current potential, which is defined only in Ω_e, we next consider the following expansion:

$$W(R, \theta, \epsilon) = W_0(R, \theta) + \epsilon W_1(R, \theta) + O(\epsilon^2). \tag{59}$$

Notice that $\epsilon\partial_N(U+V)|_e = -\kappa_w \partial_N W|_e$ on $\partial\Omega_{es}$, where $N := n/\epsilon$, implies $\partial_N W_0|_e = 0$. Also note that, because W is not defined in Ω_g, $\partial_N W_0|_e = 0$ on $\partial\Omega_{ge}$. Thus, since W_0 must be finite at $(X, Y) = (0, 0)$ and must match the previously found outer solution, $W_0 = w^\infty$.

Next, one must find a representation for $U + V$. The level curves for $U + V$ suggest $(U + V)_0$ does not depend on R'. Thus, the expansion can be written as

$$(U+V)(R', \theta', \epsilon) = (U+V)_0(\theta') + \epsilon(U+V)_1(R', \theta') + O(\epsilon^2). \tag{60}$$

Since the level curves are also equally spaced, $(U+V)_0$ appears to be linear in θ_0, so we look for something of the form:

$$(U+V)(R', \theta', \epsilon) = \alpha\theta' + \epsilon(U+V)_1(R', \theta') + O(\epsilon^2), \tag{61}$$

where α is constant. Note that, by the chain rule,

$$\begin{aligned}0 = R'\frac{\partial(U+V)_0}{\partial R'} R'\frac{\partial(U+V)_0}{\partial X}\frac{\partial X}{\partial R'} + R'\frac{\partial(U+V)_0}{\partial Y}\frac{\partial Y}{\partial R'} \\ = R'\frac{\partial(R'\cos\theta' - X_0)}{\partial R'}\frac{\partial(U+V)_0}{\partial X} + R'\frac{\partial(R'\sin\theta')}{\partial R'}\frac{\partial(U+V)_0}{\partial Y} \\ = (X+X_0)\frac{\partial(U+V)_0}{\partial X} + Y\frac{\partial(U+V)_0}{\partial Y}\end{aligned} \tag{62}$$

and

$$\begin{aligned}\alpha = \frac{\partial(U+V)_0}{\partial\theta'}\frac{\partial X}{\partial\theta'}\frac{\partial(U+V)_0}{\partial X} + \frac{\partial Y}{\partial\theta'}\frac{\partial(U+V)_0}{\partial Y} \\ = \frac{\partial(R'\cos\theta' - X_0)}{\partial\theta'}\frac{\partial(U+V)_0}{\partial X} + \frac{\partial(R'\sin\theta')}{\partial\theta'}\frac{\partial(U+V)_0}{\partial Y} \\ = -Y\frac{\partial(U+V)_0}{\partial X} + (X+X_0)\frac{\partial(U+V)_0}{\partial Y}.\end{aligned} \tag{63}$$

Note also that

$$\begin{aligned}\frac{\partial(U+V)_0}{\partial\theta} &= \frac{\partial(U+V)_0}{\partial X}\frac{\partial X}{\partial\theta} + \frac{\partial(U+V)_0}{\partial Y}\frac{\partial Y}{\partial\theta} \\ &= -Y\frac{\partial(U+V)_0}{\partial X} + X\frac{\partial(U+V)_0}{\partial Y}.\end{aligned} \tag{64}$$

Thus, using (64), equation (63) can be rewritten as

$$\alpha = \frac{\partial(U+V)_0}{\partial\theta} + X_0\frac{\partial(U+V)_0}{\partial Y}. \tag{65}$$

Using (64) and (62),

$$\frac{\partial(U+V)_0}{\partial Y} = \frac{\alpha(X+X_0)}{Y^2+(X+X_0)^2} \tag{66}$$

and

$$\frac{\partial(U+V)_0}{\partial X} = \frac{\alpha(-Y)}{Y^2+(X+X_0)^2}. \tag{67}$$

Noting that $\partial_N X = -\sin\theta_0$ and $\partial_N Y = -\cos\theta_0$, and using the chain rule again, we can write

$$
\begin{aligned}
\frac{\partial(U+V)_0}{\partial N} &= \frac{\partial(U+V)_0}{\partial X}\frac{\partial X}{\partial N} + \frac{\partial(U+V)_0}{\partial Y}\frac{\partial Y}{\partial N} \\
&= \frac{Y\alpha\sin\theta_0}{Y^2+(X+X_0)^2} - \frac{\alpha\cos\theta_0(X+X_0)}{Y^2+(X+X_0)^2} \\
&= \frac{Y\alpha\sin\theta_0 - \alpha\cos\theta_0(X+X_0)}{(R')^2} \\
&= \frac{Y\alpha\sin\theta_0 - \alpha\cos\theta_0 X - \alpha\cos\theta_0 X_0}{(R')^2} \\
&= \frac{-\alpha R\sin^2\theta_0 - \alpha R\cos^2\theta_0 X - \alpha\cos\theta_0 X_0}{(R')^2} \\
&= \frac{-\alpha R - \alpha\cos\theta_0 X_0}{(R')^2}
\end{aligned} \tag{68}
$$

Recall that, earlier in this section, an inner solution for the current potential was found, namely: $W_0 = w^\infty + O(\epsilon)$. Now using this, one can find the boundary condition on $\partial\Omega_{es}$: $\partial_N(U+V)_0 = w^\infty - (U+V)_0$. Using this equation, along with equation (61) and equation (68), we find that

$$
\begin{aligned}
\frac{\partial(U+V)_0}{\partial N}(R')^2 &= -\alpha R - \alpha\cos\theta_0 X_0 \\
(w^\infty - (U+V)_0)(R')^2 &= -\alpha R - \alpha\cos\theta_0 X_0 \\
(w^\infty - \alpha\theta')(R')^2 &= -\alpha R - \alpha\cos\theta_0 X_0 \\
(\alpha\theta' - w^\infty)(R')^2 &= \alpha R + X_0\alpha\cos\theta_0.
\end{aligned} \tag{69}
$$

Now we find parameter values so the last equation is approximately satisfied when $\theta' \ll 1$ and the outer solution found previously is matched. The first term of (69) drops out given the smallness of θ'. Similarly, R is negligible, causing the αR term to drop out and R' to be approximated by X_0 on $\partial\Omega_{es}$. Then, (69) will hold to zeroth order when

$$
\alpha = \frac{-w^\infty X_0}{\cos\theta_0}. \tag{70}
$$

To match the inner and outer solutions,

$$
\alpha\theta' = \frac{-w^\infty X_0\theta'}{cos\theta_0} = \frac{2w^\infty(\theta_0-\theta)}{\theta_0}. \tag{71}
$$

On $\partial\Omega_{es}$, $\theta = 0$ and, when considering points far enough away from the origin, $-\theta' \approx \theta_0$, giving

$$
X_0 = \frac{2\cos\theta_0}{\theta_0}. \tag{72}
$$

Note that, for all values of θ,

$$\begin{aligned}
-X_0 \sin\theta' &= R\sin(\theta' + \theta_0 - \theta) \\
-X_0 \sin\theta' &= R(\sin\theta' \cos(\theta_0 - \theta) + \cos\theta' \sin(\theta_0 - \theta) \\
-X_0 &= R\cos(\theta_0 - \theta) + R\cot\theta' \sin(\theta_0 - \theta) \\
\cot(\theta') &= \frac{-X_0 - R\cos(\theta_0 - \theta)}{R\sin(\theta_0 - \theta)} \\
\cot(\theta') &= \frac{-X_0}{R}\csc(\theta_0 - \theta) - \cot(\theta_0 - \theta) \\
-\theta' &= \cot^{-1}\left(\frac{\epsilon X_0}{\beta r}\csc(\theta_0 - \theta) + \cot(\theta_0 - \theta)\right).
\end{aligned} \tag{73}$$

Since $(U + V)_0 = \alpha\theta'$, we now have an equation for (u+v) that satisfies both the inner and outer solution:

$$(u + v)(r, \theta) = \frac{2w^\infty}{\theta_0}\cot^{-1}\left(\frac{\epsilon_2 X_0}{\beta r}\csc(\theta_0 - \theta) + \cot(\theta_0 - \theta)\right) + O(\epsilon_2, \theta'^2). \tag{74}$$

Next, we turn our attention to $u - v$, which, combined with the calculations above, will give the solutions for u and v. Consider the outer solution

$$(u - v)(r, \theta, \epsilon_2) = (u - v)_0(r, \theta) + \epsilon_2(u - v)_1(r, \theta) + O(\epsilon_2^2). \tag{75}$$

Since the outer solution for $(u + v)_0$ was found to be $2w^\infty(\theta_0 - \theta)/\theta_0$ in Ω_e and $u_0 = v_0$, $u_0 = v_0 = w^\infty(\theta_0 - \theta)/\theta_0$ in that region.

Now, consider the inner solution in terms of the inner variables defined above for $U + V$, this time with an expansion for V. Noting that the level curves for V suggest V_0 does not depend on $R^{'}$, an expansion for V can be written as

$$V(R^{'}, \theta^{'}, \epsilon) = V_0(\theta^{'}) + \epsilon V_1(R^{'}, \theta^{'}) + O(\epsilon^2). \tag{76}$$

Since the level curves are also equally spaced, V_0 appears to be linear in θ_0 and V can be written as

$$V(R^{'}, \theta^{'}, \epsilon) = \alpha\theta^{'} + \epsilon V_1(R^{'}, \theta^{'}) + O(\epsilon^2). \tag{77}$$

Note that in Ω_e,

$$\begin{aligned}
\epsilon_2 \triangle V &= \alpha(V - U) \\
\Rightarrow \frac{\triangle v}{\epsilon_2} &= \alpha(V - U) \\
\Rightarrow \triangle v_0 &= 0.
\end{aligned} \tag{78}$$

Also, on $\partial\Omega_{ge}$,

$$\begin{aligned}
\partial_N V &= 0 \\
\Rightarrow \partial_n v_0 &= 0
\end{aligned} \tag{79}$$

Finally, on $\partial\Omega_{es}$,

$$\begin{aligned} &\epsilon_2 \partial_N V = \beta(W-V) \\ \Rightarrow &\, \partial_n v = \beta(W-V) \\ \Rightarrow &\, \partial_n v_0 = \frac{\beta^2}{\epsilon_2}(w-v) \\ \Rightarrow &\, v_0 = w_0 = w^\infty. \end{aligned} \tag{80}$$

In order to match the previously found inner solution,

$$v_0 = \frac{w^\infty}{\theta_0} \cot^{-1}\left(\frac{\epsilon_2 X_0}{\beta r} \csc(\theta_0-\theta) + \cot(\theta_0-\theta)\right). \tag{81}$$

Therefore, given the solution for $u+v$ above,

$$u_0 = \frac{w^\infty}{\theta_0} \cot^{-1}\left(\frac{\epsilon_2 X_0}{\beta r} \csc(\theta_0-\theta) + \cot(\theta_0-\theta)\right). \tag{82}$$

Finally, one can use the current potentials to find an expression for the current density.

$$\begin{aligned} i_F &= \beta(w-v)/F \\ &= \frac{\beta w^\infty}{F\theta_0}\left[\theta_0 - \tan^{-1}\left(\frac{\tan(\theta_0)}{1+\epsilon/(\theta_0\beta r)}\right)\right] + O(\epsilon, \theta_0^2). \end{aligned} \tag{83}$$

This can be integrated to give the total current produced in the wedge,

$$\begin{aligned} \int_0^{r^\infty} i_F dr = \frac{\varepsilon w^\infty}{F\theta_0} &\left[R^\infty\left(\theta_0 - \tan^{-1}\left(\frac{\tan\theta_0}{1+1/(\theta_0 R^\infty)}\right)\right)\right. \\ &+ \frac{X_0 \sin\theta_0}{2} \ln\left(\left(\frac{R^\infty}{X_0}\right)^2 + 2R^\infty\theta_0 + 1\right) \\ &\left.- X_0\cos\theta_0\left(\theta_0 - \tan^{-1}\left(\frac{\tan\theta_0}{1+R^\infty/(X_0\cos\theta_0)}\right)\right)\right] \\ &+ O(\epsilon^2, \theta_0^2), \end{aligned} \tag{84}$$

where $R^\infty := r^\infty\beta/\varepsilon$. These results are essentially the same as those for the EWP [4].

7 Conclusion

Existence and uniqueness of solutions to (1) has been established, and numerical and asympotic analysis has been used to approximate the solution of the problem. Additionally, the asymptotics in the previous section have given expressions for the current density and the total current produced along the electrolyte-solid interface. If one were to approximate the distribution in the electrode of the electrolyte wedges studied in this problem, then use that information along with the expression for the total current obtained, one could in principle approximate the total current produced by the entire electrode.

References

[1] Adams, R. A. (1975) *Sobolev Spaces.* Academic Press.

[2] Carrier, G. F. and Pearson, C. E. (1988) *Partial Differential Equations: Theory and Technique.* Academic Press.

[3] Evans, Lawrence. (1998) *Partial Differential Equations.* Graduate Studies in Mathematics. **19**. AMS.

[4] Fehribach, J.D. (2001) Diffusion-reaction-conduction processes in porous electrodes: the electrolyte wedge problem. *Euro. J. Applied Mathematics.* **12**, 77-96.

[5] Fehribach, J.D., Prins-Jansen, J.A., Hemmes, K., de Wit, J.H.W., & Call, F.W. (1998) *The derivation of electrochemical-potential models for molten carbonate fuel-cell cathodes.* WPI Mathematical Sciences Preprints. **MS-01-98-03**, 1-24.

[6] Kuller, Robert Garlin. (1969) *Topics in Modern Analysis* Prentice-Hall.

[7] Makkus, R., Hemmes, K., & de Wit, J.H.W. (1990) *Proc. of the Second Symposium on Molten Carbonate Fuel Cell Technology.* The Electrochemical Society. **90-16** 454.

[8] Miranda, Carlo. (1970) *Partial Differential Equations of Elliptic Type.* Springer-Verlag.

[9] Newman, J.S. (1991) *Electrochemical Systems (2nd ed.).* Prentice Hall.