NUMERICAL AND EXPERIMENTAL CHARACTERISATION OF CONVECTIVE TRANSPORT IN SOLID OXIDE FUEL CELLS

BY
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A thesis submitted to the Department of Mechanical Engineering in conformity with the requirements for the degree of Master of Science (Engineering)

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Kingston, Ontario, Canada
(October, 2008)

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Abstract

In this work, numerical and experimental methods are used to characterise the effects of convective transport in an anode-supported tubular solid oxide fuel cell (SOFC). To that end, a computational fluid dynamics (CFD) model is developed to compare a full transport model to one that assumes convection is negligible. Between these two approaches, the variations of mass, temperature, and electrochemical performance are compared. Preliminary findings show that convection serves to reduce the penetration of hydrogen into the anode, and becomes more important as the thickness of the anode increases.

The importance of the permeability of SOFC electrodes on the characterization of convection is also investigated. Experiments performed on Ni-YSZ anodes reveal that permeability is a function of the cell operating conditions, and increases with increasing Knudsen number. An empirical Klinkenberg relation is validated and proposed to more accurately represent the permeability of electrodes in a CFD model. This is a departure from an assumption of constant permeability that is often seen in the literature. It is found that a varying permeability has significant effects on pressure variation in the cell, although according to the electrochemical model developed in this work, variation in permeability is only found to have minor effects on the predicted performance.

Furthermore, it is revealed that an electrochemical model which makes the simplifying assumption of constant overpotential is in error when predicting current and temperature variation. In this work, this is found to predict an unrealistic spatial variation of the current. It is suggested that this approach be abandoned for the solution of a transport equation for potential which couples the anodic and cathodic currents. This will lead to a more realistic prediction of temperature and performance.
Acknowledgements

This work could not have been produced without support from many people. First, and foremost, I would like to thank my family and friends, especially Tony, DJ, and Debbie, for your support throughout this undertaking. Also, I would like to thank my supervisor, Dr. Jon Pharoah, for giving me the opportunity to study fuel cells; this thesis would not have been possible without his ideas and guidance. Thanks go out to the following people for helping me wrap my head around some tough concepts, and work through some challenging coding projects: Ben, Craig, Ed, and all the previous students in the CTPL. As well, I would like to express my gratitude to everyone at the Fuel Cell Research Centre, especially Jason and Barbra, for the great spirit of cooperation that exists there. The supply of materials from the National Research Council is also greatly acknowledged.
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# Nomenclature

**Roman** – *Note: bold typeface in the text indicates a vector quantity*

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>area</td>
<td>(c_K)</td>
<td>Klinkenberg constant</td>
</tr>
<tr>
<td>(D)</td>
<td>diameter</td>
<td>(c_p)</td>
<td>specific heat</td>
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<td>(D_{ij})</td>
<td>molecular diffusivity</td>
<td>(d_p)</td>
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<td>Knudsen diffusivity</td>
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<tr>
<td>(L)</td>
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<td>(q)</td>
<td>heat flux</td>
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<td>(r,z)</td>
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<td>(Q)</td>
<td>volumetric flow rate</td>
<td>(t)</td>
<td>time, thickness</td>
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<td>universal gas constant, resistance</td>
<td>(u,u)</td>
<td>axial and radial velocity components</td>
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<td>(V)</td>
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<td>(Y_i)</td>
<td>mass fraction of species (i)</td>
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<tr>
<td>(Z)</td>
<td>moles of charged species</td>
<td>(Z)</td>
<td>moles of charged species</td>
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**Greek**

<table>
<thead>
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<td>(\kappa)</td>
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<td>(\tau)</td>
<td>tortuosity</td>
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<td>(\xi)</td>
<td>diffusion volume</td>
</tr>
<tr>
<td>(\delta)</td>
<td>distance</td>
</tr>
<tr>
<td>(\phi)</td>
<td>potential, scalar quantity</td>
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Chapter 1

Introduction

1.1 Background and Motivation
As humanity warms up to the idea that current habits of energy consumption are affecting the planet, research and development of fuel cell technology is expanding for several important reasons. First, fuel cells offer improved efficiency in using resources for energy; unlike conventional power systems, fuel cells convert the stored chemical energy in fuel directly into electrical energy, bypassing conventional conversion of fuel into mechanical and then electrical energy. Second, fuel cells can operate with water as their only by-product. Depending on the fuel source, this could potentially affect air pollution in a dramatic way, and help to change an undesirable geopolitical system based on the fossil fuel economy. Lastly, fuel cells have the promise of changing the structure of regional energy systems. Their modular nature allows cells to be stacked into systems of all power ranges, which could lead to further efficiencies by locally producing and distributing electricity.

1.2 SOFC Basics
Fuel cells certainly present opportunities to advance the way in which societies produce and consume energy. SOFCs, in particular, have proven to be some of the most efficient devices for the direct conversion of fuel energy into electricity.
especially in combined heat and power (CHP) applications, for which some companies are claiming system efficiencies of nearly 90%. SOFCs generate electricity based on a widely seen concept, that of the battery. The similarities between these two types of cells are twofold; both have a positive and negative electrode, separated by an electrolyte, and both convert chemical energy directly into electrical energy. Fuel cells differ in that the fuel is supplied externally, and this enables them to run until the fuel is spent.

Figure 1.1: Schematic of an SOFC [2].

Figure 1.1 details the basic operation for a typical hydrogen-fuelled SOFC. There are two separate reactions that take place within the anode and the cathode. When connected in an external electric circuit, these reactions create a current of charged particles through the positive electrode, across the electrolyte, and into the negative electrode (this structure is herein referred to as the PEN, for Positive Electrode/Electrolyte/Negative electrode) which can be used to do
useful work. In the cathode, oxygen gas combines with electrons to form adsorbed oxygen ions in its half-cell reaction

\[
\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \quad (1.1)
\]

Passing through the electrolyte, the oxygen ions diffuse through the solid electrolyte lattice. To complete the circuit, hydrogen is oxidized to form water and electrons at the triple phase boundary (TPB) of the anode

\[
H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (1.2)
\]

The TPB is a region containing the confluence of gaseous hydrogen, oxygen ion species, and electrons in the solid cell matrix, as shown in Figure 1.2.

![Figure 1.2: Detail of anodic reaction in the TPB region [3].](image)

The net reaction for the cell is

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O + heat \quad (1.3)
\]
As depicted in this overall cell reaction, water and heat are the only products of operation, and if one assumes that the hydrogen fuel is produced ecologically, the environmental benefits of this form of electricity generation are obvious.

1.2.1 SOFC materials and microstructure

Fuel cells are generally categorized according to the material composition of the electrolyte. For example, SOFCs are so named because the electrolyte is composed of a dense, solid oxide, and in a majority of SOFCs, this material is yttria-stabilized zirconia (YSZ). The electrode materials tend to change often as new materials are tried, and thus they are not considered in the classification. For the cell models developed in this work, the anode is composed of a mixture of Nickel and YSZ, while the cathode is composed of lanthanum strontium manganite (LSM) and YSZ. The combining of the electrode and electrolyte materials creates a composite electrode, which is an advancement that extends a conventional reaction zone from the planar electrode/electrolyte surface to create an extended TPB region. This is common in modern SOFC science and has the effect of increasing the surface area for the respective charge-transfer reaction, and thus increasing cell performance. Figure 1.3 shows a scanning electron microscope (SEM) image of the PEN for the micro-SOFC upon which the models in this work is based. The cell microstructure can be seen to consist of sintered, relatively spherical particles of the respective electrode and electrolyte material.
1.2.2 Types and Sizes of Cells

There are in general three types of SOFCs: Planar, which have the advantage of compactness, and high power density; Tubular, which have the advantage of excellent sealing characteristics; and other SOFCs that have irregular shapes.

1.2.2.1 Planar

Planar cells have the advantage that, due to their flat shape, they are easily assembled in stacks to give high power density. Furthermore, current collection is easily applied over the electrode surface area, and this results in low interconnection losses. A major disadvantage, however, is the sealing of the cell layers to prevent the fuel and oxidant from bypassing the electrolyte (referred to as crossover). A planar cell is depicted in Figure 1.4.
1.2.3 Tubular

Tubular cells have the advantage that their geometry results in an inherent seal between layers of the PEN, and fabrication can be simple. However, these cells tend to be long and small in diameter, and are susceptible to reliability and failure issues due to induced thermal stresses. A typical anode-supported tubular cell is shown in Figure 1.5. Companies like Siemens-Westinghouse and Acumentrics have developed these types of cells.
1.2.4 Irregular Shapes

Hybrid cell designs are currently being developed by companies like Rolls-Royce and Siemens-Westinghouse to combine the best aspects of both the traditional planar and tubular designs. Due to irregular shapes, these cells are more difficult to manufacture and handle. An example is shown in Figure 1.6.

![Figure 1.6: Example of a mono-block layer-built (MOLB) type cell [4].](image)

The type of cell considered in this work is of the tubular variety, and in one case has a cell diameter of roughly 2mm and active cell length of approximately 2cm. These dimensions are both an order of magnitude smaller than standard tubular cells. The small size, and associated small thermal mass, tends to mitigate the thermal stress problems that plague typical tubular SOFCs. Other issues, such as start-up time, cell fragility, and volumetric power density are improved by the reduced size as well.
1.2.5 Operating Temperature

Depending on the technology, an SOFC operates over a range of 600°C-1000°C; the main reason for this is to ensure the acceptable conductivity of oxygen ions through the electrolyte. One specific development goal is the reduction of this temperature in order to use metal materials; this would reduce overall cost and improve durability. As temperatures get lower, materials become less expensive, and there is a reduced need for expensive heat exchangers and other balance of plant components.

A further benefit of high temperature operation is that SOFCs can reform a variety of hydrocarbons such as methane and diesel, and use the reformate as an operating fuel. While hydrocarbons as a fuel would quicken the uptake of this technology (due to existing infrastructure), their use in cells still presents some issues such as carbon deposition that leads to loss of electrode activity [1].

1.3 Electrochemistry and Fuel Cell Performance

This work includes a CFD model that can predict the performance of a SOFC under a given set of conditions. It is a common approach to define the performance of a fuel cell by considering some thermodynamically ideal potential, and then subtracting the various losses which result in departure from this ideal value. Considering the SOFC in Figure 1.1 to not be connected to an external circuit, a potential difference develops across the anode and the cathode. This
open-circuit potential, also known as the Nernst potential, $E_{\text{Nernst}}$ represents the maximum electrical potential available under electrochemical equilibrium. For a hydrogen-fuelled cell (with half-cell reactions defined by equations (1.1)-(1.3)), the Nernst potential is

$$E_{\text{Nernst}} = -\frac{\Delta G}{ZF} = E^0 + \frac{RT}{ZF} \ln \frac{p_{H_2}p_{O_2}^0}{p_{H_2O}}$$

(1.4)

where $\Delta G$ is the change in Gibbs energy for the overall reaction, $Z$ is the number of electrons exchanged, $R$ is the universal gas constant, $F$ is Faraday’s constant, and $p_i$ is the partial pressure for each $i$ species.

The Nernst potential depends on two terms: the standard potential $E^0$ for the overall reaction, which is derived from thermodynamics and is a function of temperature, and a second term which involves the change in chemical potential with reactant and product concentrations [1]. There is departure from this equilibrium potential when the cell is connected in an electrical circuit and a current is drawn. This is due to various irreversibilities associated with operation, generally accepted to be caused by driving the electrochemical reaction (known as activation effects), ohmic losses due to charge transport, and mass transport (concentration) effects that reduce the Nernst potential and slow the reaction kinetics. One can thus measure performance of a fuel cell as the difference of these various losses and the ideal Nernst potential.
\[ E_{\text{cell}} = E_{\text{Nernst}} - (\eta_{\text{activation}} + \eta_{\text{ohmic}} + \eta_{\text{concentration}}) \quad (1.5) \]

where \( \eta \) denotes the overpotentials. The term overpotential refers to losses related to the departure from the equilibrium potential in order to drive a given current.

![Polarization curve for a micro-tubular cell](image)

**Figure 1.7:** Polarization curve for a micro-tubular cell. Data courtesy of the Alberta Research Council.

The characteristic visualization of fuel cell performance is the polarization curve, and Figure 1.7 shows a typical curve for the micro-tubular cell that was under investigation in this work. The polarization curve shows the relation between the potential and the average current flowing through the cell.
1.3.1 Cell Current

When a cell is connected in a circuit and departs from the open-circuit Nernst potential, a net current results from the charge transfer reactions, and this net current can be related to the electrode overpotential by the Butler-Volmer equation

\[ i_{\text{electrode}} = i_0^{\text{electrode}} \left( \exp \left( \frac{\alpha_a F \eta}{RT} \right) - \exp \left( \frac{-\alpha_c F \eta}{RT} \right) \right) \]  

Equation (1.6) describes the relationship between the current density for an electrode, \( i_{\text{electrode}} \), the exchange current density at equilibrium \( i_0 \), the overpotential \( \eta \), and temperature. The charge transfer coefficients, \( \alpha_a \) and \( \alpha_c \), express the fraction of the electrical energy resulting from the overpotential \( \eta \) that affects the rate of electrochemical transformation. This equation is based in general reaction kinetic theory, and will be discussed at length in Chapter 4. For more insight into its origins, the reader is referred to a more thorough discussion in the text by Bockris and Reddy [6].

The half-cell reactions at each electrode have the effect of, in the case of the anode, injecting mass, and for the cathode, removing mass, from each respective gas stream. This phenomenon is governed by Faraday’s law, which relates the moles of a substance consumed or produced to the current of charged species in an electrochemical reaction.
where $n$ is number of moles of the substance, $Z$ is the number of moles of charged species, and $I$ is the current. In this way, the sources of mass, momentum, and species are quantified and can be included in the governing equations of transport to represent the effects of electrochemical reaction.

1.4 Development Issues

While the benefits of fuel cells are apparent, there are many technological hurdles to overcome before they can become viable competitors to other forms of energy conversion. An introduction to SOFCs should include a discussion of some of these hurdles. Simply put, SOFCs are currently limited by cost and temperature. Research efforts are strongly aimed at reducing the high material costs associated with SOFCs, and this will happen when a SOFC design is achieved that avoids a temperature-limited scenario, and shows good electrochemical performance. Such a design would exhibit the following characteristics: a) maximization of heat transfer to avoid thermal stresses in the cell and ensure that the mechanical stability of the cell is not compromised; b) cell performance is not limited by the transport of fuel and oxidant to the electrochemical reaction sites; c) electron and ion transport losses are minimized. It is a very difficult practise to manage these criteria; often enhancing one may negatively affect another. For example, by increasing the porosity of the electrode to achieve higher mass transport, the
mechanical strength and charge transport characteristics of the cell may be lessened.

1.5 Convective transport in SOFCs
One way in which we can advance SOFC design is to better understand the fundamental processes that affect performance. Specifically, the highly coupled transport of mass, momentum, and heat needs to be fully understood. Currently, the literature seems to have a collective view that convective transport is secondary, if not negligible in SOFCs. Justification for this is rarely given, but this view is seemingly based in the fact that fuel and oxidant feed rates tend to be very low in magnitude, and the permeability of SOFC electrodes is usually fairly low as well. However, it may be that convection is more important than is generally thought, and if so, perhaps this convection could be maximised to achieve desirable effects, such as lower electrical losses due to reactant concentration, and higher heat transfer rates. It is a central goal of this thesis to investigate this.

1.6 CFD Modeling of SOFCs
Due to the many problems faced by SOFC development, the field of SOFC modeling has become prolific over recent years, especially because it helps to elucidate the complex, coupled processes that control fuel cell performance. Potential time and cost savings compared to building costly prototypes are one
reason for this, but perhaps more important is that a numerical model, through simple parametric studies, can shed light on favourable operating conditions and guide development of optimal SOFC design. In addition, a model can provide an idea of field information that is unobtainable through conventional measuring methods, such as local temperature and gas pressure in the PEN structure.

1.7 Goals of Research

The principal goal of this research is to better understand the physical and electrochemical processes in a SOFC by developing an accurate, cell-level model using CFD. This model will be used to investigate the importance of convective transport in SOFCs, and will do so by comparing an approach that solves the full transport equations, to a common approach in the literature that does not include convection. Between these two approaches, the differences in variation of mass, temperature, and electrochemical performance will be analysed.

To better understand convective transfer, a further goal of this work is to accurately characterise the permeability of SOFC electrodes and determine its importance on predicted cell performance. To that end, experimental work was performed whose results will be discussed and used to investigate the implications of the widely held view that permeability is a constant parameter. With a better understanding of the role of convection, it is hoped to suggest how it can be improved and used to improve the design and performance of a SOFC.
1.8 Organization of Thesis

Following this introduction, Chapter 2 contains a literature review of recent modeling approaches in SOFCs, including an investigation into assumptions about convective transport. The case is made that, too often, convection is ignored in the modeling literature and this practise needs to be analysed. In Chapter 3, this discussion is continued and the importance of convective transfer investigated with an analytical study. Chapter 3 also describes and presents the results of experiments that characterise the permeability of SOFC anodes. In Chapter 4, the CFD model is developed, validated, and verified, while Chapter 5 presents and analyses the results of modeling studies that elucidate the questions surrounding convective transfer in SOFCs. Chapter 6 summarizes and draws conclusions from the work, as well as suggests directions for future research.
Chapter 2

Literature Review

This chapter presents a survey of topics in the SOFC literature that will acquaint the reader with concepts that are discussed in this work. First, basic approaches to SOFC modeling, including presentation of governing equations of mass, momentum, and heat transport, are presented. This is followed by a survey of modeling approaches in the literature, from which an argument is formulated against the common approach of assuming that convection is negligible in SOFC electrodes. With a focus on convection, a review of the permeability of electrode materials is also presented, and a discussion of accurate characterization of permeability is developed in support of the experimental work that was performed in this work. The chapter ends by considering recent approaches to modeling heat transfer in SOFCs.

2.1.1 Governing Equations

As the performance, lifespan, and reliability of an SOFC are directly related to the myriad processes that occur within a cell, it is essential to have an understanding of the physical and chemical laws that predict the variation of mass, fluid motion, and energy in a fuel cell. To begin, we can consider the steady-state general transport equation for a variable $\phi$ over a control volume of interest
Equation (2.1) mathematically expresses the conservation of $\phi$, relating it to a source term within the control volume and the divergence of the difference of a convective flux, $J_C$, and a diffusive flux, $J_D$ [7], where

$$J_C = \rho \nu \phi$$

(2.2)

$$J_D = -\Gamma \nabla \phi$$

(2.3)

and $\rho$ is the density of the fluid, $\nu$ is the fluid velocity, $\Gamma$ is a diffusion coefficient, and $S_{\phi}$ is a source term. The general transport equation can be manipulated to express the physical conservation laws that govern fluid flow. For example, when $\phi=1$, equation (2.1) takes the form of conservation of mass

$$\nabla \cdot (\rho \nu) = S_m$$

(2.4)

Similarly, when $\phi=\nu$, an expression for conservation of momentum can be derived. For a Newtonian fluid, momentum conservation is governed by the Navier-Stokes equations

$$\nabla \cdot (\rho \nu_k \nu - \mu \nabla \nu) = -\nabla p + S_{mom,k}$$

(2.5)

where $\mu$ is the viscosity of the fluid, $p$ is pressure, and $u$ is the velocity component for a direction, $k$. Neglecting viscous dissipation, conservation of energy can be expressed as
\[ \nabla \cdot (\rho v c_p T) = \nabla \cdot \left( k \nabla T - \sum_i h_i J_{D,i} - q_{rad} \right) + S_T \]  

(2.6)

where \( c_p \) is the heat capacity of the fluid, \( k \) is the thermal conductivity, \( h_i \) is the specific enthalpy of species \( i \), and \( q_{rad} \) is the heat flux due to radiation. This equation balances convected energy with conduction, species energy diffusion, radiation, and a source term.

2.2 Transport in SOFC Electrodes

SOFC performance is critically controlled by transport in the electrodes, as the electrochemical reaction rates depend directly on the temperature and partial pressures of species near the electrolyte. In an SOFC, there are two distinct regions in which these variables must be modeled: the fuel/oxidant channels, and the electrodes. In the non-porous fuel and oxidant channels (see Figure 1.1), the above set of conservation equations can be solved directly. However, in the electrode regions, porous media effects on mass, momentum, and heat transport must be accounted for. Accurate variable prediction then depends on considering several factors, especially the microstructure of the porous medium and the flow regime. Microstructural parameters include the average pore diameter \( d_p \), porosity \( \varepsilon \), and tortuosity \( \tau \). Tortuosity attempts to express the twistedness of the fluid path through a porous region, and is defined between two points as the actual fluid path length divided by the distance in space. The flow regime can be
characterised by the Reynolds number of the flow, $Re$, which is the ratio of inertial to viscous forces acting on the fluid

$$Re = \frac{\rho v L}{\mu}$$

(2.7)

where $L$ is some characteristic length that describes the flow. For flow in a tube, $L$ is the tube radius or diameter; for flow in a porous medium, $L$ is often taken as the average pore diameter.

For transport in porous media, when $Re$ is sufficiently low ($< 1$) viscous forces dominate over inertial forces and a fluid is said to be in the seepage or creeping flow regime [8]. In this regime, Darcy showed that the unidirectional flow rate of a fluid through a porous medium is proportional to the pressure across it

$$\nu_s = -\frac{\kappa}{\mu} \frac{\partial p}{\partial x}$$

(2.8)

where $\nu_s$ is the seepage velocity and represents the volume-averaged velocity for the entire porous medium (instead of the physical velocity in the pore channel), and $\kappa$ is the permeability of the medium. Permeability quantitatively describes the ability of a porous medium to conduct fluid flow, and it is often viewed as a fluid-independent property, in that it is a function only of the microstructure of the porous medium [8]. Numerous attempts have been made to correlate permeability with microstructural parameters, but in the fuel cell modeling literature its accurate characterization is generally of secondary concern, and $\kappa$ is
often taken as a constant. For researchers that do model permeability, the use of the Kozeny-Carman relation is prolific

\[ \kappa = \frac{d_{\text{particle}}^2 \varepsilon^3}{C_{KC} (1 - \varepsilon)^2} \]  

(2.9)

In (2.9), \( C_{KC} \) is a constant. As will be discussed in Section 2.2.3, many SOFC models have been proposed in which \( \kappa \) was an arbitrarily chosen parameter, and part of this work will investigate the implications of this on cell performance.

### 2.2.1 Transport by Diffusion in SOFC electrodes

SOFCs are generally supplied by feed gases at low flow rates, and transport by diffusion is consequently important. An informative survey on diffusive mass transfer in SOFCs was performed by Suwanwarangkul et al. [9], where Fick’s model, the Stefan-Maxwell model, and the Dusty Gas Model were all compared. The prolific usage of the Bosanquet formulation is discussed, in which equi-molar counter-diffusion is assumed among gaseous particles in binary mixture

\[ D_i = \left( \frac{1}{D_{i,k}} + \frac{1}{D_{i,j}} \right)^{-1} \]  

(2.10)

where the molecular diffusivity, \( D_{i,j} \), is calculated from Fuller et. al [10]:
In (2.11) $\xi_i$ is the diffusion volume of species $i$. Suwanwarangkul et al. concluded that, depending on electrode microstructure, Knudsen diffusion should be taken into account in SOFC electrodes. The Knudsen diffusivity, $D_{i,Kn}$, is given by

$$D_{i,Kn} = \frac{1}{3} d_i \left( \frac{8RT}{\pi M_i} \right)^{1/2}$$

(2.12)

However, Suwanwarangkul et al. recommended that the Dusty Gas model was most appropriate in predicting diffusive mass transfer in SOFC electrodes. The Dusty Gas model expresses the diffusive flux for mass fraction $i$ in an $i$-$j$ mixture as

$$J_{D,i} = \rho \left( \frac{1}{D_{Kn,eff}} + \frac{1 - \alpha_{i,j} Y_i}{D_{i,j,eff}} \right)^{-1} \nabla Y_i; \quad \alpha_{i,j} = 1 - \left( \frac{M_i}{M_j} \right)^{1/2}$$

(2.13)

In (2.13), the term $(1-\alpha_{i,j}) Y_i$ accounts for non-equimolar counter diffusion, which is an important consideration when the molecular masses of the involved species differ considerably [11], such as in the case of a $H_2$-$H_2O$ system in the anode. (2.13) refers to effective diffusivities which account for transport in porous media. These diffusivities were calculated by applying Bruggeman’s correction
\[ D_{\text{eff}} = D \varepsilon^{1.5} \]  

which accounts for transport effects through a medium characterised by a packed bed of spherical particles, which is not unlike that considered in this work [12].

\subsection*{2.2.2 Transport by Convection}

While diffusion is an important mode of transport in SOFCs, convection, which is certainly important in the fuel channels, must occur in the porous electrodes and may be considerable in the electrodes under certain conditions (e.g. high current density) [13]. Due to the difficulty in solving the full set of transport equations, however, an assumption dismissing the role of convection is often made. In general, this is done by assuming constant pressure across the electrode, and solving a diffusion transport equation for the variable of interest. However, given that electrochemical performance is highly coupled to the partial pressures of product and reactant species, this practise seems debatable.

This approach is often seen in electrode-level models that focus on detailed electrochemical modeling [14-17]. It is not only limited to those focused on electrochemistry, however, as there is a breadth of work in the cell-level modeling literature [18-30] that disregards convective transport as well. For example, in an often-cited paper, Campanari and Iora [27] solved air and fuel flow in the channels of a tubular cell using a 2-D model in FLUENT, but gas species variation in the electrodes was estimated via a simplified 1-D diffusion model.
Hussain et al. [21] also modeled 1-D diffusive transport, though used the finite volume method to solve the diffusion equations. The usefulness of a 1-D model in anything other than a small test cell (where gas concentrations are relatively uniform over the channel/electrode surface), is questionable, as significant concentration and temperature gradients do generally arise.

There were many who took this simplified approach in two and three dimensions, however. Abbaspour et al. [19] looked at isothermal 2-D transport of oxygen in the cathode by solving a diffusion equation in COMSOL, and Aguiar et al. [28] considered diffusion only of heat and mass at constant pressure in the PEN. The list continues to include the work of Chan et al.[31], as did the work by Aloui et al. [26], Bhattacharyya et al. [20], Sanchez et al.[32], Hernandez-Pacheco et al. [33] and Morel et al. [30]. Nikooyeh et al. developed a 3-D model in COMSOL with no consideration of convective transport in the electrodes [29].

The common thread through these works is an assumption of constant pressure across the electrode (and sometimes in the flow channels). Justification for this constant pressure assumption was offered by assuming no convection and also by assuming equi-molar counter-diffusion between the gaseous species in the electrode. Several researchers have shown that equi-molar counter-diffusion is in general not a safe assumption to make. In the aforementioned work on diffusion by Suwanwarangkul et al., claims were made as to its inappropriateness in a
SOFC application [9]. Other researchers discuss and share this view [11,13]. The assumption of constant pressure and zero velocity could lead to an inaccurate density, and the implications that this has on the variations of gas species could be significant.

In order to quantify convective effects on the potential of a SOFC, Beale [34] noted that at high mass transfer rates (high current density) there was significant deviation from the above approaches and one that includes convection [34]. Recently, Ni et al. [13] discussed this topic, by comparing an overpotential model that included and neglected the effects of varying pressure. It was shown in that work that predicted concentration overpotentials varied by as much 20%, again at higher current densities. While these two works have started an important discussion, it would be useful to compare, side-by-side, a simplified diffusion approach versus full solution of the governing conservation equations.

2.2.3 Gas Permeability in Electrodes

Perhaps as important as including convective transfer in a fuel cell model, is being able to predict it accurately. In laminar flow of a Newtonian fluid in porous media, such as is generally assumed in SOFCs, momentum is usually characterized by solving Darcy’s Law [35]. In the Darcy equation (2.8), it is well understood that for the ideal gases that are modeled in SOFCs (e.g. oxygen, hydrogen), viscosity varies with temperature [36]. Less well understood, however,
is how the permeability, $\kappa$, varies, and according to which parameters. In light of this, a survey was conducted to examine the treatment of electrode permeability in the literature, with the results presented in Table 2.1. It was found that for similar electrode materials, variation in the value for $\kappa$ was quite significant; ranging from $10^{-12} - 10^{-16}$ m$^2$, while permeability measurements from actual experiments fall on the lower end of that range.

**Table 2.1:** Literature $\kappa$ values for a Ni-YSZ anode or a LSM-YSZ cathode.

<table>
<thead>
<tr>
<th>$\kappa_{\text{anode}}$ [m$^2$]</th>
<th>$\kappa_{\text{cathode}}$ [m$^2$]</th>
<th>Method</th>
<th>Microstructure</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.18 x 10^{-14}</td>
<td></td>
<td>Permeametry, porosimetry</td>
<td>$\varepsilon \approx 0.4$, $1\mu m &gt; d_p &gt; 5\mu m$</td>
<td>[37]</td>
</tr>
<tr>
<td>1.4 x 10^{-14}</td>
<td></td>
<td>Permeametry</td>
<td>$\varepsilon &gt; 0.3$</td>
<td>[38]</td>
</tr>
<tr>
<td>2.96 x 10^{-14}</td>
<td></td>
<td>Permeametry</td>
<td>$\varepsilon=0.3$, $d_p=1\mu m$</td>
<td>[39]</td>
</tr>
<tr>
<td>9.83 x 10^{-15}</td>
<td></td>
<td>Permeametry</td>
<td>$d_p \approx 0.5-10\mu m$</td>
<td>[40]</td>
</tr>
<tr>
<td>1.5 x 10^{-15}</td>
<td></td>
<td>Permeametry, porosimetry</td>
<td>$0.2 &gt; \varepsilon &gt; 0.5$</td>
<td>[41]</td>
</tr>
<tr>
<td>$10^{-12}$</td>
<td>$10^{-12}$</td>
<td>constant parameter</td>
<td>$\varepsilon=0.38-0.5$, $d_p=1-2\mu m$</td>
<td>[42,43]</td>
</tr>
<tr>
<td>1.7 x 10^{-12}</td>
<td>1.7 x 10^{-12}</td>
<td>constant parameter</td>
<td>$\varepsilon=0.3$, $d_p=1\mu m$</td>
<td>[44]</td>
</tr>
<tr>
<td>1.57 x 10^{-12}</td>
<td>1.57 x 10^{-12}</td>
<td>constant parameter</td>
<td>$d_p=1\mu m$</td>
<td>[4]</td>
</tr>
<tr>
<td>1.76 x 10^{-11}</td>
<td>1.76 x 10^{-11}</td>
<td>constant parameter</td>
<td>$\varepsilon=0.5$</td>
<td>[2]</td>
</tr>
<tr>
<td>1.0 x 10^{-7}</td>
<td>1.0 x 10^{-7}</td>
<td>constant parameter</td>
<td>$\varepsilon=0.9$</td>
<td>[5]</td>
</tr>
<tr>
<td>2.18 x 10^{-14}</td>
<td>3.6 x 10^{-14}</td>
<td>Kozeny-Carman</td>
<td>$\varepsilon=0.35$, $d_p=0.5\mu m$</td>
<td>[45]</td>
</tr>
<tr>
<td>1.27 x 10^{-14}</td>
<td>1.27 x 10^{-15}</td>
<td>Kozeny-Carman</td>
<td>$\varepsilon=0.3$, $d_p=0.5\mu m$</td>
<td>[16]</td>
</tr>
<tr>
<td>9.237 x 10^{-15}</td>
<td>9.237 x 10^{-15}</td>
<td>Kozeny-Carman</td>
<td>$\varepsilon=0.5$, $d_p=2.5\mu m$</td>
<td>[17]</td>
</tr>
<tr>
<td>1.9 x 10^{-15}</td>
<td>1.9 x 10^{-15}</td>
<td>Kozeny-Carman</td>
<td>$\varepsilon=0.3$, $d_p=1\mu m$</td>
<td>[46]</td>
</tr>
<tr>
<td>8 x 10^{-16}</td>
<td>8 x 10^{-16}</td>
<td>Kozeny-Carman</td>
<td>$\varepsilon=0.4$, $d_p=0.9\mu m$</td>
<td>[47]</td>
</tr>
<tr>
<td>(6 x 10^{-15})</td>
<td>(6 x 10^{-15})</td>
<td>Kozeny-Carman (numerical experiment)</td>
<td>$\varepsilon=0.4$, $d_p=0.9\mu m$</td>
<td>[47]</td>
</tr>
<tr>
<td>1.27 x 10^{-15}</td>
<td>1.27 x 10^{-15}</td>
<td>Kozeny-Carman</td>
<td>$\varepsilon=0.3$, $d_p=0.5\mu m$</td>
<td>[26]</td>
</tr>
</tbody>
</table>

It is noteworthy that only a handful of papers in the SOFC literature have actually reported gas permeability measurements. From the few that have, two
methods were employed to characterise the electrodes. *Permeametry* was one method, which involves measuring the permeability of a fluid through a sample under a known applied pressure, and subsequent measurement of the flow rate. The permeability can then be determined from Darcy’s Law. Another method was *porosimetry*, which involves the intrusion of a non-wetting liquid (often mercury) at high pressure into a sample. The porosity and pore size distribution of a sample can then be determined based on the external pressure needed to force the liquid into a pore against the opposing force of the liquid's surface tension [37,40].

Currently in the SOFC modeling literature, permeability is almost exclusively seen as depending only on electrode morphology. It is often estimated by the Kozeny-Carman equation (2.9), which has been used to model materials characterized by packed spherical particles, whose diameters fall within a narrow range [8]. In general, this situation is suitable for the porous geometry of an SOFC. Glass and Green [48] noted, however, that for studies which compared Kozeny-Carman to permeability experiments on sintered ceramics, there was good agreement at relative porosities of greater than 25%, but at lower porosities, predictions tended to deviate from experimental values. This was attributed to the fact that as porosity decreased, pores shrunk and closed, which created a more tortuous and impermeable path for mass transport.
From the survey in Table 2.1, there seems to be reasonable correlation between measured permeability and estimates derived from the Kozeny-Carman equation, however. The variance spans two orders of magnitude, however, and this certainly warrants further investigation. But perhaps more remarkable than the variance between these informed values, is the actual values used when permeability is taken as a parameter. Many papers have used permeability values 3-4 orders of magnitude lower than what has been measured, often without discussion or justification. Given the doubt around the values for permeability, it was deemed appropriate to perform experiments on electrodes to not only add to values reported in the literature, but to investigate other factors such as permeability at the high temperatures under which SOFCs operate.

2.3 Heat Transport

It must be acknowledged that heat transfer in SOFCs critically affects cell performance, as the rates of the charge transfer reactions depend directly on the local temperature. While there are several modes of heat transfer in an SOFC, temperature is chiefly controlled by the anode and cathode gas streams. In the majority of cells, heat is removed by the cathode air supply, where the oxidant is generally supplied at approximately 4-10x the stoichiometric ratio required for the overall reaction [1]. This can mean high electric demand for auxiliary blowers and large heat exchanger areas for preheating the cathode air; from a system
efficiency perspective, these are two solutions that are undesirable. The efficient
control of heat in SOFCs is thus of utmost importance.

2.3.1 Temperature Boundary Conditions

In a model, the prediction of an accurate temperature field is also of chief
importance, because temperature can have a profound effect on cell performance
and mechanical stability. Boundary conditions at exterior boundaries (i.e.
channel walls) play a large role in this prediction, and in the literature these
boundaries have been taken as isothermal walls and adiabatic walls.

Fixed temperature conditions were used in [49,50]. This is a somewhat
reasonable condition, as cells are usually tested and operated in controlled
temperature environments such as a furnace, and because current and voltage
plots are usually given for a specific operating temperature. However, this
approach may over-predict heat transfer from the cell and lower the predicted
temperature. If the boundary at the exterior of the cell is a furnace wall,
however, then a fairly uniform temperature may be plausible.

Of interest to this discussion, Li and Chyu [51] proposed a 2-D analysis of a
tubular cell as part of a stack, in which adiabatic conditions were imposed on
exterior boundaries to simulate non-interaction between cells in the stack.
Temperature results were surprising in this study in that the maximum
temperature and the temperature gradients along the cell decreased with
increasing current density. This could be a consequence of the assumption of constant exchange current density, which is a kinetic parameter that should rightly vary with local species concentrations and temperature.

Other tubular SOFC models employed adiabatic boundary conditions at channel walls [25,32,45], and the choice in differing types of external boundaries is likely due to the simulation of differing environments (i.e. a cell stack environment vs. a furnace). A study by Suwanwarangkul et al. [46] imposed adiabatic boundary conditions at the exterior boundaries of a cell-level model of a tubular SOFC (radiation was included). Results from this study showed a reasonable temperature profile along the cell length.

2.3.2 Radiation

A more recent development in SOFC modeling involves the incorporation of radiative heat transfer. Recently, Austin, VanderSteen, and Pharoah [50,52] performed extensive analysis on the radiative heat transfer characteristics of SOFCs. Their findings showed that the inclusion of radiative transfer reduces the peak temperatures and temperature gradients in an SOFC, and results in a more uniform temperature field within the cell. A further important result of these studies was that the feed tube used in tubular cells profoundly increased heat transfer to and from the gas which flows through it.
Suwanwarangkul et al. and others have noted from 2-D simulations that in long tubular cells (greater than 20cm in length), mechanical failure can occur due to induced thermal stresses, and modeling radiation can help accurately predict the susceptibility to this phenomenon. The importance of considering radiation in a tubular design where there is a pre-heating gas feed tube (as in this work) was also stressed [46]. Models which neglect radiation may be in substantial error and these findings are echoed in the literature. However, this opinion is not unanimous, as several groups found that radiation was negligible, especially when compared to the moderating effects of the channel feed flows [53].

2.4 Summary
This chapter has presented surveys of the literature that have shed light not only on modeling practises that ignore convective transport, but on the characterization of SOFC permeability and different approaches to modeling heat transfer. It was found that permeability values for SOFC electrodes should be on the order of $10^{-14} \text{m}^2$ or lower; anything above this order of magnitude was generally unjustified and chosen arbitrarily. From the heat transfer survey, it was found that radiation effects are important, and consideration should be taken for temperature boundary conditions at exterior walls. It was also deemed appropriate to investigate the implications of ignoring convection in a model. Solving a diffusion equation with a constant pressure does not properly simulate
the chemical reactions in the electrodes. This may have important effects, and is investigated further in Chapter 5.
Chapter 3
Convective Transfer in Porous Electrodes

A cornerstone of this thesis is the notion that a clear and thorough understanding of mass, momentum and heat transport is necessary in order to accurately predict the performance of a fuel cell. To that end, this chapter continues the discussion in the Literature Review on the characterization of convective transport in SOFC electrodes. It presents a study that investigates and discusses characteristic indicators of convective flow, such as the Peclet number, and the pressure change across an electrode layer. The discussion also looks deeper into microstructural effects on flow in the electrodes, specifically at Knudsen (pore-wall) effects on convective flow characteristics. An empirical relation that relates Knudsen effects to gas permeability is suggested to incorporate these effects into the modeling approach, and it is believed that these considerations will lead to a better representation of the flow physics and a more accurate performance prediction for a SOFC.

3.1 The Importance of Convective Flow in SOFC Electrodes
This section investigates the importance of convection in SOFC electrodes by way of a simple analytical study that estimates the magnitude of convection and pressure drop for a grouping of cells of varying sizes.
3.1.1 The Peclet Number

In order to ascertain whether it is justifiable to neglect convection in models, some kind of criterion is needed. One such criterion is the Peclet number, $Pe$, which is the dimensionless ratio of convective to diffusive transport of a flow

$$Pe = \frac{vL}{D}$$  \hspace{1cm} (3.1)

In (3.1), $L$ is some characteristic length, and $D$ is a diffusion coefficient. In this discussion, $L$ is the thickness of the porous electrode layer under consideration. A simple study was performed on planar cells of varying thicknesses to characterise Peclet numbers for typical SOFCs under typical operating conditions.

3.1.2 Analytical Study

In this study, a planar SOFC with the anode as a support layer (i.e. it is thicker to provide mechanical support) was considered, reflecting many current designs. A schematic of this is shown in Figure 3.1.

![Figure 3.1: Cell geometry for Peclet number study.](image-url)
The fuel and oxidant in each electrode were assumed to have a constant composition. Material properties ($\rho$, $\mu$, $c_p$) were calculated based on a representative system pressure and temperature from the ideal gas law, and from the polynomial expressions proposed by Todd and Young [36]. Operating conditions assumed for this study are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
</tr>
<tr>
<td>$p$</td>
</tr>
</tbody>
</table>

Anode fluid composition 20/80 mass% $\text{H}_2/\text{H}_2\text{O}$ (constant)

Cathode fluid composition 23/77 mass% $\text{O}_2/\text{N}_2$ (constant)

$d_{\text{particle}}$ (electrodes) Anode= 1$\mu$m Cathode= 0.75$\mu$m [41]

<p>| Table 3.1: Conditions and data used in Peclet number studies. |</p>
<table>
<thead>
<tr>
<th>Source</th>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode fluid composition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hao &amp; Goodwin [54]</td>
<td>$t_a=700\mu$m</td>
<td>$t_a=10\mu$m</td>
</tr>
<tr>
<td>$\varepsilon=0.35$, $\tau=3.5$</td>
<td>$\varepsilon=0.35$, $\tau=3.5$</td>
<td></td>
</tr>
<tr>
<td>$K=1.01\times10^{-16}\text{m}^2$</td>
<td>$K=1.01\times10^{-16}\text{m}^2$</td>
<td></td>
</tr>
<tr>
<td>$r_{\text{pore}}=0.5\mu$m</td>
<td>$r_{\text{pore}}=0.5\mu$m</td>
<td></td>
</tr>
<tr>
<td>Greene et al. [55]</td>
<td>$t_a=1.0\text{mm}$</td>
<td>$t_a=20\mu$m</td>
</tr>
<tr>
<td>$\varepsilon=0.3$, $\tau=3.5$</td>
<td>$\varepsilon=0.3$, $\tau=3.5$</td>
<td></td>
</tr>
<tr>
<td>$K=2.19\times10^{-16}\text{m}^2$</td>
<td>$K=2.19\times10^{-16}\text{m}^2$</td>
<td></td>
</tr>
<tr>
<td>$r_{\text{pore}}=1.0\mu$m</td>
<td>$r_{\text{pore}}=1.0\mu$m</td>
<td></td>
</tr>
<tr>
<td>Janard, et al. [56]</td>
<td>$t_a=1.0\text{mm}$</td>
<td>$t_a=25\mu$m</td>
</tr>
<tr>
<td>$\varepsilon=0.4$, $\tau=2^*$</td>
<td>$\varepsilon=0.4$, $\tau=2^*$</td>
<td></td>
</tr>
<tr>
<td>$K=2.42\times10^{-15}\text{m}^2$</td>
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</tr>
<tr>
<td>$r_{\text{pore}}=1.40\mu$m</td>
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<td></td>
</tr>
<tr>
<td>Zhu &amp; Kee [17]</td>
<td>$t_a=500\mu$m</td>
<td>$t_a=30\mu$m</td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>$K=9.27\times10^{-17}\text{m}^2$</td>
<td>$K=9.27\times10^{-17}\text{m}^2$</td>
<td></td>
</tr>
<tr>
<td>$r_{\text{pore}}=5.0\mu$m</td>
<td>$r_{\text{pore}}=5.0\mu$m</td>
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<tr>
<td>Jung et al. [45]</td>
<td>$t_a=1.0\text{mm}$</td>
<td>$t_a=50\mu$m</td>
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<tr>
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<td>$\varepsilon=0.35$, $\tau=2$</td>
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<td>$r_{\text{pore}}=1.0\mu$m</td>
<td></td>
</tr>
</tbody>
</table>

*value was assumed*
Also found in Table 3.1 are microstructural data from five published modeling studies that were used as a basis for comparison [17,45,54-56]. These data are not actual measured cell data, except for that from [56]. For all data sets listed in Table 3.1, permeability values were calculated using the Kozeny-Carman equation (2.9). In all cases, the value for tortuosity was simply an unreferenced parameter, but according to the work by Wilson et al. [57], the tortuousity values were the right order of magnitude. With this data, the Peclet numbers were then estimated by the following method:

1. A constant current density was assumed across the entire electrode/electrolyte interface. A net volumetric flow rate, $Q$, was then calculated from Faraday’s law for each electrode reaction

$$Q_{\text{electrode}} = \frac{IM}{ZF \rho_{\text{electrode}}} \quad (3.2)$$

$$Q_{\text{anode}} = \frac{I}{2\rho_{\text{anode}}} F\left(M_{H_2O} - M_{H_2}\right) \quad (3.3)$$

$$Q_{\text{cathode}} = -\frac{I}{4\rho_{\text{cathode}}} F\left(M_{O_2}\right) \quad (3.4)$$

This volumetric flow rate represents the mass flux in the electrodes that is created by the electrochemical reactions. The molecular diffusivity for the species $i$, (incorporating both binary and Knudsen effects), was calculated using the Bosanquet Formula [58]:
\[ D_i = \left( \frac{1}{D_{i,k}} + \frac{1}{D_{i,j}} \right)^{-1} \] (3.5)

2. This diffusivity was corrected for porosity by applying either the Bruggeman or \( \varepsilon/\tau \) correction. Both corrections were applied and compared to test the effects of tortuosity on \( Pe \).

3. The physical velocity in the pores was calculated by dividing the volumetric flow rate by the cross-sectional area of pores

\[ v = \frac{Q_{\text{electrode}}}{A_c \varepsilon} \] (3.6)

4. The Peclet number was then calculated from equation (3.1).

5. The pressure drop due to the flow driven by electrochemical reaction was calculated using the flow rates from (3.3) and (3.4), and Darcy’s Law.

### 3.1.3 Results of Peclet Number Study

A set of figures is now presented to investigate effects of the differing physical parameters on the indicators of convection. Figure 3.2 and Figure 3.3 show \( Pe \) variation with current density, while Figure 3.4 and Figure 3.5 show the calculated pressure drop versus current density.
We can get an idea of the relative importance of convection from these plots. From the examination of Figure 3.2, it is shown that the magnitudes for $Pe$ under typical cell conditions were in the range of 0.01-0.1. This implies that the rate of convection, in the best-case scenario, is roughly 10% of that of diffusion. This signifies that convection plays a relatively minor role, but certainly noticeable when the $\varepsilon/\tau$ correction is used.
Figure 3.3 shows the variation of $Pe$ for the cathode. Again, the range spans an order of magnitude, though in this case from approximately 0.005 – 0.05. This is quite obviously a consequence of the very thin cathode layers, which were at least an order of magnitude smaller than the anodes. The Peclet number magnitudes suggest that for thin cathodes, convection plays a minor role and is perhaps negligible in predicting mass variation.
Figure 3.4 shows the calculated pressure drop across the anode, with a pressure differential range of 0.25x~3.25x atmospheric. This suggests a potentially significant pressure change that drives mass flow away from the electrolyte and out into the fuel channel. This pressure difference is created by the anodic half-cell reaction, and it serves to move water out of the reaction zone, but also to inhibit hydrogen transport into the reaction zone. This could mean significant differences in predictions of species partial pressures throughout the electrode, compared to a model that would assume a constant pressure. The variation in $\kappa$ has a large effect on pressure variation, and this highlights the importance of
obtaining accurate values for this parameter, and suggests important implications on predicted performance.

The cathodic pressure changes shown in Figure 3.5 were much smaller in magnitude; again, this was a consequence of the thinness of the electrode. The reaction-driven mass flux in this case draws flow towards the electrolyte, and convection helps increase oxygen transport to the TPB reaction zone. This also has implications for predicted cell performance, though the pressure drop is a
maximum of 20% of atmospheric, so large effects on predicted performance are not expected.

The differing pressure magnitudes were affected by two varying parameters, $L$ and $\kappa$. From the data in Table 3.1, it is shown that $L$ varied at most by an order of magnitude; generally, for SOFCs of similar type, thicknesses will be quite similar. For permeability, however, values were found to vary over several orders of magnitude, according to the Kozeny-Carman relation (see also Table 2.1). This was a direct result of the varying microstructural parameters ($\varepsilon$, $\tau$, $d_{\text{part}}$), and reinforced the idea that permeability can have significant effects on the predicted pressure change.

The above results suggest that, for the cells under consideration, convection plays a minor role in mass transport in the anode, while in cells with thin cathodes it is likely not very significant; the same can be said of the predicted pressure changes. However, it should be noted that this study was based on small SOFC button cells that are commonly seen in experimental work, and the results are not representative of cells in actual stacks. Such cells would have larger dimensions, and the greater electrode thicknesses would result in higher Peclet numbers and pressure changes.

A further consideration from this study is that one must be aware of the implications of the approach to permeability in a numerical model, as it was
shown that $\kappa$ has a significant effect on the predicted pressure change in a given electrode region. This could have a significant effect on the predicted cell Nernst potential, and thus performance. In the interest of completeness, it must be mentioned that one important aspect was not considered in this study: heat transfer. The various physico-chemical processes in a fuel cell can create significant amounts of heat, and in order to manage cell performance effectively, this heat needs to be controlled and removed [1]. Ignoring convection then not only has important implications on a predicted electrochemical solution, but it likely has a significant effect on a predicted temperature field as well. These issues warrant further investigation, and will be the subject of modeling studies and discussion in a later chapter of this thesis.

3.2 Knudsen Effects in Porous Electrodes

To further investigate convection, the discussion now shifts to consideration of the flow regime. Generally, in SOFC modeling, it is a common practise to assume a continuum flow regime and to define macroscopic flow parameters, such as permeability, viscosity, and porosity that are used to solve the Navier-Stokes equations. If a continuum flow regime is assumed, the interactions between the gaseous molecules of a fluid usually define how such a fluid behaves, in terms of the continuity of properties such as viscosity, density, and the like.
However, if the pore sizes of a particular medium are very small, such that a substantial percentage of the molecules that make up the gas stream are experiencing contact with the pore walls instead of other molecules, then the traditional continuum approach to solving the flow field might not be accurate. This is because wall surface interactions begin to have significant effects on the average flow characteristics. In SOFCs, fuel and oxidant gases in the electrode regions generally flow through pores of an average size in the range of 0.5-5μm [37-41]. When considering the implications of flow regime assumptions, this dimension is important as it helps to quantify the effects of pore walls on the flow of gases. In fact, if the number of wall surface collisions is comparable to the inter-molecular collisions, then the flow does not necessarily satisfy continuum criteria [59].

### 3.2.1 The Knudsen Number

Insight into the occurrences of inter-molecular collisions can be gained by considering the mean free path of a gas, $\lambda$, which is defined as the average distance traveled by a gas molecule between two inter-molecular collisions [35]

$$
\lambda = \frac{1}{\sqrt{2}\pi D_{\text{molec}}^2 n^*}
$$

In equation (3.7), $D_{\text{molec}}$ is the diameter of a molecule of the gas under consideration, and $n^*$ is the number density of the gas, calculated from ideal gas theory.
\[ n^* = \frac{p}{k_B T} \]  \hspace{1cm} (3.8)

where \( k_B \) is the Boltzmann constant. This formulation is valid only under the assumption of a pure gas, which would not hold true under operation in a fuel cell. In the simplest case of SOFC operation, there exists a binary gas mixture in each electrode. The mean free path for gas \( a \) in the \( a-b \) mixture is then [60]

\[ \lambda = \frac{1}{\sqrt{\frac{1}{M_a} + \sum \frac{1}{M_b}}} \]  \hspace{1cm} (3.9)

The mean free path is used to define the Knudsen number, which is the ratio of mean free path to the characteristic length \( L \) of the flow, and expresses the probability of a molecule-molecule collision compared to that of a molecule-wall collision

\[ Kn = \frac{\lambda}{L} \]  \hspace{1cm} (3.10)

As mentioned, \( L \) is often taken as the average size of a pore in the medium under consideration. The Knudsen number can be used to give an estimate of the accuracy of using Navier-Stokes to obtain a flow solution. For example, if \( Kn<<1 \), then the flow is mostly experiencing intermolecular collisions and falls under the continuum regime. However, if \( 0.1<<Kn<<1.0 \), then wall effects have an increasingly important effect on the flow, and a no-slip velocity assumption for
walls is no longer be valid. At Knudsen numbers of one and greater, the concept of macroscopic property distributions all but breaks down [59].

One should note that the preceding numerical limits for Kn are based on empirical information from channel flow studies, and may not be the same for porous media. Moreover, as Kn depends on the inverse-square of molecular diameter, which is on the order of Angstroms, the above flow regime boundaries are even more difficult to rigidly define, due to variation in tabulated data for these molecular diameters [61-63]. Nonetheless, they provide a basis to classify the flow and justify consideration of Knudsen effects.

3.2.2 Parametric Knudsen Number Study

With this in mind, characteristic Kn for flow in SOFC media were subsequently investigated under typical operating conditions, and for typical electrode microstructural parameters. This was done by carrying out a simple parametric study using equation (3.10), with oxygen as the gas under consideration. The results of this study are presented next.

To visualize the variation of Kn with temperature, pressure, and average pore diameter, two plots were constructed. Figure 3.6 shows varying Knudsen numbers versus characteristic pore diameter, L, for two temperatures at constant pressure, while Figure 3.7 shows another perspective, the variance of Kn with pressure for different L at constant temperature.
Some interesting trends are seen in these plots. First, it can be seen that increasing the gas temperature has the effect of raising $\lambda$ and $Kn$; this is because raising temperature raises the average molecular velocity, and molecules will tend to travel further before collision with another. Increasing the pressure has the opposite effect; due to a higher number density, a given molecule will likely travel a smaller distance to come into contact with another molecule.
Based on the earlier convection study, and on typical geometrical properties found in the literature reviewed (see Table 2.1 in literature review), these plots predict a range of $Kn$ numbers in SOFC electrodes of between 0.05 and 0.5. According to several sources, [35, 59, 64] this places the flow in the “transitional” flow regime, which means that a continuum assumption may still be valid, but Knudsen effects need to be considered. This is an important finding, because while it is common to see in the SOFC modeling literature the inclusion of Knudsen effects in expressions for the diffusive flux, it is extremely uncommon to find expressions for the convective mass flux that consider Knudsen effects – to
this author’s knowledge, only Ackmann et al. have done so [65]. It was deemed necessary, then, to further investigate a convective transport model that did.

3.2.3 Knudsen Effects on Permeability

As previously mentioned, Knudsen effects are significant in any flow situation where the mean free path of gas molecules in the porous media approaches the characteristic pore dimension. Under these circumstances, the characteristic physical dimension begins to affect the definition of flow properties from a continuum assumption. It is useful to define exactly what Knudsen effects are. Physically, it means that the fluid velocity at wall boundaries can no-longer be assumed zero, and this results in higher permeabilities through a medium due to lower wall shear effects, or ‘wall slip’ [35,59,66-68].

It is, however, a widely held view that the permeability constant of a porous medium is a physical property of the medium, and is independent of the fluid that passes through this medium. This is reflected in the literature by countless modeling papers that take permeability as a constant parameter. If one were to consider the flow regime predicted by the previous Knudsen number study, however, and the above referenced work showing that permeability is increased by slip (Knudsen effects), then it seems categorically necessary to account for the Knudsen transitional effects on permeability. Recall in Chapter 3 the effects of \( \kappa \) on a predicted pressure field. This pressure field may have significant effects on
predicted concentrations and electrochemical performance, and understanding of this could be of great importance to the advancement of SOFC science.

One of the pioneers to study Knudsen effects on permeability was Klinkenberg, who, in 1941, looked at the permeability of various fluids in porous media, with relevance to oil and gas extraction in rock formations [67]. An important finding of this study was that, in general, with highly permeable media, the differences between liquid and gas permeabilities were small, whereas these differences could be considerable for media of relatively low permeability. Klinkenberg explained this difference by invoking the theory of wall slip, whereby a fluid close to a wall has a finite velocity. A consequence of this is that the quantity of gas that flows through a pore channel is larger than would be predicted from Poiseuille’s formula. From wall-slip theory, Klinkenberg derived a relation to incorporate Knudsen effects on gas permeability

\[
\kappa_{\text{ef}} = \kappa_\infty (1 + c_K \text{Kn})
\]  

(3.11)

where \(c_K\) is some constant (herein called the Klinkenberg constant), and \(\kappa_\infty\) is the absolute permeability unaffected by wall slip, or in other words, permeability at very low \(Kn\). Klinkenberg performed a series of experiments to validate equation (3.11). It was found that permeability increased linearly with decreasing mean pressure over a sample. Conversely, with increasing mean pressure (when \(Kn\) decreases) slip effects were found to decrease until they became negligible and the
permeability for a given material approached a single value, $K_{\infty}$. This permeability is a physical characteristic of the porous medium only.

From the preceding Knudsen number study, it was shown that under typical SOFC operation, $Kn$ may be high enough such that there is significant deviation from a constant permeability at standard conditions. From the few reported experiments in the literature which have measured SOFC electrode permeability, they have all been taken at room temperature under fairly significant applied pressures (i.e. $p >> p_{\text{atmospheric}}$ - see Table 2.1).

Klinkenberg’s method has recently been validated by at least the following experiments on ceramic materials [68-70]. However, a literature search resulted in no Klinkenberg-like experiments that were performed on SOFC electrode materials. It seems appropriate then to apply Klinkenberg’s method to characterise SOFC electrode permeability under typical SOFC operating conditions, and this is taken up in the next section that presents the experiment work that did just that.

### 3.3 Experimental Procedure

Experiments were carried out to determine the behaviour of gas permeability under different operating conditions. Tests were done on Nickel anode support layers that were provided by the National Research Council of Canada-Institute
for Fuel Cell Innovation (NRC-IFCI). SEM images for which are shown in Figure 3.8 and Figure 3.9. These anodes were roughly 30% porous.

Figure 3.8: Anode ID#1: SEM image of surface at 10000x magnification.

Figure 3.9: Anode ID#1: SEM image of sample anode cross-section at 10000x magnification.

3.3.1 Theory

Permeability tests were carried out on this material using diffusion permeametry, as the technique characterises permeability by measuring flow rate from both
pressure and concentration differences across a porous sample. Permeametry is the systematic measurement of permeability, while the nomenclature of diffusion permeametry is specific to the company, which developed this technique and manufactured the permeameter for this experiment, Porous Materials Inc. (PMI) of Ithaca, NY.

The technique of permeametry in this study is relatively straight-forward, and involves measuring the change in pressure over time across a sample. The implementation of this concept in this experiment is illustrated in Figure 3.10. The anode sample is placed in a sample chamber and sealed with o-rings and a pneumatic piston. When doing so, this separates the chamber in two. One

![Figure 3.10: Schematic of experimental sample chamber.](image-url)
chamber is on the inlet side of the sample and the other is on the outlet side, and the exact volumes of the chambers are known. Each chamber is then evacuated, and a quantity of test gas at known conditions is introduced to the chamber on the inlet side. The pressure is then recorded on both sides of the sample over some test time, and this data is used in subsequent calculation of the flow across the sample by employing a time rate of change formulation of the ideal gas law

\[
\frac{\partial n_{\text{out}}}{\partial t} = \frac{\partial p_{\text{out}}}{\partial t} \frac{V_{\text{out}}}{RT} \quad (3.12)
\]

where the subscript \( \text{out} \) denotes variables in the outlet chamber. Note that \( V_{\text{out}} \) and \( T \) are known. The molar flow rate in (3.12) can also be expressed in terms of changing volume at standard temperature and pressure

\[
\frac{dn_{\text{out}}}{dt} = \frac{p_{s,\text{out}}}{RT_s} \frac{dV_{s,\text{out}}}{dt} \quad (3.13)
\]

By combining equations (3.12) and (3.13), the standard volumetric flow rate across the sample and into the outlet chamber can be expressed as

\[
\frac{dV_{s,\text{out}}}{dt} = \frac{V_{\text{out}}T_s}{p_tT} \frac{dp_{\text{out}}}{dt} \quad (3.14)
\]

With knowledge of the pressure change and flow rate across the sample, the permeability is then calculated using Darcy’s law [71].
3.3.2 Experimental Setup and Procedure

All permeability experiments were performed using a DP-100 ACTROX Diffusion-Permeameter (see Figure 3.11), which is an automated permeability testing unit that is equipped to characterise low flow rates in porous media. This was desirable given the range of very low permeabilities of SOFC electrodes that were reported in the literature (see Table 2.1).

Figure 3.11: Automated diffusion permeameter showing sample chamber (a.) and concentric insulation chamber (b.).
The sample chamber that was described above is shown in Figure 3.11. The anode samples were placed in the chamber by fixing them to a custom holder plate. The anodes were sealed to this plate with epoxy, as shown in Figure 3.12.

Figure 3.12: Detail of sample holder plate.

The plate was machined from steel and contained a 1cm diameter hole through its centre for flow to pass from the inlet to outlet chamber. The samples, which measured roughly 1.4cm in diameter, were placed over the hole, and the edges were sealed with high-temperature epoxy. This is important because it ensured that only through-plane permeability was measured in the experiments. The sample plate was then placed in the permeameter on top of a hollow cylindrical pedestal, and it was sealed and held in place by a pneumatic, hollow piston that lowered from above. This is shown in Figure 3.13. Compression of the o-rings on
the top and bottom of the sample plate by the piston created a seal to force flow through the sample and not out into the insulation chamber.

![Figure 3.13: Close-up of sample plate within test chamber.](image)

The interiors of the piston and pedestal constituted the inlet and outlet volume in the schematic in Figure 3.10. To control the temperature in the experiments, the test chamber is surrounded by a pneumatic insulating chamber for thermal insulation; this chamber is shown in Figure 3.13 in the raised position.

### 3.3.3 Validation of Permeameter Results

To have some confidence in the permeability measurements of the device, a room temperature experiment was performed on an anode sample. Results from this experiment were compared with permeability results from a similar device that had the ability to measure permeability. This device was a CFP-1500-AL
Capillary Flow Porometer, also manufactured by MPI. It measures the flow rates for a known pressure drop across a sample to give permeability.

The two approaches to measuring permeability of the anode sample were compared, and found to be within the same order of magnitude (Porometer – $2.76 \times 10^{-15}$, Permeameter – $1.78 \times 10^{-15}$). Results from this comparison are shown in Appendix A. The large difference between the two could be due to the accuracy involved with the mass flow controller on the Porometer. It is rated for flow rates up to 200 litres per minute (LPM), and is accurate to within 1% of the full scale. However, as flow rates across the sample in the Porometer were on the order of 1-2 LPM, the mass flow controller was clearly within its range of inaccuracy. The only conclusion that can be drawn from this comparison is that the two results are within the same order of magnitude. It was therefore deemed that the diffusion permeameter results were reasonable and further experiments were carried out.

3.3.4 Experimental Method

Once the samples were sealed with the piston inside the insulating environment, a series of experiments were carried out to measure permeability at different operating temperatures. Experiments were performed on a total of four sample anodes, according to the following standard procedure:
1. Inlet chamber pressure was set to 500 Torr. Experiments were run at intervals of 75°C, starting at 75°C. One hour was given for $T$ to reach equilibrium between each interval.

2. Experiments were run for two minutes, and $p$ measurements were taken at intervals of three seconds. Three experiments were run for each $T$.

3. Due to temperature limits imposed by the o-rings and the epoxy, experiments were run to a maximum of 450°C.

3.4 **Permeability Experiments: Results and Discussion**

The results of the diffusion permeameter experiments are now presented. Sample experimental data can be found in Appendix B, while the permeability data is plotted versus the ratio of $T$ to mean pressure. This presentation was chosen to directly compare trends with the experiments by Klinkenberg. This is essentially the same as plotting $\kappa$ versus $Kn$, as the other parameters in the Knudsen number calculation are constants.
Figure 3.14 shows experimental results for the first sample. Only three temperature plots are shown, as data for the experiments at \( T=75^\circ C \) are omitted due to error in device settings. This temperature trial was not repeated before the sample was removed from the holder plate (and subsequently damaged). This first experiment was performed to only 300\(^\circ\)C, due to failure of the seal. Over a limited temperature range, however, there is a clear trend of permeability increasing with \( Kn \).
Experiments on the second sample provided results that are more complete; these are shown in Figure 3.15. This sample was subjected to a wider temperature range, up to 450°C, without sealing failure. The trend of increasing permeability with increasing $Kn$ is clearly seen.
Results for the third sample were limited due to failure of the epoxy sealant near 450°C and are shown in Figure 3.16. Experiments for the fourth sample were similar to the third, with failure of the epoxy seal after 375°C. Results for sample 4 are shown in Figure 3.17.
It can be seen that there is some variation in the trend and magnitude of $\kappa$ across the samples, with experiments for sample 4 showing the smallest measured values for permeability, and also the smallest variation with $Kn$. This variation between samples is better seen in Figure 3.18, which shows $\kappa$ averaged for each trial and for each temperature interval. The variation between the different samples can perhaps be explained by the following reasons. First, there is possibly a difference in pore structure across the samples, specifically in the quality of porosity. For sample 1, note the differences in porosity of the anode.
surface compared to that of the cross section, as shown by SEM in Figure 3.8 and Figure 3.9; the surface seems much less porous than does the cross section.

![Figure 3.18: Permeability vs. temperature/mean pressure for all samples.](image)

These samples were prepared using the tape-casting method, and it seems unlikely that under this method the microstructure through the anodes would vary appreciably from sample to sample. There could be significant variation, however, in surface porosity from sample to sample, and this has to do with how the samples are sintered and reduced (further steps in manufacturing process). Variation in surface porosity would certainly have an effect on the gas permeability. Second, all of the four samples that were tested were not completely flat disks, but were curved to a small degree. The curvature was
caused by uneven heating during the reduction process of the manufacturing of the anodes. Disks 3 and 4 were curved the most, and it is thought that the curvature had some part in the variation across the samples, as it could have affected the underlying microstructure.

3.4.1 Experimental Uncertainty

Variation in results draws attention to experimental error. In these experiments, systematic uncertainties inherent in the measurements that were taken lead to accuracy errors. First, pressure was measured with a Model 1000 pressure transducer, manufactured by (Spectre Sensors of Avon Lake, OH). According to the manufacturer, this transducer was accurate to 0.5% of the measured value. Temperature measurements were taken by a series 998D temperature controller, which, according to the manufacturer (Watlow of St. Louis, MO), was accurate to 0.1% of the span $+$ $1^\circ$C, with a minimum span of 1186$^\circ$C. Random uncertainties resulted from measurement of the electrode thicknesses and diameters using dial callipers. It was estimated that the error of these measurements was half of the smallest readable division.

Referring again to Figure 3.18, the experimental data (averaged for pressure) is presented in the form of Klinkenberg’s equation, which is repeated again for convenience
The trendline equations in the legend of Figure 3.18 allow the experimental results to be directly compared to the Klinkenberg equation, where the y-intercept directly gives the slip-independent permeability $K_\infty$ that occurs at high pressures and low temperatures (low Knudsen numbers). The value for the Klinkenberg constant $c_K$ is found by calculating the Knudsen number for the test conditions (equation (3.7)) and then comparing with the trendline equation for each sample. The results for the 4-trial-averaged experiments are summarized in Table 3.2, and the experimental curves mirror trends that are reported in the work by Klinkenberg, and others [67-70].

Table 3.2: Average results from Klinkenberg experiments.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$\kappa_\infty$ [m$^2$]</th>
<th>$c_K$</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>$1.26 \times 10^{-15} \pm 4.1%$</td>
<td>$2.23 \pm 4.1%$</td>
</tr>
<tr>
<td>2</td>
<td>$1.43 \times 10^{-15} \pm 3.6%$</td>
<td>$2.73 \pm 3.6%$</td>
</tr>
<tr>
<td>3</td>
<td>$1.19 \times 10^{-15} \pm 3.8%$</td>
<td>$2.21 \pm 3.8%$</td>
</tr>
<tr>
<td>4</td>
<td>$1.18 \times 10^{-15} \pm 3.8%$</td>
<td>$1.69 \pm 3.8%$</td>
</tr>
<tr>
<td>Average</td>
<td>$1.26 \times 10^{-15} \pm 3.8%$</td>
<td>$2.22 \pm 3.8%$</td>
</tr>
</tbody>
</table>

for $Kn$ calculation: $d_p=1\mu m$, $D_{argon}=3.5\AA$ [72]

Average permeabilities for the four samples show a significant amount of variation: a maximum of 14% from the mean for $\kappa_\infty$, and a maximum of 24% from the mean for $c_K$. Confidence is limited in these average values as experiments were performed on only four samples. If more anode samples were tested, this could perhaps better explain the variation in permeability as being a
function of different microstructures across the samples, or as being a function of experimental inaccuracy. This was not possible to ascertain, however, as more samples were not made available before the culmination of this work. Nonetheless, the values for $\kappa_\infty$ are comparable to those obtained by other researchers (see Table 2.1).

3.5 Summary  
This chapter discussed concepts relating to the characterization of convective flow in SOFC electrodes. It was shown in a simple analytical study that even though the Peclet numbers may be small, the pressure changes across an electrode could be significant. Furthermore, the permeability (and the parameters upon which it is based) was found to have large influence on this pressure drop. It was further shown that significant Knudsen effects may affect the flow in electrodes, and those effects must be considered. With the goal of proper characterization of permeability, experiments were performed to investigate the relationship between permeability and Knudsen number, and results from those experiments supported Klinkenberg’s empirical relationship. It is left to determine the importance of a Klinkenberg permeability on performance predictions in a SOFC. This will be one of the topics explored in the CFD model that is developed and discussed in the next chapter.
Chapter 4  
Model Development  

As part of this research work, several modeling studies were performed to investigate the importance of convection in SOFCs. This chapter will describe the development of the SOFC model, where the spatial variations of velocity, pressure, temperature, gaseous species, and cell current are predicted by computational fluid dynamics (CFD).

This chapter is organized in terms of increasing complexity. The discussion begins with the introduction of the governing transport equations and outlining of their numerical solution. It then continues to discuss the measures that have been employed to ensure that the simulation results will be physical and relevant. The results of these verification measures are analysed, and discussed.

4.1 Computational Domain
The model in this work was developed using the commercial CFD package, FLUENT 6.3.26. The computational domain and detailed dimensions are shown below in Figure 4.1 and Table 4.1. The dimensions in Table 4.1 reflect those of a real cell under development by the Alberta Research Council (ARC), except for the entrance/exit lengths, L-e, which were arbitrarily chosen. These lengths were
added at the recommendation of the FLUENT user manual [73], to avoid any entrance/exit effects at boundaries on the solution.

<table>
<thead>
<tr>
<th>Label</th>
<th>Description</th>
<th>Dimension</th>
</tr>
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<tbody>
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</tr>
<tr>
<td>L</td>
<td>Cell length</td>
<td>20mm</td>
</tr>
<tr>
<td>L-st</td>
<td>Length of fuel supply tube</td>
<td>24mm</td>
</tr>
<tr>
<td>r-st</td>
<td>Radius of fuel supply tube</td>
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</tr>
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<td>r-fc</td>
<td>Radius of fuel channel</td>
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</tr>
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<td>Supply tube thickness</td>
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<tr>
<td>t-ai</td>
<td>Anode inactive layer thickness</td>
<td>275μm</td>
</tr>
<tr>
<td>t-aa</td>
<td>Anode active layer thickness</td>
<td>7.5μm</td>
</tr>
<tr>
<td>t-el</td>
<td>Electrolyte thickness</td>
<td>5μm</td>
</tr>
<tr>
<td>t-ca</td>
<td>Active cathode thickness</td>
<td>15μm</td>
</tr>
<tr>
<td>t-ci</td>
<td>Cathode inactive layer thickness</td>
<td>60μm</td>
</tr>
<tr>
<td>t-ac</td>
<td>Air channel thickness</td>
<td>1mm</td>
</tr>
</tbody>
</table>

Figure 4.1: Schematic of computational domain (not to scale)

4.2 Governing Transport Equations

A two-dimensional, axi-symmetric model was developed in this work. The choice of axi-symmetry reduced computational requirements compared to the case of modeling the entire volume. This is a reasonable assumption if there is no...
consideration of phenomena which vary circumferentially, such as current collection, and this approach is often seen in the literature. The conservation equations which describe the transport of fluid variables were introduced earlier, and these equations are presented here for 2-D, cylindrical, axi-symmetric conditions. For laminar \((Re < 10)\), steady flow, conservation of mass is

\[
\frac{\partial}{\partial z} (\rho u) + \frac{\partial}{\partial r} (\rho v) + \frac{\rho v}{r} = S_m
\]

where \(S_m\) is a mass source, and the density \(\rho\) varies in the anode and cathode streams according to a mixing law based on ideal gas theory \[73\]

\[
\rho = \frac{p_{local}}{RT_{local} \sum_i Y_i / M_i}
\]

In (4.2), \(M_i\) is the molecular weight of species \(i\) in the mixture, \(T_{local}\) and \(p_{local}\) are the local temperature and pressure, respectively, \(R\) is the universal gas constant, and \(Y_i\) is the species mass fraction.

For the axial and radial directions, respectively, conservation of momentum is

\[
\frac{\partial}{\partial z} (\rho w) + \frac{1}{r} \frac{\partial}{\partial r} (rwv) = -\frac{\partial p}{\partial z} + \frac{\partial}{\partial z} \left( \frac{\mu}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{\mu}{\partial r} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{\mu}{\partial r} \right) + S_{mom,z}
\]

\[
\frac{\partial}{\partial z} (\rho u) + \frac{1}{r} \frac{\partial}{\partial r} (r\rho u) = -\frac{\partial p}{\partial z} + \frac{\partial}{\partial z} \left( \frac{\mu}{\partial z} \right) + \frac{\partial}{\partial z} \left( \frac{\mu}{\partial z} \right) + \frac{2}{r} \frac{\partial}{\partial r} \left( \frac{\mu}{\partial r} \right) - \frac{2\mu v}{r^2} + S_{mom,r}
\]

with the molecular viscosity \(\mu\) determined using a mixing law based on kinetic theory \[73\]
\[ \mu = \sum_i \sum_j X_i \mu_i \frac{\phi_{ij}}{X_j \phi_{ij}} \text{ with } \phi_{ij} = \frac{\left[ 1 + \left( \frac{\mu_i}{\mu_j} \right)^{1/2} \left( M_j / M_i \right)^{1/4} \right]^2}{8 \left( 1 + M_i / M_j \right)^{1/2}} \] (4.5)

For an ideal gas, conservation of energy of a fluid can be cast as a temperature equation, which, in axi-symmetric conditions becomes

\[
\frac{\partial \left( \rho u c_p T \right)}{\partial z} + \frac{1}{r} \frac{\partial \left( r \rho v c_p T \right)}{\partial r} = \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} + h J_{D,i,z} + \frac{\partial q_{rad}}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \left( k \frac{\partial T}{\partial r} + h J_{D,i,r} + \frac{\partial q_{rad}}{\partial r} \right) \right) + S_T
\] (4.6)

In equation (4.6) any viscous heating effects were assumed negligible, and the specific heat capacity, \( c_p \), and thermal conductivity, \( k \), are calculated from mixing laws

\[ c_p = \sum_i Y_i c_{p,i} \] (4.7)

\[ k = \sum_i \sum_j \frac{X_i k_i}{X_j \phi_{ij}} \] (4.8)

where \( \phi_{ij} \) is defined in equation (4.5). It should be noted that all individual species properties (\( \mu_i, k_i, c_{p,i} \)) are calculated from temperature-dependent polynomial expressions, as proposed in the work by Todd and Young [36]. In equation (4.6), the variation of the radiative heat flux, \( q_{rad} \), is given by
\[ \nabla \cdot q_{rad} = a \left( 4\sigma T^4 - \int_{4\pi} I_{rad} d\Omega \right) \]  

(4.9)

where \( \sigma \) is the Stefan-Boltzmann constant, \( I_{rad} \) is radiative intensity, which is integrated over the \( 4\pi \) solid angular space to account for incident radiation, and \( a \) is the absorption coefficient of the medium, which accounts for effects of participating gaseous media [50]. In this work, the absorption coefficient was taken from the evaluation of the HITRAN and HITEMP databases by Zhang and Modest, who showed that the absorption of water vapour at 1 bar and in the temperature range of 600°C was approximately 0.05 [74]. It was also assumed that scattering of radiation by participating media was negligible, and the Discrete Ordinates Model (DOM) was used to solve the radiative intensity field and quantify its contribution to the radiative heat flux.

To predict the variation of gaseous species, the axi-symmetric species equation is

\[ \frac{\partial}{\partial z} \left( \rho u Y_i \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho v Y_i \right) = \frac{\partial}{\partial z} \left( J_{D,i,z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r J_{D,i,r} \right) + S_i \frac{dy}{dx} \]  

(4.10)

where \( Y_i \) is the mass fraction of species \( i \), \( S_i \) is a species source term, and the diffusive flux \( J_{D,i} \) is given by

\[ J_{D,i,k} = \rho D_{i,j} \frac{\partial Y_i}{\partial x_k} \]  

(4.11)

Note that in equation (4.11), the subscript \( k \) denotes direction. In this work, the species making up each stream were two-component binary systems (\( \text{H}_2-\text{H}_2\text{O} \) on
the anode side, O₂-N₂ on the cathode side), and the molecular diffusivity, $D_{i,j}$, was calculated from Fuller et al [10]

$$D_{i,j} = \frac{1 \times 10^{-7} T^{4.75} \left(1/M_i + 1/M_j\right)^{1/2}}{\left(\xi_i^{1/3} + \xi_j^{1/3}\right)^2 p}$$

where $\xi_i$ is the diffusion volume of species $i$.

### 4.2.1 Porous Regions

This model considered flow through porous solids, which add considerable complexity to the approach. Porous regions can be thought of as obstructions to the bulk flow of mass and heat, and the effect of these obstructions needs to be incorporated into the above governing equations. How this was implemented in this work is now described.

### 4.2.2 Porous Effects on Mass Transport

As discussed in the introduction, it was assumed that Darcy’s Law governs the relationship between pressure and flow rate in the porous regions. The velocity that it predicts is known as the superficial or seepage velocity, $\nu_s$, which is related to the velocity in the pore conduits by

$$\nu_s = \varepsilon \nu$$

Conservation of mass (equation (4.1)) then becomes [8]
\[
\frac{\partial}{\partial z}(\rho \varepsilon u) + \frac{\partial}{\partial r}(\rho \varepsilon v) + \frac{\rho \varepsilon v}{r} = S_m \tag{4.14}
\]

### 4.2.3 Porous Effects on Momentum Transport

For momentum transport, porous regions have the effect of removing momentum from the flow. This was simulated by adding a sink term to the momentum equation that is based on Darcy’s law

\[
S_{\text{mom},k} = -\frac{\mu}{\kappa} v_{s,k} \tag{4.15}
\]

Because of low flow rates considered in this study, inertial losses were assumed negligible. Conservation of momentum (equations (4.3) and (4.4)) are then corrected for porosity and solved for the seepage velocity, as in equation (4.14).

### 4.2.4 Porous Effects on Species Transport

The species transport equations were also formulated differently in porous regions, with the incorporation of porous effects on the convective and diffusive fluxes in the species transport equation

\[
\frac{\partial}{\partial z}(\rho \varepsilon u Y_i) + \frac{1}{r} \frac{\partial}{\partial r}(\rho \varepsilon v Y_i) = \frac{\partial}{\partial z}(\varepsilon J_{D,i,z}) + \frac{1}{r} \frac{\partial}{\partial r}(r \varepsilon J_{D,i,r}) + S_{Y,i} \tag{4.16}
\]

In the porous electrodes, the diffusive flux \(J_{D,i,k}\) was derived from the extended Dusty Gas Model for a binary component system, and includes both Knudsen and molecular diffusion [9]
\[
J_{D_{i,k}} = \rho \left( \frac{1}{D_{i,Kn,eff}} + \frac{(1 - \alpha_{i,j}) Y_i}{D_{i,j,eff}} \right)^{-1} \frac{\partial Y_i}{\partial x_{i,k}}; \quad \alpha_{i,j} = 1 - \left( \frac{M_i}{M_j} \right)^{1/2}
\]  
(4.17)

In equation (4.17), the term \((1-\alpha_{i,j}) Y_i\) accounts for non-equimolar diffusion, which is an important consideration when the molecular masses of the involved species differ considerably [11], and \(D_{i,Kn,eff}\) is the effective Knudsen diffusivity, given by

\[
D_{i,Kn,eff} = \frac{1}{3} d_p \left( \frac{8RT}{\pi M_i} \right)^{1/2} \varepsilon^{1.5}
\]  
(4.18)

The molecular diffusivity \(D_{i,j,eff}\) is

\[
D_{i,j,eff} = D_{i,j} \varepsilon^{1.5}
\]  
(4.19)

where \(D_{i,j}\) is as defined in (4.12). Both the Knudsen and molecular diffusivities were multiplied by the factor \(\varepsilon^{1.5}\), which is application of the Bruggeman correction and accounts for the effect of transport through a medium characterised by a packed bed of spherical particles, which is not unlike that considered in this work [12].

### 4.2.5 Porous Effects on Heat Transport

Within the porous electrodes, the momentum and mass transport equations are quite different from in the channel. The energy equation, however, was applied inside the porous region with little modification from that used in the channels. As a porous medium will generally have lower thermal conductivity than a solid made of the same material, a correction to the thermal conductivity was
implemented to combine the properties of the electrode material and the gas filling its pores

\[ k_{\text{eff}} = \varepsilon k_i + (1 - \varepsilon) k_s \]  

(4.20)

where \( k_i \) and \( k_s \) are the thermal conductivities of the fluid and solid, respectively.

### 4.3 Modeling of Electrochemistry

As was discussed in the introduction, there are two fundamental relations that describe the electrochemical performance in a fuel cell. These are, respectively, the Nernst and Butler-Volmer equations

\[ E_{\text{Nernst}} = -\frac{\Delta G}{ZF} = E^\alpha + \frac{RT}{ZF} \ln \frac{p_{H_2}p_{O_2}^{0.5}}{p_{H_2O}} \]  

(4.21)

\[ i_{\text{electrode}} = i_{o,\text{electrode}} \left( \exp \left( \frac{\alpha_F \eta}{RT} \right) - \exp \left( -\alpha_F \eta \right) \right) \]  

(4.22)

Expressions for the exchange current density, \( i_{o,\text{electrode}} \), are proposed in the literature [23,27,75-77], and take the following form in this work

\[ i_{o,\text{ano}} = k_{ano} \left( \frac{p_{H_2}}{p_{H_2}^o} \right) \left( \frac{p_{H_2O}}{p_{H_2O}^o} \right)^{-0.5} \exp \left( -\frac{E_{a,\text{ano}}^o}{RT} \right) \]  

(4.23)

\[ i_{o,\text{cat}} = k_{cat} \left( \frac{p_{O_2}}{p_{O_2}^o} \right)^{0.375} \exp \left( -\frac{E_{a,\text{cat}}}{RT} \right) \]  

(4.24)

where \( k^o \) is some reference equilibrium constant, and \( E_a \) is the activation energy required to drive the charge transfer reaction. These are empirically derived
models which are based on studies of electrodes of the same composition as those used in this work. Equations (4.23) and (4.24) have important implications for the predicted performance, because the exchange current density is related to how polarisable the electrolyte-electrode interface is; as \( i_o \) increases, the overpotential required to drive a given current decreases, and vice versa [6]. It must be stressed, however, that even though these relations are derived from reaction mechanisms, they are empirical in nature and will be used in this work to fit the model to experimental data.

**4.3.1 Electrode Overpotentials**

The overpotential term in (4.22) is the difference between the Nernst potential of the electrode and the actual potential difference between the electrode and the electrolyte

\[
\eta_{electrode} = \Delta \phi_{electrode} - \Delta \phi_{Nernst} \tag{4.25}
\]

This overpotential can be broken down into two components: an activation overpotential and a concentration overpotential [6], where

\[
\eta_{electrode} = |\eta_{act}| + |\eta_{conc}| \tag{4.26}
\]

The activation overpotential quantifies the voltage loss that results from driving the charge-transfer reaction in the active regions of the cell. The concentration overpotential quantifies the voltage loss due to mass transfer limitations in the porous regions, or, more simply put, the change in the Nernst potential from
some value based on gas partial pressures in the channel, to one that is based on the partial pressures in the active electrode region, which will always be smaller under operation. The concentration overpotential is then

\[ \eta_{\text{conc}} = \left( \frac{RT}{ZF} \ln \frac{p_{H_2} P_{O_2}^{0.5}}{p_{H_2O}} \right)_{\text{PB region}} - \left( \frac{RT}{ZF} \ln \frac{p_{H_2} P_{O_2}^{0.5}}{p_{H_2O}} \right)_{\text{channel}} \]

Equation (4.27) provides an explicit measure of mass transfer effects on the cell performance, and subtraction of this term from the Butler-Volmer overpotential gives the activation overpotential.

4.3.2 Ohmic Losses

Further losses result from the resistance to flow of ions and electrons within the cell materials. These are termed ohmic losses because they are characterised by Ohm’s law, and are linearly proportional to the ionic/electronic current. Ohmic losses were assumed to be composed of resistances in the PEN structure only

\[ \eta_{\text{ohmic}} = I \left( R_{\text{electrolyte}} + R_{\text{ano}} + R_{\text{cal}} \right) \]

while the contribution from any current collector is not considered. This assumption is reasonable, as in most SOFCs, the main ohmic contribution comes from the electrolyte’s resistivity to oxygen ion transport [1]. The individual resistances in (4.28) depend on the material resistivity, the average distance that charged particles travel through the material, and the material temperature.
Expressions for resistivities for the cell components are taken from the work by Besette [78] and have the form

$$\rho_{c,i} = C_{1,i} \exp\left(\frac{C_{2,i}}{T}\right)$$

(4.29)

where the resistivity for a specified material $i$ is $\rho_{c,i}$, which depends on two material constants $C_{1,i}$ and $C_{2,i}$ and the local temperature. The individual cell resistances are calculated from

$$R_{\text{cell}} = \frac{\rho_{c,i} \delta_{\text{avg},i} V_{\text{cell}}}{A_i V_i}$$

(4.30)

where $\delta_{\text{avg},i}$ is the average distance that a charged particle travels through a cross sectional area $A_i$, for a particular cell region of volume $V_i$. It was assumed in this work that $\delta_{\text{avg},i}$ the cell layer thickness in the radial direction. While this is most likely an underestimation of the true current path in the electrodes, it is reasonable if the assumption is made that the current collector is applied evenly over both electrode surfaces, and is justified given that the majority of charge-transfer resistance is attributed to the $O^2$ transport through the electrolyte [1,78].

### 4.3.3 Iterative Procedure for Calculation of Current

As was previously mentioned, the local current was calculated iteratively using the Butler-Volmer equation; the procedure for doing so required some assumptions. First, an average overpotential was assumed over the entire electrode of interest; this was because potential distribution was not solved in
this work. This assumption was made to overcome the nonlinearity and instability of iterative Butler-Volmer calculations, and is a common practise in the literature. The consequences of this assumption include overestimating the electroodic overpotential in regions where the exchange current density is high, and underestimating it when the exchange current density is low.

The current calculation was implemented via a User-Defined Function (UDF) in the FLUENT solver. It is outlined below:

1. A while loop is entered:

2. A current is calculated in each cell of the active electrode region, based on local conditions and some guessed overpotential.

3. Newton’s method is employed on the Butler-Volmer equation to find the average overpotential that matched a specified current, $I_{sp}$, for the cell. Mathematically, this can be expressed as finding the zero of the discretized Butler-Volmer equations

$$f(\eta_{avg}) = I_{sp} - \sum_{cell} V_{cell}i_{cell} \left( \exp\left[ \frac{\alpha_{an} F \eta_{avg}}{RT_{cell}} \right] - \exp\left[ \frac{-\alpha_{cat} F \eta_{avg}}{RT_{cell}} \right] \right)$$  (4.31)

4. Equation (4.31) is iterated by adjusting $\eta_{avg}$ and solved until the difference between the specified current and the summation over the individual cell currents is less than some tolerance ($10^{-7}$ in this case). The new current values for each cell are then stored.
4.3.4 Determination of Cell Potential

In comparison to solutions for current and other field properties, calculation of the cell potential was rather trivial. The cell overpotentials described above were subtracted from the ideal Nernst potential based on flow in the channels to give an approximate cell voltage for a specified current draw

\[ E(i) = E_{\text{Nernst}} - \eta(i)_{\text{anode}} - \eta(i)_{\text{cathode}} - \sum I_{\text{cell}} R_{\text{cell}} \]  

(4.32)

4.3.5 Electrochemical Source Terms

A set of source terms was included to account for mass, momentum, energy, and species consumption and generation due to the charge transfer reactions.

4.3.5.1 Mass Sources

Faraday’s law relates the current to the mass consumed/produced by the charge transfer reactions, and in equation (4.14) the mass source takes the form

\[ S_{m,i} = \frac{i M_i}{Z F} \]  

(4.33)

with the total mass source in the anode equal to \( S_{m,H_2} + S_{m,H_2O} \) and the cathode mass source equal to \( S_{m,O_2} \).

4.3.5.2 Momentum Sources

To account for the effect on the momentum balance due to mass injection/removal by electrochemical reaction, a source term was included in the momentum conservation equations, and for species \( i \) has the form
4.3.5.3 Heat Sources

During cell operation, both reversible and irreversible losses account for heat generation. As discussed previously, the irreversible losses are due to lost energy to drive the electrochemical reaction and transfer charge. These losses are quantified by the product of the local current and the respective overpotential

\[ S_{c,\text{irr},i} = i_{\text{local}} \left( |\eta_{\text{act},i}| + \eta_{\text{ohmic},i} \right) \]  \hspace{1cm} (4.35)

Heat sources also arise from the entropy changes of the electrochemical reactions

\[ S_{c,\text{rev},i} = T\Delta S_i \frac{i}{ZF} \]  \hspace{1cm} (4.36)

where \( \Delta S_i \) is the change in entropy for each electrode half-cell reaction:

\[ \Delta S_\text{anode} = S_{H_2O} + 2S_e - S_{H_2} - S_{O^2-} \]  \hspace{1cm} (4.37)

\[ \Delta S_\text{cathode} = S_{O^2-} - \frac{1}{2}S_{O_2} - 2S_e \]  \hspace{1cm} (4.38)

In (4.37) and (4.38), the transported entropy for an electron is not known; instead, the entropy change for the overall reaction (4.39) was calculated

\[ \Delta S_{\text{total}} = S_{H_2O} - S_{H_2} - \frac{1}{2}S_{O_2} \]  \hspace{1cm} (4.39)

and half of this total was assigned to each electrode region. According to [1], the majority of the reversible heat generation is located in the cathode, although the
work of Austin shows these entropic effects to be marginal, and the fraction assigned to each electrode has little effect on the final solution [50].

4.3.5.4 Scalar Species Sources

Scalar transport equations were solved for each species in each fluid stream. Species are consumed/produced by the half-cell reactions in the active regions, and the source terms have the same form as those for conservation of mass

\[
S_{\phi,i} = \frac{i M_i}{ZF} \tag{4.40}
\]

To summarize this section, the source terms that influence a particular governing equation in a particular location within the domain are tabulated in Table 4.2.

<table>
<thead>
<tr>
<th></th>
<th>Inactive Layer</th>
<th>Active Layer</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mass</strong></td>
<td></td>
<td>( S_{m,a} = \frac{\mu}{\kappa_a} (M_{H_2O} - M_{H_2}) )</td>
<td>( S_{m,c} = \frac{\mu}{\kappa_c} M_{O_2} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( S_{mom,a,i} = -\frac{\mu}{\kappa_a} v_{i,a} )</td>
<td>( S_{mom,c,i} = -\frac{\mu}{\kappa_c} v_{i,c} )</td>
</tr>
<tr>
<td><strong>Momentum</strong></td>
<td></td>
<td>( S_{mom,a,i} = -\frac{\mu}{\kappa_a} v_{i,a} )</td>
<td>( S_{mom,c,i} = -\frac{\mu}{\kappa_c} v_{i,c} )</td>
</tr>
<tr>
<td><strong>Energy</strong></td>
<td>( S_{e,a} = \eta_{local} \left( \frac{T \Delta S_a}{ZF} +</td>
<td>\eta</td>
<td>+ i_{local} R_e_{local} \right) )</td>
</tr>
<tr>
<td></td>
<td>( S_{e,c} = \eta_{local} \left( \frac{T \Delta S_c}{ZF} +</td>
<td>\eta</td>
<td>+ i_{local} R_e_{local} \right) )</td>
</tr>
<tr>
<td><strong>Species</strong></td>
<td>( S_{H_2} = -\frac{\eta_{local}}{ZF} M_{H_2} )</td>
<td>( S_{H_2O} = -\frac{\eta_{local}}{ZF} M_{H_2O} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( S_{O_2} = -\frac{\eta_{local}}{ZF} M_{O_2} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

N.B. a,c subscripts denote anodic and cathodic terms, respectively.
4.4 Discretization

The numerical procedure employed to solve the governing equations is now described. The approach in this work follows the Finite Volume Method (FVM), which is a well-established CFD technique that approximates the solution to physical problems by integrating the governing equations over the finite volumes in a discretized domain to create a set of discretized algebraic equations. The FVM has the merit of ensuring that each discretized form preserves the conservation properties of the governing differential equations, for each computational cell and for the domain as a whole [7].

The process of transforming the continuous governing equations into algebraic expressions on a finite spatial grid is known as discretization. To illustrate how this is implemented, let us consider a domain such as that pictured in Figure 4.1, with a grid overlaid. First, the relevant governing equation is integrated over a control volume of interest

\[ \oint \nabla \cdot (\rho \mathbf{v} \phi - \Gamma_{\phi} \nabla \phi) dA = \int_{s_{\phi}} s_{\phi} dV \]  

(4.41)

The values of the variables such as \( \rho \), \( \phi \), \( \Gamma \), and \( \mathbf{v} \), are evaluated at discrete points called nodes, and the control volumes in a domain are centred around these nodes. To solve (4.41), face values and gradients of the flow variable \( \phi \) are required. These terms are approximated by means of some finite differencing
method, and are then substituted into the integrated governing flow equations to create a set of discrete algebraic equations

\[ \sum_{\text{faces}} \rho_j \bar{u}_j \phi_j \cdot \bar{A}_j = \sum_{\text{faces}} \Gamma_j \nabla \phi_j \cdot \bar{A}_j + S_\phi V \]  

(4.42)

where the subscript \( f \) denotes values at faces. In this work, the variable values at cell faces that are required to solve (4.42) are calculated using the QUICK differencing scheme, which is based on a weighted average of second-order-upwind and central interpolations of the variable \( \phi \). It should be noted that diffusion terms in FLUENT are always approximated using the central differencing scheme. Both methods are second order accurate, based on a Taylor-series formulation around the cell-centred value [73,79].

4.5 Solution Method

Equation (4.42) represents a set of discrete algebraic equations for all variables of interest. As the solution of velocity can present difficulties due to non-linearity in the momentum equations, the SIMPLE algorithm was adopted to link the solution of the pressure and velocity fields via the continuity equation. The system of equations was then solved by an iterative numerical algorithm, until a converged solution was reached.

The procedure of implementing this model in FLUENT was quite involved, and brief description of this is now given. To begin, initial values were guessed for
the temperature, pressure, and species mass fraction fields. Following this, the FLUENT solver entered an iterative loop to solve the governing equations by the FVM. The structure of the iterative loop, which is visualized in Figure 4.2, can be described by the following steps:

*Beginning of loop*

1. Flow properties were updated from previous run (or initialization).

2. Cell potential, local current and local overpotential fields were solved based on user-defined code written by the author.

3. Local diffusion coefficients (and local permeabilities, depending on the study) were solved, based on user-defined code.

4. The SIMPLE algorithm was implemented to solve velocity and pressure.

5. The temperature and scalar species fields were solved.

6. An approximate solution was reached. If the solutions had not converged, the fields were updated and another iteration performed.

*End of loop*
4.5.1 Convergence Criteria

Ultimately, a converged solution implies that the solution has stopped changing beyond some reasonable threshold. In this work, convergence was judged based on several criteria: mass and species conservation, the temperature field, and equation residuals. First, mass conservation was checked by calculating the difference between the inlet mass flow rate, and that at the outlet. The difference between the two should equal the sum of the source terms for a respective stream

$$m_{in} - m_{out} = \sum_{\text{cells}} m_{source}$$  \hspace{1cm} (4.43)
Conservation of species was similarly checked for each species $i$ in each stream, according to

$$m_{i,in} - m_{i,out} = \sum_{\text{cells}} m_{i,source} \ ?$$  \hspace{1cm} (4.44)

These were considered converged when the normalized difference $\text{abs}(m_{in} - m_{out} - \sum_{\text{cells}} m_{source})/m_{in}$ was less than $10^{-3}$.

Figure 4.3: Plot of average temperature over the active anode/electrolyte interface.

Another measure of convergence was monitoring of the temperature field, which, compared to other variables, required the most iterations to stop changing; this was due to the slow convergence of conjugate heat transfer problems. Given the
strong coupling between temperature, electrochemistry, and fluid flow, it was an especially necessary measure to ensure that the temperature field in the model stopped changing. To be sure that it had, the average temperature across the electrolyte was monitored versus number of iterations, as in Figure 4.3.

For the monitoring of residuals, it was deemed sufficient that the absolute residuals fell below a reasonably small value and stopped changing. Absolute residuals are defined by considering the discretized conservation equation for a variable \( \phi \) (equation (4.42)) in the following form

\[
a_p \phi_p = \sum_{nb} a_{nb} \phi_{nb} + S
\]  

(4.45)

where \( p \) denotes the variable for a particular point, and \( nb \) denotes neighbouring cell values. The absolute residual \( R_\phi \) is then [73]

\[
R_\phi = \sum_{cells} \left( \sum_{nb} a_{nb} \phi_{nb} - a_p \phi_p + S \right)
\]  

(4.46)

The default convergence criteria in FLUENT was ignored, and the fields were judged to have converged when the residual values stopped changing with iterations, this usually happened after roughly 2000 iterations. If the residual curves had not yet flattened out, then the model was run for as many iterations as was necessary in order to achieve this. This was only done after the other convergence checks had been carried out. A typical residual plot is shown in Figure 4.4.
4.6 Model Validation and Verification

To have confidence in the output of a numerical simulation, it must also be shown that measures were undertaken to ensure the modeling approach was reasonable. This can be referred to as verification and validation. Verification involves ensuring that the correct equations are solved, and that the model is appropriate for the identified problem. This involves application of the model to another problem of similar physics, for which there is a known or accepted solution. Validation, on the other hand, checks that the computer code does what is expected of it, and involves performing a grid study to ensure that the
solution is independent of the spatial discretization. It also involves the comparing modeling predictions with previous numerical and experimental data.

### 4.6.1 Validation of Momentum Approach

The approach to modeling the mass flux in the porous regions was investigated by comparison to an analogous problem researched by Yuan and Finkelstein [80]. The physics of the Yuan and Finkelstein study were duplicated and implemented for a domain that is similar to that of Figure 4.1, but with a simplified geometry. Figure 4.5 shows this domain, along with the prescribed boundary conditions.

![Figure 4.5: Schematic of the domain used in the validation study (not to scale).](image)

The radius of the channel, $R$, mirrors the fuel channel radius (r-fc) in Figure 4.1, as do the lengths $L$ and $L-e$. In their study, laminar, tubular flow with mass injection/removal at the wall was considered, and analytical solutions to the cylindrical Navier-Stokes equations were obtained. These are given by equations
(4.47) and (4.48), where \( \lambda = \rho v_o R / \mu \), \( Re_R = \rho u_o R / \mu \), \( \eta \) is the non-dimensional radius \( r/R \). The variables \( u_o, v_o \) and \( R \) are as shown in Figure 4.5.

\[
u = u_o \left( 1 - \frac{\lambda}{18} + \frac{83}{5400} \lambda^2 \right)^{-1} + \frac{4 \lambda x}{Re R} \times \\
\left( 1 - \eta + \frac{\lambda}{36} ( -2 + 9 \eta - 9 \eta^2 + 2 \eta^3 ) + \frac{\lambda^2}{10800} ( 166 - 760 \eta + 825 \eta^2 - 300 \eta^3 + 75 \eta^4 + 6 \eta^5 ) \right)
\]

\[
v = \frac{2 u_o \lambda^2}{Re 72 \eta} \left( \eta - \frac{\eta^2}{2} + \frac{\lambda}{72} ( -4 \eta + 8 \eta^2 - 6 \eta^3 + \eta^4 ) \right) + \\
\frac{\lambda^2}{10800} ( 166 \eta - 380 \eta^2 + 275 \eta^3 - 75 \eta^4 + 15 \eta^5 - \eta^6 )
\]

The porous wall region was treated as described in section 4.2.1, and Faradaic source terms were implemented in a simulated active electrode region (near the porous/solid interface) for the mass and momentum equations. The sources were based on a constant current density along the \( z \) direction in this region. 2-D axi-symmetric, incompressible, isothermal, steady state flow of hydrogen gas was then solved in the channel, with specified values found in Table 4.3.

| \( u_o \) | \( 8.8 \text{cm/s} \) |
| \( v_o \) | \( 0.54 \text{mm/s} \) |
| \( Re_R \) | \( 0.9 \) |
| \( \lambda \) | \( 0.00478 \) |
| \( \kappa \) | \( 1 \times 10^{-15} \text{ m}^2 \) |
4.6.2 Momentum Validation Results

Figure 4.6 and Figure 4.7 show the converged results of the model validation study. Very good agreement was obtained with Yuan & Finkelstein, with some difference in the axial velocity at \( z=0.0 \). This is attributed to the gradients that are created near the exit of the inlet channel (before the porous wall begins) where the effect of the wall suction begins. The Yuan & Finkelstein study would not show this behaviour because it does not consider any length of tube that does not have wall suction. These extra lengths were added in FLUENT to avoid any inlet/outlet effects near the region of interest in the domain.

![Diagram showing normalized axial velocity vs. r/R at three different axial locations.](image)

Figure 4.6: Normalized axial velocity vs. \( \eta \) at three different axial locations.
4.7 Grid Independence

With the momentum approach validated, a further step was taken to ensure the model would give physically meaningful results. Cognisant of the fact that, in the FVM, errors in the solution decrease as the grid becomes more resolved, a grid study was performed to determine what grid resolution stops appreciably changing the solution. The procedure for the grid study was to create grid meshes of increasing spatial resolution and examine the solution of variables that will have important implications on the cell performance predictions. The variables considered were flow velocity and temperature. The grid used in this
study is identical to that employed in the modeling studies in the next chapter. The domain in Figure 4.1 was meshed using GAMBIT 2.4.6, and Figure 4.8 shows the base grid of lowest resolution in this grid study.

![Figure 4.8: Grid resolution for the base case (1x), showing 11,250 cells.](image)

The mesh is rectangular and structured, but it is not a uniform grid in that it is composed of varying grid sizes. To elaborate, the mesh is more refined in areas of large expected gradients; particularly near the 180° turn-around cavity in the anode channel; this, to reduce error due to lack of spatial resolution. The mesh is also much more refined in the “fuel cell layers” (as demarcated in Figure 4.8); this was to have a very fine resolution of the species partial pressures and temperature in the regions that directly affect cell performance. Subsequent meshes were created by doubling the resolution in both radial and axial directions. Increasing the grid resolutions resulted in an increase of computational cells (roughly 38,000 for the 2x resolution, and roughly 140,000 cells for the 4x resolution).
4.7.1 Grid Study Boundary Conditions

The boundary conditions for the grid study and the final model are shown below in Figure 4.9, while material properties for solid/porous materials are detailed in Table 4.4. Inlets were specified with uniform velocities that were based on a utilisation factor, $u_i$, where

$$ u_i = \frac{I/ZF}{\dot{n}_{inlet,i}} \quad (4.49) $$

and $\dot{n}_{inlet,i}$ is the molar flow of species $i$ at the inlet. This factor provides a useful normalization for measuring performance across different cell types. For the studies, $u$ for hydrogen and oxygen varied from 0.2 to 0.8. Pressure outlet boundary conditions were prescribed where the flows leave the domain, with gauge pressure set to zero. The flow is assumed to be fully developed at the outlet, where a zero gradient condition exists. Zero gradient means that the change in a variable in the direction normal to the outlet is zero (except for $p$).

![Figure 4.9: Schematic of boundary conditions](image)
All other external boundaries are set as fixed walls that do not allow mass flux. As these boundaries are radiation walls, they can, however, exchange heat with the surroundings, and the emissivity for these exterior walls and the furnace walls were assumed to be 1. This approach was chosen to simulate the conditions of a furnace, in which SOFCs are generally tested and operated. At the symmetry axis, there is a no-flux condition, and here the normal velocity to the symmetry axis is set to zero. Inlet temperatures were set to 873K, fuel and oxidant utilisation factors were set to 0.1, and current density was set to 10000A/m². $Re_{melt}$ for fuel and oxidant were, respectively, on the order of 6 and 8. Material properties for the solid and electrode regions are given in Table 4.4.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Ni-YSZ</td>
<td>Ni-YSZ</td>
<td>YSZ</td>
<td>LSM-YSZ</td>
<td>LSM-YSZ</td>
<td>Ni-YSZ</td>
</tr>
<tr>
<td>$\rho$ [kg/m³]</td>
<td>3030</td>
<td>3030</td>
<td>5160</td>
<td>3310</td>
<td>3310</td>
<td>3943</td>
</tr>
<tr>
<td>$k$ [W/mK]</td>
<td>5.21</td>
<td>6.38</td>
<td>2.86</td>
<td>2.13</td>
<td>1.8</td>
<td>5.21</td>
</tr>
<tr>
<td>$c_p$ [J/kg-K]</td>
<td>450</td>
<td>595</td>
<td>600</td>
<td>573</td>
<td>573</td>
<td>595</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>25%</td>
<td>10%</td>
<td>&gt;1%</td>
<td>20%</td>
<td>30%</td>
<td>0</td>
</tr>
<tr>
<td>$d_{pore}$ [μm]</td>
<td>10</td>
<td>1</td>
<td>n/a</td>
<td>1</td>
<td>10</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Sources [39,78,81-83]

4.7.2 Grid Study Results

The results of the grid study are now presented. Figure 4.10 shows a plot of centerline temperatures for the electrolyte, anode channel, and cathode channel.
Figure 4.10: Plot of centerline temperatures, with values blanked out to show points from each grid resolution.
Figure 4.11: Velocity magnitude results from grid study.
In Figure 4.10, hardly any deviation in temperature can be seen for the different resolutions. Similarly, the velocity magnitude plots in Figure 4.11, show virtually no variation with increasing resolution. From these results, the conclusion was drawn that the base case grid is sufficiently resolved to provide accurate answers, and this grid was used in the modeling studies in for rest of this work.

4.8 Electrochemical Verification

In order to have confidence in the electrochemical model, results should be compared to those from a real cell. In this work, the tubular cell geometry was based on a cell developed by the Alberta Research Council (ARC), and electrochemical data was obtained for one of their test cells for varying temperatures. It is again stressed that due to the empirical nature of the expressions for exchange current density (equations (4.23) and (4.24)), the parameter \( k^o \) was adjusted to tune the activation portion of the polarization curve to match the ARC results. To match the ohmic loss profile of the ARC results, the constant \( C_i \) in the expressions for the resistivity of the cell materials (equation (4.29)) was also adjusted. Both of these variables were discussed in sections 4.3.1 and 4.3.2, respectively.

4.8.1 Operating Conditions

The operating conditions for this study were set to match those given for experimental data for the ARC cell. An inlet flow rate of 25sccm was specified,
and operating temperatures were varied from 600°C to 800°C. The physical domain that was developed for the grid study, including all boundary conditions and material properties, was the same used for this study.

4.8.2 Verification Results

Figure 4.12 shows relatively good agreement between the model and ARC data. The profiles are well-matched at low current density, but as $i$ increases, we begin to see deviation in the two sets of results, with maximum deviation of 9% at 800°C. While it was a goal of this work to capture the effects on overpotential by studying mass transfer in detail, the accuracy of other electrochemical considerations was secondary. In that light, one must be reminded that the model results were tuned to match the ARC experimental profiles, chiefly by adjusting constants for the electroic exchange current densities. It is perhaps appropriate that there is some deviation in the profiles, so as to remind the reader that these results are merely predictions derived from tuning model parameters. Furthermore, because the decision was made to ignore the losses due to current collection, which can be significant, adjusting the expressions for material resistivity was a way to account for other losses that should have been included. To avoid relying on these tuning assumptions, the model would need to solve for the potential distribution throughout the cell, and this was considered to be outside the scope of this work.
4.9 Summary

This chapter has covered the development of the CFD model, from the discretization of the governing equations, to the validation and verification of the modeling approach. The results of the validation and verification give confidence in the modeling approach taken thus far, and provide context for the modeling studies that are presented in the next chapter.
Chapter 5
Modeling Studies and Analysis

In this thesis, it has been argued that accurate characterization of convective transport is important in predicting the various physical and electrochemical processes in fuel cells. In support of this argument, this chapter will present results and analyses from two modeling studies. First, the implications of different permeability values on the predicted flow and cell performance will be explored via a parametric study. This study incorporates results from the Klinkenberg experiments that were discussed in Chapter 3. Second, the role of convective transport is explored by comparing simulations in which the transport equations are solved normally, to ones in which convection is set to zero in the electrode layers. This is to simulate the constant pressure approach that was highlighted in the literature review.

In both studies, the modeling domain is based on that of the micro-tubular SOFC that has been discussed so far. However, a domain based on a larger cell was also developed to investigate whether convective effects would be more pronounced as electrode thickness increased. According to the literature review, a larger cell could be reasonably approximated by increasing the μSOFC dimensions by a factor of 10, excepting the active anode, electrolyte, and both cathode layers. All electrode properties were kept the same as in Table 4.4. These studies will reveal
several considerations pertaining to electrochemistry, and mass and heat transport that prior to this work were not discussed in the literature.

5.1 Permeability Study
This first study was carried out to investigate the effects of a range of permeability values on cell predictions. Simulations were run with a high and low permeability ($10^{-14}$ and $10^{-16}$ m$^2$, according to the literature survey), and a Klinkenberg permeability that was a function of Knudsen number, according to the experimental results of Chapter 3. The Klinkenberg permeability was implemented via a UDF, and it was found that it did not vary appreciably throughout the cell in the model; its value varied between 1-3 x $10^{-15}$m$^2$. Unless otherwise indicated, the following conditions apply in this permeability comparison study:

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{operation}$</td>
<td>873K</td>
</tr>
<tr>
<td>$P_{operation}$</td>
<td>101325Pa</td>
</tr>
<tr>
<td>$I$</td>
<td>7400 A/m$^2$</td>
</tr>
<tr>
<td>$k$</td>
<td>$10^{-14} - 10^{-16}$ m$^2$</td>
</tr>
<tr>
<td>Fuel composition at inlet</td>
<td>H$_2$ with 5mol% H$_2$O</td>
</tr>
<tr>
<td>Oxidant composition at inlet</td>
<td>21mol% O$_2$, 79mol% N$_2$</td>
</tr>
<tr>
<td>$ufuel/ox$</td>
<td>0.2</td>
</tr>
</tbody>
</table>
The first results of this permeability study show the pressure and density variation across the anode/electrolyte interface (Figure 5.1 and Figure 5.2) and the cathode/electrolyte interface (Figure 5.4).

In Figure 5.1, substantial differences in pressure drop across the anode are shown for the range of permeability values, with lower permeability predicting the highest pressures. The large cell produced the largest pressure changes (~10x atmospheric) and, compared to the higher permeability, this should result in a
predicted performance increase as well. In all cases, the Knudsen-dependent permeability displayed pressure and density profiles that were between the high and low permeabilities, as expected. While the differences in pressure variation are significant, the associated difference in density variation, except for the lowest permeabilities, was very small over the whole anode.

Figure 5.2: Variation of density along the anode-electrolyte interface for varying $\kappa$.

The impetus for studying a larger cell was to observe whether the relative importance of convective effects would increase, and this is difficult to ascertain
from Figure 5.2. Moreover, Figure 5.3 shows that variations in pressure and density predicted by different permeability values did not have a discernable effect on mass fraction variation for the micro- and large-sized cells. What is interesting to see, however, is that the difference in anode thicknesses for the two models showed significantly different predictions in hydrogen mass fraction.

Figure 5.3: Mass fraction variation along anode-electrolyte interface for varying $\kappa$.

We can see that the difference in electrode thickness results in convective effects that, in the case of the large cell, flatten the mass fraction profiles quite significantly. Furthermore, the convective flux in the anode flows away from the electrolyte, and Figure 5.3 shows the effects of this flux and how it opposes the diffusion of hydrogen towards the electrolyte layer. For the large cell, this effect
causes a dramatic decrease in $Y_{H2}$ compared to the $\mu$SOFC. This is evidence that convection can have an important effect when the electrode layer is thick enough.

Figure 5.4: Pressure (upper plot) and density (lower plot) along cathode-electrolyte for varying $\kappa$. 

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When the electrode is thin, however, as in the case for the cathode, significantly less variation is seen. Figure 5.4 shows the differences in pressure and density variation for the different permeabilities. The reader should note that variation in oxygen mass fraction is predictably small, and is not shown. As the cathode shows much smaller pressure changes than the anode, changing its permeability will probably have small effects on electrochemistry. However, the significant pressure variation in the anode should have some appreciable effect on performance predictions. The electrochemical model that is developed in this work, however, does not show strong differences in the polarization curves for the different permeability cases.

![Figure 5.5: Polarization curve for varying $\kappa$.](image-url)
This is shown in Figure 5.5, where the potential is barely higher for the lowest permeabilities, and overall, the trends show very understated differences in potential with pressure. This is likely a consequence of the electrochemical model that is developed in this work, and to explore this, one would be wise to perform a sensitivity analysis with respect to the tuning of the exchange current density. This will be discussed at greater length in Section 5.2.2.

![Figure 5.6: Temperature along electrolyte centerline for varying $\kappa$.](image)

To comment on a different trend in Figure 5.5, the differences in potential with anode thickness are explained by the difference in $Y_{H_2}$ (shown in Figure 5.3) and in temperature (shown in Figure 5.6). The larger cell predicts a much higher temperature, and this is chiefly due to the longer resident time of the anode fuel.
stream in the fuel supply tube. Because of the longer length, the anode fuel stream has more time to absorb heat and is at a hotter temperature by the time it reaches the cell’s active regions. In Figure 5.6, it is seen that varying permeability has a minor effect on temperature, and a lower value for $\kappa$ resulted in a slightly lower temperature profile. The reason for this is unclear, but an explanation perhaps lies in the fact that the higher densities predicted with lower permeability have a greater heat capacity. The minor temperature variation with $\kappa$ over the whole cell is shown for the $\mu$SOFC in Figure 5.7; similar figures for the larger cell are not shown, as no appreciable differences were seen for the different permeability cases.

Figure 5.7: Variation of $T$ with changing $\kappa$. 
5.2 Investigation of Convective Mass Transfer

The results of the previous study provide evidence of some important convective effects; namely on the hydrogen mass fraction profile between the micro and large cells. With the goal of further investing the importance of convection, the next study compares the solution of the standard model developed in Chapter 4 (herein referred to as the “standard model”), to a case where transport is modeled by diffusion only (herein referred to as the “diffusion model”). To implement the diffusion model, the following changes were made to the standard model: The axial and radial velocities were set to zero in the porous electrodes via an option in FLUENT. This simulated setting convection to zero and resulted in not solving transport equations for axial and radial velocities. However, if momentum is not solved, then nor is continuity, as they are inextricably linked in the pressure-velocity coupling algorithms in FLUENT [7]. Diffusion-only forms of conservation of energy and species were still solved in these regions. The conditions in Table 5.2 apply in the current study.

<table>
<thead>
<tr>
<th></th>
<th>873K, 101325Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{operation}, P_{\text{operation}}}$</td>
<td></td>
</tr>
<tr>
<td>$I$</td>
<td>7400 A/m²</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>$1 \times 10^{-16}$ m²</td>
</tr>
<tr>
<td>Fuel composition at inlet</td>
<td>H₂ with 5mol% H₂O</td>
</tr>
<tr>
<td>Oxidant composition at inlet</td>
<td>23mol% O₂, 77mol% N₂</td>
</tr>
<tr>
<td>$u_{\text{fuel/ox}}$</td>
<td>0.2, 0.4, 0.8</td>
</tr>
</tbody>
</table>
5.2.1 Results

Comparisons between the standard and diffusion models are now presented, beginning with a set of contour plots that show variation of species mass fractions and temperature over the computational domain. In these plots, the standard solutions are presented above those for diffusion to facilitate direct comparison. The reader should note models were investigated for three different utilisation factors (0.2, 0.4, and 0.8). Figure 5.8 - Figure 5.16 show the differing mass fraction solutions for each species of interest, where generally there is an appreciable variation between the two models. Following the mass-fraction plots are similar ones for temperature, where, again, marked difference is seen.
Figure 5.8: Variation of $Y_{H2} - u_{fuel}=0.2$. Lower plot neglects convection in anode.

Figure 5.9: Variation of $Y_{H2} - u_{fuel}=0.4$. Lower plot neglects convection in anode.

Figure 5.10: Variation of $Y_{H2} - u_{fuel}=0.8$. Lower plot neglects convection in anode.
Figure 5.11: Variation of $Y_{H_2O} - u_{fuel}=0.2$. Lower plot neglects convection in anode.

Figure 5.12: Variation of $Y_{H_2O} - u_{fuel}=0.4$. Lower plot neglects convection in anode.

Figure 5.13: Variation of $Y_{H_2O} - u_{fuel}=0.8$. Lower plot neglects convection in anode.
Figure 5.14: Variation of $Y_{O_2} - u_{O_2} = 0.2$. Lower plot neglects convection in cathode.

Figure 5.15: Variation of $Y_{O_2} - u_{O_2} = 0.4$. Lower plot neglects convection in cathode.

Figure 5.16: Variation of $Y_{O_2} - u_{O_2} = 0.8$. Lower plot neglects convection in cathode.
Figure 5.17: Variation of $T$. $u_{fuel,ox}=0.2$. Lower plot neglects convection in electrodes.

Figure 5.18: Variation of $T$. $u_{fuel,ox}=0.4$. Lower plot neglects convection in electrodes.

Figure 5.19: Variation of $T$. $u_{fuel,ox}=0.8$. Lower plot neglects convection in electrodes.
In the preceding mass-fraction plots, the diffusion-only model shows the depletion of $Y_{H_2}$ occurring much sooner along the length of the domain; as a binary gas mixture is considered, the opposite is true for $Y_{H_2O}$. Interestingly, at the highest fuel utilisation (0.8), the hydrogen is completely depleted; this is clearly wrong as it violates the definition of the utilisation factor, which was used to set the inlet flow rate. On the cathode side, $Y_{O_2}$ variation is much less marked between the two modeling approaches, although at high utilisation, we begin to see disparity. This cathode is opposite to the anode in that oxygen seems to be used up less than its utilisation factor would predict.

The temperature variation in Figure 5.17, Figure 5.18, and Figure 5.19 also shows marked difference between the two flow models, with the diffusion model showing higher temperatures for all fuel utilisations. This is as expected, as convection should help remove heat from the anode, and bring cooler air into the cathode. One must note that the temperature boundary conditions are seen to have a significant effect on the predicted field; this explains why any fluid near exterior walls is relatively cool. The linkage amongst the above plots requires a more detailed understanding of the underlying flow phenomena, and the assessment of the two approaches is helped by looking more closely at the processes occurring in the electrodes.
5.2.2 Anode Regions

Figure 5.20: Variation of $Y_{H_2}$ throughout anode active region.

Figure 5.20 shows the variation of $Y_{H_2}$ throughout the active anode for both the standard and diffusion models. The profiles are as expected, in that hydrogen mass fraction decreases along the length of the cell in the direction of flow. In the radial direction, there is not a large variation in $Y_{H_2}$ through the thickness of the anode, but in general, it is lower closer to the electrolyte. Both situations are due to consumption of...
hydrogen by the half-cell reaction. The differences between the two models are surprising in that hydrogen mass fractions are almost always lower (except for \( u_{fuel}=0.2 \)), and depleted sooner, in the diffusion model. This is interesting because one would expect that, for the diffusion model, \( Y_{H_2} \) would be higher due to the lack of convective flow, especially near the 180° bend of the fuel channel.

An explanation for the rapid depletion of \( H_2 \) in the diffusion model lies in the fact that mass is not properly being conserved. Specifically, in the FVM implementation in FLUENT, the approach to simulating diffusion results in an erroneous mixture density that does not properly include the mass change due to chemical reaction. It was resolved that due to the implementation of the zero velocity and pressure conditions in Fluent, the SIMPLE algorithm does not properly enforce conservation of mass via the pressure-correction equation, and this results in an improper coupling between the mass flux in the porous media and that in the channel. Erroneous predictions for the utilisation factors are a direct result of this, and this is shown by the following differences between what the utilisation should be (as in the standard model) and what it is in the diffusion model:

- When \( u \) should be 0.2: \( u_{fuel} \) is 0.30, \( u_{ox} \) is 0.17
- When \( u \) should be 0.4: \( u_{fuel} \) is 0.78, \( u_{ox} \) is 0.33
- When \( u \) should be 0.8: \( u_{fuel} \) is 1.00, \( u_{ox} \) is 0.70
Much effort was expended to try to overcome these errors. Different velocity-pressure coupling algorithms, discretization schemes, and density formulations were tried. Furthermore, to bypass the FLUENT facility for zeroing the $v$ and $p$, and thus enforce the solution of mass and momentum, it was further attempted to write UDFs to control every flux term in the transport equations. A correct solution that conserved mass and that zeroed the pressure and velocity in the diffusion model was not achieved, however, and, unfortunately, this is something that needs to be solved in future work.

The variation of $H_2O$ throughout the active anode is shown in Figure 5.21. As expected, the profiles complement those of $H_2$, due to the constraint that $Y_{H_2} + Y_{H_2O} = 1$. Variation of $H_2O$ in the radial direction is small, a consequence of the thin active region. Towards $z=0.005$, the high mass fractions of water have important implications on electrochemistry, as they will drive the current lower (recall equations (4.23) and (4.24)). Towards $z=0.025m$, the mass fraction profiles decrease, which is interesting. This is likely due to the lower temperature and currents at the end of the cell (near $z=0.025$), compared to the neighbouring cell region (say at $z=0.0245$). The lower temperatures are, again, a direct consequence of the temperature boundary conditions for the external walls of the cell, (radiation exchange with black environment at $T_{operation}$).
Figure 5.21: Variation of $Y_{H2O}$ throughout anode active region.

To better understand the coupling that exists between species partial pressures and electrochemistry, the current density variations for the standard/diffusion models are shown in Figure 5.22. The current density profiles are reminiscent of those for the hydrogen plots, in that they are markedly higher near the 180° turn in the fuel channel, where hydrogen is most abundant and water is lowest. This stands to reason, however, as this phenomenon is magnified by the erroneous mass fraction predictions in the diffusion model, and in the case of the highest
fuel utilisation, highly unrealistic skewing of the current is seen. This is likely due to several reasons: first, at higher $u_{fuel}$ there is less hydrogen to feed a fixed current draw, and so the tendency will be that current production due to $H_2$ will be shifted towards $z=0.025$.

![Figure 5.22: Variation of anodic current density throughout anode active region.](image)

The skewed current profile is magnified in the diffusion model by the conservation of mass errors just discussed, however, they are also explained by...
considering the electrochemistry model. Recall in that approach (discussed in section 4.3.3), a constant overpotential was assumed over the entire electrode of interest. This leads to under-predicting the true overpotential in situations when the exchange current density is normally low. This would happen when the variables that affect electrochemical charge transfer, species partial pressures and temperature, are low. The opposite is also true, where the overpotential overpredicts when conditions are favourable for a high current.

Examining Butler-Volmer (4.22), it can be seen that a larger overpotential results in a larger predicted current. This, coupled with the non-linearity of the current-overpotential relationship, results in the nonlinear increases in current gradients that come with increasing the utilisation factor. Combined, these factors cause the excessive skewing of the current. In reality, there would be a more balanced current profile, but it would still be higher towards z=0.025m. This can be further understood by considering the temperature profile in Figure 5.23, where the temperature differences are quite pronounced, and they reflect the current profile throughout the cell. First, a comment is appropriate on the skewed location of heat in the cell. The fuel is pre-heated as it travels through the supply tube towards the 180° bend, thus it is at a high temperature when it reaches the electrode regions. This would be favourable for higher current
production near the 180° bend in the fuel channel, and is partly responsible for the high anodic current in this region.

Furthermore, it is reiterated that the decrease in temperature towards the extremities of the cell is a direct result of the imposed radiative heat flux with environment. Recalling the temperature contour plots at the beginning of this chapter, it is seen that higher temperatures are predicted in the diffusion model.
This makes sense as there is one less mode of heat transfer. This further explains the steep current gradients and the tendency for higher consumption of $H_2$ towards $z=0.025\text{m}$.

![Gauge pressure variation throughout the anode.](image)

Finally, the anodic pressure variation is shown in Figure 5.24. Consistent with the predictions made in Chapter 3, a permeability on the order of $10^{-16}\text{m}^2$ results in very significant pressure drops across the anode. In general, the anodic...
pressure profiles reflect those for current density, and this is predicted in Darcy’s Law.

5.2.3 Cathode Regions

Some trends observed in the anode are repeated in the cathode. To begin, there was no discernable difference in temperature between the anode and the cathode; this is reasonable given that there is only a 5μm electrolyte separating the two.

Figure 5.25: Variation of $Y_{O_2}$ throughout cathode active region.
While temperature differences may be small, the oxygen variation should look quite different compared to hydrogen variation in the anode. Figure 5.25 shows \( Y_{O_2} \) variation in the cathode active layer. For low utilisation, the minor difference between the two models is interesting. The main reason for this is, again, the thinness of the cathode layers, which minimizes the convective effect across the layers. However, at high utilisation, the convective contribution should be to \textit{increase} \( Y_{O_2} \) in the cathode. In fact, the results show the opposite, with the diffusion model predicting higher mass fractions that, again, violate the definition of the utilisation factor. This is a direct consequence of not properly conserving mass and momentum.

Figure 5.26: Gauge pressure along the electrolyte/active cathode interface.
Figure 5.26 shows the pressure variation through the cathode. Where pressure drops are greatest, the current and associative convective flux should be the highest; this we know from Darcy’s law. This direct coupling between the pressure and the current is reinforced in Figure 5.27. In shape, the pressure and current plots are mirror images of each other.

Figure 5.27 shows that, compared to the anode, the axial gradients of the cathodic current are significantly reduced. This can be explained by considering
that oxygen is in high concentration towards $z=0.005\text{m}$, while higher temperatures are found towards $z=0.025\text{m}$; as both of these factors are favourable for current production, their locations tend to balance out the current profile. This generality breaks down for high utilisation, where the high temperatures outweigh the effects of concentration. Also, the same explanation for the skewing of the anodic current with fuel utilisation applies in the cathode. Namely, the assumption of constant $\eta$ overpredicts current densities when conditions are favourable for charge transfer, and underpredicts when they are not.

5.2.3.1 Constant Current Density

Figure 5.28 shows the predicted temperature profile when the current density and heat sources were constrained constant throughout the active electrode regions.
The main reason for doing this is to remove the skewed current effect and see if the difference in heat transfer between the two models can be better ascertained. Due to the extra mode of heat transfer, the standard model should predict lower, flatter temperature profiles, both by bringing in cooler air to the cathode, and by removing hot reaction products from the anode. As seen in Figure 5.28, the constant current case does not show an appreciable temperature difference between the two models, except for at high utilisation. Towards \( z=0.025 \) m, and at the lowest utilisation factors, it is seen that the diffusion model predicts a slightly higher temperature. A probable explanation for this is that the diffusion model predicts a higher density, which results in a higher heat capacity and lower temperature. To properly investigate the difference in temperature predictions would require a diffusion model that would conserve mass; while this was not possible to implement in FLUENT and include in this work, this would certainly be an interesting area for future study.
Chapter 6
Conclusions and Future Work

The principal goal of this research was to better understand the role of convection in SOFC electrodes, and with that in mind, this thesis has presented both numerical and experimental work.

The experimental work showed that the permeability of a sample anode increased with Knudsen number (and cell operating conditions), and increased wall-slip effects were used as an explanation for this coupling. It was found that electrode permeability was generally on the order of $10^{-15} \text{m}^2$, which is in agreement with the experimental results of the few other researchers who have measured SOFC permeability. The results obtained provide SOFC researchers that use CFD with values for permeability that are based on scientific methods, instead of having to make assumptions.

On the numerical side, a detailed CFD model was developed to not only study the variation of permeability on performance predictions, but also to compare the solutions of a full transport model to one that considered diffusion only. It was found that over a range of reasonable values for SOFC electrode permeabilities, large pressure differences were predicted. However, it was found that these large pressures had little effect on predicted temperature or cell potential. According to the methodology adopted in this work, it can be concluded that the
permeability does affect cell performance, but the electrochemical model herein needs to be further developed in order to better quantify these effects.

It was further found that the approach to electrochemistry in this work resulted in skewing of the anodic and cathodic currents towards the incoming fuel and oxidant flow. This finding has important implications on the temperature field, as the model predicted a skewed profile that mimicked that of the current. As accurate temperature predictions are of utmost importance in fuel cell performance models, it is recommended that the practise of assuming a constant overpotential in a simplified electrochemical model be abandoned in favour of solving a transport equation for a varying potential field, where the anodic and cathodic currents are coupled in the model, as they are in reality.

Concerning the study that compared the standard transport model to a diffusion model, it must be concluded that the highly non-physical concentration, temperature, and current predictions in the diffusion model were the result of not properly solving conservation of mass and momentum. Unfortunately, fixing this error within the framework of the FLUENT software was not accomplished, and this makes direct comparison between the two models speculative at best. For this reasons, this thesis is partially inconclusive because a rigorous comparison of convection and diffusion in SOFCs was not fully carried out. To be able to do this using CFD, a customized model must be written where the user can control
the flux terms in the transport equations. Access to all parts of a CFD code are necessary for this, and it is likely that in most commercial CFD packages such as FLUENT, this access will be restricted.

Nevertheless, some insight was still gained into the role of convection in SOFCs. When the size of the cell was taken into consideration, it was found that a larger cell with a thicker electrode not only decreased the concentration gradients in the cell, but also decreased the penetration of hydrogen into the active anode zone. This decrease in hydrogen mass fraction is believed to be caused by the convective flux that flows out of the anode, and needs to be taken into consideration if one of the electrodes is much thicker than the other cell layers.

Finally, it would be instructive to look for evidence of convective effects on the heat transfer solution within the porous electrodes. This could be done by removing the channels in a model and forcing the flow through the electrodes under a significant applied pressure. The inclusion of convection can indirectly affect the temperature by changing the location of current density, and one must consider that controlling and reducing the temperature gradients in a cell is critically important to advancing SOFC development. Future work could involve investigating whether convection can be used to more effectively achieve this.
References


[38] D Simwonis, H Thülen, FJ Dias, A Naoumidis, D Stöver. Properties of Ni/YSZ porous cermets for SOFC anode substrates prepared by tape casting and


[80] SW Yuan, AB Finkelstein. Laminar pipe flow with injection and suction through a porous wall, Trans ASME. (1956) 719-724.


Appendix A

Validation results for the same sample anode. Results from the Porometer (top) and the Diffusion Permeameter (bottom) are shown.

### Porometer Results for Air
(Anode cross-sectional area=4.06e-4m²)

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### Diffusion Permeameter Results for Argon
(Anode cross-sectional area=4.06e-4m²)

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Appendix B

The following tables show diffusion permeameter results for anode sample ID #2.
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