THE DEVELOPMENT OF A COUPLED PHYSICS AND KINETICS MODEL TO COMPUTATIONALLY PREDICT THE POWDER TO POWER PERFORMANCE OF SOLID OXIDE FUEL CELL ANODE MICROSTRUCTURES

by

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"We can’t solve problems by using the same kind of thinking we used when we created them."

-Albert Einstein
Abstract

A numerical model was developed to evaluate the performance of detailed solid oxide fuel cell (SOFC) anode microstructures obtained from experimental reconstruction techniques or generated from synthetic computational techniques. The model is also capable of identifying the linear triple phase boundary (TPB) reaction sites and evaluating the effective transport within the detailed structures, allowing a comparison between the structural properties and performance to be conducted. To simulate the cell performance, a novel numerical coupling technique was developed in OpenFOAM [1] and validated. The computational grid type and mesh properties were also evaluated to establish appropriate mesh resolutions to employ when studying the performance. The performance of a baseline synthetic electrode structure was evaluated using the model and under the applied conditions it was observed that the ionic potential had the largest influence over the performance.

The model was used in conjunction with a computational synthetic electrode manufacturing algorithm to conduct a numerical powder to power parametric study investigating the effects of the manufacturing properties on the performance. An improvement in the overall performance was observed in structures which maximized the number of reaction sites and had well established transport networks in the ion phase. From the manufacturing parameters studied a performance increase was observed in
structures with low porosity and ionic solid volume fractions near the percolation threshold, and when the anodes were manufactured from small monosized particles or binary mixtures comprising of smaller oxygen ion conductive particles. Insight into the anode thickness was also provided and it was observed that the current distribution within the anode was a function of the applied overpotential and an increase in the overpotential resulted in the majority of the current production to increase and shift closer to the electrode-electrolyte interface.
Acknowledgments

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Thank you all!
Nomenclature

**Roman**

\[ a_i \] Activity of species \( i \)

\[ a^\text{prod}_i \] Activity of the product to the power of the stoichiometric value

\[ a^\text{react}_i \] Activity of the reactant to the power of the stoichiometric value

\[ c_i \] Concentration of species \( i \)

\[ c_{x,\text{ave}} \] Volume average concentration of species \( x \)

\[ c_{x,\text{localtpb}} \] Volume average concentration of species \( x \) adjacent to a TPB line

\[ D_{i,j} \] Diffusivity of species \( i \) through species \( j \)

\[ D^\text{Bos}_{i,j} \] Bosanquet diffusion coefficient of species \( i \) through species \( j \)

\[ D^\text{Bulk}_{i,j} \] Bulk diffusion coefficient of species \( i \) through species \( j \)

\[ d_{p,\text{ore}} \] Characteristic pore length

\[ d_{\text{ele}} \] Spherical partial diameter of electronic conductive material

\[ d_{\text{ion}} \] Spherical partial diameter of ion conductive material

\[ d_{\text{H}_2}^2 \] Molecular diameter of a hydrogen molecule

\[ E_{\text{rev}} \] Reversible Cell Voltage

\[ E_{\text{a,H}_2} \] Activation Energy of Hydrogen

\[ F \] Faraday Constant

\[ \Delta \hat{g}_{\text{rxn}} \] Change in Gibbs free energy of a reaction

\[ I \] Current

\[ i \] Current density

\[ i^\circ \] Exchange current density

\[ i^*_{\text{H}_2} \] Reference exchange current density

\[ J_i \] Flux for species \( i \)

\[ K^\prime \] Knudsen number

\[ k_B \] Boltzmann constant

\[ L \] Domain length

\[ l_{\text{anode}} \] Anode domain length

\[ M_i \] Species \( i \) molar mass

\[ n \] Number of electrons transferred in reaction

\[ \partial n \] Surface normal
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>Power</td>
</tr>
<tr>
<td>$p_{H_2}$</td>
<td>Adsorption/desorption equilibrium of hydrogen gas</td>
</tr>
<tr>
<td>$p_i$</td>
<td>Partial pressure of species $i$</td>
</tr>
<tr>
<td>$P_o$</td>
<td>Standard atmospheric pressure</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas Constant</td>
</tr>
<tr>
<td>$R_{loss}$</td>
<td>Resistance losses within a fuel cell</td>
</tr>
<tr>
<td>$S$</td>
<td>Surface Area</td>
</tr>
<tr>
<td>$S_i$</td>
<td>Volumetric source term of species $i$</td>
</tr>
<tr>
<td>$S_{pore}$</td>
<td>Wetted surface Area of the pore phase</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_{ref}$</td>
<td>Reference temperature</td>
</tr>
<tr>
<td>$t_{a,node}$</td>
<td>Anode thickness</td>
</tr>
<tr>
<td>$u_i$</td>
<td>Velocity of species $i$</td>
</tr>
<tr>
<td>$V$</td>
<td>Voltage</td>
</tr>
<tr>
<td>$V_{pore}$</td>
<td>Voltage</td>
</tr>
<tr>
<td>$V_{localtpb}^{ele}$</td>
<td>Computational cell volume adjacent to a TPB line</td>
</tr>
<tr>
<td>$V_{localtpb}^{Tot}$</td>
<td>Total computational cell volumes of all cell adjacent to the same TPB line</td>
</tr>
<tr>
<td>$w$</td>
<td>Anode domain width</td>
</tr>
<tr>
<td>$Z_i$</td>
<td>Species $i$ charge number</td>
</tr>
</tbody>
</table>

**Greek**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Transport coefficient</td>
</tr>
<tr>
<td>$\alpha^{eff}$</td>
<td>Effective transport coefficient</td>
</tr>
<tr>
<td>$\alpha_a$</td>
<td>Anodic charge transfer coefficient</td>
</tr>
<tr>
<td>$\alpha_c$</td>
<td>Cathodic charge transfer coefficient</td>
</tr>
<tr>
<td>$\eta_{act}$</td>
<td>Activation overpotential</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Particle mean free path</td>
</tr>
<tr>
<td>$\lambda_{TPB}$</td>
<td>Triple phase boundary length</td>
</tr>
<tr>
<td>$\lambda_{TPB length,local}$</td>
<td>Local computational TPB length</td>
</tr>
<tr>
<td>$\psi_{ele}$</td>
<td>Electron phase solid volume fraction</td>
</tr>
<tr>
<td>$\psi_{ion}$</td>
<td>Ion phase solid volume fraction</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Conductivity of species $i$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Potential distribution within region $\Omega$</td>
</tr>
<tr>
<td>$\phi_{ele}$</td>
<td>Electronic potential</td>
</tr>
<tr>
<td>$\phi_{ele,ave}$</td>
<td>Volume average electronic potential</td>
</tr>
<tr>
<td>$\phi_{ele,localtpb}$</td>
<td>Volume average electronic potential adjacent to a TPB line</td>
</tr>
<tr>
<td>$\phi_{\Omega^+}$</td>
<td>Ionic potential</td>
</tr>
<tr>
<td>$\phi_{ion,ave}$</td>
<td>Volume average ionic potential</td>
</tr>
<tr>
<td>$\phi_{ion,localtpb}$</td>
<td>Volume average ionic potential adjacent to a TPB line</td>
</tr>
<tr>
<td>$v_i$</td>
<td>Species $i$ diffusion volume</td>
</tr>
</tbody>
</table>
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Chapter 1

Introduction

1.1 Motivation

Today’s globalized society is heavily dependent on an intricate energy system to drive our industrial, technological, and economic sectors. For the past century the dominant source of energy for this system has been fossil fuels (coal, oil, natural gas) with current estimates suggesting 80% of the energy consumed in the world is generated from these fuels [2]. The prolonged use of these fuels has begun to quantitatively destabilize our environment as the previously sequestered carbon are burned and discharged back into the environment [3]. Increases in the ocean acidity, CO and CO$_2$ gases in the atmosphere, and in the average global temperature all illustrate examples of the environmental changes associated with the overuse of fossil fuels, with the continued use expected to increase the severity of these environmental changes.

To mitigate the environmental issues resulting from fossil fuels, there is a strong trend towards developing alternative fuel sources and energy technologies. However,
the simultaneous development of high efficiency and clean burning fossil fuel technologies have been identified as a more immediate solution and can be just as pivotal in helping wean the world off its dependence on this fuel source. One technology which has been the focus of much research and development due to its ability to operate on a variety of fuels\footnote{Including both renewable and conventional fuels} at high efficiencies is the fuel cell.

1.2 Fuel Cells

Fuel cells are an energy conversion technology which use an electrochemical reaction to convert the Gibbs energy of a fuel directly into electrical energy. The major benefits of this technology are high energy efficiency, renewable fuel sources, quiet operation, and lack of mechanical parts. The first functioning fuel cell was demonstrated around 1839 by Sir William Grove when he produced an electrical current by bubbling hydrogen and oxygen gas over two connected platinum electrodes submerged in a sulfuric acid solution \cite{4}. The basic premise of Grove’s fuel cell was to decompose the fuel combustion reaction into two intermediate half-cell electrochemical reactions and harness the movement of electrons between these reactions to extract useful electrical work. All fuel cells operate using this general principle and are comprised of three major components: two electrodes (an anode and cathode) which facilitate the half-cell reactions, and an electrolyte which separates the two electrodes and permits only ionic species transport. Fuel cells can employ a variety of ion conducting materials and the chosen electrolyte material will dictate the overall performance, operational conditions and component materials. This particular body of work will focus on Solid Oxide Fuel Cells. For further information on other types of fuel cells, please refer to

1.3 Solid Oxide Fuel Cells

Solid Oxide fuel cells (SOFCs) are a type of fuel cell which employ a solid ceramic oxygen conductive material as the electrolyte. The most widely used electrolyte material is Yttria-Stabilized Zirconia (YSZ) with 8 molar % doping of Yttrium, but other materials are also under development like samaria- or gadolinia- doped ceria [5]. These electrolyte materials require high operational temperatures (600°C - 1000°C) in order to become effective conductors of oxygen anions, $O^{-2}$. The major benefits of SOFCs include fuel flexibility†, clean combustion process, high electrical efficiency (≈50-60%), use of non-noble metal catalyst materials, and high temperature waste heat useful for combined heat and power (CHP) generation [5] ‡. Suitable applications for SOFC systems include large scale CHP facilities (100 kW), household CHP generation (≈5 kW) and auxiliary power units for long haul trucking (1-5 kW) [6].

1.4 Solid Oxide Fuel Cell Performance

To generate electricity, SOFCs employ the same electrochemical principles covered in section 1.2 to extract useful electrical work from the fuel. Using hydrogen gas as the working fuel the combustion reaction, equation 1.1, is decomposed into an oxygen reduction reaction, equation 1.2, and a hydrogen oxidation reaction, equation 1.3, which occur within the cathode and anode respectively.

†SOFCs can operate using hydrogen gas, methane, carbon monoxide, and reformed hydrocarbons like diesel gas, natural gas and biogas.
‡Potentially boosting the energy efficiency up to 90% [5]
\[
H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O \tag{1.1}
\]
\[
\frac{1}{2}O_2 + 2e^- \rightleftharpoons O^{2-} \tag{1.2}
\]
\[
H_2 + O^{2-} \rightleftharpoons H_2O + 2e^- \tag{1.3}
\]

These two half-cell reactions take place at triple phase boundary (TPB) interfaces between the electron, ion and gas transport phases at or near the electrode-electrolyte interface, where all three species are present to react. An example of the macro species transport throughout a SOFC cell can be seen in Figure 1.1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{sofc_diagram.png}
\caption{A schematic of a solid oxide fuel cell.}
\end{figure}

Energy is converted in a SOFC by supplying a continuous flow of air and fuel over the electrode surfaces, which is simultaneously transported into the cathode and anode. At the cathode-electrolyte triple phase boundary (TPB) interface, the oxygen
gas in the air reacts with incoming electrons to form oxygen ions, equation 1.2. These ions are then transported through the electrolyte to the anode where they oxidize the hydrogen gas to form water and release electrons, equation 1.3. The two electrodes are then connected by an external circuit and an electrical potential difference between the electrodes force electrons from the anode towards the cathode inducing an electric current. By placing an electric load in the external circuit, useful electrical work can be harnessed from the cell.

The total power output from a cell is a function of the potential difference/voltage between the electrodes and the current being drawn from the external load. To increase the total power output multiple cells can be arranged in series or parallel stack configurations to increase either the voltage or current. The total power drawn from a single or stack of cells can be determined using equation 1.4.

\[ P = IV \]  

(1.4)

The relationship between the cell voltage, power, and current can be seen in figure 1.2. When no current is being drawn from the cell it is said to be at open circuit voltage (OCV) and the maximum theoretical potential difference can be calculated from thermodynamic properties of the reacting species. As current is drawn from the system, reaction and species transport inefficiencies within the fuel cell reduce the overall performance. The three major types of losses in a fuel cell are the activation loss, ohmic loss and concentration/mass transport loss.
CHAPTER 1. INTRODUCTION

Figure 1.2: The typical performance of an SOFC cell. The cell voltage and power curves are a function of the current density.

Reversible Voltage

The reversible voltage of the SOFC cell can be calculated using the Nernst equation to evaluate the difference in the Gibbs free energy of the reactants and products, equation 1.5. In this equation the first term is the cell voltage at the operating temperature and the second term accounts for a deviation from standard state activity. The cell voltage is determined by calculating the Gibbs free energy of the reaction at the operating temperature while the activity term for an ideal gas is a ratio of the species partial pressure and a reference pressure at standard temperature and pressure (STP)\(^1\), equation 1.6. The Nernst equation can also be used to determine the galvani potential of the two electrodes, which when summed together equals the reversible

\(^1\)At STP temperature is 273.15\(^\circ\)K and pressure is 1 atm
cell voltage.

\[
E_{rev} = -\frac{\Delta g_{rxn}}{nF} - \frac{RT}{nF} \ln \frac{\prod a_{prod}^{n_i}}{\prod a_{react}^{n_i}}
\]  
\hspace{1cm} (1.5)

\[
a_i = \frac{p_i}{P_o}
\]  
\hspace{1cm} (1.6)

**Activation Loss**

As previously mentioned, electron/current production within a fuel cell is dependent on the two electrochemical half-cell reactions, 1.2 and 1.3. To increase the rate of these reactions, the electrical potential difference at the reaction sites can be modified by sacrificing a portion of the operating voltage, known as the activation overpotential \( \eta_{act} \). To determine an expression for these rates the two half-cell reactions are decomposed into elementary reaction steps which proceed in multiple series and parallel steps\(^\dagger\). The slowest of these elementary reactions is assumed to limit the overall reaction and an expression of this step is used to quantify the overall half-cell reaction\(^\ddagger\). An example of an elementary charge transfer reaction can be seen in equation 1.7; where A(m) and AB(m) are adsorbed species on the electrode, (m) is an metal vacancy, \( B^- (e) \) is an ionized species adsorbed on the electrolyte surface, and \( e^- (m) \) is an electron in the metal lattice.

\[
A(m) + B^- (e) \rightleftharpoons (m) + AB(e) + e^- (m)
\]  
\hspace{1cm} (1.7)

\(^\dagger\)Examples of these reactions include species adsorption/desorption onto the electrode/electrolyte surface, species surface diffusion, species chemisorption, and charge transfer reactions.

\(^\ddagger\)The assumption normally is made that the rate limiting step occurs much slower than the other steps, making this expression valid to use for the whole reaction.
This reaction proceeds in both the forward and reverse direction, and the dominant reaction direction is determined by the probability that a species gains enough energy to overcome the energy/activation barrier between the two states. In the case that the forward and reverse reactions occur at the same rate, the reaction is said to be in equilibrium and the equilibrium reaction rate can be expressed as an exchange current density. Figure 1.3 illustrates an example of the energy barriers of equation 1.7 in equilibrium. To bring this system out of equilibrium the activation barrier can be modified by using a portion of the cell voltage to make one direction more favourable. Normally in a fuel cell is it assumed that the rate limiting step is a charge transfer reaction, making the Butler-Volmer equation 1.8, a suitable expression to describe the current density as a function of the overpotential. This equation can also be rewritten as a function of a unit area ($A/m^2$), known as a current density, which expresses the amount of current which can be produced per unit area.

\[
i = i_o \left\{ \exp \left( \frac{\alpha_a nF}{R T} \eta_{act} \right) - \exp \left( \frac{-\alpha_c nF}{R T} \eta_{act} \right) \right\}
\] (1.8)

Fuel cells have two activation losses expressing the voltage loss attributed to the anodic and cathodic reactions. The elevated operational temperature of the SOFC minimizes the activation losses which are small when compared to lower temperature fuel cells.

**Ohmic Loss**

In a SOFC both electronic and ionic species are transported throughout the cell in response to an applied voltage. The voltage drop or ohmic loss, $\eta_{ohm}$ is caused by finite species conductivity between the electrochemically active regions and is a function of
Figure 1.3: The energy potential difference across the reaction interface for a charge transfer reaction in equilibrium, solid line, and non-equilibrium, dashed line. In equilibrium, the potential difference between the forward and reverse reactions, $\delta G_{E,\text{equ}}^\ast$, are equal allowing both reactions to occur at a constant rate. When an overpotential is applied, the potential difference between the forward, $\delta G_f^\ast$, and reverse, $\delta G_r^\ast$, reactions are manipulated by $-\alpha n F \eta$, leading to a higher reaction rate in one direction. In this example, the overpotential has reduced the potential difference in the forward reaction, increasing the forward reaction rate.
the charge carrier concentration and carrier mobility. Electron conduction within the SOFC is a result of either N- or P-type conduction. N-type conduction occurs when there is an abundance of mobile free electrons† within the atomic lattice, while P-type conduction occurs when lattice site defects cause positively charged holes which permit electron hopping. Due to the higher charge carrier concentration and mobility of free electrons, N-type conduction occurs faster than P-type. Anodes normally employ N-type conductive materials while cathodes normally use materials with P-type conductivity, which is why ohmic losses are normally higher in the cathode.

Ion conduction in the SOFC is a result of atomic lattice site defects like vacancies‡ and interstitial sites§ which permit ionic transport through the material. Due to lower species mobility and site concentration, ion transport occurs at a much slower rate than electron transport and therefore accounts for a large portion of the ohmic loss of a SOFC cell.

Poor contact between different transport layers also contributes to ohmic loss in SOFCs and is a result of poor physical connection between layers. This problem can be mitigated by employing manufacturing techniques which ensure good contact between layers. Each ohmic loss within the cell can be expressed as a resistance and the overall voltage drop can be calculated using equation 1.9.

\[ V = I \sum R_{\text{loss}} \quad (1.9) \]

† detached valence electrons
‡ sites with missing atoms
§ locations within a crystalline lattice structure with extra atoms
Concentration Loss

Mass transport within the SOFC flow structure and porous electrodes allow for the continuous supply and removal of gas species from the TPB reaction sites within the electrodes. As a result of the difference in length scale, mass transport in the flow structure is dominated by convection, while gas diffusion normally dominates within the porous electrode. Convection in the flow structure, which is primarily a result of a pressure differential between the gas inlet and outlet, provides a constant supply/removal of gas species throughout the cell. In the electrode, molecular diffusion is a result of a concentration gradient which develops due to the constant consumption/production of gas species at the reaction interface. Both types of mass transport have inherent losses which reduce the gas concentration at the reaction sites and this decrease is known as the concentration or mass transport loss. The concentration loss affects the local half-cell reversible potential and activation loss at the TPB sites and can be calculated either: indirectly with an empirical expression or directly by accounting for the species transport loss when calculating the local half-cell reversible potential, equation 1.5, and the activation loss, equation 1.8, at the TPB sites. In this work the latter method is used to determine the effects of the concentration loss, as the local species distributions are evaluated within the electrode structures.

1.5 SOFC Electrodes

Solid oxide fuel cell electrodes are fundamental to cell operation as they house the TPB reaction sites and facilitate the transport of species to and from these reaction sites. The electrodes are a porous multiphase structure which must exhibit high
mass transport, electrical conductivity and catalytic activity. To maximize the cell performance the electrodes are normally comprised of two distinct layers: a thin, dense porous layer near the electrolyte interface and an adjacent thicker, coarser porous transport/current collector layer [7]. The thin layer promotes both ionic and electronic conductivity and is electrochemically active with small particles and pores to provide a high density of TPB reaction sites. The thicker layer has larger pores and particles which promotes high mass transport and electronic conductivity between the channel, bipolar plate, and active layer. The electrode materials employed need to be chemically stable in highly reactive environments and have similar thermal expansion characteristics to avoid fracturing and delamination under high temperature thermal cycling [5]. To achieve the thermal and chemical stability cermets† or composite ceramics are commonly used within the electrode.

Anode Materials

The most commonly used anode material is a Ni-YSZ cermet which is chemically stable in the highly reducing environment of the anode. The nickel component of the cermet provides the electron conductivity which is high due to the N-type electron conductance. The nickel also has a low charge transfer resistance with YSZ making it a good electrocatalyst [5]. The YSZ component allows better thermal matching with other components and permits ionic conductance into the anode, increasing the TPB reaction sites in the active layer. The YSZ structure is also known to mitigate nickel coarsening, which reduces the performance of the cell. The effect of each component on the cermet is dependent on the mixture concentration and initial powder size of

†composite ceramic/metal materials
each material, and is currently being studied.

Cathode Materials

Cathode materials need to be able to withstand a highly oxidizing environment and thus normally utilize composite ceramic materials, as cermets are unstable at these conditions. Strontium-doped $LaMnO_3$ (LSM) and YSZ are commonly mixed together to form the cathode composite material and demonstrate good structural and chemical stability. LSM provides good electrical conductivity and catalytic activity, while YSZ provides similar benefits as in the anode. In addition, mixed ionic electronic conducting (MIEC) materials like LSCF$^{†}$ are being developed which have the ability to conduct electrons and ions simultaneously. These materials would allow for reactions to occur on the material surface instead of solely at the TPB and could potentially improve the overall cell performance [8].

Electrode Mass Transport

Mass transport within the electrode is dominated by diffusion as a result of the micrometre/nanometre length scales of the porous media [5]. Diffusive species transport in a fluid occurs as a result of a continuous series of intermolecular collisions which induce a general motion to each molecule of the gas species. At the continuum level this type of diffusion results in the transport of species from high to low concentrations and is referred to as molecular diffusion. In a binary fluid, like the hydrogen/water (fuel mixture) or oxygen/nitrogen (air), the rate of molecular diffusion can be described using Fick’s first law, equation 1.10. Where $J_i$ is the species flux$^\dagger$, $D_{i,j}$ is the

$^{†}(La, Sr)(Co, Fe)O_3$

$^\dagger$A measure of the quantity of a species which flows through a normalized area per unit time
diffusivity of species $i$ through species $j$, and $\nabla c_i$ is the concentration gradient.

$$J_i = -D_{i,j} \nabla c_i$$ (1.10)

In the porous electrode structure it is possible that gas molecules will collide with a solid interface instead of other molecules, and diffusion caused by molecule-to-wall collisions is referred to as Knudsen Diffusion. To determine the main diffusion mode, a dimensionless number known as the Knudsen number defines the ratio between inter-molecular and wall collision, and is expressed as a ratio between the molecular mean free path†, $\lambda$, and the characteristic pore length, $d_{pore}$; equation 1.11.

$$Kn = \frac{\lambda}{d_{pore}}$$ (1.11)

At low Knudsen numbers, $Kn \to 0$, bulk diffusion dominates, at high Knudsen numbers, $Kn \to \infty$, Knudsen diffusion dominates and between $0.01 < Kn < 10$ both bulk and Knudsen diffusion will affect species transport [9]. The diffusion coefficient within this transition regime is determined using the Bosanquet equation, the harmonic average of the two diffusion coefficients. For simplicity, the Bosanquet equation can be expressed as a function of the bulk diffusion and Knudsen number, equation 1.12. Refer to reference [9] for the derivation.

$$D_{i,j}^{Bos} = \frac{D_{i,j}^{Bulk}}{1 + Kn}$$ (1.12)

†An average length a molecule will travel before colliding with another molecule
1.6 SOFC Modelling with CFD

The complex coupled transport phenomena and small length scale of SOFC components make computational fluid dynamic (CFD) models an important tool for performance analysis. The development of this tool has enabled studies to be conducted at a fraction of the cost it would take to determine through experimentation, leading to faster development times of new designs, manufacturing methods, and components. Numerical modelling can also provide the ability for detailed component and in-situ studies to be conducted, minimizing the need for difficult experimental studies. In addition the development of multiscale models can allow for detailed performance characteristics to be determined and coupled between different length scales, increasing the realism and capability of CFD models.

1.7 Scope

The main goal of this research is to develop a better understanding of the intricate species transport and current production within electrode structures, and determine better electrode designs and manufacturing parameters. To achieve this a CFD model was developed in MicroFOAM† [10] which couples the multiphase species transport equations to an electrochemical kinetic expression to estimate electrode performance. The current model has been developed to analyze the performance of Ni/YSZ cermet anodes but can easily be modified to analyze the performance of other anode or cathode composites. Both synthetic and experimentally reconstructed electrode structures can be analyzed with this model, allowing for the direct comparison of both species transport and current production within electrode structures, and determine better electrode designs and manufacturing parameters. To achieve this a CFD model was developed in MicroFOAM† [10] which couples the multiphase species transport equations to an electrochemical kinetic expression to estimate electrode performance. The current model has been developed to analyze the performance of Ni/YSZ cermet anodes but can easily be modified to analyze the performance of other anode or cathode composites. Both synthetic and experimentally reconstructed electrode structures can be analyzed with this model, allowing for the direct comparison of both species transport and current production within electrode structures, and determine better electrode designs and manufacturing parameters. To achieve this a CFD model was developed in MicroFOAM† [10] which couples the multiphase species transport equations to an electrochemical kinetic expression to estimate electrode performance. The current model has been developed to analyze the performance of Ni/YSZ cermet anodes but can easily be modified to analyze the performance of other anode or cathode composites. Both synthetic and experimentally reconstructed electrode structures can be analyzed with this model, allowing for the direct comparison of both species transport and current production within electrode structures, and determine better electrode designs and manufacturing parameters. To achieve this a CFD model was developed in MicroFOAM† [10] which couples the multiphase species transport equations to an electrochemical kinetic expression to estimate electrode performance. The current model has been developed to analyze the performance of Ni/YSZ cermet anodes but can easily be modified to analyze the performance of other anode or cathode composites. Both synthetic and experimentally reconstructed electrode structures can be analyzed with this model, allowing for the direct comparison of both species transport and current production within electrode structures, and determine better electrode designs and manufacturing parameters. To achieve this a CFD model was developed in MicroFOAM† [10] which couples the multiphase species transport equations to an electrochemical kinetic expression to estimate electrode performance. The current model has been developed to analyze the performance of Ni/YSZ cermet anodes but can easily be modified to analyze the performance of other anode or cathode composites. Both synthetic and experimentally reconstructed electrode structures can be analyzed with this model, allowing for the direct comparison of both

†A modified version of the open-source CFD software OpenFOAM
performance and geometric features between structures to be made. In this work synthetic anodes produced from a numerical generation algorithm are used to develop and analyze the numerical model. A parametric study is then conducted to investigate the effects of different anode structural parameters on the overall performance. The effects of the solid volume fraction, porosity, and particle size are all investigated to help identify favorable electrode manufacturing parameters. Insight into the manufacturing thickness of the anode is provided by analyzing the relationship between the overpotential and current distribution in elongated electrode structures.

1.8 Thesis Overview

The remainder of this thesis is divided into five chapters. Chapter 2 provides a literature review on general electrode manufacturing methods and various microstructure discretization, analysis and modelling techniques. In Chapter 3 development of the performance model is outlined, while Chapter 4 provides verification and analysis of the model. The results of a parametric study examining microstructure effects on the performance is presented and discussed in Chapter 5, along with insight into the anode thickness. Chapter 6 summarizes the conclusions drawn and suggests future areas of research.
Chapter 2

Literature Survey

Energy conversion within a fuel cell is a complex process occurring over multiple length scales and requires a thorough understanding of the processes and interactions between these length scales to further the development of fuel cell systems [11–13]. Of particular interest are the species interactions within the detailed porous electrodes, and the effects of the manufacturing process on the intricate microstructure. To investigate these effects in detail, methods have been developed to analyze the structural, transport and performance properties of electrode structures attained from numerical and experimental methods. In this chapter, an general overview of the electrode manufacturing process is discussed, followed by a review of different methods used to obtain discretized electrode structures. Methods used to compare and evaluate these structures are then reviewed, with particular emphasis on methods used to quantify and analyze the different geometric properties. The chapter is then concluded by a review of different transport and performance models used to further analyze the discretized electrode structures.
2.1 Electrode Manufacturing

The SOFC electrode and electrolyte layers are manufactured in succession to produce a structure with intimate contact between layers, commonly referred to as a PEN\(^{\dagger}\) structure. The optimal geometric shape of the PEN structure is still under development with planar, tubular and to a lesser extent hybrid designs being investigated [14, 15]. In an attempt to reduce the SOFC operational temperature down to 600-800°C a shift from electrolyte supported to electrode/anode supported PEN structures has been observed in the literature. This shift reduces the thermal stress during operational cycling, and allows for thinner electrolyte layers to be employed, increasing the performance by decreasing the ohmic loss [7,14,15].

A review article by Menzler et al. [7] thoroughly investigated different fabrication techniques for the PEN structure and divided the process into three main manufacturing technologies: ceramic technologies, thermal spraying technologies, and gas phase deposition techniques. Ceramic technologies use ceramic and cermet solutions to build and coat the mechanical support and substrate layers. The composite solution consists of initial ceramic and/or metal powders\(^{\dagger}\) of submicron sizes\(^{\S}\) which are ball-milled and mixed in a solution with organic additives. Planar cells normally employ tape casting and screen printing techniques to fabricate and coat the substrate, while in tubular cell designs extrusion and spraying methods are common. These methods are applicable for both porous and dense layers and the porosity is controlled by the organic additives used in the initial solution. After deposition the layers are heat treated to remove the organic additives, and allow the powders to

\(^{\dagger}\)PEN - Positive electrode-Electrolyte-Negative electrode

\(^{\dagger}\)Metal powers are only added for cermet layers

\(^{\S}\)Vivet et al. reported submicron sizes of 0.55\(\mu m\) and 0.9\(\mu m\) for the nickel and YSZ powders [16], while Kenney et al. reported 0.73\(\pm\)0.3\(\mu m\) and 0.51\(\pm\)0.3\(\mu m\) for the LSM and YSZ powders [17]
sinter and form percolation networks.

Thermal spray techniques look to remove the sintering process by heating up the powder precursor solution with a plasma flame before deposition. The high temperature powders then sinter upon contact with the substrate forming the required percolation networks without the need for additional heat treatment. This method is ideal for metallic substrates which oxidize during the sintering process and can withstand the large temperature gradients that develop. Gas phase deposition techniques are used to deposit a thin dense coating of material and are an ideal technique for the electrolyte layer [7].

2.2 Microstructure Reconstruction and Generation

Analysis of electrode microstructures is important in establishing a relationship between the electrode manufacturing process and overall performance [18]. Three dimensional (3D) structures in particular are of interest as they allow for the identification of heterogeneous structures and anisotropic properties. To examine the influence of the manufacturing methods on the 3D electrode microstructure two different techniques have been developed to produce 3D structures: experimental reconstruction techniques, and numerical generation techniques.

2.2.1 Experimental Reconstruction Techniques

Experimental reconstruction techniques are used as a diagnostic tool to directly study the effects of manufacturing parameters on the electrode microstructure. Two common techniques are focused ion beam-scanning electron microscopy (FIB-SEM)
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[16,18–32] and X-ray computed tomography (XCT) [33–37]. The FIB-SEM method involves a repetitive FIB milling and SEM imaging process which sequentially captures a series of 2D images that are digitally assembled into a 3D structure. The resolution of this destructive process depends on the SEM for the plane resolution and the FIB milling thickness for the in-plane resolution and both resolutions are on the order of tens of nanometres. This method has been widely employed due to the ease of image acquisition and ability to automate reconstruction steps within the image assembly process [24,28]. The XCT method utilizes a dual-lens system to focus and magnify the x-rays as they penetrate the sample and are absorbed by an x-ray detection device. The sample is rotated through 180 degrees with X-ray emission and detection occurring at small increments to obtain a series of cross sectional images [34,35]. The cross sectional images are then processed to obtain a 3D image and resolutions on the order of tens of nanometres have been reported in studies which utilize a synchrotron radiation source [34–37]. The non-destructive nature of the XCT technique allows for in-situ analysis of the electrode microstructure, however in order to detect multiple solid phases a strong radiation source is required, normally from a synchrotron [33]. In both techniques the resulting 3D structures form a discretized structure comprising of small 3D volumes or uniform voxels designated as one of the three phases. The experimental setup for both techniques can be found in a review paper by Shearing et al. [33]

2.2.2 Numerical Generation Techniques

Numerical generation techniques to construct synthetic electrodes have been developed in an attempt to circumvent the continuous need of experimental reconstructions
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when analyzing different manufacturing processes. Three such methods have been identified within the literature: stochastic techniques based on stereology [38–40], randomized particle placement methods [41–47], and particle packing from induced motion methods [17, 47–52]. Stochastic methods involve the processing of 2D electrode images to determine the size and dispersion of material species, and generate random 3D structures from this information [38]. While simplistic in its approach, Wilson et al. [19] questioned the accuracy of stochastic methods when investigating non-isotropic properties and determining percolation networks. The latter two methods, commonly referred to as Monte-Carlo techniques, use controllable parameters like the powder size distribution, composition, and shape to generate 3D structures of packed particles. The structures are generated by either: randomly placing particles on a lattice structure, randomly placing particles in contact with previously placed particles, or by inducting particle motion and allowing them to naturally settle. The sinter effect can then be added through simple particle expansion or detailed analysis of the intrinsic particulate sintering nature [48] to insure adequate phase percolation between the particles. The particle size used in these simulations can be determined through direct measurement of the powders [17], estimated from the average particle sizes of 2D imaging/experimental reconstructions [38, 41], or arbitrarily set to investigate size dependence on other microstructural effects [46]. Many authors have commented on the heterogeneous nature of the structures produced from Monte Carlo techniques [9, 10, 17, 28, 42–44, 46].
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2.3 Microstructure Analysis

The resulting discretized structures from the generation techniques outlined in Section 2.2 are compared in this section. To provide an accurate comparison between the generation techniques, the inherent differences in the discretization and analysis process are first compared. Following this, studies investigating the effects of independent manufacturing parameters like the phase fraction, porosity and powder size on geometric properties are reviewed.

2.3.1 Quantifying Structural Properties

Experimental reconstruction techniques normally obtain structural information directly from the discretized geometry by summing voxel edges, surface areas and volumes. While structural information about synthetic electrodes is obtained by either: discretization and summing volume data, or by using analytical equations of placed particles to obtain volume, surface and TPB length information.

Berson et al. [9] investigated the difference in volume and surface area calculations between an analytical and discretized method and concluded around 10 voxels per particle diameter was sufficient for estimating the volume of a discretized structure. The group also noted the tendency for a discretized structure to overestimate the surface area by a factor of 3/2 at high resolutions and suggested that at attainable FIB-SEM voxel resolutions of 10-30 voxels per particle the error between the methods would be 8-20%, after applying the overestimation correction factor (3/2). Kenney et al. [17] compared the difference in TPB lengths obtained from discretized and analytical methods, and reported that the TPB length was always overestimated when using discretized structures. They attributed the overestimation to the voxel
edge counting method, which is commonly used in the literature to estimate the TPB length of discretized structures [17, 29, 44–46].

Analytical approaches for structural characterization have limits as they can only determine the TPB length of 3D structures comprised of well-defined analytical shapes and decrease in accuracy as particle overlap increase [17, 43, 48, 51, 52]. Iwai et al. [22] developed two methods to increase the accuracy of the TPB length estimation from discretized structures: the volume expansion method and the centroid method. Both methods were found to produce results within 3% of each other and were validated against an analytical solution. The study suggested reasonable results for a resolution of 10 voxels per particle diameter or higher. Shikazono et al. [29] compared the centroid method with a midpoint method and voxel edge count method and found the latter two methods overpredicted the TPB length when compared to the centroid method.

In parallel to TPB length estimation, the identification of active TPB lines requires determining percolation networks within the three phases. The interpretation of the criteria of percolating regions varied between studies: Vivet et al. [16] considered a phase to be percolating if it was connected to all six boundaries, Wilson et al. [53] identified regions to be percolating if a connected phase made contact with two different boundaries, while Shearing et al. [27] considered directional specific percolation beginning from a specified domain wall. The different percolation criteria affect the overall active TPB length and species transport within the structures, and is important to understand when comparing properties between studies.

The domain size of the studied electrodes is also influential in estimating percolation and structural properties, with the possibility of local structural defects biasing the values of these properties. Shearing et al. [27] outlined the need for a large
domain size when analyzing FIB-SEM reconstruction, and reported a large nickel agglomeration in one of their sample structures. Gunda et al. [28] also identified a large pore crater within their reconstructed structure and attributed the calculated local anisotropy to this anomaly. Shearing et al. [27] suggested the possibility of FIB-SEM methods being used to obtain cubic samples as large as $20\mu m$ per edge.

Kenney et al. [17] also investigated the domain size of synthetic electrodes and reported little variation in structural properties when cubic domain lengths of 15 and 20 $\mu m$ were populated with monosized 1 $\mu m$ particles. Metcalfe et al. [41] also looked at the effects of the domain size on the structural properties and suggested a reasonable domain size was achieved when the edges were approximately 14 times larger than the mean particle size. Cai et al. [45] found that with a particle resolution of 20-40 voxels per particle diameter, the structural percolation networks were fully formed for a particle to domain length ratio of $\geq 7.5$. To verify this work, groups studying the synthetic electrodes performed multiple tests to provide a good statistical base for further experiments. The difference in suggested domain sizes may be attributed to the different methods used to generate and discretize the synthetic electrodes.

### 2.3.2 Comparing Structural Properties

The effects of the solid volume fraction of the TPB length and phase percolation have been investigated using both numerical and experimental methods. Several studies of synthetic electrodes at constant porosity suggest that the maximum percolating TPB length of a binary material of monosized particles occurs at a 50/50 solid volume composition of electron and ion particles [17, 41–43, 48, 54]. It has also been widely established that the size of the particles influenced the TPB length, with smaller
particles producing structures with higher TPB lengths [17, 42, 43, 45, 46, 54, 55]. The effect of size distribution on the TPB length have also been investigated by looking at binary compositions of equally sized particles per phase. Kenney et al. [17] observed that as the size ratio between the particles increased, the maximum active TPB length shifted towards the higher volume fraction of the larger particles. A trend confirmed by Abbaspour et al. [43]. Kenney et al. [17] also noted a decrease in the symmetry of the active TPB length curves as the size ratio increased and attributed this to the chosen method of particle placement. Synthetic electrodes of polydispersed spheres were also studied, with the results showing a decrease in the TPB length of polydispersed particles when compared to monosized particles of similar mean radii [17, 51]. In both the monosized and polydispersed cases the deviation of the maximum TPB length was attributed to a shift in the percolation threshold as a result of the particle sizes [17].

Phase percolation of synthetic electrodes were also investigated to determine the percolation threshold. This threshold was either reported directly as the percent of connected volumes or can be inferred from the TPB active length. It was observed that between solid volume fractions of 30-40% percolation within the structure rapidly increases, becoming widely established above this range for a monosized bi-composite material [17, 42, 43, 47]. Similar to the TPB length it was observed that the maximum phase percolation of both solid regions occurred at equal solid volume fractions [42, 43]. In polydisperse particle structures it was observed that phase percolation occurred slower in response to an increase in volume phase fraction than for monosized particles and a much higher solid volume fraction was required in order to well establish a percolation phase [17].
The porosity of the synthetic electrodes was also studied to determine its importance on various geometric properties. In these structures the pore phase is comprised of the void space between the solid particles and normally does not have an established shape like the solid phase\footnote{When pore forming particles are used the spherical shape is recognizable within the pore phase}. Phase percolation of the pore space was initially investigated in two studies and found to be close to 100% percolating at porosities greater than 20\% \cite{17, 41}. The porosity was also found to have an impact on the active TPB length, which was higher in structures with low porosities \cite{17, 41, 51}. Metcalfe et al. \cite{41} found that in their structures the maximum active TPB length was obtained at a porosity of 0.21, which was also very close to the pore phase percolation threshold which they reported. The size of the pore space was investigated by Kenney et al. \cite{17} who determined the pore size using a combined sphere growth and chord length method. Their results found pore sizes smaller than the commonly assumed pore size range of 0.5-1 \textmu m and that the pore size was dependent on the particle size with larger particles producing larger pores.

The effects of the volume fraction on TPB length and percolation were also investigated experimentally. Vivet et al. \cite{23} reconstructed five different cermet anodes of varying NiO and YSZ composition and used the FIB-SEM technique coupled with a passive voltage contrast technique (PVC). The PVC technique allowed percolating nickel particle to be identified during the FIB-SEM process. The group reported good solid phase percolation at volume fractions above 22\% and identified no percolation in the Ni phase below 16\% phase volume fraction(\approx 25\% solid volume fraction). The group also reported their highest active TPB length at a nickel volume fraction of 26\% (44\% solid volume fraction) manufactured from 56 weight \% NiO powder. Wilson et al. \cite{20} also conducted a study which used the FIB-SEM method but determined
phase percolation with numerical methods. The group identified an initial powder composition of 50 weight % NiO as producing the highest TPB length density (≈40% Ni solid volume fraction). In both studies good phase connectivity was observed for solid volume fractions above 20%. It was also observed that the nickel and pore volume fractions were linked to the initial NiO composition increasing as the composition increased. Vivet et al. [23] comment on these results stating the need for further studies due to the structural dependency on the fabrication processes and precursor composition.

2.4 Microstructure Modelling

To extend the useful information obtained from the 3D electrodes, several groups have begun to develop numerical models to extract and evaluate the transport and performance properties of the structures. Development of these models allows for additional insight into favourable manufacturing and structure parameters through evaluation of the structural interdependencies. This information also provides important transport/performance properties which can be directly used in cell models [56, 57]. The literature reviewed in this section looks at models which: predict the effective transport/tortuosity within porous media, and estimate the overall electrode performance.

2.4.1 Effective Transport Properties

The multicomponent nature of the porous SOFC electrodes results in multiple material and transport properties being present throughout the composite. The semi-continuous distribution of these phases leads to tortuous transport networks which
constrain transport through confined pathways. To compare these structures, expressions which approximate the interstitial transport throughout the porous media have been developed to give approximations of the normalized effective transport coefficients and tortuosity.

Initially, analytical expressions which rely on structural properties were first developed to determine the effective transport properties. In the solid region, percolation theory was developed to estimate the effective diffusive/conductive transport and assumes a rigid packing a spherical particles of known size and composition [51,56–58]. In the pore phase, the Bruggeman equation is commonly used to estimate the effective diffusion coefficient as a function of the porosity and tortuosity.

Validation of these analytical expressions has been conducted with synthetic electrode structures. To investigate the effective transport within the solid phases, Sanyal et al. [47] compared two synthetic electrode generation techniques against a percolation model and found that modification of the model was required in order to get matching results. Bertei et al. [52] also compared synthetic structures against an extended percolation theory expression and found relative agreement between the methods. However the group found that as particle sintering increased\(^1\), the extended percolation theory was unable to accurately predict the effective transport. In the pore phase, Berson et al. [9] compared the Bruggeman equation with a random walk simulation for similar structures and found the Bruggeman equation overpredicted the effective diffusivity and suggested a corrected equation for porosities below 40%.

Effective transport coefficients can also be determined directly from the 3D electrode structures, allowing for directional transport properties to be determined [42–44,46]. The Laplacian equation is a common method employed in the literature to

\[^1\text{This group modelled sintering by setting the particle-to-particle contact angle.}\]
determine the phase potential distribution within the discretized geometry \([10,16,18,21,24,59,60]\) and is described in more detail in section 3.1.3. Resistor network models, which simulate the inter-particle transport as a resistance, have also been used to determine the effective conductivity of the solid phases \([43,48]\). Choi et al. \([10]\) compared the effective transport within the pore phase of a BCC structure using the Laplace method and a random walk method. They found that the laplacian method results were affected by the mesh type, with a body-fitted/cell-cut mesh providing the best agreement with the random walk simulation. The group also determined that for random spherical packings, the sample domain should be at least 10 times larger than the mean particle size to obtain accurate effective properties \([10]\).

Gunda et al. \([28]\) and Vivet et al. \([16,23]\) investigated the local anisotropic effects of reconstructed electrodes, by determining transport properties in the three principle directions. Vivet et al. \([23]\) analyzed the nickel phase tortuosity under different nickel loadings and found higher local anisotropy at lower nickels loadings and relatively constant tortuosity values at higher loadings. In another study, Vivet et al. \([16]\) compared the local tortuosity of the nickel and YSZ phases. They reported an anisotropic tortuosity in the nickel phase and relatively homogeneous properties in the YSZ phase, suggesting anisotropic transport in nickel phase. Gunda et al. \([28]\) evaluated the normalized effective transport of a two phase LSM/pore material and observed a reduced effective transport value in the FIB milling direction, in both the solid and pore phases. They suggested the local anisotropy might be attributed to the presence of a large crater and/or due to the milling direction of the reconstruction method, highlighting the need for multiple samples of large size. The group also compared their results to synthetic electrodes and did not find matching results, with
exception to the normalized diffusivity in the SEM plane direction.

**2.4.2 Electrode Performance Modelling**

Performance models have been developed and employed to gain a better understanding of the complex energy conversion process within the fuel cell. The majority of these models investigate the performance at the cell level and used continuum properties to model the transport through the porous structures [55–58,61,62]. While these models facilitate multicomponent cell analysis, they simplify the transport and current production throughout the detailed porous structure decreasing the accuracy of the predicted performance. To improve the predictive capability, detailed component models have been developed to analyze the performance within detailed 3D electrode structures.

The developed models initially used the techniques described in sections 2.2 and 2.3 to construct and analyze the detailed electrode structures. Suzue et al. [38] and Golbert et al. [44] both published papers in 2008 outlining the development of models to determine the performance within detailed electrode microstructures. In both models the performance is determined by coupling the multiphase species transport equations with a kinetic expression at reactions sites within the structures. The models use charge transfer and binary Fickian diffusion equations to solve for the species transport within the solid and pore phases. In the model developed by Suzue et al. [38], a stochastic geometry was evaluated using the lattice Boltzmann method (LBM) to solve species transport and the Knudsen diffusion was accounted for with an analytical expression. This model coupled the transport equations with a kinetic expression at cell volumes sharing a common TPB line. Golbert et al. [44] used a
volume of fluid (VOF) method to evaluate synthetic electrodes structures† and model the coupled transport. The VOF model was used to determine the phase fraction and TPB length density within the VOF cells, and used this information to approximate the localized effective transport and current production within these volumes. Both models used a Butler-Volmer type kinetic expression‡ to couple the local transport, with Suzue et al. [38] using an expression formulated from the thesis work of De Boer [63] and Golbert et al. [44] using a general expression and experimental values from Sukeshini et al. [64]. Kishimoto et al. [32] also developed a sub-grid scale (SGS) model which utilized the sub-grid structural information of the electrode, normally lost during the image resampling process, when solving the performance. The method initially determines the local volumetric effective transport and effective surface flux between the computational volumes from the sub-grid structure, and uses these properties when evaluating species transport. The authors demonstrate the potential of this model to reduce the computational load while improving the simulation accuracy, and suggest the applicability of this model in cell-scale analysis.

Shikazono et al. [29] employed the model developed by Suzue et al. [38] to determine the performance of a reconstructed FIB-SEM structure and the group used the centroid method to improve the estimate of the TPB length. Shikazono et al. also derived in detail the local and component overpotential expressions and added the dusty gas equation to model the gas transport, with a constant total pressure assumption. The group investigated the grid dependence of the solution, determined the cell performance at two different inlet fuel conditions, and compared their results with experimental data finding good agreement at low $H_2O$ concentrations. The group also

†Constructed from a random particle placement technique to generate the structures
‡Both studies also assumed that the rate limiting step was a charge transfer reaction
provided insight into the active layer thickness. Kanno et al. [30] elaborated on this work by analyzing three reconstructed FIB-SEM structures of varying domain size, the largest structure had a volume of $\simeq 17400\mu m^3$ and spanned the entire electrode thickness. They used two different electrochemical expressions to determine the performance of the structures and compared the results to experimental work, finding a weaker steam dependence of the models when compared to the experiments. The group also suggested avoiding mirrored structures which they found created artificial nickel networks which reduced the effective reaction area.

In parallel, the model developed by Golbert et al. [44] was used by Shearing et al. [26] who used a combined modelling and experimental approach to estimate a length-specific exchange current. The group initially measured the electrode performance at varying temperatures and compared their results to the predicted performance of a FIB-SEM reconstruction, altering the model’s length-specific exchange current until the performance matched. The resulting exchange current was then compared with literature and reported to be consistent with published values. Cai et al. also conducted a study, using the initial model of Golbert et al. [44], to investigate the computational parameters [45] and active thickness [46] of synthetic electrodes constructed from random monosized spherical packings. The group found that the active layer ranged between 5 - 15 $\mu m$ and was a function of the operation overpotential, with high overpotentials reducing the active thickness. The group observed the highest cell performance at equal solid volume fractions and a porosity of 0.21, and commented on the larger current generation near the electrode/electrolyte interface. In addition, the group found that a reduction in the particle size increased the current production and lead to a thinner active electrode thickness [46]. Cai et al. [46]\footnote{Obtained from the experimental work of De Boer [63] and Bieberle [65]}
also reported the importance of using a kinetic expression which accounts for the local gas phase concentrations, citing that models without this restrict the predictive applicability to low current densities.

**Kinetic Models**

The accuracy of kinetic expression in the performance model is important as it couples the species transport equations and predicts the overall performance of the electrode. To obtain a realistic kinetic expression groups have conducted studies to investigate the elementary reaction steps of both the reduction and oxidation reactions, employing both experimental and numerical techniques. Patterned electrode studies [63–66] have been developed to measure the performance of structures with well defined reaction sites at controlled operating conditions. From these studies important experimental parameters can be determined and expressions for the current production rate can be established for use in performance prediction models. Numerical models have also been developed to analyze the multi-step elementary reaction, estimate a rate limiting step(s), and establish an overall kinetic performance expression [12,61,62,67–71]. This work utilizes a numerically derived kinetic expression from the work of by Zhu et al. [57,62,67] to predict the overall current production from the hydrogen reduction reaction in equation 1.3. The model was validated by Goodwin et al. [68], who found the kinetic expression was suitable for predicting the current production when compared to the experimental patterned anode work of Mizusaki et al [66].
CHAPTER 2. LITERATURE SURVEY

2.5 Summary

This chapter begins by summarizing the electrode manufacturing methods used in industry and academia. Different techniques used to experimentally reconstruct and computationally generate the porous electrode microstructures were identified. Methods employed to analyze these microstructures were reviewed and the evaluated properties are compared. Models developed to further analyze the transport and performance properties of the microstructures are also reviewed along with kinetic models used to help predict the performance. The need for a model which can be used to determine and compare the structural properties and performance of the electrode microstructures has been identified from the literature survey. In addition, the need to investigate microstructural properties which maximize the electrode performance was identified from the literature. The remainder of this work is focused on developing a computational model to meet the previously identified needs and employing this model to investigate way to improve the electrode performance.
Chapter 3

Model Development

The development of an electrode performance model in MicroFOAM† [10] to predict the performance and evaluate structural properties of detailed electrode geometries is presented in this chapter. The model predicts the performance by coupling the multiphase species transport equations with an electrochemical kinetic expression at reaction sites within the structures. To investigate the dependency of the performance on various microstructure properties, a numerical generation technique which allows direct control of the initial structural properties was employed. Techniques used to discretize and analyze these structures in MicroFOAM are then presented, followed by an overview of the transport and kinetic equations used in the model. The novel method developed to couple these expressions is then presented along with the computational setup for the benchmark and parametric studies conducted in the following chapters. The combination of the synthetic manufacturing code and the performance model enables a powder to power analysis of the anode structures to be conducted.

†A modified version of the open-source CFD software OpenFOAM
3.1 Electrode Structure

3.1.1 Structure Generation

The structure generation technique used in this work was developed at the Queen’s-RMC Fuel Cell Research Centre (FCRC) and was presented in the work of Kenney et al. [17]. The technique replicates the ceramic electrode manufacturing process and constructs synthetic electrode structures comprised of overlapping spherical particles. The composite structures consist of three transport phases: two solid (electron and ion conduction) phases constructed from randomly distributed spherical particles, and a pore phase consisting of the void space between the particles. The utilization of this generation technique allows for a wide range of structures to be generated as the particle size distribution, solid volume fraction and porosity can all be modified within the code. This work studies structures composed of mono- and binary sized particle distributions at varying particle sizes, solid volume fractions, and porosities.

The synthetic electrode structures are generated using a "drop-and-roll" algorithm to distribute the particles throughout the domain. The algorithm randomly generates a seed particle, at a reduced size, above the domain and simulates the dropping and rolling of the particle over previously placed seed particles. A final stationary position for the dropping particle occurs when it either: makes contact with the bottom of the domain or three previously settled particles. The process is then repeated until the domain boundary is fully populated by spherical particles. To control the solid volume fraction of the structures, a weighted probability function is used when determining the phase of the dropped particle. The sintering of the rigid structure is simulated by
allowing the seed particles to uniformly expand† and overlap each other, establishing transport networks within the overlapping spherical particles. The porosity of the settled structure is then checked and altered, if necessary, by repeating the packing process with a different initial seed particle size. Since this model relies on rigidly packed seed particles to construct the initial structure, manipulation of the porosity affects the initial size of the seed particle, particle-particle contact angle, and the number of particles placed within the domain. This leads to structures with low porosities having a greater number of particles within the domain and larger contact angles when compared to structures of higher porosity and constant particle size. An example of the particle-particle contact angle can be seen in figure 3.1. Upon completion of the algorithm, the analytical structure information of the synthetic electrodes‡ is stored for use within the MicroFOAM [10] model. An example of a structure obtained from the drop-and-roll algorithm if displayed in figure 3.2

![Figure 3.1: The particle-particle contact angles, $\theta_n$, of two overlapping particles. Also shown are the analytical positions, $(x_n, y_n, z_n)$, the particle radii, $r_n$, and the distance between the two particles, $d$, where $n$ is the particle number.](image)

---

†The spherical particle expands to the user defined particle size
‡Particle position, size, and phase
Figure 3.2: The packed structure of spherical particles obtained from the drop-and-roll algorithm.
3.1.2 Mesh Generation

A cut-cell/body-fitted mesh technique is used to discretize the synthetic electrode structures [72,73] and a modified version of the meshing procedure common to OpenFOAM [1] is employed. The method begins by constructing a coarse Cartesian background mesh with the blockMesh program and uses the structural information from section 3.1.1 to then identify and group the three transport regions in the mesh. A custom algorithm was developed and then applied to the background mesh to identify and refine cells at the regional boundaries and TPB interfaces using an octree cutting technique within OpenFOAM. This custom refinement procedure is based on the thesis work of Khakbazbaboli [74] and was used iteratively to refine the background mesh until appropriate cell-to-diameter ratios were achieved, as outlined in section 4.1.

The refined background mesh is then processed using the snap function within snappyHexMesh† to produce a body-fitted mesh. This function also uses the synthetic electrode data to project the individual spherical surfaces into the computational domain and identify cells intersected by these surfaces. An algorithm in OpenFOAM is used to manipulate the vertices of the intersected cells onto the projected surfaces, altering the shape of the computational mesh. The integrity of the manipulated cells are then verified to ensure adequate orthogonality between computational cells. This method has been shown to accurately capture the spherical surfaces of the structures [74] but has issues resolving the curvilinear interfaces between the spheres, producing jagged interfaces at these locations. The jagged refinement of the interfaces can be attributed to the surface snapping method used by snappyHexMesh and the error

†A mesh generation tool designed specifically for OpenFOAM
CHAPTER 3. MODEL DEVELOPMENT

associated with this interface was reduced by increasing refinement at this interface. Further improvement of this interface is possible but is currently beyond the scope of this thesis. An example of the meshing procedure is illustrated in figure 3.3.

![Figure 3.3: The steps used in the OpenFOAM meshing procedure: (a) the analytical surfaces are projected into the computational domain shown in red, (b) and (c) an octree cut-cell process is used to refine the cell multiple times, (d) the surface snapping procedure is then applied to snap the refined cells to the projected surfaces.](image)

3.1.3 Structural Analysis

The finalized mesh structures are then analyzed to determine the percolating transport regions within the three phases using the splitMeshRegions feature in OpenFOAM. This feature uses a marching cell-face-cell process to select and group connected sub-regions, and the sub-region with the largest volume fraction is selected as
the percolating transport phase. The global mesh is then subdivided into six regional meshes and the percolating transport regions are then used for the remainder of the analysis process, and will subsequently be referred to as the general electron, ion and pore phases.

The volume fractions of the structures can then be determined directly from the six regional meshes and are used to calculate the total solid volume fractions, percolating solid volume fraction and the porosity of the synthetic electrodes. The surface area of the regional boundaries is also obtained directly from the regional meshes and is used to estimate the mean cord length of the pore phase, section 3.2.1. The TPB length of the structures is extracted directly from the meshed geometry using a new algorithm developed within MicroFOAM. The algorithm uses a cell/point selection method to initially identify the regional cells and points at the junction between the three percolating phases. This structural information is then processed to determine the linear junctions between the three phases and couple these lines to the adjacent cell volumes. Once completed, the length of the percolating TPB lines can then simply be summed to evaluate the total percolating TPB length of the structure. An example of the percolating solid transport phases and TPB lines can be seen in figure 3.4.

†Percolating and non-percolating mesh regions for each phase
Figure 3.4: The identified TPB lines, in red, are shown within a sample electrode structure of monosized spherical particles. The white particles are the ion conducting phase while the blue particles are the electron conducting phase.

The effects of the porous structure on the species transport is then evaluated by determining the normalized effective transport coefficients. To evaluate the transport coefficients, the boundary conditions in section 3.3.2 are applied and a Laplace equation, equation 3.1, used to evaluate the potential, $\phi$, distribution throughout each of the three percolating phases, $\Omega$. The flux through the two transport boundaries
are then evaluated and compared to fluxes through a unit volume to determine the
normalized effective transport coefficient, equation 3.2.

\[ \nabla \cdot (\alpha \nabla \phi) = 0 \quad (3.1) \]

\[ \frac{\alpha^{eff}}{\alpha} = \frac{\int_{\Omega} (\partial \phi / \partial n) dS}{(\Delta \phi / L) S} \quad (3.2) \]

The \( \alpha^{eff} \) and \( \alpha \) terms are the effective and bulk transport coefficients. On the
RHS of equation 3.2, the numerator is the total surface flux, \( \int_{\Omega} (\partial \phi / \partial n) \), through
the phase surface, dS, of the detailed geometry. The denominator is the normalized
surface flux of a known potential difference, \( \Delta \phi \), across a normalized length, L, and
surface area, S.

### 3.2 Performance Model

The performance of SOFC electrodes is dependent on both the species transport and
electrochemical reactions within the porous structure as previously noted in Chapter
1. An example of the current production process within a Ni/YSZ cermet anode
is illustrated in figure 3.5. To model this phenomena, a solver in MicroFOAM was
developed. The model initially evaluates the individual species transport equations
within the three percolating phases. At the TPB locations where all three species
are present to react, the model couples the transport equations with an electrochem-
ical kinetic expression to evaluate the local current production. To enable the local
species coupling, a novel technique was developed and added to MicroFOAM. The
development of this model allows for the current production within the electrode to
be a function of the local species values, enabling the relationship between the microstructure and performance to be studied in detail.

![Figure 3.5: The coupled species transport and the local species production and consumption at the TPB reaction sites is shown in the anode microstructure.](image)

### 3.2.1 Transport Equations

The transport of the electron and oxygen ion species are governed by the Nernst-Planck equation which expresses the charged species flux, $J_i$, as a function of the concentration gradient, potential gradient, and species convection, equation 3.3.

$$ J_i = -D_i \nabla c_i - \frac{\sigma_i}{(|Z_i|F)} \nabla \phi + c_i \vec{u}_i $$  \hspace{1cm} (3.3)

Under the assumption of a constant species concentration throughout the conduction phases and neglecting convection within the solid transport regions, the potential
gradient within the transport regions will govern the charged species transport. Under these assumptions the Nernst-Plank equation, 3.3, can be rewritten to Ohm’s law and be used to solve the electronic, 3.4, and ionic, 3.5, potential fields.

\[
\nabla \cdot (\sigma_{ele} \nabla \phi_{ele}) = S_{ele}
\]

(3.4)

\[
\nabla \cdot (\sigma_{ion} \nabla \phi_{ion}) = -S_{ion}
\]

(3.5)

In equations 3.4 and 3.5, \(\phi_{ele}\) is the electronic and \(\phi_{ion}\) the ionic potential, \(\sigma_{ele/ion}\) is the material conductivity, and \(S_{ele/ion}\) is the local charge consumption or production source term. In the electronic region the source term is applied as a sink, decreasing the local electrical potential in comparison to the boundary, leading to the transport of species away from the reaction sites and out of the anode. While in the ionic region, the source term is applied as a source, increasing the local potential and leading to the transport of oxygen ions into the anode towards the reaction sites. In both equations the source terms are only applied to the potential fields at the cell volumes directly adjacent to a TPB line, as described in section 3.2.3. The model assumes the electron phase is comprised of pure Nickel, while the oxygen ion phase is comprised of pure YSZ and the respective conductivities are given in equations 3.6 [61,62] and 3.7 [67,75]. It was also assumed that each solid region conducts only one charged species†.

\[
\sigma_{ele} = 3.27 \times 10^6 - 1065.3T \quad [S/m]
\]

(3.6)

†Electron conduction only occurs in the percolating electron phase and ion conduction in the percolating ion phase
\[ \sigma_{\text{ion}} = (3.6 \times 10^7)T^{-1} \exp \left( \frac{-8.01 \times 10^4}{RT} \right) \quad [\text{S/m}] \quad (3.7) \]

In the porous region, the transport of the fuel mixture is assumed to be purely diffusive and Fickian diffusion is used to solve for the gas species concentration distribution. The model assumes a binary fuel mixture of hydrogen gas and water vapour and employs equimolar isobaric isothermal counterdiffusion to simplify the gas species transport. Under these assumptions equation 3.8 is used to solve for the hydrogen species transport.

\[ \nabla \cdot (D_{H_2,H_2O}^{\text{Bos}} \nabla c_{H_2}) = \frac{S_{H_2}}{nF} \quad (3.8) \]

Where \( D_{H_2,H_2O}^{\text{Bos}} \) is the Bosanquet diffusion coefficient of hydrogen gas in water vapour, \( c_{H_2} \) is the concentration of hydrogen gas, \( n \) is the number of electrons transferred in the reaction \(^\dagger\), \( F \) the Faraday constant and \( S_{H_2} \) is the consumption term of hydrogen gas in the electrochemically active regions\(^\ddagger\). To determine the diffusion coefficient of the fuel mixture, the Knudsen number is first calculated to determine the dominant mode of diffusion\(^\S\), equation 3.9. In this equation both the mean free path, \( \lambda_{H_2} \), and the characteristic pore length, \( d_{\text{pore}} \), are determined globally.

\[ Kn = \frac{\lambda_{H_2}}{d_{\text{pore}}} \quad (3.9) \]

The mean free path\(^\P\) of the hydrogen gas molecules can be calculated using equation 3.10 and is a function of the Boltzmann constant, \( k_B \), gas temperature, \( T \),

\(^1\)In the hydrogen reduction reaction \( n=2 \)
\(^\dagger\)This is again set to zero in non-reactive regions
\(^\ddagger\)Bulk, transition, or Knudsen diffusion
\(^\S\)Which is a measure of the average distance between intermolecular collisions
molecule diameter, $d_{H_2}$, and gas pressure, $P$.

$$\lambda_{H_2} = \frac{k_B T}{P \sqrt{2\pi d_{H_2}^2}} \quad (3.10)$$

The characteristic pore length of a computational structure comprising of spherical particles can be evaluated using equation 3.11, as seen in the work of Berson et al. [9]. In this work the authors reported that for an exponential chord-length distribution as expected in monodisperse/polydisperse structures, $\langle l^2 \rangle/2\langle l \rangle^2 = 1$. They also suggested that to best model the wall collisions, $\beta = 4/13$ [9]. The mean chord length, $\langle l \rangle$, was then calculated with equation 3.12 and used the pore domain surface area, $S_{pore}$, and volume, $V_{pore}$, evaluated directly from the meshed structure.

$$d_{pore} = \left[ \frac{\langle l^2 \rangle}{2\langle l \rangle^2} - \beta \right] \langle l \rangle \quad (3.11)$$

$$\langle l \rangle = \frac{4V_{pore}}{S_{pore}} \quad (3.12)$$

Using these equations to determine the Knudsen number at the operational conditions shown in table 3.4, it was established that all the structures studied in this work were within the diffusion transition regime, $0.01 < Kn < 10$, and the Bosanquet equation was then used to calculate the diffusion coefficient, equation 3.13.

$$D_{Bos}^{H_2,H_2O} = \frac{D_{Bulk}^{H_2,H_2O}}{1 + Kn} \quad (3.13)$$

The bulk gas diffusivity of the binary mixture of hydrogen gas and water vapour, $D_{Bulk}^{H_2,H_2O}$, was taken from the work of Wesselingh et al. [76] and is a function of the gas temperature, $T$, total pressure, $P_{tot}$, species diffusion volume, $v_i$, and species molar
mass, $M_i$, equation 3.14.

$$D_{H_2,H_2O}^{Bulk} = 3.16 \times 10^{-8} \frac{T^{1.75}}{P_{tot}^{1/3}(v_{H_2}^{1/3} + v_{H_2O}^{1/3})^2} \left( \frac{1}{M_{H_2}} + \frac{1}{M_{H_2O}} \right)^{1/2} \tag{3.14}$$

### 3.2.2 Electrochemical Kinetic Expression

The electrochemical kinetic expression used to couple the transport equations was taken from the work of Zhu et al. [62], who developed a Butler-Volmer type kinetic equation, 3.15, to determine the current production for the hydrogen reduction reaction.

$$i = i_o \lambda_{tpb} \left[ \exp \left( \frac{\alpha_a F \eta_{act}}{RT} \right) - \exp \left( -\frac{\alpha_c F \eta_{act}}{RT} \right) \right] \tag{3.15}$$

This equation expresses the local current production and as a function of the local activation overpotential, $\eta_{act}$, reaction length, $\lambda_{tpb}$, exchange current density, $i_o$, temperature, $T$, and experimental anodic, $\alpha_a$, and cathodic, $\alpha_c$, symmetry coefficients. An expression for the local exchange current density was also developed by Zhu et al. [62], equation 3.16.

$$i_o = i_{H_2}^* \left( \frac{p_{H_2}/p_{H_2}^*}{p_{H_2}/p_{H_2}^*} \right)^{(1-\alpha_a/2)} \left( \frac{p_{H_2O}}{p_{H_2O}} \right)^{(\alpha_a/2)} \frac{1 + (p_{H_2}/p_{H_2}^*)^{1/2}} \tag{3.16}$$

The exchange current density, $i_o$, is a function of the the gas phase partial pressure, $p_i$, adsorption/desorption equilibrium of hydrogen gas, $p_{H_2}^*$, a reference exchange current density value, $i_{H_2}^*$, and the anodic symmetry coefficient, $\alpha_a$. A general expression for the hydrogen adsorption/desorption rate was also given in the initial work by Zhu et al. [67]. An Arrhenius equation was also used by Zhu et al. [62] to account for
the temperature dependence of the reference change current density, equation 3.17

\[ i^*_{H_2} = i^*_{\text{ref},H_2} \exp \left[ -\frac{E_{a,H_2}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \] (3.17)

The local activation overpotential was also required to calculate the local current production in equation 3.15. The local activation overpotential, a measure of the voltage used to drive the reaction, is determined locally by calculating the difference between the local half-cell reversible potential and the local electronic and ionic potential fields, equation 3.18.

\[ \eta_{\text{act}} = E_{\text{equ}}^o \frac{RT}{2F} \ln \frac{a_{H_2}O}{a_{H_2}} - \left[ \phi_{O_2^-} - \phi_{e^-} \right] \] (3.18)

The first two terms in this equation calculate the local reversible half-cell potential, while \( \phi_{O_2^-} \) and \( \phi_{e^-} \) are the local electronic and ionic potentials. This equation is also valid to determine the overall anode overpotential using the potential and species values set at the boundaries. The experimental parameters used here were taken from the works of Zhu et al. [62] and Goodwin et al. [68] and are displayed in tables 3.4, 3.5, and 3.6 in section 3.3. The reference exchange current density take from the work of Goodwin et al. [68] was compared and corrected against the exchange current densities reported in the literature [26, 29, 32, 45, 46].

### 3.2.3 Multi-regional Coupling

A novel coupling method was developed to allow the volumetric source terms to be coupled at the linear TPB reaction sites. The method relies on the coupled linear and volumetric regions from section 3.1.3 to enable direct communication between the
TPB lines and adjacent cell volumes. The coupling process of the transport regions initially determines the volume average species values at the cell volumes adjacent to the TPB lines, equations 3.19, 3.20 and 3.21. These averaged values are then passed to the local TPB line and used to solve equations 3.16, 3.18, and 3.15 to evaluate the local current production at the TPB line segment, illustrated in figure 3.6.

\[
\begin{align*}
\bar{c}_x &= \frac{\sum_{i=1}^{n} c_{x,i_{\text{localtpb}}} \times V_{i_{\text{localtpb}}}}{V_{\text{Tot}_{\text{localtpb}}}} \quad (3.19) \\
\bar{\phi}_{\text{ele,ave}} &= \frac{\sum_{i=1}^{n} \phi_{\text{ele,i}_{\text{localtpb}}} \times V_{i_{\text{localtpb}}}}{V_{\text{Tot}_{\text{localtpb}}}} \quad (3.20) \\
\bar{\phi}_{\text{ion,ave}} &= \frac{\sum_{i=1}^{n} \phi_{\text{ion,i}_{\text{localtpb}}} \times V_{i_{\text{localtpb}}}}{V_{\text{Tot}_{\text{localtpb}}}} \quad (3.21)
\end{align*}
\]

**Figure 3.6:** The local average species values coupling of the three transport regions to the linear TPB reaction site.
The local current value is then distributed back to the adjacent cell volumes as a volumetric source, equation 3.22, and applied to the species transport equations, illustrated in figure 3.7.

\[ S_x = S_{ele} = S_{ion} = \frac{\left( i_{local} \cdot \lambda_{tpb} \right) \cdot \lambda_{tpb.length,local}}{V_{Tot,local}} \tag{3.22} \]

**Figure 3.7:** The local distribution of the calculated current to the coupled transport regions.

The volumetric sources are then coupled to the transport equations explicitly and the coupling procedure is applied at the beginning of every computational iteration. The use of volume averaged species values and source terms was implemented to take advantage of the already present finite volume method source code in OpenFOAM. These volume averaged terms are sufficient at approximating the local potential and
species concentrations surrounding the TPB line. The approximation could be improved by modelling the species diffusion from the cell centre to the reaction length or potentially modelling adsorbed species diffusion, but these improvements are beyond the scope of the present work.

3.3 Benchmark Model Setup

The structural and performance parameters presented in this section were employed to setup and model the initial benchmark performance test case and are also the default parameters used within the parametric study presented in Chapter 5.

3.3.1 Electrode Structure

The manufacturing parameters used to generate the baseline synthetic electrode structures are presented in table 3.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Size Distribution</td>
<td>Monosized</td>
</tr>
<tr>
<td>$d_{ele}/d_{ion}$</td>
<td>$1\mu m/[1\mu m]$</td>
</tr>
<tr>
<td>Solid Volume Fraction $(Electron/Ion)$</td>
<td>50%/50%</td>
</tr>
<tr>
<td>Porosity $\psi$</td>
<td>30%</td>
</tr>
<tr>
<td>Electrode Domain Size $(l_{anode} \times w_{anode} \times t_{anode})$</td>
<td>$(10 \times d_{average,Max}) \times (10 \times d_{average,Max}) \times (1 \times d_{average,Max})$</td>
</tr>
<tr>
<td>Electrolyte Domain Size $(l_{electrolyte} \times w_{electrolyte} \times t_{electrolyte})$</td>
<td>$(10 \times d_{average,Max}) \times (10 \times d_{average,Max}) \times (1 \mu m)$</td>
</tr>
</tbody>
</table>

A particle-to-edge ratio† of 10:1 was found to produce an adequately converged TPB density when the electrode domain size was evaluated, presented in more detail

†The ratio between the domain edge length and the spherical particle diameter.
In section 4.2. In the benchmark structure this amounted to a cubic domain size of 1000 \( \mu m^3 \) when a particle size of 1\( \mu m \) is used. When the effects of the structural particle sizes are investigated in the parametric study the domain size is set to be ten times larger than the average size of the larger particle and the domain thickness is kept constant at 10 \( \mu m \). This allows for the structural properties and performance to be normalized with respect to the surface area allowing for direct comparison. To enable electrochemical reactions at the electrode and electrolyte interface, a thin electrolyte layer, 1/10\(^{th}\) the thickness of the electrode, was added to the bottom domain and the computational structure is illustrated in figure 3.8.

![Figure 3.8: The dimensions of the anode/electrolyte computational domain](image)
3.3.2 Boundary Conditions

An example of the computational structures used to evaluate the effective transport properties and the performance are shown in figure 3.9 with the only difference between these structures being the omission of the thin electrolyte layer when evaluating the effective transport.

Figure 3.9: An example of the three transport regions, electron (blue), ion (grey) and pore (void space) used to calculate the (a) effective species transport and (b) performance, compared to (c) a manufactured cell assembly taken for the work of Menzler et al. [7].

Within the electron and pore phases ten boundary conditions were required to solve the transport equations, five domain boundaries and five internal boundary conditions, while in the ion phases six domain and five internal boundary conditions were required due to the added electrolyte interface at the z-min boundary wall. In figure 3.9 the two solid phases are the electron (blue) and ion (grey) conducting regions. The pore transport phase is comprised of the void space encompassed by the black bounding box, excluding the non-percolating regions which have not been included. Bulk transport within these structures occurs primarily along the z-axis, as oriented in figure 3.9, as electrons and gas species are transported from the substrate into the anode through the z-max domain boundary and oxygen ion species are transported through the electrolyte from the z-min domain boundary. The x and y domain boundaries have been modelled using symmetry boundary conditions and a Neumann zero flux boundary condition was used at the phase interfaces. When evaluating the effective transport of these structures, only transport in the z-direction was determined and the boundary conditions used in each phase, Ω, are given in table 3.2.

**Table 3.2:** Outlines the boundary conductions used in each phase, Ω, to calculate the effective transport in the z-direction

<table>
<thead>
<tr>
<th>Domain Boundary/Phase Interface</th>
<th>Phase Boundary Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-max.</td>
<td>Symmetry ((\nabla \phi_\Omega \cdot \hat{n} = 0))</td>
</tr>
<tr>
<td>X-min.</td>
<td>Symmetry ((\nabla \phi_\Omega \cdot \hat{n} = 0))</td>
</tr>
<tr>
<td>Y-max.</td>
<td>Symmetry ((\nabla \phi_\Omega \cdot \hat{n} = 0))</td>
</tr>
<tr>
<td>Y-min.</td>
<td>Symmetry ((\nabla \phi_\Omega \cdot \hat{n} = 0))</td>
</tr>
<tr>
<td>Z-max.</td>
<td>Fixed Value ((\phi_\Omega = 1))</td>
</tr>
<tr>
<td>Z-min.</td>
<td>Fixed Value ((\phi_\Omega = 0))</td>
</tr>
<tr>
<td>Phase Interfaces</td>
<td>Zero Flux ((\nabla \phi_\Omega \cdot \hat{n} = 0))</td>
</tr>
</tbody>
</table>

The boundary conditions used to evaluate the performance of the anode structures are presented in table 3.3.
### Table 3.3: Outlines the regional boundary conditions used in the performance model

<table>
<thead>
<tr>
<th>Domain Boundary/Phase Interface</th>
<th>Electron Phase</th>
<th>Ion Phase</th>
<th>Pore Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-max.</td>
<td>Symmetry</td>
<td>Symmetry</td>
<td>Symmetry</td>
</tr>
<tr>
<td></td>
<td>( \nabla \phi_{ele} = 0 )</td>
<td>( \nabla \phi_{ion} = 0 )</td>
<td>( \nabla C_{H_2} = 0 )</td>
</tr>
<tr>
<td>X-min.</td>
<td>Symmetry</td>
<td>Symmetry</td>
<td>Symmetry</td>
</tr>
<tr>
<td></td>
<td>( \nabla \phi_{ele} = 0 )</td>
<td>( \nabla \phi_{ion} = 0 )</td>
<td>( \nabla C_{H_2} = 0 )</td>
</tr>
<tr>
<td>Y-max.</td>
<td>Symmetry</td>
<td>Symmetry</td>
<td>Symmetry</td>
</tr>
<tr>
<td></td>
<td>( \nabla \phi_{ele} = 0 )</td>
<td>( \nabla \phi_{ion} = 0 )</td>
<td>( \nabla C_{H_2} = 0 )</td>
</tr>
<tr>
<td>Y-min.</td>
<td>Symmetry</td>
<td>Symmetry</td>
<td>Symmetry</td>
</tr>
<tr>
<td></td>
<td>( \nabla \phi_{ele} = 0 )</td>
<td>( \nabla \phi_{ion} = 0 )</td>
<td>( \nabla C_{H_2} = 0 )</td>
</tr>
<tr>
<td>Z-max.</td>
<td>Dirichlet</td>
<td>Neumann</td>
<td>Dirichlet</td>
</tr>
<tr>
<td></td>
<td>( \phi_{ele,inlet} = \text{constant} )</td>
<td>( \nabla \phi_{ion} = 0 )</td>
<td>( C_{H_2,inlet} = \text{constant} )</td>
</tr>
<tr>
<td>Z-min.</td>
<td>No contact with interface due to electrolyte layer</td>
<td>Dirichlet</td>
<td>No interface due to electrolyte</td>
</tr>
<tr>
<td></td>
<td>( \phi_{ion,inlet} = \text{constant} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In these structures the electric potential and gas species are only set at the z-max domain boundary at the anode-substrate interface, while the ion potential is set at the z-min domain boundary in the electrolyte. It is assumed that the substrate interface at the z-max domain is not conductive of oxygen ions, thus a zero flux condition is used at the z-max domain. Species transport through the x and y boundary domains are assumed to be symmetric, while species transport is confined within each percolating region resulting in zero species flux through the domain boundaries with exception to the coupled TPB reaction sites.
3.3.3 Numerical Setup and Parameters

The operating conditions used within this work are presented in table 3.4, and the present model assumes the that the electrode environment is both isobaric and isothermal.

**Table 3.4:** Operating conditions used within the anode structures

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>800°C(1073 K)</td>
</tr>
<tr>
<td>Fuel Pressure</td>
<td>101325 Pa</td>
</tr>
<tr>
<td>Fuel Composition</td>
<td>97%H₂ - 3%H₂O</td>
</tr>
</tbody>
</table>

Using the operation conditions from table 3.4, the transport and electrochemical parameters employed in this study are presented in table 3.5.

**Table 3.5:** Transport and electrochemical parameters used within the anode

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ_{ele}</td>
<td>2.12 · 10^6 S/m</td>
</tr>
<tr>
<td>σ_{ion}</td>
<td>4.27 S/m</td>
</tr>
<tr>
<td>D_{H₂,H₂O}^{bulk}</td>
<td>8.14 · 10^{-4} m²/s</td>
</tr>
<tr>
<td>α_a</td>
<td>1.3</td>
</tr>
<tr>
<td>α_c</td>
<td>0.7</td>
</tr>
<tr>
<td>P_{H₂}^*</td>
<td>206053 Pa</td>
</tr>
<tr>
<td>i_{ref,H₂}^*</td>
<td>4.04 · 10^{-4} A/m</td>
</tr>
<tr>
<td>E_{a,H₂}</td>
<td>1.2 · 10^5 J/mol</td>
</tr>
<tr>
<td>T_{ref}</td>
<td>700°C(973 K)</td>
</tr>
</tbody>
</table>

The boundary condition values are presented in table 3.6. The Dirichlet boundary values used for the three phases were applied such that the overall activation overpotential, $\eta_{anode}$, between the z-max and z-min domains was 0.1V. The electrode activation overpotential was calculated using equation 3.18, replacing the local values with the boundary species values. The gas concentration applied at the domain boundary was assumed to be that of the inlet fuel, as mass transport losses through the flow structure and dense porous transport layer/substrate were neglected. The
OCV of the anode was set such that the first two terms from equation 3.18 were equal to the OCV of the hydrogen combustion reaction at the specified operating conditions, $E^{\text{eq}}_{\text{equ}}$.

### Table 3.6: Boundary values and anode overpotential

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_{\text{anode}}$</td>
<td>0.1 V</td>
</tr>
<tr>
<td>$E^{\text{eq}}_{\text{equ}}$</td>
<td>0.84 V</td>
</tr>
<tr>
<td>$C_{\text{H}_2,\text{inlet}}$</td>
<td>$\approx 11.02 \text{mol/m}^3[98285 \text{Pa}]$</td>
</tr>
<tr>
<td>$\phi_{\text{ele, inlet}}$</td>
<td>$\approx 0.9 \text{ V}$</td>
</tr>
<tr>
<td>$\phi_{\text{ion, inlet}}$</td>
<td>0 V</td>
</tr>
</tbody>
</table>

#### 3.3.4 Solution Convergence

The solution convergence of the developed model was monitored by observing the residuals of the boundary species fluxes at Dirichlet boundaries and the total current generation. The inlet boundary flux values and total current production were also monitored to insure species conservation was upheld within the solution. The solution was considered to be solved when the residuals achieved an asymptotic value approaching zero and residuals between the boundary fluxes and total current generation also approached zero.

#### 3.4 Summary

This chapter reviews the development of the anode performance model which couples the three transport equations with an electrochemical kinetic expression. The chapter initially outlines the procedure used to generate, discretize, and analyze the synthetic electrode structures. The multiphase transport equations and electrochemical kinetic expression used within the performance model are also reviewed. The novel method
used to couple the volumetric sources of the species transport equations to a linear reaction site is also presented. The general benchmark model setup used to verify the model and analyze the anode structures is then outlined. In chapter 4 the coupling of the transport equations in the developed model will be verified and the predictive capabilities demonstrated.
Chapter 4

Model Verification

The predictive capabilities of the developed coupled transport model are verified in this chapter. A mesh independence study is first presented to determine the mesh parameters required to adequately resolve the TPB length of the analytical electrode structures. The effects of the domain size on the TPB density are then analyzed to investigate an appropriate domain size to use when predicting the anode performance. The ability of the model to couple the three transport regions is then examined and the performance prediction capabilities of the model are verified against an analytical solution.

4.1 Mesh Independence Study

A mesh independence study was conducted to investigate the resolution of the percolating TPB length as a function of the mesh resolution. In this study the mesh resolution of the refined Cartesian background mesh was varied in proportion to the
analytical particle diameter size, before the body-fitted meshing procedure was applied. To minimize the number of computational cells produced during meshing, two different octree refinement levels were used when refining the particle surface and TPB interface. The results in this section are expressed using the mesh resolution at the TPB interface. Three random synthetic electrode structures with the same initial parameters, outlined in section 3.3, were generated, meshed, and analyzed using the procedures outlined in section 3.1. The results are presented in figure 4.1 which shows a comparison of the percolating TPB length density of the three synthetic electrode structures before and after the body-fitted mesh was applied.

![Figure 4.1](image.png)

**Figure 4.1:** The mesh independence of the percolating TPB length density before and after the body-fitted mesh procedure was applied. The mesh resolution was varied by modifying the average number of Cartesian cell per particle before the body-fitted procedure.

The results in figure 4.1 show that the TPB length estimates from the refined
CHAPTER 4. MODEL VERIFICATION

Cartesian and body-fitted meshes both approach an asymptotic value as the mesh resolution increases. For both the refined Cartesian and body-fitted meshes a resolution of 16 cells per particle diameter was found to be sufficient to keep the variation difference in the percolating TPB length below 1.5%. This resolution was subsequently used for the remainder of this work. From the results it can also be seen that the estimated TPB length density obtained from the two meshing methods varies by roughly 20%. It is commonly known that the TPB estimate from a Cartesian mesh overestimates the TPB length [17], thus the 20% lower TPB length obtained from the body-fitted mesh shows the ability of this meshing procedure to better resolve this interface. The converged TPB density of the body-fitted mesh also agrees well with the TPB density obtain from the work of Kenney et al. [17], who used a analytical approach to estimate the TPB length, validating the uses of this meshing procedure.

4.2 Domain Size

The domain size of the porous electrode was investigated to establish an appropriate size to be used when evaluating performance. The domain size must adequately capture the effective transport properties and performance of the electrode, while minimizing the overall computation time and resources. To establish the appropriate size, the domain was varied in proportion to the monosized spherical particles which had a constant diameter of 1 µm. For each domain size three random structures using the initial parameters outlined in section 3.3 were generated and the resulting percolating TPB length density was determined and used to establish the minimal domain size required. At a particle-domain length ratio of 10, six structures were generated to observe the variance in the TPB estimate.
Figure 4.2: The effects of the domain size on the calculated percolating TPB length density. The domain length is a function of the spherical particle diameter used to construct the electrode.

Figure 4.2 demonstrates the effect of the domain size on the percolating TPB length density which shows an asymptotic trend as the domain size increases. When observing the change in the average percolating TPB length density between domain sizes there is a much larger change between the domain ratios of 6-10, \( \approx 14\% \), in comparison to 10-14, \(<2\%\). It also appears that at a particle-to-domain length ratio of 10 or greater, the variance in the percolating TPB length density becomes constant. This small change between domain ratios of 10-14 and stable sample variance demonstrate that a minimal domain size of 10 times the average particle size is appropriate for determining the performance. Choi et al. [10] found similar results when determining the minimal sample domain size to use when determining the normalized effective transport properties within porous electrode structures, further verifying the uses of
CHAPTER 4. MODEL VERIFICATION

4.3 Performance Model Verification

Verification of the coupled transport model is now presented in order to demonstrate the ability of the model to properly couple the three transport equations with an electrochemical expression. The performance of a baseline sample structure is also evaluated and the impact of the species on the performance is discussed.

4.3.1 Direct Comparison with an Analytical Solution

The ability of the performance model to properly couple the three transport regions with a kinetic expression was verified in this section. This was tested by comparing the current production from the performance model to the kinetic expression from equation 3.15. To allow for the performance model to evaluate the kinetic expression, the species transport in the three regions was neglected and the species and potential regions throughout the electrode were set to constant values. The current production from the model and the kinetic expression were then compared and both values were found to be equal. This was repeated multiple times and in all cases the current production between the modified model and the kinetic expression equated. These results demonstrate the ability of the model to properly couple the three transport equations and evaluate the kinetics.
4.3.2 Baseline Sample Species Distributions

The ability of the performance model to account for the species transport losses and local species consumption/production is then demonstrated from the species distribution within the three phases of a fully converged solution, as seen in figure 4.3.

![Figure 4.3: The distribution of the (a) electrical potential, (b) gas concentration, and (c) oxygen ion potential in the benchmark structure for a fully converged simulation using the parameters outline in section 3.3.](image-url)
Figure 4.3 shows the species distribution within the benchmark structure simulated using the parameters from section 3.3. As is demonstrated, local species gradients develop within each of the phases as a result of the coupled transport at the reaction regions. In the electron region the potential gradient is very small but still demonstrates species transport out of the anode through the z-max domain boundary as expected. In the pore phase a larger species concentration gradient develops and demonstrates hydrogen gas diffusion into the anode or water vapour exiting the structure. In the oxygen ion transport region a large potential gradient develops which was shown to dominate the local overpotential calculation. The development of the ionic potential in this regions also properly shows the directional transport of oxygen ions into the anode through the electrolyte domain boundary at min-Z. To further demonstrate the coupled regions, the calculated overpotential field within in the oxygen ion phase is shown in figure 4.4.

\[†\]This model assumed binary diffusion thus the concentration gradient of the water vapour will be the inverse of the hydrogen concentration, once a reference total molar concentration is applied
Figure 4.4: (a) The overpotential distribution within the entire ion transport region and (b) the overpotential distribution when the non-reactive regions are removed.

Figure 4.4a shows the local overpotential within each computational cell which is zero in non-reactive cells and >0 in reactive cells. Figure 4.4b better illustrates the distribution of the overpotential within the anode by removing the non-reactive regions. As expected the largest overpotential occurs near the electrode/electrolyte interface and decreases in magnitude at reaction regions further away from this interface. The distribution of the local overpotential also appears to coincide with the oxygen ion potential distribution in figure 4.3c, noting the inverse relationship between the ionic potential and overpotential demonstrated in equation 3.18. When the two are compared as it can be observed that a potential drop of approximately 0.05V, figure 4.3c, corresponds to a overpotential drop of approximately 0.05V, figure 4.4,within the anode. The ionic potential is expected to limit the overall overpotential due to the low conductivity of the ionic region.
4.3.3 Performance Analysis

The ability of the performance model to evaluate the steady state performance of detailed anode structures is analyzed in this section and a structure was randomly generated using the initial conditions outlined in section 3.3. In addition the boundary conditions and operating conditions used in this section are outlined in sections 3.3.2 and 3.3.3. The performance curve of the anode structure was generated by varying the applied overpotential to simulate applied electrical loads on the anode. This was accomplished through modification of the Dirichlet ionic boundary condition of the Z-min boundary in the oxygen ion transport region. The resulting performance curve can be seen in figure 4.5 and has been compared to the maximum theoretical current obtainable from the anode structure, calculated with equation 3.15. The theoretical current production neglects species transport throughout the electrode and calculates the current production at constant potentials and species concentrations. The range of overpotentials examined in the performance model was between 0.05V - 0.55V and the range for the maximum theoretical current was 0.05V - 0.35V, with the overpotentials increasing by 0.05V in each case.

\[^{1}\text{It is important to note that the performance curve generated in this section is only the performance on the anode component and not the entire cell. Thus the behaviour of the component performance curve will be different then the behaviour of the cell performance curve.}^1\]
Figure 4.5 compares the performance curves of the theoretically ideal performance of the structure against the modelled performance of the benchmark structure which accounts for species consumption, production, and transport. As expected the predicted performance is less than the theoretical performance due to the ability of the model to couple the transport equations and capture the effects of the species consumption, production, and transport within the detailed geometry. When comparing the lowest half-cell voltage/overpotentials there was around 46% difference between the theoretical current production and the predicted current from the coupled model. This difference clearly demonstrates the importance of the species distribution within the anode structure when determining the performance, and highlights the need for the development of a performance model which can use the local species distributions.
to accurately predict the current production within these detailed structures.

The species distributions within the three phases were then examined as the applied overpotential was varied. Similar to section 4.3.2 it was observed that a small electrical potential gradient developed within the electron phase, even at high potentials. The small gradient was attributed to the very high conductivity of the nickel phase. In the pore phase the species concentration gradient was also shown to increase as the overpotential increased as more species were being consumed. However, at the largest overpotential studied, 0.55V, only a small change in the species concentration, approximate 1.5% change from the z-max to z-min boundaries was observed. This demonstrates that for the structure studied there is only a small species concentration loss within the anode layer, even at high overpotentials. The largest species distributions were observed within the ion phase and the ionic potential difference across the domain boundaries was seen to increase as the applied overpotential increased. This is expected since the overpotential was set by modifying the ionic boundary potential and because of the low ionic conductivity of the ionic phase. The ionic potential distributions were again compared to the overpotential distributions and it was again observed that the ionic potential distribution directly influenced the overpotential distribution. These results clearly demonstrate that the ionic potential has the largest influence on the current production as the overpotential is varied.

4.4 Summary

In this chapter verification the performance model developed in chapter 3 is conducted. Two mesh sensitivity studies were conducted and it was found that a mesh
resolution of 16 refined cells per particle diameter before the body-fitted mesh procedure was applied and a domain size ten times larger than the mean particle size both provided adequately meshed geometric structures. The proper coupling of the three transport equations and ability of the developed model to evaluate the half-cell performance was also demonstrated. It was also observed that ionic potential had the largest influence on the overall performance for the conditions studied. In chapter 5 the performance model is employed to identify anode manufacturing parameters which improve the performance of the anode.
Chapter 5

Anode Structure Characterization

In this chapter the validated anode performance model is used to conduct a numerical powder to power parametric study investigating the effects of different anode structural parameters on the overall performance. The results of this study are used to infer beneficial anode structural properties and manufacturing parameters to help improve the anode performance. A study investigating the effects of the anode thickness on the overall performance was also conducted to provide insight into the manufacturing thickness of the anode layer. The effects of the thickness on the current production was studied by varying the overpotential at a constant anode thickness, and monitoring the depth and intensity of the accumulative current density within the anode structures.

5.1 Parametric Study of Anode Microstructure

A numerical powder to power parametric study investigating the effects of the porosity, solid phase volume fraction, and powder size distributions on the anode half-cell
performance is conducted in this section. The effects of these manufacturing parameters on the TPB length density and effective transport properties is also investigated to better establish the impact of the structural properties on the overall performance.

To facilitate the study of multiple structures, this work employs the synthetic electrode structure generation technique and analysis methods outlined in section 3.1. With the exception of the study in section 5.1.4, six structures are generated and analyzed per parameter to enable the statistical variation of the structure generation process to be studied. The operating conditions and computational parameters used for the parametric study are outlined in section 3.3 and the important parameters are shown again for convenience in table 5.1.

**Table 5.1:** Displays the baseline parameters used in the parametric study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Size Distribution</td>
<td>Monosized</td>
</tr>
<tr>
<td>$d_{el}[d_{ion}]$</td>
<td>$1\mu m[1\mu m]$</td>
</tr>
<tr>
<td>Solid Volume Fraction $[\vartheta_{ele}/\vartheta_{ele}]$ (Electron/Ion)</td>
<td>50%/50%</td>
</tr>
<tr>
<td>Porosity $\psi$</td>
<td>30%</td>
</tr>
<tr>
<td>Temperature</td>
<td>1073 K</td>
</tr>
<tr>
<td>Fuel Pressure (Composition)</td>
<td>101325 Pa (97%H₂ − 3%H₂O)</td>
</tr>
<tr>
<td>$\eta_{anode}$</td>
<td>0.1V</td>
</tr>
</tbody>
</table>
5.1.1 Porosity

The effects of the porosity on the anode structural properties and performance were investigated. Table 5.2 outlines the structural properties examined in this study.

<table>
<thead>
<tr>
<th>Target Porosity</th>
<th>Average Measured Porosity ($\mu \pm \sigma$)</th>
<th>Average Knudsen Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.2528 ± 0.002</td>
<td>0.846</td>
</tr>
<tr>
<td>0.30</td>
<td>0.3043 ± 0.004</td>
<td>0.763</td>
</tr>
<tr>
<td>0.35</td>
<td>0.3518 ± 0.004</td>
<td>0.697</td>
</tr>
</tbody>
</table>

The effects of the porosity on the percolating TPB length density, normalized effective species transport, and performance are shown in figures 5.1, 5.2, and 5.3 respectively.

![Figure 5.1](image)

**Figure 5.1:** The variation of percolating TPB length density with respect to the porosity. The solid line connects the sample averages at each porosity.

In figure 5.1 the trend between the electrode porosity and the TPB length density,
which increases as the porosity decreases, can be observed. As outlined in section 3.1.1, a decrease in porosity will increase the number of particles populating the domain and increase the particle-particle contact angle, both of which were observed and explain the increase in the overall TPB length density. An increase in the number of particles within the domain increases the number of particles available to form TPB reaction sites, while an increase in the contact angle leads to a larger contact area between contacting particles resulting in a larger TPB reaction length. The increase in TPB length density with a decrease in porosity has also been reported in Metcalfe et al. [41] and Cai et al. [46]. From their work it is also expected that as the porosity decreases further, the TPB density will increase until a local maxima is reached. As the porosity is further decreased a sharp decline in the TPB density is expected as the pore phase percolation threshold is reached. Although the porosity range studied does not clearly show this maxima and subsequent threshold, it can be assumed that porosities 0.25 or less are ideal for maximizing the TPB length density. The previous studies reported that the maximum electrode TPB length occurred around a porosity of 0.21 [41, 46].
In figure 5.2 a linear relationship between the normalized effective transport in all three transport phases and the porosity can be observed. Within the pore phase the normalized effective diffusivity decreases as the porosity decreases, while in table 5.2 it can be seen that the average Knudsen number increases as the porosity decreases, reflecting a decrease in the molecular gas diffusion coefficient. In the solid transport regions there is an increase in the normalized effective transport coefficient as the porosity decreases. The variation in the rate of change of the effective transport within these regions is attributed to the change in the phase volume fractions as the porosity decreases. In the pore phase, the sample variation clearly follows a linear pattern when compared to the sample average at each porosity setting. Due to the initial structural properties used, a 50:50% solid volume fraction and the constant particle size, the
normalized effective transport in the two solid phases can be directly compared. It can be observed that the normalized effective transport in the electron and ion regions are also a linear function of the porosity, with a larger sample variation observed when compared to the pore phase. The rate of change of the effective diffusivity in the pore phase is more dramatic since the porosity decreases by 5% each interval, while the rate of change of the effective transport in the solid regions is less since the volume fraction of the solid regions only increases by around 2.5% at each interval. It can also be observed that at a porosity of 0.25 the effective transport within the three regions is similar.

![Figure 5.3: The effects of the porosity on the overall current production. The solid line connects the sample averages at each porosity.](image)

A linear relationship between the anode half-cell performance and porosity is illustrated in figure 5.3. Similar to the relationship between the TPB density and
porosity, there is a steady increase in the performance as the porosity decreases. The similarity between the trends suggests that the TPB density and performance are directly related and that maximizing the reaction length is important in increasing the overall performance. When the performance is compared to the effective transport in figure 5.2 and average Knudsen number in table 5.2, it appears that the decrease in the effective transport in the pore region and the gas diffusivity coefficient have a negligible effect on the overall performance. This suggests that the porosity and pore size could be reduced further to increase the TPB length and performance, without incurring major transport losses within the pore phase. However the effects of the species concentration on the performance should also be explored to verify this conclusion. To a lesser extent the increased effective transport in the solid regions could also be attributed to the increase in the performance as is suggested in section 5.1.2.

5.1.2 Solid Volume Fraction

This section investigates the effects of the solid volume fraction on the anode structural properties and performance. The target and measured structural solid volume fractions of the electron phase, along with the average Knudsen number are displayed in table 5.3. It should be clarified that the solid volume fraction, which is the phase fraction of the solid regions, is the variable being studied in this section as opposed to the phase volume fraction, which is a phase fraction of the entire domain volume.
Table 5.3: Shows the initial and measured electron solid volume fractions of the structures analyzed

<table>
<thead>
<tr>
<th>Target Electron Solid Volume Fraction</th>
<th>Measured Electron Solid Volume Fraction ($\mu \pm \sigma$)</th>
<th>Average Knudsen Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>0.3002 ± 0.0008</td>
<td>0.763</td>
</tr>
<tr>
<td>0.35</td>
<td>0.3513 ± 0.001</td>
<td>0.760</td>
</tr>
<tr>
<td>0.40</td>
<td>0.3992 ± 0.001</td>
<td>0.764</td>
</tr>
<tr>
<td>0.50</td>
<td>0.5015 ± 0.002</td>
<td>0.763</td>
</tr>
<tr>
<td>0.60</td>
<td>0.6020 ± 0.001</td>
<td>0.765</td>
</tr>
<tr>
<td>0.70</td>
<td>0.7035 ± 0.002</td>
<td>0.766</td>
</tr>
</tbody>
</table>

The measured effects of the solid volume phase fraction on the percolating TPB length density, normalized effective transport and performance are shown in figures 5.4, 5.5, and 5.6 respectively.
The relationship between the percolating TPB density and the solid volume fraction is shown in figure 5.4. It can be observed that the maximum percolating TPB length density occurs at a solid volume fraction of 50-50%, as has been previously reported [17, 43, 48, 51]. The percolating TPB density threshold was identified to occur between the solid volume fractions of 30%-40% and 60%-70%. Outside these ranges one solid region becomes completely isolated, while the other region becomes fully percolating. This is illustrated by the sudden decrease in percolating TPB density.
and reported in the work of Kenney et al [17]. Also reported in the literature was that a deviation from the 50-50% solid volume fraction resulted in a symmetric decrease in the TPB length. This was attributed to there being less particles available to form percolation networks at lower solid volume fractions, directly impacting the number of percolating TPB interfaces. In this work a deviation from the 50-50% solid volume fraction was observed to result in an asymmetric decrease in the TPB length density outside the percolation threshold, as illustrated by the sample average trendline. At an electron solid volume fraction of 70% a higher TPB length density can be observed when compared to a ion solid volume fraction of 70%, best illustrating the observed asymmetry. This asymmetric decrease is a result of the added electrolyte layer at the bottom of the domain which promotes TPB density production near this interface at high electron solid volume fractions. It is expected that as the electron solid volume fraction is increased further the TPB length density will approach an asymptotic value and will be concentrated around electrode-electrolyte interface.
Figure 5.5: The effects of the solid volume fraction on the normalized effective transport in the z-direction of the three transport regions. The solid line connects the sample averages at each solid volume fraction.

The normalized effective transport as a function of the solid volume fraction is illustrated in figure 5.5. It can be observed in the solid volume regions that there is a non-linear increase in the normalized effective transport which transitions into a linear increase after percolation within the phase is established. In the pore phase, since the porosity was kept constant at 30% there was no significant change observed in the normalized effective diffusivity or the Knudsen number, table 5.3. Also as
expected, at equal solid volume fractions the normalized effective transport in the electron and ion regions were equal.

The relationship between the solid volume phase fraction and the performance can be seen in figure 5.6. Applying the trend which was observed during the porosity study, it is expected that the maximum performance will occur at the maximum TPB density. However, the results show that the maximum current production actually occurs at a 60% ion solid volume fraction (40% electron solid volume fraction) which

\[
\begin{align*}
d_{\text{ele}} &= d_{\text{ion}} = 1 \mu\text{m} \\
\psi &= 0.3 \\
\eta &= 0.1 \text{V}
\end{align*}
\]

Figure 5.6: The effects of the solid volume fraction on the overall current production. The solid line connects the sample averages at each solid volume fraction.
was identified as being the ion and electron phase percolation thresholds. These results demonstrate the importance of a well established ionic transport network within the anode to overcome the poor ionic conductivity limitations. The importance of the percolating TPB density is still demonstrated by the sudden drop in performance at the electron phase percolation threshold, between solid volume fractions of 30-40%. The slow performance decrease and better overall performance above an electron solid volume fraction of 40% is attributed to an increase in the current production at the electrode/electrolyte interface. From this study it is clearly demonstrated that an optimal solid volume fraction can be expected to occur around the ionic percolation threshold at an ionic solid volume fraction of approximately 60%.

5.1.3 Monosized Particle Structures

The effects of the initial particle size of the synthetic anode structures on the structural properties and performance is investigated in this section. The average Knudsen number and particle sizes employed in this study are shown in table 5.4. In this study, the anode thickness (z-domain length) was kept constant at 10\(\mu m\) to remove the dependence of the thickness on the performance. The ratio between the particle diameter and the x- and y-domain lengths was kept at 10:1 which was determined acceptable in section 3.3.1, but note that the results are normalized per unit surface area to take the unequal domain surface areas into account.
Table 5.4: Shows the initial spherical particle sizes used to construct the synthetic anode structures.

<table>
<thead>
<tr>
<th>Structure Particle Diameter</th>
<th>Average Knudsen Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1µm</td>
<td>0.763</td>
</tr>
<tr>
<td>0.75µm</td>
<td>1.056</td>
</tr>
<tr>
<td>0.5µm</td>
<td>1.563</td>
</tr>
</tbody>
</table>

The effects of the initial particle size on the percolating TPB length density, normalized effective transport and the performance are presented in figures 5.7, 5.8, and 5.9.

Figure 5.7: The variation in the percolating TPB density when a monosized powder composition is used to manufacture the synthetic anode. The solid line connects the sample averages at each particle size.

In Figure 5.7 the relationship between particle size and the percolating TPB length density can be observed. The results demonstrate a non-linear increase in the number
of percolating reaction sites within the structures as the particle size decreases. The increase in TPB density is a result of the increased number of particles within the synthetic structure which are available to form reaction sites and has previously been reported \[17, 42, 43, 45, 46, 54, 55\]. In addition, the TPB length densities obtained in this work compare well with the analytical TPB densities reported in the work of Kenney et al. \[17\]

![Graph showing the variation of the normalized effective transport in the z-direction of the three transport regions.](image)

**Figure 5.8:** The variation of the normalized effective transport in the z-direction of the three transport regions when a monosized powder composition is used to manufacture the synthetic anode. The solid line connects the sample averages at each particle size.

The relationship between the particle size and the normalized effective transport within the synthetic electrode structures is shown in figure 5.8. There appears to be no significant change in the normalized effective transport of the three transport
regions as the particle size decreases. While an increase in the average Knudsen number as the particle size decreases is observed in table 5.4 and demonstrates a decrease in the gas diffusivity coefficient as the particle size decreases. In the solid regions the roughly constant normalized effective transport values have been attributed to the relationship between the particle size and contact area between particle. At large particle sizes the contact area between the particles is also large, with the contact area being a function of the particle radius. As the particle size decreases the contact area also decreases but is counterbalanced by an increase in the number of contacting particles, demonstrated through the non-linear increase in the percolating TPB density and the relative constant normalized effective transport. In the pore region the constant normalized effective transport is attributed to the constant porosity of the structures studied. However a decrease in the particle size will decrease the average pore size which was observed in this work and demonstrated by Kenney et al. [17]. The decreased pore size will increase the average Knudsen number, which leads to a decreased diffusivity coefficient as is demonstrated in equations 3.9 and 3.13.
Figure 5.9: The variation of the current production within the anode when a monosized powder composition is used to manufacture the synthetic anode. The solid line connects the sample averages at each particle size.

The relationship between particle size and the performance is shown in figure 5.9. From the result it can be seen that for a constant applied overpotential of 0.1V, the anode performance was improved as the particle size decreased. Since the normalized effective transport properties showed little variation with the particle size and the decrease in the gas diffusivity coefficient had no negative effect on the performance, the improved performance was attributed to the larger number of reaction sites produced when smaller particles were used to construct the anode. The improved performance at smaller particles sizes clearly demonstrates the benefits of using smaller powder sizes to manufacture anodes.
5.1.4 Binary-Sized Particle Structures

In this section, synthetic electrode structures composed of binary distributions of monosized particles per phase are studied to investigate the effects of the particle size distribution on the structural properties and performance. The domain size employed was set using the larger of the two particle sizes and, due to the computational cost of meshing and analyzing the binary distribution, only one structure per setting was analyzed. While the current sample size allows for general trends to be observed and commented upon, it should be noted that the sample size does not allow the sample variance to be examined which reduces the confidence in some of observed trends. Table 5.5 outlines the average Knudsen number and the binary particle sizes studied in this section.

Table 5.5: Shows the binary spherical particle size distributions used to construct the synthetic anode structures.

<table>
<thead>
<tr>
<th>Electron Particle Diameter</th>
<th>Ion Particle Diameter</th>
<th>Average Knudsen Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 ( \mu m )</td>
<td>1 ( \mu m )</td>
<td>1.210</td>
</tr>
<tr>
<td>( \approx 0.71 \mu m )</td>
<td>1 ( \mu m )</td>
<td>0.943</td>
</tr>
<tr>
<td>1 ( \mu m )</td>
<td>1 ( \mu m )</td>
<td>0.763</td>
</tr>
<tr>
<td>1 ( \mu m )</td>
<td>( \approx 0.71 \mu m )</td>
<td>0.945</td>
</tr>
<tr>
<td>1 ( \mu m )</td>
<td>0.5 ( \mu m )</td>
<td>1.228</td>
</tr>
</tbody>
</table>

The effects of the binary size distribution on the percolating TPB length density, normalized effective transport, and the performance are shown in figures 5.10, 5.11 and, 5.12.
Figure 5.10: The variation in the percolating TPB density when a binary powder composition is used to manufacture the synthetic anode. The solid line connects the sample averages at each particle size.

The relationship between the percolating TPB length density and the binary particle mixtures are shown in figure 5.10. It can be observed that the lowest percolating TPB density occurs when the phase particle diameters are equal and that the percolating TPB length density increases as the monosized particles of either the electron or ion phase decreases. This trend is expected since a larger number of smaller particles are required to meet the specified solid volume fraction, and both the greater number and smaller size of particles increases the probability of TPB reaction sites occurring within the structures. This trend was also observed in the work of Kenney et al. [17] for structures comprising of polydisperse particles. It is also of interest to note that the highest percolating TPB length density occurs when the electron and ion particle diameters are 0.5µm and 1µm respectively. In the structure with the
opposite particle sizes, electron and ion particle diameters of 1µm and 0.5µm, the TPB density was found to be roughly 16% lower. The increased TPB density when smaller electron particles are used could be attributed to a greater number of smaller electron particles forming TPB reaction sites near the electrode-electrolyte interface, but a larger sample size will be required to conclusively comment on this possible trend.

![Figure 5.11](image)

**Figure 5.11:** The variation of the normalized effective transport in the z-direction of the three transport regions when a binary powder composition is used to manufacture the synthetic anode. The solid line connects the sample averages at each particle size.

The relationship between the normalized effective transport and the binary particle size distribution is shown in figure 5.11. In the pore phase it was observed that for a constant porosity the normalized effective diffusion was unaffected by the binary particle size distribution. However, an increase in the Knudsen number was observed
as the particle size ratio increased, demonstrating a decrease in the gas diffusivity in the pore phase as the particle size ratio increases. In the solid regions it was observed that the normalized effective transport of both the electron and ion phases are equal when the particle sizes are equal, as is expected and was seen in sections 5.1.1, 5.1.2, and 5.1.3. However, as the particle size ratio increased it was observed that the normalized effective transport increased in the smaller monosized particles, while a decrease in the normalized effective transport was observed in the monosized particles held constant at $1\mu m$. This indicates that the particle size ratio has a positive effect on the transport within the smaller particles and a negative effect on the transport within the larger particles. Kenney et al. [17] analyzed the effect of the particle size ratio using the same structure generation code and commented on the tenancy of the larger particles to impede the distribution of the smaller particles during the synthetic manufacturing process. The group also reported the agglomeration of the smaller particles around the larger particles. The agglomeration of the smaller particles as the particle size ratio increases would simultaneously promote the formation of percolating networks within the smaller particle phase and suppress the formation of percolation networks in the larger particle phase.
The impact of the binary particle size distribution on the anode performance is shown in figure 5.12. It was observed that when smaller electron particles were employed in the binary distribution there was an initial increase in the overall performance, as demonstrated by a local maxima at an electron:ion particle size of 0.71\(\mu m : 1\mu m\), followed by a decrease in performance as the electron particle size decreased further. The local performance maxima at an electron:ion particle size of 0.71\(\mu m : 1\mu m\) coincides with the increase in TPB density, while the subsequent performance decrease at smaller electron particle sizes appears to occur because of the reduction in the normalized effective transport in the ion phase. This trend demonstrates the interplay between the percolating TPB length density and the normalized ionic phase transport and highlights the importance of the ionic transport in the
anode. When the ion particle size was manipulated and smaller ion particles were employed in the binary distribution, a constant increase in the anode performance was observed with the maximum performance occurring when the electron and ion particle diameters are $1\,\mu m$ and $0.5\,\mu m$ respectively. The observed performance increase when smaller particles were used is due to the increase in both the percolating TPB length density and the normalized effective transport in the ion phase. It should be noted that the improved transport within the ion phase was crucial in improving the performance, as was made apparent when smaller electron particles were employed. As the sample size is increased it is expected that the observed trends in the performance will remain. The decrease of the gas diffusion coefficient as the particle size ratio increased had no noticeable effects on the performance. This initial investigation into binary distributions suggests that the use of smaller ion conductive powders may lead to better performance within the anode.
5.2 Anode Thickness

The effects of the anode thickness on the current production is investigated in this section to provide insight into the optimal manufacturing thickness for the anode layer. The purpose of this study is to provide insight into the minimal anode thickness required to maximize the overall current production. In this study, the structure generation procedure outlined in section 3.3 was used with an elongated domain length of 20 $\mu m$ in the direction normal to the anode/electrolyte interface. The reference overpotential was then applied and varied, and the accumulative current production within the anode was evaluated as a function of the thickness. The accumulative current is simply the total current produced at a given thickness from the electrode-electrolyte interface. Similar to the parametric study, six synthetic electrodes were generated and analyzed. The synthetic electrode parameters and operating conditions used in this study are outlined in table 5.6 and the results from this study are shown in figure 5.13.

Table 5.6: Displays the structural parameters and operating conditions used to evaluate the optimal electrode thickness

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron Size Distribution</td>
<td>Monosized</td>
</tr>
<tr>
<td>$d_{ion}$</td>
<td>$1\mu m$</td>
</tr>
<tr>
<td>Solid Volume Fraction $\varrho_{ele}/\varrho_{ele}$ (Electron/Ion)</td>
<td>50%/50%</td>
</tr>
<tr>
<td>Porosity $\psi$</td>
<td>30%</td>
</tr>
<tr>
<td>Electrode Domain Size $l_{anode} \times w_{anode} \times t_{anode}$</td>
<td>$10\mu m \times 10\mu m \times 20\mu m$</td>
</tr>
<tr>
<td>Electrolyte Domain Size $l_{electrolyte} \times w_{electrolyte} \times t_{electrolyte}$</td>
<td>$10\mu m \times 10\mu m \times 2\mu m$</td>
</tr>
<tr>
<td>Temperature</td>
<td>1073 K</td>
</tr>
<tr>
<td>Fuel Pressure (Composition)</td>
<td>$101325$ Pa ($97%H_2 - 3%H_2O$)</td>
</tr>
<tr>
<td>$\eta_{anode}$ ($\Delta \eta_{anode}$)</td>
<td>0.1V-0.5V (0.1V)</td>
</tr>
</tbody>
</table>
Figure 5.13: The accumulative current production as a function of the anode thickness at overpotentials of (a) 0.1V, (b) 0.2V, (c) 0.3V, (d) 0.4V, (e) 0.5V starting from the electrode/electrolyte interface (thickness = 0) to the support layer interface (thickness = 20). Locations within the anode where the current production reaches 95%, green line, and 99%, red line, of the total current production within the anode are shown.
Figure 5.13 illustrates the accumulative current production within the anode microstructures as a function of the thickness at five different overpotentials. Common to all five tests it can be observed that the majority of the current production occurs near the electrode/electrolyte interface (thickness = 0) as demonstrated by the steep linear current production rate. This is followed by a decrease in the current production rate until a production plateau exhibiting a very low current production rate is established. The aforementioned production plateau can be clearly observed at higher overpotentials, $\eta_{\text{anode}} \geq 0.3V$.

To provide insight into the optimal anode thickness interval locations within the anode where the accumulative current production is 95% and 99% of the overall current production were established, as demonstrated by the green and red lines in figure 5.13. It is observed that at low overpotentials, 0.1V and 0.2V, the 95% and 99% intervals occur deep within the anode close the anode active/support layer interface. From this it can be inferred that the majority of the anode is utilized in the energy conversion process. As the overpotential increases from 0.3 to 0.5V, the current production plateau is established and the 95% and 99% intervals are seen to occur closer to the electrode/electrolyte interface. This indicates that there are limited gains from the current produced within the plateau region and the overall thickness could be reduced without greatly reducing the overall performance. It was also observed that as the applied overpotential increased, the distance between the 95% and 99% intervals increased, demonstrating the small increase of the current production rate in the production plateau region at higher overpotentials.
5.3 Discussion

The parametric study clearly demonstrates that the anode performance can be improved by increasing the number of percolating TPB reaction sites and improving the species transport through the ion phase. While the electron phase is also identified as being important for the production of percolating TPB sites, it was found to be less influential on the overall performance due to the high electronic conductivity of the nickel phase, which is several orders of magnitude higher than the ionic conduction in the YSZ phase. In the structures studied there was also little influence of the gas phase on the performance which could be attributed to: the high hydrogen concentration used at the boundary, global calculation of the Knudsen/diffusion mechanism, or the high porosity of the structures studied. Further studies addressing these effects on the performance will be investigated in the future.

The parametric study demonstrated that an increase in the overall performance could be achieved by increasing the number of percolating TPB reactions sites as indicated by the TPB length density. The results from this work demonstrate that the TPB density could be increased by either decreasing the porosity or decreasing the powder/particle size used to manufacture the porous structure. From the parametric study of the porosity it was found the a porosity of 0.25 provided the highest TPB length and best performance. Using the work of Metcalfe et al. [41] to supplement the porosity range of this work, it is suggested that TPB length density can be maximized at a porosity of 0.21. Using the current conclusions that the TPB length will have the largest impact on the performance, it is suggested that the optimal performance will occur around a porosity of 0.21. However this will not be the true if the gas species transport begins to limit the performance, which will occur at low porosity or at low
fuel concentrations. It was also widely reported in numerical studies that a decrease in the particle size increased the TPB length density [17, 42, 43, 45, 46, 54, 55] and performance [45,46]. The increase in performance with smaller powder sizes was also experimentally shown in the work of Fukui et al. [77]. The current results support these finding and show that the overall anode performance is improved as the particle size decreased, with the highest performance seen at the lowest particle/powder size of 0.5 µm. It was also shown that the normalized multiphase effective species transport was generally not affected by the reduced particle size. Nonetheless the gas diffusivity coefficient, which is a function of the pore size, is affected by the particle size and decreases as the particle size decreases, demonstrating a limitation to a continual decrease of the particle size to increase the performance.

The parametric study also demonstrated that the anode performance was increased by improving the species transport network within the ionic phase. This was achieved by either: increasing the solid volume fraction of the ion transport phase or, in the case of binary structures, using smaller ion conductive particles and powders. For packings of spherical particles the optimal performance was found to occur at the ionic phase percolation threshold at ion-election solid volume percentages of 60-40%. The use of smaller ionic conductive powders was also shown to both increase the number of TPB sites and the overall ionic transport which increase the overall performance of the anode. The smaller powder/particle size may also help suppress nickel agglomeration as the intimate contact between the small ionic particles and the larger electronic particles may constrain nickel phase. The difference in powder sizes can also provide insight into the performance after nickel agglomeration has occurred from smaller particle sizes.
The results from the parametric study clearly demonstrate that significant performance improvements can be made through optimization of the anode microstructure. It was identified that structures with porosities $\leq 0.25$, ion solid volume fraction $\approx 60\%$ and particle/powder sizes at or below $0.5\, \mu m$, increase the current production within the anode. In addition when using a binary composition of electronic and ionic conductive powders, the uses of smaller ionic powders was shown to increase the overall performance.

Insight into the optimal anode thickness was also provided and a clear trend between the optimal thickness and the operational overpotential was observed. It was shown that as the applied overpotential increased, the portion of the anode thickness utilized in the current production process decreased. This was demonstrated by the 95% and 99% production intervals occurring closer to the anode/electrolyte interface at higher overpotentials. The relationship between the anode thickness and the gas species distribution makes commenting on the effects of a reduced anode thickness difficult. However, it was observed that the anode thicknesses at the 95% current production intervals agreed relatively well with the optimal thicknesses reported by Cai et al. [46], even though the anode composition slightly differed. This preliminary comparison suggest the ability to use an analysis of the accumulative current production to refine a starting thickness for subsequent thickness optimization studies.

5.4 Summary

In this chapter a parametric study was conducted which explored the effects of the porosity, solid volume fraction and initial particle/powder size on the current production. An improvement in the overall performance was observed in structures which
maximized the number of reaction sites and had well established transport networks in the ion phase. Anode structures with low porosities \( \leq 0.25 \), high ionic solid volume fractions near the ionic percolation threshold, small monosized particles \( \approx 0.5\mu m \), and powder compositions with smaller ionic conducting particles were all found to increase the performance within the respective studies of these parameters. The anode thickness was also studied in this chapter with the findings showing the relationship between the applied overpotential and utilization thickness. Insight into starting locations for future studies of the optimal anode thickness was also provided.
Chapter 6

Conclusions and Future Work

6.1 Summary

The primary objective of this thesis was to develop a SOFC anode performance model to predict the current produced within detailed anode microstructures obtained from experimental or numerical techniques. To achieve this, a novel coupling technique was developed in MicroFOAM [10] to enable the coupling of volumetric sources terms to linear reaction sites. The technique was then applied to couple the multiphase species transport equations to the current production sites to enable the overall performance to be evaluated. A sensitivity analysis of the mesh resolution and the domain size was conducted and the performance model validated to insure the coupling procedure was properly implemented.

The developed performance model was then employed in a parametric study to investigate the effects of the porosity, solid volume fraction and particle size distributions on the overall performance of the anode. The effects of these manufacturing properties on the production of TPB reaction sites and the normalized effective
transport were also evaluated and reported to provide further insight into beneficial structural properties. The effects of the overpotential on the optimal anode thickness was also investigated to help establish an optimal manufacturing thickness for the anode layer.

6.2 Conclusions

The computational parameters to be used in conjunction with the performance model were investigated. It was determined that a mesh resolution of \( \approx 16 \) computational cells per particle diameter at the TPB interfaces provided a converged mesh interface. It was also determined that the cut-cell/body-fitted provided a better TPB length estimate when compared to a Cartesian mesh. A boundary domain packed with monosized particles provided a converged TPB length density estimate when the domain edges were 10 times larger than the particle diameter. This domain size was also found to be acceptable when determining the normalized effective phase transport, as reported by Choi et al. [10].

The finding from this work with the performance model enhances the literature by enabling the relationship between the TPB length, normalized effective transport and anode performance to be studied in detail. In addition the added electrolyte layer, which was found to be omitted in other studies, was included in this work and shown to have an influence on both the TPB length and the performance.

The performance model, used in conjunction with a particle packing code, was employed in a parametric study to investigate the effects of anode manufacturing and structural properties on the performance. From the results it was identified that the current production within the anode was improved in structures which maximized
the number of TPB sites and promoted good species transport within the ion phase. In a supplementary study the ionic potential was also found to be highly influential over the current production. The parametric study found that the performance was maximized in structures with low porosities, \( \leq 0.25 \), and small particle/powder sizes, \( \leq 0.5 \mu m \), due to the percolating TPB length being maximized, and in structures near the ionic phase percolation threshold (\( \approx 60\% \) ion solid volume fraction for spherical powders) and composed of binary powders with smaller ionic conductive particles due to the improved species transport in the ion phase. The thickness of the anode was also investigated and it was found that as the applied overpotential increased, the overall anode thickness utilized in the current production process decreased.

### 6.3 Future Work

There are many interesting research areas which can now be explored with the SOFC anode performance model. The next most logical step would be to continue the research into the optimal anode composition by numerically synthesizing new anode microstructure compositions based on the optimal structural properties identified in the parametric study. Once an optimal composition has been identified a parametric study of the thickness could be conducted by generating synthetic electrode structures of varying thickness. The optimized parameters could then be manufactured and tested. The particle size, composition and shape could also be expanded in additional parametric studies to investigate the effects of binary and polydispersed powder size distributions, and cylindrical and agglomerated particle geometries on the structural properties and performance.
Further validation between the synthetic manufacturing method and real manufacturing method would be beneficial in advancing the synthetic powder to power analysis tools which this work has helped to develop. To accomplish this a direct comparison between synthetic electrodes and manufactured electrodes from similar initial conditions should be studied and analyzed in depth with the performance model. This would enable the realism of the synthetic manufacturing model to be investigated and improved upon, and demonstrate the full potential of these tools.

The predictive capability of the developed anode half cell performance model could also be further improved by adding additional modules to predict internal fuel reforming, surface gas species diffusion, temperature distribution and thermal stresses. It would also be feasible to modify the anode model into a cathode half-cell performance model and enable mixed ion electron conductive (MIEC) materials to be analyzed. A PEN model could also be developed by merging the anode and cathode models and adding a thicker electrolyte layer. This would enable the analysis of detailed PEN structures obtained from synthetic or experimental methods and allow for the PEN structure in cell models to be simplified.
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