A Computational Study of Linking Solid Oxide Fuel Cell Microstructure Parameters to Cell Performance

Chao Wang
Wright State University

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A COMPUTATIONAL STUDY OF LINKING SOLID OXIDE FUEL CELL MICROSTRUCTURE PARAMETERS TO CELL PERFORMANCE

A dissertation submitted in partial fulfillment of the requirements of the degree of
Doctor of Philosophy

By

CHAO WANG
B.E., Dalian University of Technology, 2007
M.S. Egr., Wright State University, 2010

2013
Wright State University
WRIGHT STATE UNIVERSITY

GRADUATE SCHOOL

May, 02, 2013


____________________
George P. G. Huang, Ph.D.
Dissertation Director

____________________
Ramana V. Grandhi, Ph.D.
Director, Ph.D. in Engineering Program

____________________
R. William Ayres, Ph.D.
Interim Dean, Graduate School

Committee on Final Examination

____________________
George P. G. Huang, Ph.D.

____________________
Ryan Miller, Ph.D.

____________________
Daniel Young, Ph.D.

____________________
Hong Huang, Ph.D.

____________________
Robert Wilkens, Ph.D.
ABSTRACT


Solid Oxide Fuel Cell (SOFC) has been considered as a promising technology to replace the traditional fossil fuels due to high efficiency, low emission, and silent operation. The configuration of microstructures throughout the electrodes plays a significant role in improving cell performance. However, current research did not capture the connections of the microstructure parameters, which is vital to simulate the SOFC behavior under practical circumstances. This study explored the correlations of microstructure parameters from a microscale level, together with mass transfer and electrochemical reactions inside the electrodes, providing a novel approach to predict the SOFC performance numerically. The results then compared with available experimental data with encouraging outcome. Sensitivity of each microstructure parameter is also tested aiming to deliver a benchmark for micro-scale analysis of SOFC in the future. Additional effort focuses on exploring the cell performance of functionally graded electrodes by taking the microstructure sub-model correlations into consideration. Present results exhibit that micro-scale graded electrodes have the potential to enhance SOFC efficiency by boosting mass diffusion and fastening electrochemical reactions and hence demonstrate a strong improvement of cell performance compared with conventional uniform composite electrodes.
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<th>Meaning</th>
<th>Unit</th>
</tr>
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<tbody>
<tr>
<td>$A_0$</td>
<td>Specific surface area</td>
<td>m$^{-1}$</td>
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<tr>
<td>$ASR$</td>
<td>Area specific resistance</td>
<td>Ω·m$^{-2}$</td>
</tr>
<tr>
<td>$A_{des}$</td>
<td>Pre-exponential factor</td>
<td>s·cm$^{-2}$/mol</td>
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<tr>
<td>$A_{O_2}$</td>
<td>Pre-exponential factor</td>
<td>atm</td>
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<tr>
<td>$B_0$</td>
<td>Permeability</td>
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<td>$c$</td>
<td>Concentration</td>
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<tr>
<td>$d$, $D$</td>
<td>Diameter</td>
<td>m</td>
</tr>
<tr>
<td>$den$</td>
<td>Density</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$d_0$</td>
<td>Pore diameter</td>
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</tr>
<tr>
<td>$d_h$</td>
<td>Hydraulic diameter</td>
<td>m</td>
</tr>
<tr>
<td>$D_{i,k}^{eff}$</td>
<td>Effective Knudsen diffusion coefficient for species $i$</td>
<td>m$^2$/s</td>
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<td>$D_{i,j}^{eff}$</td>
<td>Effective binary diffusion coefficient</td>
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<td>Equilibrium potential</td>
<td>V</td>
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<td>kJ/mol</td>
</tr>
<tr>
<td>$E_{O_2}$</td>
<td>Activation energy</td>
<td>kJ/mol</td>
</tr>
<tr>
<td>$E_{des}$</td>
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<td>$F$</td>
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<td>Gas species</td>
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<tr>
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<td>Gibbs free energy of species $i$</td>
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<td>Current density of electronic conductors</td>
<td>A/m$^2$</td>
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<td>$j_c$</td>
<td>Current density of ionic conductors</td>
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<tr>
<td>$j^*$</td>
<td>Imperial constant</td>
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<tr>
<td>$J_0$</td>
<td>Exchange current density</td>
<td>A/m$^2$</td>
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<td>$K$</td>
<td>Contact area fraction of two spheres</td>
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<tr>
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<td>Equilibrium constant of reaction $i$</td>
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<td>Forward reaction constant of reaction $i$</td>
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<td>$k_B$</td>
<td>Boltzmann constant</td>
<td>J·K$^{-1}$</td>
</tr>
<tr>
<td>$l$</td>
<td>Thickness of electrode</td>
<td>m</td>
</tr>
<tr>
<td>$l_{TPB}$</td>
<td>TPB length</td>
<td>m</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar weight</td>
<td>g/mol</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass</td>
<td>kg</td>
</tr>
<tr>
<td>$n$</td>
<td>Number fraction; adjustable parameter</td>
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</tr>
<tr>
<td>$N$</td>
<td>Molar flux</td>
<td>mol/m$^2$·s</td>
</tr>
<tr>
<td>$n_t$</td>
<td>Total number of particles per unit volume</td>
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</tr>
<tr>
<td>Symbol</td>
<td>Meaning</td>
<td>Unit</td>
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<td>---------</td>
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</tr>
<tr>
<td>$P$</td>
<td>Probability</td>
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<td>Partial pressure</td>
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<td>$R$</td>
<td>Ideal gas constant</td>
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<tr>
<td>$r$</td>
<td>Radius of particle</td>
<td>m</td>
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<td>$S$</td>
<td>Sticking coefficient</td>
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<tr>
<td>$s_i$</td>
<td>Entropy of species i</td>
<td>J/mol·K</td>
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<td>$S_v$</td>
<td>Active surface area per unit volume</td>
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<td>Reference temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>$U$</td>
<td>Practical voltage</td>
<td>V</td>
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<tr>
<td>$U_{rf}$</td>
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<tr>
<td>$v$</td>
<td>Convection velocity</td>
<td>m/s</td>
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<tr>
<td>$V$</td>
<td>Potential</td>
<td>V</td>
</tr>
<tr>
<td>$V_{ol}$</td>
<td>Volume</td>
<td>$m^3$</td>
</tr>
<tr>
<td>$W_{elec}$</td>
<td>Electrical work</td>
<td>J</td>
</tr>
<tr>
<td>$W$</td>
<td>Weight</td>
<td>kg</td>
</tr>
<tr>
<td>$x$</td>
<td>X axis</td>
<td>m</td>
</tr>
<tr>
<td>$y$</td>
<td>Molar fraction</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>$Y$</td>
<td>Doping composition</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>$z$</td>
<td>Number of charges transferred per unit fuel gas</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>$Z$</td>
<td>Overall average number of contact</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>$Z_0$</td>
<td>Average total coordination number in a random packing of mono-sized spheres</td>
<td>Dimensionless</td>
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<td>$Z_{i-e}$</td>
<td>Average number of electronic conductor in contact with an ionic conductor</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>$Z_{i-i}$</td>
<td>Average number of ionic conductor in contact with an ionic conductor</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>$Z_{e-i}$</td>
<td>Average number of ionic conductor in contact with an electronic conductor</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>$Z_{e-e}$</td>
<td>Average number of electronic conductor in contact with an electronic conductor</td>
<td>Dimensionless</td>
</tr>
<tr>
<td>$Z_i$</td>
<td>Average number of contacts of both ionic conductor and electronic conductor with an ionic conductor</td>
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</tr>
<tr>
<td>$Z_e$</td>
<td>Average number of contacts of both ionic conductor and electronic conductor with an electronic conductor</td>
<td>Dimensionless</td>
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<th>Meaning</th>
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<td>Ionic and electronic particles size ratio</td>
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</tr>
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<td>Symbol</td>
<td>Dimensionless</td>
<td>Subscript</td>
</tr>
<tr>
<td>--------</td>
<td>---------------</td>
<td>-----------</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Charge transfer coefficient</td>
<td></td>
</tr>
<tr>
<td>$\delta$</td>
<td>Mass fraction</td>
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<tr>
<td>$\varepsilon$</td>
<td>Porosity</td>
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<td>$\epsilon$</td>
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<td>$\eta$</td>
<td>Overpotential voltage</td>
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</tr>
<tr>
<td>$\theta$</td>
<td>Contact angle</td>
<td>°</td>
</tr>
<tr>
<td>$\theta_i$</td>
<td>Coverage of species i</td>
<td></td>
</tr>
<tr>
<td>$\mu_{mix}$</td>
<td>Viscosity of mixture</td>
<td>kg / m·s</td>
</tr>
<tr>
<td>$\nu_i$</td>
<td>Stoichiometric coefficient of species i</td>
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<tr>
<td>$\xi$</td>
<td>Lennard-Jones energy</td>
<td>J</td>
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<tr>
<td>$\rho$</td>
<td>Resistivity</td>
<td>$\Omega \cdot m$</td>
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<tr>
<td>$\sigma$</td>
<td>Conductivity</td>
<td>S/m</td>
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<td>Pre-exponential coefficient</td>
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<tr>
<td>$\tau$</td>
<td>Tortuosity</td>
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<td>$\Gamma$</td>
<td>Surface site density</td>
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<td>$\Omega_D$</td>
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<td>$a$</td>
<td>Anode</td>
</tr>
<tr>
<td>$act$</td>
<td>Activation overpotential</td>
</tr>
<tr>
<td>$c$</td>
<td>Cathode</td>
</tr>
<tr>
<td>$con$</td>
<td>Concentration overpotential</td>
</tr>
<tr>
<td>$e$</td>
<td>Electronic conductor</td>
</tr>
<tr>
<td>$i$</td>
<td>Ionic conductor</td>
</tr>
<tr>
<td>$L, D$</td>
<td>Large particle</td>
</tr>
<tr>
<td>$ohm$</td>
<td>Ohmic overpotential</td>
</tr>
<tr>
<td>$S$</td>
<td>Small particle</td>
</tr>
<tr>
<td>sat</td>
<td>saturated</td>
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<tr>
<td>1</td>
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<tr>
<td>0</td>
<td>At standard conditions for temperature and pressure</td>
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<td>$eff$</td>
<td>Effective</td>
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<tr>
<td>$eq$</td>
<td>Equilibrium</td>
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<tr>
<td>1</td>
<td>Inlet</td>
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</table>
Acknowledgement

I am heartily grateful to my advisors, Dr. George Huang and Dr. Ryan Miller, for their guidance and inspiration during my past four years of studies. Their continuous support from the initial to the final level enabled me to achieve this dissertation. I owe my deepest gratitude to them. I also would like to extend my thanks to the rest committee members: Dr. Daniel Young, Dr. Hong Huang, and Dr. Robert Wilkens for their help in my studies.
Dedicated to

This dissertation is dedicated to my beloved wife and parents who have always supported me through my studies.
Chapter 1 Introduction

1.1 Motivations and Objectives
Scientists are tirelessly working on sources of alternative energy so that we can have a better substitute for fossil fuels in near future, since the amount of recoverable fossil fuels is finite and is likely to get more expensive as resources are depleted. Furthermore, evidence suggests that the rise of atmospheric CO$_2$ due to the combustion of fossil fuels is correlated with the global warming. Thus, considerable effort should be made to develop efficient energy conversion devices with minimal negative environmental impact. The solid oxide fuel cell (SOFC) is considered as an attractive alternative because of its silent operation, high efficiency and low emission. In the last few years people have realized its huge potential and many experimental researches have been reported to improve the cell performance by applying new materials. However, for the further development of SOFC technology the combination of numerical and experimental evaluation is indispensable. Instead of spending lots of time on the complex cell fabrication and testing processes, accurate numerical models taking into consideration the whole physical-chemical processes can easily predict the cell performance and saves expense of the costly equipment as well. The objectives of this project are listed below. The primary objective of this thesis is to develop a numerical model that can simulate the mass transfer and electrochemical reactions within the electrodes by taking microstructure parameters into account. The second task is to explore the interactions and sensitivities of these cell microstructure parameters in order to understand the performance of a SOFC from the micro-scale level. The next goal is to conduct comparison between the functionally graded electrodes (FGEs) and conventional non-graded electrodes (uniform random composites) to investigate the potential of FGEs for SOFCs.

1.2 Introduction of Fuel Cells

1.2.1 Fuel Cell Definitions
A fuel cell is an electrochemical device that directly converts the chemical energy from a fuel into electricity through a chemical reaction with oxygen or another oxidizing agent. Hydrogen is the most common fuel, but methanol and hydrocarbons such as natural gas can also be used. Fuel cells are different from batteries. They require a continuous supplement of fuel and oxygen to
run. As long as these inputs are satisfied, the cells can produce electricity unceasingly. A fuel cell is comprised of an anode (negative side), a cathode (positive side), and an electrolyte that allows charges to move between the two sides of the fuel cell. Electrons are drawn from the anode to the cathode through an external circuit, producing direct current electricity. The electrolyte layer is sandwiched between the anode and cathode. Fuel cells can be manufactured in a variety of sizes. Individual fuel cells only produce very small amounts of electricity. In order to increase the voltage and current output to meet an application’s power generation requirements, cells are stacked, or placed in series or parallel circuits. In addition to electricity, fuel cells produce water, heat and, depending on the fuel source, very small amounts of carbon dioxide and other emissions. The energy conversion efficiency of a fuel cell is generally between 40-60%. However, it could go up to 85% if the waste heat is captured for use.

1.2.2 Types of Fuel Cell
Fuel cells are classified according to the types of electrolyte employed. There are five major types of fuel cells: polymer electrolyte membrane fuel cell (PEMFC); phosphoric acid fuel cell (PAFC); alkaline fuel cell (AFC); molten carbonate fuel cell (MCFC), and the solid oxide fuel cell (SOFC). The properties of different types of fuel cells such as electrolyte materials, operation temperature, catalyst, fuel gases, charge carriers, and cell efficiency are listed in Table 1. The reaction mechanisms of 5 types of fuel cells are provided in Figure 1 (1).

<table>
<thead>
<tr>
<th>Table 1 Fuel cell types</th>
</tr>
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<tbody>
<tr>
<td><strong>Electrolyte</strong></td>
</tr>
<tr>
<td>Polymer membrane</td>
</tr>
<tr>
<td><strong>Operating Temperature</strong></td>
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<tr>
<td><strong>Catalyst</strong></td>
</tr>
<tr>
<td><strong>Fuel</strong></td>
</tr>
<tr>
<td><strong>Charge Carrier</strong></td>
</tr>
<tr>
<td><strong>Efficiency</strong></td>
</tr>
</tbody>
</table>
1.3 Solid Oxide Fuel Cells

1.3.1 Basic Principles and Operations

The basic operational principle for the solid oxide fuel cell is illustrated in Figure 2 (2). The charge carrier in the SOFC is the oxygen ion. At the cathode, the oxygen molecules from the air decompose into oxygen ions by reacting with electrons from the external circuit. The oxygen ions transport through the electrolyte and combine with hydrogen at anode to form water and release electrons. The electrons travel an external circuit providing electric power and producing by-product heat. For unit mole of hydrogen, the number of electrons generation is 2. Therefore, the overall reaction and the half reactions at both anode and cathode can be written as:

Anode: \( \text{H}_2 + \text{O}^{2-} \leftrightarrow \text{H}_2\text{O} + 2\text{e}^- \)

Cathode: \( \frac{1}{2}\text{O}_2 + 2\text{e}^- \leftrightarrow \text{O}^{2-} \)

Overall Reaction: \( \text{H}_2 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{H}_2\text{O} \)
1.3.2 Advantages and Disadvantages of SOFC
The SOFC stands out as a promising technology because it has a number of advantages. First of all, SOFCs offers very high-energy conversion efficiency as compared with conventional fossil fuel. Second, the solid component structure will make it simpler to design and manufacture. Since the reaction zone at the electrode-electrolyte interface becomes a gas-solid contact, complex electrolyte management is not required. Also, the problems of electrolyte such as material depletion, lifetime, and the server corrosion of the cell are avoided completely if compared with liquid-based electrolyte such as PAFC and AFC. Next, because SOFCs are operated at high-temperature conditions, the relevant electrochemical kinetics at the electrodes proceeds sufficiently fast without the need of noble metals as catalysts. Furthermore, such high operating temperatures also make it possible for the internal reforming of methane and other hydrocarbons to produce hydrogen gas and carbon monoxide. Therefore, SOFCs have a better ability to allow flexible fuel choices in the reactant gas streams. Finally, the high-temperature SOFC operation provides a high-quality waste heat for co-generation applications such as heat engines.

On the other hand, the solid oxide fuel cell has its drawbacks, as well. The challenges include stack hardware, sealing, and cell interconnects issues due to high operating temperatures. The high operating temperature also makes materials requirements, mechanical issues, reliability concerns, and thermal expansion matching tasks more difficult.
1.3.3 Components Requirements
Each of the components of an SOFC: anode, cathode and electrolyte must be thermally, chemically, and mechanically stable at the operating conditions. In addition to those requirements, the individual layers have additional microstructure, property, and processing target requirements, as summarized in Table 2. (3)

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Anode</th>
<th>Electrolyte</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous, many triple-phase boundaries, stable to sintering.</td>
<td>Dense, thin, free of cracks and pinholes</td>
<td>Porous, many triple-phase boundaries, stable to sintering.</td>
<td></td>
</tr>
<tr>
<td>Electronically and preferably ionically conductive.</td>
<td>Ionically but not electronically conductive.</td>
<td>Electronically and preferably ionically conductive.</td>
<td></td>
</tr>
<tr>
<td>Compatible with other layers, especially electrolyte</td>
<td>Compatible with other layers especially structural support layers.</td>
<td>Compatible with other layers, especially electrolyte</td>
<td></td>
</tr>
<tr>
<td>Minimal reactivity with electrolyte and interconnect</td>
<td>Minimal reactivity with anode and cathode</td>
<td>Minimal reactivity with electrolyte and interconnect</td>
<td></td>
</tr>
</tbody>
</table>

1.3.4 Materials

1.3.4.1 Electrolyte
The electrolyte materials for SOFCs are generally oxygen ion conductors, in which current flow occurs by the movement of oxygen ions through the crystal lattice. This movement is a result of thermally activated hopping of the oxygen ion, moving from one crystal lattice to its neighbor site. To achieve this movement, the crystal must contain unoccupied sites equivalent to those occupied by the lattice oxygen ions. Yttria-stabilized zirconia (YSZ) is the common electrolyte materials for SOFCs. YSZ is created by doping $\text{ZrO}_2$ with a certain percentage $\text{Y}_2\text{O}_3$. The doping concentration is typically around 8 mol% because it has been reported (4) that the ion conductivity reaches peak at that yttria content. In the crystal structure two zirconium cations
(Zr$^{4+}$) are replaced by two yttrium cations (Y$^{3+}$), thus one oxygen site (O$^{2-}$) will be left vacant to maintain charge balance. The vacancy production can also be expressed by Kroger-Vink notation.

$$Y_2O_3^{\text{ZrO}_2} \rightarrow 2Y'_2 + V'_0 + 3O_0^X$$

1.3.4.2 Anode

The most common SOFC anode material is Ni-YSZ cermet, since Ni-YSZ cermet materials meet most of the electrode requirements aforementioned. In a porous Ni-YSZ cermet anode, the Ni metal provides the required electronic conductivity and catalytic activity, while the relatively low thermal expansion of YSZ ceramic prevents Ni from coarsening. In addition, YSZ also provides ionic conductivity to the electrode, thus effectively broadening the triple phase boundary (TPB). The electrical conductivity is strongly dependent on the Ni composition. Fig. 3 (5) shows the conductivity as a function of nickel measured at 1000 °C for different sintering temperatures of the Ni/ZrO$_2$ (Y$_2$O$_3$) cermet. The percolation threshold plays an important role in the conductivity of composite materials. Percolation threshold of a SOFC means the critical configuration of same type of particles connecting with each other to form a bridge through the electrodes. It relies on composition, porosity, particle sizes and other physical parameters of electrode. In this particular case, the percolation threshold for nickel (which drives the electronic conductivity) is at approximately 30 volume percent. Below the threshold, the cermet exhibits predominantly ionic conduction behavior. Above this threshold, the electrical conductivity increases by about three orders of magnitude. Moreover, it can be found from Fig. 3 that higher sintering temperature, in the range given, will result in higher conductivity. In general, the anode and electrolyte are co-sintered in the range of 1300°C and 1400°C to achieve a dense electrolyte while maintaining an anode with about 30% porosity. (6)
1.3.4.3 Cathode
SOFC cathodes must provide high activity for the electrochemical reduction of oxygen. In order to maximize the number of TPB sites, SOFC cathodes must provide both ionic and electronic conductivity, as well as catalytic activity. Because metal conductors are typically not stable in high temperature oxidizing environments, SOFC cathodes are almost always purely ceramic. In YSZ-based SOFCs, the dominant cathode material is strontium-doped lanthanum manganite (LSM) with the general formula La$_{1-x}$Sr$_x$MnO$_3$, where $x$ describes the doping level and is usually in the range of 10-20% (7) (8). It has a high electronic conductivity, crucial for reducing the ohmic polarization, especially when the cathode is made thick to provide the structure support. This material also has proper catalytic properties and maintains mechanical and chemical stability under high temperature operating conditions. Unfortunately, oxygen-ion conductivity is very low in LSM. Therefore, LSM-based cathodes are typically mixed with YSZ to form a LSM-YSZ composite cathode, where the YSZ can provide high ionic conductivity in order to possess mixed electronic and ionic conductivity and expand the reaction zone.

1.3.5 Equilibrium Potential
The maximum possible electrical energy output and the corresponding electrical potential difference between the cathode and anode are achieved when a fuel cell is operated under the thermodynamically equilibrium condition. This maximum possible cell potential is called
equilibrium cell potential, or reversible potential. Combing the first and second law of thermodynamics with Gibbs free energy, we have:

\[ W_{\text{elec}} = zF E^0 = -\Delta g^0 = \sum_{\text{react}} (v_i g_i^0) - \sum_{\text{prod}} (v_i g_i^0) \]  (1.1)

Where \( W_{\text{elec}} \) is electrical work; \( z \) is the number of charges transferred in the reaction per unit fuel gas, (for SOFC, \( z=2 \)); \( F \) is the Faraday constant (96485 C/mol); \( E^0 \) is equilibrium potential of the cell; \( v_i \) is the stoichiometric coefficient of the \( i^{th} \) constituent, \( g_i^0 \) is the Gibbs free energy (J/mol) of \( i^{th} \) constituent and the superscript 0 means at standard conditions for temperature and pressure (STP), which are 25°C (298K) and 1 atm (101325Pa).

The reversible voltage can be approximately calculated as a function of temperature using the Gibbs free energy and entropy under STP condition. (9)

\[ E = E^0 + \frac{\Delta s^0}{zF} (T - T_0) = -\frac{\Delta g^0}{zF} + \frac{\Delta s^0}{zF} (T - T_0) \]  (1.2)

Where \( \Delta s^0 = \sum_{\text{react}} (v_i s_i^0) - \sum_{\text{prod}} (v_i s_i^0) \), which is the entropy difference of the chemical reaction at STP condition; \( T_0 \) is the standard temperature (298K); and \( T \) is the operating temperature (K). For all of the fuel cell reactions \( \Delta s^0 \) is negative, thus fuel cell reversible potential will drop due to increasing of temperature. The reversible cell voltage can also be directly calculated by using the Gibbs free energy of each component at operating temperature, and can be written as

\[ E = -\frac{\Delta g(T)}{zF} = -\frac{\sum_{\text{react}} [v_i g_i(T)] - \sum_{\text{prod}} [v_i g_i(T)]}{zF} \]  (1.3)

Also from the Gibbs energy expression above, the variation of the reversible cell voltage can be written in terms of to the pressure change of fuel and oxidant gases, as given below

\[ E = -\frac{\Delta g^0}{zF} + \frac{RT}{zF} \ln \frac{\prod_{\text{react}} p_i^{v_i}}{\prod_{\text{prod}} p_i^{v_i}} \]  (1.4)

Where \( R \) is the ideal gas law constant (8.314 J/mol·K); \( p_i \) is partial pressure (atm) of species \( i \).

The full expression describing how the reversible voltage of SOFC varies with temperature and pressure can be written as
1.3.6 Overpotential
For most of the occasions, the measured open-circuit voltage (OCV) will equal the equilibrium potential. The cell actual output voltage will drop due to the growth of internal losses as the current flow increases. In other words, at finite current part of the available potential is lost due to internal losses and is often called overpotential. There are three different types of overpotentials. These are activation overpotential, ohmic overpotential, and concentration overpotential. The performance of an SOFC is often described by its current density-voltage (I-V) curve, shown in Fig. 4. The practical cell voltage can be expressed by \[ U = E - \eta_{\text{act}} - \eta_{\text{ohm}} - \eta_{\text{con}} \] (1.6)
Where U is practical voltage, \( \eta_{\text{act}} \) is activation overpotential; \( \eta_{\text{ohm}} \) represents ohmic overpotential; \( \eta_{\text{con}} \) represents concentration overpotential.

**Figure 4 Typical SOFC I-V Curve**

### 1.3.6.1 Activation Overpotential
Activation overpotential is due to the energy barriers of the charge-transfer reactions. At low and midrange currents, the response is mostly dominated by the charge transfer reaction kinetics, which can be seen from Fig. 4, and is often described by the well-known Butler-Volmer equation.
1.3.6.2 Ohmic Overpotential
Ohmic overpotential is associated with ion transport through the electrolyte and electron transfer through the electrodes, which is normally solved by Ohm’s law. In Fig. 4, a linear central region is often attributed to ohmic resistance and the slope is the summation of the electrodes and electrolyte ohmic resistance.

1.3.6.3 Concentration Overpotential
Concentration overpotential is caused by non-reacting mass transport process in the gas-diffusion region of the electrodes. As shown in Fig. 4, the effect of this type of loss is most pronounced at the high current region, where a limiting or maximum current occurs. Concentration overpotential is important because it defines the maximum current achievable from the device and it is strongly dependent on the concentration of fuel gas and reactant at fuel channel and electrode-electrolyte (EE) interface. In other words, it is driven by the gas diffusion process. Theoretically, the limiting current density occurs when the concentration of fuel gas drops to zero at EE interface. The mathematical expression of concentration overpotential is listed below

\[
\eta_{\text{con}} = - \frac{RT}{zF} \left[ \left( \ln \frac{\prod_{i} p_{i}^{\text{vol}}}{\prod_{i} p_{i}^{\text{react}}} \right)_{\text{at \ channel}} \right] - \left( \ln \frac{\prod_{i} p_{i}^{\text{vol}}}{\prod_{i} p_{i}^{\text{react}}} \right)_{\text{at \ EE}} \]  

(1.7)

1.3.7 Microstructure Parameters

1.3.7.1 Porosity
Porosity (ε) is a parameter that measures the void part of the material and can be expressed by a fraction of the volume of voids over the total volume. According to the definition a large porosity value means more vacant space in the structure. The range of porosity is between 0 and 1, or as a percentage between 0 and 100%. Porosity value is vital to SOFC performance. For a low porosity, the number of particles will increase to occupy the empty spots with decreasing porosity, which in turn causes the available reaction sites near TPB region to increase considerably. The disadvantage of low porosity is that fewer channels are available for the gas to transport through the electrodes and hence block the diffusion process. On the other hand, if the porosity is too high, the electrode will suffer from poor particle connectivity, poor percolation, and thus poor electrochemical performance. However, large porosity will benefit the gas diffusion by providing more unobstructed channels. Therefore, it is a trade-off and the porosity
range of SOFC is usually between 30% - 70%. (10) The measurement of porosity can be achieved by applying Archimedes’ method. (11) Basically, a dry weight ($W_{dry}$), saturated weight ($W_{sat}$), and wet weight ($W_{wet}$) of a fuel cell sample need to be measured and the porosity can be calculated using the eqn. (1.8).

$$
\varepsilon = \frac{W_{sat} - W_{dry}}{W_{sat} - W_{wet}} \times 100\%
\quad (1.8)
$$

1.3.7.2 Tortuosity
Tortuosity is a property used in porous media describing how the porous structure is twisted. The definition of tortuosity ($\tau$) can be expressed by eqn. (1.9) and it is always greater or equal to 1. In a SOFC the higher that number is, the longer the distance that the reactant gas has to travel before it reaches the TPB region. Therefore, in order to improve diffusion efficiency, tortuosity needs to be retained as small as possible.

$$
\tau = \frac{\text{typical diffusion path between two points through the pores}}{\text{straight distance between the same two points}}
\quad (1.9)
$$

1.3.7.3 Particle Size
Particle size, also called grain size, refers to the diameter of individual “spherical” particles that can be used to represent the grain structure of an SOFC electrode. Obviously, the conductors in the electrodes of SOFC are not perfect spherical shapes. Still, it is valid and reasonable assumption. Currently, particle radius of SOFC electrodes ranging from 0.03 to 10.0 $\mu$m have been reported (12). The overpotential drops with decreasing particle size due to the expansion of reactive surface area. However, if the particle keeps reducing, eventually electrodes will become dense and block the mass transfer of gases and increase the resistance, increasing the overall overpotential.

1.3.8 Functionally Grade Electrodes
FGE have been applied to SOFCs in recent years aiming to improve the cell performance by altering the microstructure including porosity, particle size, and composition of electronic and ionic conductors near the TPB region. The advantages of FGEs include expanding the electrochemical reaction area, optimizing the electrical/ionic conductivity, and improving the gas
transport. Other than that it was also found by Liu (13) that applying FGE can help to reduce operating temperature. It is known that reducing the operating temperature down to 600–800 °C brings both dramatic technical and economic benefits. The cost of SOFC technology may be dramatically reduced since much less expensive materials can be used in cell construction and novel fabrication techniques can be applied to the stack and system integration. Furthermore, as the operating temperature is reduced, system reliability and operational life increase, as does the possibility of using SOFCs for a wide variety of applications.

The three major types of FGEs are shown in Figure 5. It can be seen that porosity, particle size, and concentration of the electronic conductor starts to drop closer to the electrolyte so that the cell can perform more efficiently. In other words, this configuration of microstructure in electrodes can significantly improve the mass transport process and enhance the electrochemical reactions. For porosity grading, large porous space near the fuel channel will help the diffusion process of the gas, whereas the small porosity near EE will bring more ion and electron conductors into the reaction zone to aid the electrochemical reaction. For composition grading, more electron conductors near the fuel channel can facilitate the delivery of electrons generated by the half reaction. On the contrary, having more ion conductors near EE is a way to continue the ion transportation to the inside of the electrodes so that the TPB region can be extended. For particle size grading, larger particles (or grains) near the fuel channel can generate more vacant space to assist gas diffusion. On the other hand, smaller particles near EE can provide more active surface area and boost the electrochemical reaction.

(a) Porosity grading, (b) Composition grading, and (c) Particle size grading

Figure 5 Schematics of functionally graded electrodes
1.4 Scopes and Contributions of Thesis Work
A comprehensive numerical model taking consideration of microstructure parameters of SOFC will be implemented to study the cell performance from a micro-scale. In addition to that, we will take one step further to explore and establish firm relationships and assumptions the for the definition of the physical and microstructure parameters of the fuel cell in order to produce predictions of real cell performance. Furthermore, in order to determine if the numerical model and sub model correlations of microstructure parameters have the potential to accurately describe the mass transfer and electrochemical reactions of the cell, model validation will be carried out. If the numerical results and experimental data show reasonable agreement, the model can be considered as a proper assumption to resemble the experimental study of SOFC. We can take advantages of that and perform sensitivity study for all the physical and microstructure parameters. For the parameters with noticeable sensitivity, they should be highlighted and noted for accurate measurement during experimental analysis. In contrast, for the parameters with trivial sensitivity the significance may be neglected and perhaps conventional values may be used in the analysis. In the end, a sensitivity table of each parameter will be provided so that model users can make their own judgment on which error range is affordable to them and then determine if the measurement is necessary for that particular parameter. Another goal of our research is to modify our adapted numerical model so that it can be applied in more complicated scenarios, such as FGEs. After that, a detailed analysis of FGEs will be examined and compared with uniform composite electrodes. The purpose is to find out under which circumstances applying FGEs will be necessary and can provide better performance. The numerical results need to be reasonable and represent physics as well. That is to say, by taking sub-model correlations into account, micro structural parameters will not be treated separately during the grading process. In contrast, as one factor changes, the affected factors will alter correspondingly. Multiple approaches of grading will also be tested and the one that can improve SOFC performance most will be determined.
Chapter 2 Literature Review

2.1 Numerical Simulation of SOFC
In order to investigate SOFCs mathematically, efforts have been put into development of models including mass transportation and electrochemical reactions. Zhu et al. (14) presents a new computational modeling framework for SOFC simulation that takes the whole system including flow channels and planar membrane-electrode assemblies into consideration. SOFCs can be operated with a variety of fuels, such as hydrogen, carbon monoxide, hydrocarbons, and mixtures of those. His work employed multistep reaction mechanisms in terms of detailed elementary heterogeneous chemical kinetics so that hydrocarbons could be treated as fuel input, in addition to pure hydrogen. Mass diffusion is calculated by using the dusty-gas model. Detailed charge transfer reactions are analyzed by separating the mechanism into several elementary steps, with activation overpotential being determined by the dominating single rate-limiting step.

Won Yong Lee (15) extended Zhu’s study and predicted the activation overpotential of SOFC by proposing two rate-limiting reactions with a switch-over mechanism. Instead of using only one rate-limiting reaction, the author claims that two rate-limiting reactions with a switch-over mechanism is in accordance with actual observations and is also helpful to simulate cell performance, especially near the limiting current density region.

Regarding mass transport, Suwanwarangkul et al. (16) implement and compare three different numerical models inside a porous SOFC anode. It was found that current density, reactant concentration, and pore size are the three key factors in selecting the appropriate mass transport model. The dusty gas model is considered to be the best approximation for describing mass transport, especially for multicomponent systems, small porosity, high current density, and low fuel gas concentrations. However, this model does not have an analytical solution. Therefore, an iterative approach is required to solve for the solution. Fick’s and Stefan-Maxwell models are easily to solve but can be applied in fewer occasions because they are restricted to the fuel gas system, current density region, and so on.

Since the main purpose of this project is to investigate the performances of FGEs in SOFCs by taking the micro structural parameters into account, a comprehensive mathematical model needs to be explored and implemented. Chan and Xia (17) proposed a numerical modeling approach to
simulate the polarization effects of SOFCs. Their model takes into account electronic, ionic, and gas transport together with the electrochemical reaction. They can predict the distributions of overpotentials, current densities, and gas concentrations along the electrodes. The reason Chan and Xia’s (17) model was selected to be the basis of the study is that their model is built based on the first principles and includes all the micro structural factors that are critical to the cell performances. This model can simulate the complex gas transport phenomena in electrodes and electrochemical reactions at TPB region. The disadvantage of this model is that it can only be used in uniform electrodes, i.e. fixed micro structural parameters such as porosity, particle size, and electronic/ ionic composition throughout the whole electrodes. Therefore, the model will be modified and revised so that it can be applied for both uniform electrodes and FGEs.

Several other numerical models were studied in the literature review, however they all have their drawbacks and did not fit the goal of this project. For example, in the M. Ni el al. (10) model, they applied Graham’s law to predict the relationships between the water flux and hydrogen flux. Graham’s Law states that the flux ratio of two substances is inverse proportional to their molar masses. And it may not be a reasonable assumption in this case because the flux of the reactant and product need to obey mass conservation (i.e., flux of water coming out of the electrode equals to the flux of hydrogen going in). Furthermore, their model was applied to study the FGEs as well. But all the micro structural parameters are treated separately. For instance, when they try to perform the porosity grading, particle size of electronic and ionic conductors and tortuosity stay the same through electrodes. However, physically all those parameters are observed to correlate with each other. Once one factor changes, the rest of the factors should alter correspondingly.

In some other CFD-based models such as Wilson Chiu et al. (18) and Huayang Zhu et al. (14), the activation overpotential is directly calculated by the Butler-Volmer equation and do not take the micro structural characteristics into consideration. Theoretically, these micro structural factors are critical to the size of active reaction surface sites and hence affect the rate of electrochemical reaction. Therefore, these simulations may not fully mimic the electrochemical reaction process and result in inaccurate prediction. Chan and Xia’s (17) adopt a binary random packing sphere model created by Costamagna (19) and Bouvard (20) to solve this problem so that the microstructure parameters can be taken into account when calculating the activation
overpotential. Bouvard and Lange used a numerical simulation of the random packing of particles to study the percolation within a powder mixture (20). Costamagna et al. extended the theory to propose a model for active area per unit volume (19). In the random packing sphere model, the electrode is assumed to be a random packing of spheres. By applying coordination number model together with percolation theory, this model guarantees that the same type of particles touch each other and form a network or particle chain through the electrode. That is to say, for any given combination of compositions and particle size ratios of electronic and ionic conductors, the coordination model is used to differentiate if it is above the percolation threshold and hence determine if the simulation can be proceeded or not. In other words, if the percolation threshold is not satisfied, the model will stop the simulation due to the extremely poor connectivity of particles. As abovementioned, active surface area is supposed to be taking micro structural parameters into account in order to control the rate of electrochemical reaction. In the random packing model, the active surface area formula takes all these micro scale factors such as porosity, particle size, number fraction of electronic and ionic conductors into consideration. Therefore, charge transfer processes in the TPB can be properly described. Other than activation overpotential, both ohmic overpotential and concentration overpotential in the electrodes are affected by micro structural parameters. In a porous structure, the resistivity of electronic/ionic conductors is called effective resistivity and it depends on porosity, tortuosity and volume fraction of electronic/ionic conductors of the electrodes. Concentration overpotential is related to mass transport. Effective diffusion coefficients capture the effects of micro structural parameters such as porosity, tortuosity and particle size. Our selected model will capture all these overpotentials from a micro scale level.

2.2 Microstructure of SOFC
The primary focus of our study is to investigate how the micro structural parameters are related to each other. During the literature review, it was determined that for most numerical simulations which took microstructure into account, the micro structural parameters were assumed to be some commonly used values. Most of them were neither obtained from experimental data nor had theory to back them up. This basically meant that all these parameters became tuning factors which were manipulated to allow the mathematical results to be consistent with experimental data. In order to improve the applicability of the mathematical model, our goal was to develop correlations between the micro structural parameters. The correlations are selected based on
experimental study including tortuosity/porosity relationships and porosity/particle size ratio relationships.

Perhaps the most intuitive and straightforward definition of tortuosity is the ratio of the length of true flow paths to the shortest length between any two points within the pore space. Notice that by this definition, it is evident that tortuosity is dependent on the microscopic geometry of the pores. It has been reported that the measurement of tortuosity has been made by both performing experiments and using mathematical derivation. Recent studies of SOFC using focused ion beam scanning electron microscopy (FIB-SEM), X-ray computed tomography and gas counter-diffusion provide evidence that the tortuosity for a typical anode, in an anode-supported cell is 1.33-4.0 (21) (22) (23). On the other hand, many modern SOFC models calculated the value of the tortuosity in the range of 2 to 17. (24) (25)

Several tortuosity and porosity relations were developed and organized by Cussler (26).

\[ \tau(\varepsilon) = \varepsilon^{-n} \]  
(2.1)

\[ \tau(\varepsilon) = 1 - n \ln(\varepsilon) \]  
(2.2)

\[ \tau(\varepsilon) = 1 - n(1 - \varepsilon) \]  
(2.3)

\[ \tau(\varepsilon) = [1 - n(1 - \varepsilon)]^2 \]  
(2.4)

where \( n \) is an adjustable parameter. Eqn. (2.1) was proposed for the electric tortuosity by Jiang et al. (27). Eqn. (2.2) (with \( n = 1/2 \)) was found in a theoretical study on diffusivity of a model porous system composed of freely overlapping spheres by Matyka et al. (28). The same relation (with \( n \approx 0.86 \) and \( n \approx 1.66 \)) was also reported in measurements of the hydraulic tortuosity for fixed beds of parallelepiped particles by Archie (29). Weissberg (30) measured the tortuosity in fixed beds and determined that \( n \) is dependent on the particle shape. Eqn. (2.3) is an empirical relation found for sandy (\( n = 2 \)) or clay-silt (\( n = 3 \)) sediments by Comiti et al. (31). Eqn. (2.4),
with \( n = \frac{32}{9} \pi \approx 1.1 \), was obtained in a model of the diffusive tortuosity in marine mud (the particles are assumed to be disks) by (32).

Regarding the correlation between particle size and porosity, it has been found that the porosity has nothing to do with particle size for mono-sized particle and it only relies on the packing type (33). It has been reported that the electrochemical performance of the cell was extensively improved when the size of the constituent particles was reduced so as to yield a denser microstructure (34). In binary mixture of spherical particles, porosity is dependent on composition of two species and particle size ratio. German (33) finds out that the larger the particle size ratio is, the higher the packing density at all compositions will be. Conventional non-graded electrodes and two types of FGEs, namely, particle size graded and porosity graded SOFC anodes, were compared to evaluate the potential of the SOFC by M. Ni et al. (10). Their research shows that the particle size graded electrode causes a high reduction in overpotential from that of the non-graded electrode. Besides, the graded electrode can also increase the active surface area per unit volume and allow the fuel gas to remain at a high concentration at the reaction sites. Ricardo Dias (35) explored the dependence of packing porosity on particle size ratio, but he focused on exploring the extreme limits of the particle size ratio. However, for common SOFCs, the particle size ratio of electronic and ionic conductors is more or less the same. S. Yerazunis (36) performed experiments to analyze this particular situation. In the experiment, the particles sizes are assumed to be comparable. In addition, dense-packed particles will ensure good connection of particles as it will reduce the path length of the fuel gases and allow the flow to reach the TPB faster. Based on the experimental data, the curve fitting equation of the measured data gives the correlation between particle size ratio and porosity.

A number of numerical and experimental studies have been conducted to improve the cell performance. However to the best of the author's knowledge, to carry out a mathematical study by considering the correlations of microstructure parameters has not yet been attempted.

### 2.3 Functionally Grade Electrodes of SOFC

New materials and fabrication techniques have been used in FGEs in order to enhance the performance of SOFCs. Hart et al. (37) used slurry spraying techniques to observe the cell performance by setting up electrode layers with different materials. It was found that as temperature decreases, the functionally layered cell still maintained a high level of performance.
Zha et al. (38) fabricated a four-layer cathode and the results indicated the cell performance was strongly dependent on sintering temperature and oxygen partial pressure. Liu et al. (13) found out that a functionally graded cathode fabricated by combustion CVD process can dramatically increase the rates of electrode reactions, enhance the transport of oxygen molecules to the active reaction sites, and significantly improve the compatibility between the electrodes and other cell components. As a result, extremely low interfacial polarization resistances and high power densities have been achieved at operating temperatures of 600-850°C. Efforts have also been made by examining the advantages of applying FGEs in SOFCs from a mathematical perspective. Ni et al. (10) developed a mathematical model to compare the uniform composite electrodes with two types of FGEs (particle size grading and porosity grading) in the anode. Both particle size and porosity were linearly varied from the flow channel to the electrolyte surface. The results show that applying FGEs reduced the mass transport resistance and increase the active surface area near the TPB region, thus improving cell performance. Greene et al. (18) developed computational model to explore mass transport and ohmic loss in graded SOFC electrodes from a micro-scale level. A porosity-tortuosity graded electrode is applied to demonstrate the reduction of ohmic overpotential. Gas fuel concentration and molar flux increases significantly at electrolyte surface for graded electrodes, so mass transfer is also improved as compared to a uniform pore structure. Activation overpotential is not calculated based on microstructure parameters, porosity or tortuosity, as author assumes electrochemical reactions only take place at electrode-electrolyte surface, where a very thin layer with few microstructure parameters get involved in the reactions. Thus, it is assumed that the activation overpotential may not be affected by the grading. Wang et al. (39) implemented a mathematical model to predict SOFCs performance of electrodes with one interlayer. It was found that in most cases, using an interlayer in the anode can improve the SOFC performance by reducing the overpotential. However, for the addition of an interlayer to the cathode, the improvement may vary depending on the thickness.
Chapter 3 Numerical Modeling of SOFC

In this chapter we will present a framework for the numerical simulation of SOFCs. This is a physically based, predictive, quantitative model that can be used for SOFC design and optimization at the cell level.

3.1 Anode

3.1.1 Overpotential due to electrochemical reactions and ohmic resistance

The overall charge balance relationship can be written as (17):

$$\frac{dj_{e,a}}{dx} = -\frac{dj_{i,a}}{dx} = -S_v j_{n,a} \quad (3.1)$$

\(j_{e,a}\) and \(j_{i,a}\) are the current density (A/m\(^2\)) due to transport of electronic and ionic conductors in anode; \(S_v\) is active surface area per unit volume (m\(^2\)/m\(^3\)) of the porous hydrogen electrode; \(j_{n,a}\) is the transfer current density per unit area of reactive surface (A/m\(^2\)). This equation essentially accounts for the electrochemical reaction rate of the fuel cell along the anode.

The transfer current density is normally described by the general form of the Butler-Volmer (B-V) equation.

$$j_{n,a} = j_{0,a} \left\{ \frac{y_{H_2} \exp \left( \frac{\beta zF \eta_a}{RT} \right) - 1 - y_{H_2}^f \exp \left( -\frac{(1-\beta)zF \eta_a}{RT} \right) }{1 - y_{H_2}^f} \right\} \quad (3.2)$$

Where \(j_{0,a}\)is the exchange current density of anode (A/m\(^2\)); \(y_{H_2}\)is the molar fraction of \(H_2\); \(y_{H_2}^f\) is the molar fraction of \(H_2\) at fuel channel. \(\beta\) is the charge transfer coefficient and is normally chosen to be 0.5 for “symmetric” reactions (9).

Applying Ohm’s law for the electronic and ionic conductors, we get:

$$\frac{dV_e}{dx} = \rho_{e,a}^{eff} j_{e,a} \quad \frac{dV_i}{dx} = \rho_{i,a}^{eff} j_{i,a} \quad (3.3)$$

\(\rho_{e,a}^{eff}\) is the effective resistivity (Ω·m) of the anode electronic conductors; \(\rho_{i,a}^{eff}\) is the effective resistivity of anode ionic conductors; \(V_e\) and \(V_i\) are electronic and ionic potential (V), respectively.

The effective resistivity can be determined by (40):
\[
\rho_{e,a}^{\text{eff}} = \frac{\tau}{\varphi_e(1-\varepsilon)\sigma_{e,a}} \tag{3.4}
\]

\[
\rho_{i,a}^{\text{eff}} = \frac{\tau}{(1-\varphi_e)(1-\varepsilon)\sigma_i} \tag{3.5}
\]

Where \(\varphi_e\) is the volume fraction of electronic conductors; \(\tau\) is tortuosity of the anode; \(\varepsilon\) is porosity of anode; \(\sigma_{e,a}\) is electrical conductivity (S/m) of anode electronic conductors; \(\sigma_i\) is ionic conductivity (S/m) of ionic conductors.

The anode overpotential \(\eta_a\) can be determined by the difference of equilibrium potential and practical potential.

\[
\eta_a = V^{eq} - V = (V_e^{eq} - V_i^{eq}) - (V_e - V_i) \tag{3.6}
\]

\(V_e^{eq}\) and \(V_i^{eq}\) are the equilibrium electronic and ionic potential (V), respectively.

The first derivative of \(\eta_a\) can be written as:

\[
\frac{d\eta_a}{dx} = -\left(\frac{dV_e}{dx} - \frac{dV_i}{dx}\right) = \rho_{i,a}^{\text{eff}}J_{i,a} - \rho_{e,a}^{\text{eff}}J_{e,a} \tag{3.7}
\]

Combing the charge balance equation and B-V equation, the second derivative of \(\eta_a\) is equal to:

\[
\frac{d^2\eta_a}{dx^2} = \rho_{i,a}^{\text{eff}}\frac{dJ_{i,a}}{dx} - \rho_{e,a}^{\text{eff}}\frac{dJ_{e,a}}{dx} = S_vJ_{n,a}\left(\rho_{i,a}^{\text{eff}} + \rho_{e,a}^{\text{eff}}\right)
\]

\[
= S_vJ_{n,a}\left(\rho_{i,a}^{\text{eff}} + \rho_{e,a}^{\text{eff}}\right)\left(\frac{y_{H_2}}{y_{H_2}}\exp\left(\frac{\beta zF\eta_a}{RT}\right) - \frac{1 - y_{H_2}}{1 - y_{H_2}}\exp\left(\frac{(1 - \beta)zF\eta_a}{RT}\right)\right) \tag{3.8}
\]

### 3.1.2 Overpotential due to mass transport

#### 3.1.2.1 Diffusion in porous electrodes

Diffusion processes within a porous electrode structure can be distinguished as two types. First, there is normal diffusion in which one gas diffuses through another, with negligible influence of the pore walls on the rate of diffusion. This applies when the mean free path of the molecules is much less than the pore diameter. Second, when the mean free path of the molecules is greater than the pore diameter, Knudsen diffusion occurs. For most of SOFCs, the Knudsen effects cannot be neglected (15). Therefore, for a binary gas system going through the pore structure, the
overall effective diffusion coefficient \( D_{ij}^{\text{eff}} \) can be written by combing effective normal binary diffusion coefficient \( D_{ij}^{\text{eff}} \) and the effective Knudsen diffusion coefficient \( D_{ik}^{\text{eff}} \). \( \text{(41)} \)

\[
\frac{1}{D_i^{\text{eff}}} = \frac{1}{D_{ij}^{\text{eff}}} + \frac{1}{D_{ik}^{\text{eff}}} 
\]

(3.9)

The binary diffusion coefficient can be determined from the Chapman-Enskog theory \( \text{(42)} \).

\[
D_{ij} = 0.0018583 \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2} \frac{T^{2/3}}{Pe_{ij}^2 \Omega_D} 
\]

(3.10)

\( M \) is molar weight (g/mol); \( P \) is anode pressure (atm); \( \epsilon_{ij} \) is collision diameter in Å; \( \Omega_D \) is collision integral. The equation for calculating \( \sigma_{ij} \) and \( \Omega_D \) can be expressed as:

\[
\epsilon_{ij} = \frac{\epsilon_i + \epsilon_j}{2} \quad \text{(3.11)}
\]

\[
\Omega_D = \frac{1.06}{\epsilon} + \frac{0.193}{\exp(0.476\epsilon)} + \frac{1.036}{\exp(1.53\epsilon)} + \frac{1.765}{3.894\epsilon} \quad \text{(3.12)}
\]

Where \( \epsilon \) is determined by,

\[
t = \frac{k_B T}{\xi_{ij}} \quad \text{(3.13)}
\]

The Boltzmann constant \( k_B = 1.38066 \times 10^{-23} \text{(J·K}^{-1}) \); \( \xi_{ij} \) is the Lennard-Jones energy and can be expressed as:

\[
\xi_{ij} = \sqrt{\xi_i \xi_j} \quad \text{(3.14)}
\]

The following table listed \( \sigma_i \) and \( \xi_{ij}/k_B \) values for several commonly used gases.

<table>
<thead>
<tr>
<th>( \sigma_i ) and ( \xi_{ij}/k_B ) values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \epsilon_i )</td>
</tr>
<tr>
<td>N(_2)</td>
</tr>
<tr>
<td>O(_2)</td>
</tr>
<tr>
<td>CH(_4)</td>
</tr>
<tr>
<td>H(_2)O</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>H(_2)</td>
</tr>
<tr>
<td>CO(_2)</td>
</tr>
</tbody>
</table>
The effectively diffusion coefficient depends on the microstructure of the porous anode, quantified through the porosity and tortuosity values. Thus, the effective binary diffusion coefficient can be written as: (17)

\[ D_{i,j}^{\text{eff}} = \frac{\varepsilon}{\tau} D_{i,j} \]  

(3.15)

For Knudsen diffusion, its coefficient can be described as (14),

\[ D_{i,K} = \frac{2}{3} d_0 \sqrt{\frac{8RT}{\pi M_i}} \]  

(3.16)

d_0 is the pore diameter (m) and is assumed to be approximately equal to the hydraulic diameter.

\[ d_0 \approx d_h = \frac{4}{A_0} \frac{\varepsilon}{1 - \varepsilon} \]  

(3.17)

A_0 is specific surface area based on the solid volume. For random packing of binary, A_0 is expressed as:

\[ A_0 = \frac{6 n_e + (1 - n_e) \alpha^{-2}}{d_e n_e + (1 - n_e) \alpha^{-3}} \]  

(3.18)

d_e is the diameter (m) of electronic particles, n_e is number fraction of electronic particles, \( \alpha = \eta / r_e \).

Similarly as with the effective binary diffusion coefficient, the effective Knudsen diffusion coefficient can be expressed as:

\[ D_{i,K}^{\text{eff}} = \frac{\varepsilon}{\tau} D_{i,K} \]  

(3.19)

### 3.1.2.2 Fick’s Law

Fick’s Law is the simplest form to describe the mass transfer through the porous media. The general form of the model takes into account both diffusion and convection mass transfer and can be expressed as: (15) (16)
Where \( N_i \) is molar flux (mol/m\(^2\)·s) of species \( i \); \( D_i^{eff} \) is the effective diffusion coefficient (m\(^2\)/s) of specie \( i \); \( c_i \) is the concentration (mol/m\(^3\)) of specie \( i \); \( v \) is the convection velocity (m/s); \( p \) is pressure (Pa); \( B_0 \) is the permeability (m\(^2\)); \( \mu_{mix} \) is the viscosity of mixture (kg / m·s).

The equations of diffusion for both \( \text{H}_2 \) and \( \text{H}_2\text{O} \) are listed as follows: (44)

\[
N_{\text{H}_2} = -D_{\text{H}_2}^{eff} \frac{dc_{\text{H}_2}}{dx} + c_{\text{H}_2} v 
\]

(3.21)

\[
N_{\text{H}_2\text{O}} = -D_{\text{H}_2\text{O}}^{eff} \frac{dc_{\text{H}_2\text{O}}}{dx} + c_{\text{H}_2\text{O}} v 
\]

(3.22)

The convection velocity is due to inertia. Under constant operating temperature, the ideal gas law can be written as:

\[
\frac{dp}{dx} = \frac{dc}{dx} RT 
\]

(3.23)

If pressure is uniform throughout the electrode, then \( dp/dx \) is constant. According to eqn. (3.23), \( dc/dx \) will also be constant. Then we will have:

\[
\frac{dc_{\text{H}_2}}{dx} = -\frac{dc_{\text{H}_2\text{O}}}{dx} 
\]

(3.24)

For equimolar counter-current mass transfer, \( N_{\text{H}_2} = -N_{\text{H}_2\text{O}} \). The summation of eqn. (3.21) and (3.22) will give us:

\[
0 = -(D_{\text{H}_2}^{eff} - D_{\text{H}_2\text{O}}^{eff}) \frac{dc_{\text{H}_2}}{dx} + v(c_{\text{H}_2} + c_{\text{H}_2\text{O}}) 
\]

(3.25)

Eqn. (3.25) can be rearranged as:

\[
v = \frac{D_{\text{H}_2}^{eff} - D_{\text{H}_2\text{O}}^{eff}}{c_{\text{H}_2} + c_{\text{H}_2\text{O}}} \frac{dc_{\text{H}_2}}{dx} 
\]

(3.26)

Substitute above equation back into \( \text{H}_2 \) and \( \text{H}_2\text{O} \) flux equations, which are eqn. (3.21) and eqn. (3.22), we have:
According to flux and current density relations as well as ideal gas law, 

\[ N_{H_2} = -\left( \frac{c_{H_2O}}{c_{H_2O} + c_{H_2}} D_{H_2}^{eff} + \frac{c_{H_2}}{c_{H_2O} + c_{H_2}} D_{H_2O}^{eff} \right) \frac{dc_{H_2}}{dx} \]

\[ = -(y_{H_2O} D_{H_2}^{eff} + y_{H_2} D_{H_2O}^{eff}) \frac{dc_{H_2}}{dx} \]  

(3.27)

\[ N_{H_2O} = -\left( \frac{c_{H_2O}}{c_{H_2O} + c_{H_2}} D_{H_2}^{eff} + \frac{c_{H_2}}{c_{H_2O} + c_{H_2}} D_{H_2O}^{eff} \right) \frac{dc_{H_2O}}{dx} \]

\[ = -(y_{H_2O} D_{H_2}^{eff} + y_{H_2} D_{H_2O}^{eff}) \frac{dc_{H_2O}}{dx} \]

(3.28)

According to flux and current density relations as well as ideal gas law,

\[ N_{H_2} = \frac{J_{e,a}}{2F} \]  

(3.29)

\[ \frac{dc_{H_2}}{dx} = \frac{dy_{H_2}}{dx} \frac{p}{RT} \]  

(3.30)

Eqn. (3.27) turns into:

\[ \frac{dy_{H_2}}{dx} = - \frac{1}{y_{H_2O} D_{H_2}^{eff} + y_{H_2} D_{H_2O}^{eff}} \frac{RT J_{e,a}}{p \cdot 2F} \]

\[ = - \frac{1}{(1-y_{H_2}) D_{H_2}^{eff} + y_{H_2} D_{H_2O}^{eff}} \frac{RT J_{e,a}}{p \cdot 2F} \]  

(3.31)

\[ 3.1.2.3 \text{ Dusty Gas Model} \]

The Dusty Gas Model (DGM) (16) is another commonly used diffusion model. It is assumes that the pore walls consist of giant molecules (dust) uniformly distributed in space. These dust molecules are considered to be dummy, pseudo, species in the mixture. The general form of the DGM is shown as

\[ \frac{N_i}{D_{i,K}^{eff}} + \sum_{j=1, j \neq i}^{n} \frac{y_j N_i - y_i N_j}{D_{i,j}^{eff}} = - \frac{dc_i}{dx} - \frac{1}{p} \frac{dp}{dx} \left( 1 + \frac{B_0 p}{D_{i,K}^{eff} \mu_{mix}} \right) \]  

(3.32)
The first term on the left hand side (LHS) expresses Knudsen diffusion. The second term indicates the multi-component diffusion and is described by the Stefan-Maxwell Model. The first term on the right hand side (RHS) denotes the concentration gradient along the electrode. The second term takes into consideration the effect of total pressure gradient on mass transport. If we assume pressure is uniform along the entire electrode, then this term drops out. The DGM reduces to:

\[
\frac{N_i}{D_{i,k}^{\text{eff}}} + \sum_{j=1,j\neq i}^{n} \frac{y_j N_i - y_i N_j}{D_{i,j}^{\text{eff}}} = -\frac{dc_i}{dx}
\]  

(3.33)

For a H₂ - H₂O binary system, the DGM can be rewritten as:

\[
\frac{N_{H_2}}{D_{H_2,K}^{\text{eff}}} + \frac{y_{H_2O} N_{H_2} - y_{H_2} N_{H_2O}}{D_{H_2,H_2O}^{\text{eff}}} = -\frac{d c_{H_2}}{dx}
\]  

(3.34)

Under steady state, \( y_{H_2O} = 1 - y_{H_2} \) and \( N_{H_2O} = -N_{H_2} \). The above equation turns into:

\[
\frac{N_{H_2}}{D_{H_2,K}^{\text{eff}}} + \frac{N_{H_2}}{D_{H_2,H_2O}^{\text{eff}}} = N_{H_2} \left( \frac{1}{D_{H_2,K}^{\text{eff}}} + \frac{1}{D_{H_2,H_2O}^{\text{eff}}} \right) = -\frac{d c_{H_2}}{dx}
\]  

(3.35)

Then hydrogen flux can be expressed as:

\[
N_{H_2} = -D_{H_2}^{\text{eff}} \frac{d c_{H_2}}{dx}
\]  

(3.36)

This above equation is exactly the same as Fick’s Model if the pressure term is neglected.

### 3.1.3 Anode governing equations and boundary conditions

In our simulation, the Fick’s model is selected to calculate the mass transfer over anode. Combining with the electrochemical reaction formulas, we get a total of three governing equations. They are:
The boundary conditions for the governing equations can be derived as follows: At the fuel gas inlet, which is also the location of the current collector, the hydrogen molar fraction is equal to the bulk flow value. The total current density only comes from the transport of electrons. As a result, the boundary conditions can be expressed as:

\[
\begin{align*}
\frac{d^2 \eta_a}{dx^2} &= S_v j_{0,a} \left( \rho_{i,a}^{eff} + \rho_{e,a}^{eff} \right) \left( \frac{y_{H_2}}{y_{H_2}^{l}} \exp \left( \frac{\beta z F \eta_a}{RT} \right) \right) \\
&\quad - \frac{1 - y_{H_2}}{1 - y_{H_2}^{l}} \exp \left( - \frac{(1 - \beta) z F \eta_a}{RT} \right) \\
\end{align*}
\]

(3.37)

\[
\frac{dj_{e,a}}{dx} = -S_v j_{0,a} \left( \frac{y_{H_2}}{y_{H_2}^{l}} \exp \left( \frac{\beta z F \eta_a}{RT} \right) - \frac{1 - y_{H_2}}{1 - y_{H_2}^{l}} \exp \left( - \frac{(1 - \beta) z F \eta_a}{RT} \right) \right)
\]

(3.38)

\[
\frac{dy_{H_2}}{dx} = -\frac{1}{(1 - y_{H_2})D_{H_2}^{eff} + y_{H_2}D_{H_2}^{eff 0}} \frac{RT j_{e,a}}{p} \frac{RT}{2F}
\]

(3.39)

Since the governing equation associated with solving for the overpotential is a second order partial differential equation, another boundary condition is required. At the electrode-electrolyte (EE) interface, the transport of ions is the only factor that contributes to the overall current density. Therefore, ion current density equals to the overall current density. This allows for the boundary condition of the overpotential to be from defined, as in eqn. (3.7).

\[
\begin{align*}
\left. y_{H_2} \right|_{inlet} &= y_{H_2}^{(bulk)}; \left. j_{i,a} \right|_{inlet} = 0; \left. j_{e,a} \right|_{inlet} = j_{total}; \left. \frac{d\eta_a}{dx} \right|_{inlet} = \frac{\rho_{i,a}^{eff}}{j_{i,a}} - \frac{\rho_{e,a}^{eff}}{j_{e,a}} = -\frac{\rho_{e,a}^{eff}}{j_{total}} \\
\end{align*}
\]

(3.40)

After solving the governing equations, \( \eta_a, j_{e,a} \) and \( y_{H_2} \) distribution can be obtained. Then the overall overpotential of the anode can be written as follows. At the fuel gas inlet,
\[ \eta_a|_{\text{inlet}} = (V_e^{eq} - 0) - (V_e|_{\text{inlet}} - 0) \]  
(3.42)

At the electrode-electrolyte interface,
\[ \eta_a|_{\text{interface}} = (0 - V_i^{eq}) - (0 - V_i|_{\text{interface}}) \]  
(3.43)

Adding the above two equations together, we will get anode overall overpotential:
\[ \eta_a|_{\text{overall}} = V^{eq} - V = \eta_a|_{\text{inlet}} + \eta_a|_{\text{interface}} \]  
(3.44)
\[ = (V_e^{eq} - V_i^{eq}) - (V_e|_{\text{inlet}} - V_i|_{\text{interface}}) \]

3.2 Cathode

3.2.1 Overpotential due to electrochemical reactions and ohmic resistance

The electrochemical reaction equations in cathode are similar to the ones in anode and can be derived in a similar fashion, to produce the following.

\[ \frac{d^2 \eta_c}{dx^2} = S_c J_{0.c} (\rho_{e,c}^{eff} + \rho_{e,c}^{eff}) \left\{ \frac{y_{y_2}}{y_{y_2}^0} \exp \left( \frac{\beta z F \eta_c}{RT} \right) - \exp \left( - \frac{(1 - \beta) z F \eta_c}{RT} \right) \right\} \]  
(3.45)

\[ \frac{dJ_{e,c}}{dx} = S_c J_{0.c} \left\{ \frac{y_{y_2}}{y_{y_2}^0} \exp \left( \frac{\beta z F \eta_c}{RT} \right) - \exp \left( - \frac{(1 - \beta) z F \eta_c}{RT} \right) \right\} \]  
(3.46)

Where \( \eta_c \) is cathode overpotential; \( J_{0.c} \) is cathode exchange current density; \( \rho_{e,c}^{eff} \) is effective resistivity of cathode electronic conductors. \( J_{e,c} \) is the current density due to transport of electronic current conductors in cathode.

3.2.2 Overpotential due to mass transport

3.2.2.1 Fick’s Law

The model is proposed by Berger (44). An effective Knudsen diffusion coefficient of O2 can be defined by

\[ N_{O_2} = -D_{O_2,K} \left( \frac{dc_{O_2}}{dx} \right)_{\text{Knudsen}} \]  
(3.47)
The effective normal diffusion of oxygen taking both conduction and convection transport can be defined by

\[
N_{O_2} = -D_{\text{eff},O_2,N_2}^{\text{normal}} \left( \frac{dc_{O_2}}{dx} \right)_{\text{normal}} + c_{O_2} v = -D_{\text{eff},O_2,N_2}^{\text{normal}} \left( \frac{dc_{O_2}}{dx} \right)_{\text{normal}} + \frac{N_{\text{total}}}{c_{\text{total}}} \quad (3.48)
\]

Total concentration of O\(_2\) is equal to the summation of Knudsen concentration and normal concentration.

\[
\frac{dc_{O_2}}{dx} = \left( \frac{dc_{O_2}}{dx} \right)_{\text{Knudsen}} + \left( \frac{dc_{O_2}}{dx} \right)_{\text{normal}} = -\left( \frac{1}{D_{\text{eff},O_2,K}} + \frac{1}{D_{\text{eff},O_2,N_2}} \right) N_{O_2} + \frac{c_{O_2}}{c_{\text{total}}} \frac{1}{D_{\text{eff},O_2,N_2}} N_{\text{total}} \quad (3.49)
\]

On the cathode side, nitrogen does not involve any electrochemical reaction, so flux of nitrogen at steady state is zero. Then we have \(N_{\text{total}} = N_{O_2}\). The above equation turns into

\[
\frac{dc_{O_2}}{dx} = -\left( \frac{1}{D_{\text{eff},O_2,K}} + \frac{1}{D_{\text{eff},O_2,N_2}} - y_{O_2} \frac{1}{D_{\text{eff},O_2,N_2}} \right) N_{O_2} = -\left( \frac{1}{D_{\text{eff},O_2,K}} + \frac{1 - y_{O_2}}{D_{\text{eff},O_2,N_2}} \right) N_{O_2} \quad (3.50)
\]

The O\(_2\) flux becomes

\[
N_{O_2} = -\left( \frac{1}{D_{\text{eff},O_2,K}} + \frac{1 - y_{O_2}}{D_{\text{eff},O_2,N_2}} \right)^{-1} \frac{dc_{O_2}}{dx} \quad (3.51)
\]

### 3.2.2.2 Dusty Gas Model

Assume pressure is uniform throughout cathode, and then the DGM equation becomes

\[
\frac{N_{O_2}}{D_{\text{eff},O_2,K}} + \frac{y_{N_2} N_{O_2} - y_{O_2} N_{N_2}}{D_{\text{eff},O_2,N_2}} = -\frac{dc_{O_2}}{dx} \quad (3.52)
\]
Because $N_{N_2} = 0$ and $y_{N_2} = 1 - y_{O_2}$, DGM equation becomes

$$\frac{N_{O_2}}{D_{O_2,K}^{eff}} + \frac{(1 - y_{O_2})N_{O_2}}{D_{O_2,N_2}^{eff}} = -\frac{dc_{O_2}}{dx} \tag{3.53}$$

Rearranging the above equation, we have

$$N_{O_2} = -\left(\frac{1}{D_{O_2,K}^{eff}} + \frac{1 - y_{O_2}}{D_{O_2,N_2}^{eff}}\right)^{-1} \frac{dc_{O_2}}{dx} \tag{3.54}$$

It can be found that the DGM and Fick’s Law have the same formula in this case.

According to flux and current density relations as well as ideal gas law, we have

$$N_{O_2} = \frac{j_{e,c}}{4F} \tag{3.55}$$

$$\frac{dc_{O_2}}{dx} = \frac{dy_{O_2}}{dx} \frac{p}{RT} \tag{3.56}$$

Then eqn. (3.57) becomes

$$\frac{dy_{O_2}}{dx} = -\frac{RT}{p} \left(\frac{1}{D_{O_2,K}^{eff}} + \frac{1 - y_{O_2}}{D_{O_2,N_2}^{eff}}\right) \frac{j_{e,c}}{4F} \tag{3.57}$$

### 3.2.3 Cathode governing equations and boundary conditions

Similarly as anode, three coupled governing equations for cathode can be listed as

$$\frac{d^2 \eta_c}{dx^2} = S_{e}J_{0,c}(\rho_{i,c}^{eff} + \rho_{e,c}^{eff}) \left(\frac{y_{O_2}}{y_{O_2}} \exp\left(\frac{\beta_2 F \eta_c}{RT}\right) - \exp\left(-\frac{(1 - \beta_2)zF \eta_c}{RT}\right)\right) \tag{3.58}$$

$$\frac{dj_{e,c}}{dx} = S_{e}J_{0,c} \left(\frac{y_{O_2}}{y_{O_2}} \exp\left(\frac{\beta_2 F \eta_c}{RT}\right) - \exp\left(-\frac{(1 - \beta_2)zF \eta_c}{RT}\right)\right) \tag{3.59}$$

$$\frac{dy_{O_2}}{dx} = -\frac{RT}{p} \left(\frac{1}{D_{O_2,K}^{eff}} + \frac{1 - y_{O_2}}{D_{O_2,N_2}^{eff}}\right) \frac{j_{e,c}}{4F} \tag{3.60}$$
At fuel gas inlet, which is also the location of current collector, the oxygen molar fraction is equal to the bulk flow value and the total current density only comes from the transport of electrons. The boundary conditions can then be expressed as:

\[
y_{O_2}|_{inlet} = y_{O_2}(bulk); J_{i,c}|_{inlet} = 0; J_{e,c}|_{inlet} = J_{total}; \frac{d\eta_{c}}{dx}|_{inlet} = \rho_{i,c} J_{i,c} - \rho_{e,c} J_{e,c} = -\rho_{e,c} J_{total} \quad (3.61)
\]

On electrode-electrolyte (EE) interface, the transport of ions will be the only factor contributes to the overall current density. Thus, the treatment of overpotential on the EE boundary can be obtained as follows.

\[
J_{i,c}|_{interface} = J_{total}; \frac{d\eta_{c}}{dx}|_{inlet} = \rho_{i,c} J_{i,c} - \rho_{e,c} J_{e,c} = \rho_{i,c} J_{total} \quad (3.62)
\]

After solving the governing equations, the cathode overall overpotential can be calculated as:

\[
\eta_{c}|_{overall} = V_{eq} - V = \eta_{c}|_{inlet} + \eta_{c}|_{interface}
\]

\[
= (V_{eq} - V_{i}) - (V_{e}|_{inlet} - V_{i}|_{interface}) \quad (3.63)
\]

### 3.3 Electrolyte

The overpotential from the electrolyte can be simply expressed by the Ohm’s Law.

\[
\eta_{e} = J_{total} \times ASR \quad (3.64)
\]

The area specific resistance ASR (Ω·m$^{-2}$) equals to $L/\sigma$. L is the thickness of electrolyte (m) and $\sigma$ is the ionic conductivity (S·m$^{-1}$) of electrolyte.

### 3.4 Numerical Solution Procedure

The numerical domain for anode is listed below.
Figure 6 computational domain of anode

The numerical solution procedure for anode and cathode are basically the same. Let us use the anode as an example. By analyzing the original 2\textsuperscript{nd} order partial differential equation (PDE) given in eqn. (3.37), it can be found that the value difference between the two sides of the equation is extremely large due to the exponential term on the RHS. Therefore, instead of solving the 2\textsuperscript{nd} order PDE directly, a so-called the delta form is introduced in eqn. (3.65).

\[
\frac{d^2 \Delta \eta_a}{dx^2} = \frac{d^2 \eta_a}{dx^2} - S_e j_{0,a} \left( \rho_{i,a}^{\text{eff}} + \rho_{e,a}^{\text{eff}} \right) \left( y_{H_2} \frac{\exp\left( \frac{\beta z F \eta_a}{RT} \right)}{y_{H_2}} \right) \\
- \frac{1 - y_{H_2}^{\text{ref}} \exp\left( - \frac{(1 - \beta) z F \eta_a}{RT} \right)}{1 - y_{H_2}^{\text{ref}}}
\]  

(3.65)

Instead of dealing with the original PDE, what a delta form does is try to create an infinite small value of overpotential, in this case, $\Delta \eta_a$ and force this variable to zero using an iterative method. Once the LHS of eqn. (3.65) converges to zero, the original governing equation will be satisfied automatically. The advantage of solving this 2\textsuperscript{nd} PDE by delta form is that we can manipulate the coefficient of $\Delta \eta_a$ in discretization. Eventually, $\Delta \eta_a$ is supposed to be zero, so the value of the coefficient of $\Delta \eta_a$ could be anything as long as it can benefit for solving the equation. To take advantage of that, extra terms can be added to the coefficient of $\Delta \eta_a$ in order to help balance the entire equation. In this case, derivative of the B-V equation with respect to $\eta_a$ will be the extra term added to the coefficient of $\Delta \eta_a$ such that the whole equation will have the same order of magnitude (both sides of the equation contains exponential term) and hence be more stable and easier to be solved by Tri-diagonal matrix solver. The detailed discretization of this equation is listed below.
The control volume and nodal points are generated based on the following figure.

![Figure 7 discretization of the domain](image)

The original 2nd order equation is listed as

\[
\frac{d^2 \eta_a}{dx^2} = S_{vJ,0,a} \left( \rho_{i,a}^{\text{eff}} + \rho_{e,a}^{\text{eff}} \right) \left\{ y_{H_2} \exp \left( \frac{\beta zF \eta_a}{RT} \right) \right. \\
- \left. (1 - y_{H_2}) \exp \left( -\frac{(1 - \beta) zF \eta_a}{RT} \right) \right\} \tag{3.66}
\]

Delta Form can be expressed as

\[
\frac{d^2 \Delta \eta_a}{dx^2} = S_{vJ,0,a} \left( \rho_{i,a}^{\text{eff}} + \rho_{e,a}^{\text{eff}} \right) \left\{ y_{H_2} \exp \left( \frac{\beta zF \eta_a}{RT} \right) \right. \\
- \left. (1 - y_{H_2}) \exp \left( -\frac{(1 - \beta) zF \eta_a}{RT} \right) \right\} - \frac{d^2 \eta_a}{dx^2} \tag{3.67}
\]

\[
RHS(j) - LHS(j)
\]

Where

\[
RHS(j) = S_{vJ,0,a} \left( \rho_{i,a}^{\text{eff}} + \rho_{e,a}^{\text{eff}} \right) \left\{ y_{H_2} \exp \left( \frac{\beta zF \eta_a}{RT} \right) \right. \\
- \left. (1 - y_{H_2}) \exp \left( -\frac{(1 - \beta) zF \eta_a}{RT} \right) \right\}
\]

\[
LHS(j) = \frac{d^2 \eta_a}{dx^2}
\]

Next, the second order term of \( \Delta \eta_a \) can be discretized as
In order to solve for using tri-diagonal matrix solver, the original equation in delta form must be rearranged as

\[
a_p(j) \Delta \eta_a(j) = a_e(j) \Delta \eta_a(j + 1) + a_w(j) \Delta \eta_a(j - 1) + S(j) \tag{3.69}
\]

Where

\[
a_e(j) = \frac{1}{\Delta x(j) \Delta xc v(j)}
\]

\[
a_w(j) = \frac{1}{\Delta x(j - 1) \Delta xc v(j)}
\]

\[
a_p(j) = a_e(j) + a_w(j)
\]

\[
S(j) = LHS(j) - RHS(j)
\]

The RHS term contains exponential term. Taylor series is applied in order to linearize that term.

\[
\frac{\partial \text{RHS}}{\partial \eta_a}(j) = \frac{\text{RHS}^{\text{new}}(j) - \text{RHS}(j)}{\Delta \eta_a(j)} \rightarrow \text{RHS}^{\text{new}}(j)
\]

\[
= \text{RHS}(j) + \frac{\partial \text{RHS}}{\partial \eta_a}(j) \Delta \eta_a(j) \tag{3.70}
\]

Then the updated source term is calculated as

\[
S^{\text{new}}(j) = LHS(j) - \text{RHS}^{\text{new}}(j) = LHS(j) - \text{RHS}(j) + \frac{\partial \text{RHS}}{\partial \eta_a}(j) \Delta \eta_a(j)
\]

\[
= S(j) - \frac{\partial \text{RHS}}{\partial \eta_a}(j) \Delta \eta_a(j) \tag{3.71}
\]

Substitute the old source term by the new one, we have

\[
a_p(j) \Delta \eta_a(j) = a_e(j) \Delta \eta_a(j + 1) + a_w(j) \Delta \eta_a(j - 1) + S(j) - \frac{\partial \text{RHS}}{\partial \eta_a}(j) \Delta \eta_a(j) \tag{3.72}
\]
Rearrange into the special form that can be solved by tri-diagonal matrix solver.

\[
\left[ a_p(j) + \frac{\partial \text{RHS}}{\partial \eta_a} (j) \right] \Delta \eta_a(j) = a_e(j) \Delta \eta_a(j + 1) + a_w(j) \Delta \eta_a(j - 1) + S(j) \quad (3.73)
\]

Where

\[
a_e(j) = \frac{1}{\Delta x(j) \Delta xc v(j)}
\]

\[
a_w(j) = \frac{1}{\Delta x(j - 1) \Delta xc v(j)}
\]

\[
a_p(j) = a_p^{old}(j) + \frac{\partial \text{RHS}}{\partial \eta_a} (j) = a_e(j) + a_w(j) + \frac{\partial \text{RHS}}{\partial \eta_a} (j)
\]

\[
S(j) = LHS(j) - \text{RHS}(j)
\]

Boundary conditions of this equation are

\[
\Delta \eta_a(1) = \Delta \eta_a(n) = 0 \quad (3.74)
\]

For internal points, we have

\[
a_p(2) \Delta \eta_a(2) = a_e(2) \Delta \eta_a(3) + a_w(2) \Delta \eta_a(1) + S(2)
\]

\[
a_p(3) \Delta \eta_a(3) = a_e(3) \Delta \eta_a(4) + a_w(3) \Delta \eta_a(2) + S(3)
\]

......

......

\[
a_p(n - 2) \Delta \eta_a(n - 2) = a_e(n - 2) \Delta \eta_a(n - 1) + a_w(n - 2) \Delta \eta_a(n - 3) + S(n - 2)
\]

\[
a_p(n - 1) \Delta \eta_a(n - 1) = a_e(n - 1) \Delta \eta_a(n) + a_w(n - 1) \Delta \eta_a(n - 2) + S(n - 1)
\]

We can also express the above set of equations in matrix form.
The 1st order governing used to solve electron current density can be discretized by upwind scheme.

\[
\frac{dj_{e,a}}{dx} = -S_{vJ_{0,a}} \left\{ y_{H_2} \exp\left(\frac{\beta zF \eta_a}{RT}\right) - (1 - y_{H_2}) \exp\left(-\frac{(1 - \beta) zF \eta_a}{RT}\right) \right\} \tag{3.76}
\]

Define LHS and RHS

\[
LHS = \frac{dj_{e,a}}{dx} = \frac{J_{e,a}(j^+) - J_{e,a}(j - 1^+)}{\Delta xcv(j)}
\]

\[
RHS(j) = -S_{vJ_{0,a}} \left\{ y_{H_2} \exp\left(\frac{\beta zF \eta_a}{RT}\right) - (1 - y_{H_2}) \exp\left(-\frac{(1 - \beta) zF \eta_a}{RT}\right) \right\}
\]

The original equation can be rearranged as:

\[
\frac{J_{e,a}(j^+) - J_{e,a}(j - 1^+)}{\Delta xcv(j)} = RHS(j) \tag{3.77}
\]

The electronic current density can be expressed as:

\[
J_{e,a}(j^+) = RHS(j) \times \Delta xcv(j) + J_{e,a}(j - 1^+) \tag{3.78}
\]

Apply the same treatment, and then the other 1st order governing equation can be discretized as:
\[
\frac{dy_{H_2}}{dx} = -\frac{1}{(1 - y_{H_2})D_{H_2}^{eff} + y_{H_2}D_{H_2O}^{eff}} \frac{RT \, J_{e,a}}{p} \frac{x}{2F} 
\] (3.79)

Define LHS and RHS

\[
LHS = \frac{dy_{H_2}}{dx} = \frac{y_{H_2}(j + 1) - y_{H_2}(j)}{\Delta x(j)}
\]

\[
RHS(j) = -\frac{1}{(1 - y_{H_2})D_{H_2}^{eff} + y_{H_2}D_{H_2O}^{eff}} \frac{RT \, J_{e,a}(j^*)}{p} \frac{x}{2F}
\]

Then, we have

\[
\frac{y_{H_2}(j + 1) - y_{H_2}(j)}{\Delta x(j)} = RHS(j)
\] (3.80)

Hydrogen concentration can be calculated as:

\[
y_{H_2}(j + 1) = RHS(j) \times \Delta x(j) + y_{H_2}(j)
\] (3.81)

Along x direction, the domain will be divided into 500 sections. The flow chart show that the overall numerical treatment of these three coupled governing equations is to bond the 2\textsuperscript{nd} order equation with either of the 1\textsuperscript{st} order equations and solve them together until converges. The under relaxation factor (urf) in this case can be chosen to be 0.5. After that, the third equation is coupled and all the governing equations are iterated together. Please notice that if all three equations are solved simultaneously, the code may end up not converging unless applying a heavy under-relaxation factor (0<urf<0.1). We want to avoid this because it will make the computing process very time-consuming.
Input: T, P, l, r_f, r_e, T, \Psi, I_0, I_0', I_e
Initial guess: \eta, \Psi_0, I_e

Do while sum > err

YES

Do while sum1 > err & sum2 > err

YES

Calculate 2nd order DE
Call TDMA for \Delta \eta
\eta_{new} = \eta_{old} + \Delta \eta * \text{urf}
sum1 = sum[abs(\Delta \eta)]

Calculate \Psi_{H2} by solving 1st DE
sum2 = sum[abs(\Psi_{H2\_new} - \Psi_{H2\_old})]

Check convergence {sum1, sum2}
Update \eta, \Psi_{H2}

Calculate I_e by solving 1st DE
sum = sum[abs(I_{e\_new} - I_{e\_old})]

Check convergence (sum)
Update \eta, \Psi_{H2}, I_e

End program

Figure 8 Flow chart
Chapter 4 Analysis of model parameters

In order to produce predictions of real cell performance, firm relationships and assumptions need to be established for the definition of the physical and microstructure parameters of the fuel cell. These assumptions and relationships are defined in this chapter.

4.1 Active surface area per unit volume

The active surface area per unit volume of a composite, porous material cannot be simply calculated on the basis of the properties of the pure materials or porosity/tortuosity parameters, alone. Instead, the composite material can be represented as randomly packed spheres, as was done by Costamagna and Bouvard (19) (20). They utilized the particle coordination number together with percolation theory to build a model of a porous, composite electrode. This model ensures good pathways for both electrical and ionic conduction by connecting the particles of the same type together and forming a bridge through the electrode.

The following equations describe the number of contact points on one electronic or ionic particle

\[ Z_i = Z_{i-i} + Z_{i-e} \]  
\[ Z_e = Z_{e-i} + Z_{e-e} \]
\[ Z = n_i Z_i + n_e Z_e \]
\[ n_i + n_e = 1 \]

\( Z_{i:e} \) is the average number of contact points between an electronic conductor particle and other ionic conductor particles; \( Z_{i:i} \) is the average number of contact points between an ionic conductor particle and other ionic conductor particles; \( Z_{e:i} \) is the average number of contact points between an ionic conductor particle and other electronic conductor particles; \( Z_{e:e} \) is the average number of contact points between an electronic conductor particle and other electronic conductor particles. \( Z_i \) is the average number of contacts between both ionic conductor and electronic conductor particles with an ionic conductor particle; \( Z_e \) is the average number of contacts of both ionic conductor and electronic conductor particles with an electronic conductor particle; and \( Z \) is the overall average number of contacts between particles. In addition, \( n_i \) is the number fraction of
ionic conductor particles and \( n_e \) is number fraction of electronic conductor particles. The definitions can be visualized by Fig. 6.

![Diagram](image1)

Figure 9 Schematics of particle contact

To achieve a mechanically stable position during particle packing, each particle must make contact with a minimum of three other particles, as shown in Fig. 7 (20)

![Diagram](image2)

Figure 10 Number of contact to achieve stable (20)

Thus, the average number of contacts in excess of the minimum required for stability during packing is proportional to the surface area of the particles.
\[
\frac{Z_i - 3}{Z_e - 3} = \alpha^2 \quad (4.5)
\]

\(\alpha\) is the particle size ratio of ionic to electronic conductors. Combing the above equations we get:

\[
Z_e = 3 + \frac{Z - 3}{n_e + (1 - n_e)\alpha^2} \quad (4.6)
\]

\[
Z_i = 3 + \frac{(Z - 3)\alpha^2}{n_e + (1 - n_e)\alpha^2} \quad (4.7)
\]

\(Z\) is the average coordination number, which is equal to 6 in a binary random packing of spheres.

According to Bouvard and Lange’s assumption (20), which is the fraction of contacts of electron particles with ion particles, \(Z_{e-i}/Z_e\), is proportional to the average number of contact of an ion particle with both ion and electron particles within the medium. Therefore, the coordination number between the electronic and ionic particles obeys the following relationship

\[
Z_{e-i} = n_i \frac{Z_i Z_e}{Z} \quad (4.8)
\]

Total number of particles per unit volume can be expressed as follows based on its physical meaning,

\[
n_e = \frac{1 - \varepsilon}{\left(\frac{4}{3}\right)\pi r_e^3 [n_e + (1 - n_e)(r_i/r_e)^3]} \quad (4.9)
\]

where \(r_e\) is the radius of an electronic conductor particle and \(r_i\) is the radius of an ionic conductor particle.

The probabilities of electronic and ionic particles connecting with same particles throughout the whole electrode are evaluated by (20)

\[
P_e = [1 - \left(\frac{4 - Z_{e-e}}{2}\right)^{2.5}]^{0.4} \quad (4.10)
\]

\[
P_i = [1 - \left(\frac{4 - Z_{i-i}}{2}\right)^{2.5}]^{0.4} \quad (4.11)
\]

Where,
$Z_{e-e} = \frac{Z_0 n_e}{[n_e + (1 - n_e)\alpha^2]}$  \hspace{1cm} (4.12)

$Z_{i-i} = \frac{Z_0 n_i}{[n_i + (1 - n_i)\alpha^2]}$  \hspace{1cm} (4.13)

$Z_0$ is the average total coordination number in a random packing of monosized spheres and the value is equal to 6. \hspace{1cm} (46)

Based on following figure, the contact area fraction of two spheres can be expressed as

![Figure 11 contact area fraction of two spheres](image)

The contact angle $\theta$ is normally chosen as 15°

An expression for the active surface area, $S_v$, is illustrated below:

$$S_v = \frac{4\pi K r_e^2}{\text{surface area of electronic conductor per contact}} \cdot \frac{n_e n_e}{\text{No. of electronic conductors per unit vol.}} \cdot \frac{Z_{e-i}}{\text{No. of ionic conductors in contact with electronic conductors}} \cdot \frac{P_e P_i}{\text{surface areas of ionic conductor in contact of electronic conductor per unit vol.}}$$

The overall active surface area per unit vol.

$$S_v = 4\pi K r_e^2 n_e n_e Z_{e-i} P_e P_i = \pi \sin^2 \theta r_e^2 n_e n_e n_i \frac{Z_e Z_i}{Z} p_e p_i$$

$$= 4\pi \frac{\sin^2 \theta}{4} r_e^2 \frac{1 - \epsilon}{(\frac{4}{3})^2 \pi r_e^2} \frac{1}{n_e + (1 - n_e)\left(\frac{r_e}{r_e^2}\right)^2} n_e n_i$$

$$= \left(3 + \frac{Z - 3}{n_e + (1 - n_e)\alpha^2}\right) \left(3 + \frac{(Z - 3)\alpha^2}{n_e + (1 - n_e)\alpha^2}\right)$$

$$S_v = \frac{4\pi K r_e^2 n_e n_e Z_{e-i} P_e P_i}{Z}$$  \hspace{1cm} (4.15)
4.2 Exchange current density

Exchange current density can be determined from detailed elementary reactions. (15) (14)

4.2.1 Anode exchange current density

The follow development is summarized from Lee (2001). The anode overall half reaction is

\[ H_2(g) + O^X_0(YSZ) \Leftrightarrow H_2O(g) + V_0**(YSZ) + 2e^-(Ni) \]

The detailed elementary reactions are listed below.

Absorption on the anode surface:

\[ H_2(g) + 2(Ni) \Leftrightarrow 2H(Ni) \ldots \ldots \text{I} \]

Charge transfer reaction at the triple phase boundary (TPB) region:

\[ H(Ni) + O^{2-}(YSZ) \Leftrightarrow (Ni) + OH^-(YSZ) + e^-(Ni) \ldots \ldots \text{II} \]

\[ H(Ni) + OH^-(YSZ) \Leftrightarrow (Ni) + H_2O(YSZ) + e^-(Ni) \ldots \ldots \text{III} \]

Adsorption/desorption on the YSZ surface:

\[ H_2O(YSZ) \Leftrightarrow H_2O(g) + (YSZ) \ldots \ldots \text{IV} \]

Transfer of the oxygen ion between the surface and the bulk YSZ:

\[ O^X_0(YSZ) + (YSZ) \Leftrightarrow O^{2-}(YSZ) + V_0**(YSZ) \ldots \ldots \text{V} \]
The detailed anode reactions involve six surface species, H(Ni), (Ni), OH(YSZ), O₂(YSZ), H₂O(YSZ), and (YSZ) and two gas-phase species, H₂ (g) and H₂O (g). The coverage of each species on Ni and YSZ can be expressed as

\[ \theta_H + \theta_{Ni} = 1 \]  \hfill (4.16)

\[ \theta_O + \theta_{OH} + \theta_{H_2O} + \theta_{YSZ} = 1 \]  \hfill (4.17)

\( \theta_H \) is the coverage of hydrogen atoms on the anode; \( \theta_{Ni} \) represents an empty site on the anode; \( \theta_O \) represents \( O_2^- \) on YSZ; \( \theta_{OH} \) represents OH⁻ on YSZ; \( \theta_{H_2O} \) represents H₂O on YSZ; \( \theta_{YSZ} \) represents an empty site on the YSZ.

If the reaction III is assumed to be rate-limiting (14), the relations between gaseous partial pressure and surface species coverage are

\[ \frac{\theta_H^2}{\theta_{Ni}^2 P_{H_2}} = K_4 \]  \hfill (4.18)

\[ \frac{\theta_{YSZ} P_{H_2O}}{\theta_{H_2O}} = K_4 \]  \hfill (4.19)
\[
\frac{\theta_{YSZ}}{\theta_o} = K_i
\]  
(4.20)

\(K_i\) is the equilibrium constant of reaction \(i\).

For reaction II, the current density can be written in elementary form as

\[
J_a = J_1 - J_2
\]

\[
= 2l_{TPB} F \left[ k_{2,1} \theta_o \theta_n \exp\left( \frac{\beta_2 FV}{RT} \right) - k_{2,2} \theta_{n1} \theta_{OH} \exp\left( -\frac{(1-\beta_2)FV}{RT} \right) \right]
\]  
(4.21)

At zero current density \((J_1=J_2)\), with \(K_2=k_{2,1}/k_{2,2}\), the equilibrium electrical potential can be found as:

\[
\frac{\theta_{OH}}{\theta_o \theta_n} = K_2 \exp\left( \frac{FV}{RT} \right)
\]  
(4.22)

The current density is determined by rate-limiting reaction III and can be expressed as:

\[
J_a = J_1 - J_2
\]

\[
= 2l_{TPB} F \left[ k_{3,1} \theta_n \theta_{OH} \exp\left( \frac{\beta_3 FV}{RT} \right) - k_{3,2} \theta_{H,O} \theta_n \exp\left( -\frac{(1-\beta_3)FV}{RT} \right) \right]
\]  
(4.23)

At zero current density \((J_1=J_2=0)\), with \(K_3=k_{3,1}/k_{3,2}\), substitute the surface coverage species equations, which are eqn. (4.18), eqn. (4.19), eqn. (4.20) and eqn. (4.22) into eqn. (4.23), the equilibrium electrical potential can be found:

\[
V^{eq} = \frac{RT}{2F} \ln \frac{K_3 P_{H_2,0}}{K_1 K_2 K_3 K_4 P_{H_2}}
\]  
(4.24)
Combining all equations in this section together, the current density can be expressed in terms of the activation overpotential

\[
J_a = J_{0,a} \left[ \exp \left( \frac{(1 + \beta_a)F\eta_a}{RT} \right) - \exp \left( - \frac{F\eta_a}{RT} \right) \right] 
\]

(4.25)

Where

\[
\eta_a = V_0 - V
\]

(4.26)

\[
J_{0,a} = \frac{2l_{TPB}K_{3,2}K_5p_{H_2O}}{K_4(1 + K_1^{1/2}p_{H_2}^{1/2})} \left( \frac{K_3p_{H_2O}}{K_1K_2K_3K_4p_{H_2}} \right)^{(1-\beta_a)/2}
\]

(4.27)

Then the anode exchange current density can be simplified by setting \( \beta = 0.5 \) for the “symmetric” reactions.

\[
J_{0,a} = J_{H_2}^* \left( K_1p_{H_2} \right)^{1/4} \left( p_{H_2O} \right)^{3/4}
\]

(4.28)

Where

\[
J_{H_2}^* = 2l_{TPB}K_{3,2} \left( K_5K_2 \right)^{1/4} \left( K_5 / K_4 \right)^{3/4}
\]

(4.29)

The parameter \( J_{H_2}^* \) is taken here as an empirical parameter that is adjusted to represent experimentally observed performance. Also, from eqn. (4.29) we know that \( J_{H_2}^* \) is only a function of temperature. This indicates that under the same operating temperature \( J_{H_2}^* \) is a fixed value.

According to Lapujoulade and Neil’s report (47), reasonable estimate of hydrogen adsorption-desorption rates are available. \( K_1 \) can be computed as
where the surface site density $\Gamma = 2.6 \times 10^{-9}$ mol/cm$^2$, the pre-exponential factor $A_{des} = 5.59 \times 10^{19}$ s$^{-1}$ cm$^2$/mol, and the activation energy $E_{des} = 88.12$ kJ/mol, the sticking coefficient $S=0.01$. It can be found that $K_1$ is a function of operating temperature.

Exchange current density will normally be obtained by the Electrochemical Impedance Spectroscopy (EIS) plot from experimental study. EIS plot is captured when the fuel cell is working at open circuit voltage. This means partial pressures of the fuel gases at TPB region are equal to the bulk partial pressure during the measurement. Hence, $J_{H_2}^*$ can be calculated by inputting exchange current density, temperature and fuel gas input from eqn. (4.28). Once $J_{H_2}^*$ is obtained, the exchange current density with different fuel gases input under the same operating temperature can be predicted.

$$J_{H_2}^* = J_{0,a} \left[ 1 + \left( \frac{K_1 p_{H_2}}{K_1 p_{H_2}} \right)^{1/2} \right]^{1/4} \left( \frac{p_{H_2}}{p_{H_2,0}} \right)^{1/4} = J_{0,a} \left[ 1 + \left( \frac{K_1(T) p_{H_2(bulk)}}{K_1(T) p_{H_2(bulk)}} \right)^{1/2} \right]^{1/4} \left( \frac{p_{H_2,0(bulk)}}{p_{H_2,0(bulk)}} \right)^{1/4}$$  \hspace{1cm} (4.31)

4.2.2 Cathode exchange current density

Again, summarizing from Lee (2001), the cathode overall half reaction is:

$$\frac{1}{2} O_2(g) + V_{O}^{**}(YSZ) + 2e^- (LSM) \Leftrightarrow O_0^x (YSZ)$$  \hspace{1cm} (4.32)

The detailed elementary reactions are listed below:

Adsorption/desorption on LSM surface

$$O_2(g) + 2(YSZ) \Leftrightarrow 2O_{ad}(LSM) \hspace{1cm} \text{VI}$$

Charge transfer reaction at TPB region
\[ O_{\text{ad}}(\text{LSM}) + V_o^r(\text{YSZ}) + 2e^-(\text{LSM}) \rightleftharpoons O_o^x(\text{YSZ}) + (\text{LSM}) \] ............ VII

\[ \theta_v \text{ represents the coverage of the vacancy on the cathode surface and } \theta_o \text{ represents the coverage of adsorbed oxygen on the cathode surface.} \]

\[ \theta_v + \theta_o = 1 \] ............ (4.34)

Using above two equations, the surface coverage can be expressed by the gaseous partial pressure and the equilibrium constant.
\[ \theta_o = \frac{p_{O_2}^{1/2}}{K_b^{1/2} + p_{O_2}^{1/2}} \]  
\[ \theta_v = \frac{K_b^{1/2}}{K_b^{1/2} + p_{O_2}^{1/2}} \]  

The current density can be written in elementary form from reaction VII as
\[ J_c = J_1 - J_2 = 2l_{TPB}F \left[ k_{7,1} \theta_i \exp \left( \frac{\beta_i F V}{RT} \right) - k_{7,2} \theta_o \exp \left( -\frac{(1 - \beta_7) F V}{RT} \right) \right] \]  

At zero current density \((J_1=J_2=0)\), with \(K_7=k_{7,1}/k_{7,2}\), substitute the eqn. (4.35) and (4.36) into eqn. (4.37), the equilibrium electrical potential can be found
\[ V_0 = \frac{RT}{F} \ln \frac{p_{O_2}^{1/2}}{K_b^{1/2} K_7} \]  

Combining all equations in this section together, the current density can be expressed in terms of activation overpotential
\[ J_c = J_{0,c} \left[ \exp \left( \frac{(1 + \beta_7) F \eta_c}{RT} \right) - \exp \left( -\frac{(1 - \beta_7) F \eta_c}{RT} \right) \right] \]  

Where
\[ \eta_c = V_0 - V \]  

\[ J_{0,c} = \frac{2l_{TPB} F k_{7,2} p_{O_2}^{1/2}}{\left( K_b^{1/2} + p_{O_2}^{1/2} \right)^{1-\beta}} \left( K_b^{1/2} + p_{O_2}^{1/2} \right) \]  

Then the cathode exchange current density can be simplified by setting \( \beta=0.5 \) for “symmetric” reactions.
\[ J_{0,c} = J_{O_2}^* \frac{p_{O_2}}{K_b} \left( 1 + \frac{p_{O_2}}{K_b} \right)^{1/2} \]  

(4.42)

Where

\[ J_{O_2}^* = 2J_{TPB}Fk_{1,1}^{1/2}k_{7,2}^{1/2} \]  

(4.43)

The parameter \( J_{O_2}^* \) is taken here also as an empirical parameter that is adjusted to represent experimentally observed performance.

For an LSM-YSZ interface, Matsuzaki and Yasuda (48) presented an Arrhenius expression for \( K_b \) as

\[ K_b = A_{O_2} \exp \left( \frac{E_{O_2}}{RT} \right) \]  

(4.44)

Where the pre-exponential factor \( A_{O_2} = 4.9 \times 10^8 \text{ atm} \), and the activation energy \( E_{O_2} = 200 \text{ kJ/mol} \).

Similar to the anode, cathode exchange current density of different fuel gases input under the same operating temperature can be predicted by using eqn. (4.42) once \( J_{O_2}^* \) is known.

### 4.3 Material conductivity

The conductivity of commonly used materials in the anode (nickel), cathode (LSM) and electrolyte (YSZ) are studied and expressed as only a function of temperature. The purpose is to make the model compact and reduce the unnecessary inputs.

#### 4.3.1 Electrical conductivity of anode material (nickel)

The most commonly used electron conducting material in the anode is nickel. The electrical conductivity of nickel can be expressed as a function of temperature (49).

\[ \sigma_{e,a}(T) = \frac{1}{\rho_{e,a}(T)} = \frac{1}{\rho_{e,a}(T_{\text{ref}})[1 + 0.006(T - T_{\text{ref}})]} \]  

(4.45)
The reference temperature is $T_{\text{ref}}=20^\circ\text{C}$; the resistivity of nickel at $20^\circ\text{C}$, $\rho_{\text{e,n}}(T_{\text{ref}}) = 6.99\times10^{-8}$ $\Omega\cdot\text{m}$.

### 4.3.2 Electrical conductivity of cathode material (LSM)

Lanthanum strontium manganite (LSM) is an oxide ceramic material with the general formula $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, where $x$ describes the doping level and is usually in the range of 10-20%.

The electrical conductivity of LSM measured at $P_{\text{O}_2}=1$ bar is listed as follows (50).

For $x\leq1/3$,

$$
\sigma_{e,c} = \left(\frac{2.8\times10^6}{T}\right)^{\left(\frac{-x^2 - x + 6(x^2 - 18x + 17)}{(17-x)^2}\right)} \exp\left\{ -\frac{E_{\text{act}}}{k_B T} \right\}
$$

(4.46)

Where $E_{\text{act}} = -0.59(3 + x) + 2.00\text{eV}$, $k_B = 8.617\times10^{-5}$ eV K$^{-1}$.

For $x\geq1/3$,

$$
\sigma_{e,c} = \left(\frac{2.8\times10^6}{T}\right)^{x(1-x)} \exp\left\{ -\frac{E_{\text{act}}}{k_B T} \right\}
$$

(4.47)

Where $E_{\text{act}} = -0.036(3 + x) + 0.16\text{eV}$.

The unit of eqn. (4.46) and eqn. (4.47) is in terms of S/cm.

![Figure 14](image.png)
Fig. 14 shows the how the electrical conductivity of LSM varies with oxygen partial pressure (50). It can be determined that the electrical conductivity remains almost unchanged for oxygen partial pressure in the range $-5<\log[P(O_2)/\text{bar}]<0$. Or in other words, $0.0067\text{bar}<P(O_2)<1\text{bar}$. In the cathode the most common fuel gas is air or pure oxygen, which means that partial pressure of oxygen is either 0.21 bar or 1 bar. By observing Fig. 14, it can be concluded that the conductivity of those different partial pressure keeps almost the same for doping level between 0.1 and 0.2. To sum up, the electrical conductivity keeps consistent no matter the input is air or pure oxygen.

### 4.3.3 Ionic conductivity of electrolyte material (YSZ)

YSZ ionic conductivity was studied by S.P.S. Badwal (4). In his experiments, the conductivity was measured by a 4 probe DC technique.

![Figure 15 Arrhenius plots for three different $Y_2O_3$ doping of $ZrO_2$ compositions](image)

The governing equation of ion conductivity in a crystalline solid electrolyte is given as (9)

$$
\sigma_{io} = \sigma_0 T^{-1} \exp \left( \frac{-E_{act}}{RT} \right)
$$

(4.48)

Where $\sigma_0$ (S·m$^{-1}$·K) is pre-exponential coefficient; $E_{act}$ (J/mol) is activation energy.

SOFC operation temperature is usually between 650°C and 900°C. Correspondingly, in the above Arrhenius plot x-axis is approximately from 8.5 to 10.8. The curve fitting of eqn. (4.48)
will give us two unknown variables, which are $\sigma_0$ and $E_{act}$. For different doping compositions, those two variables can be calculated as follows by least square method.

For 3 mol% Y$_2$O$_3$,

$$\sigma_0 = 2.47172 \times 10^7 \, S \cdot m^{-1} \cdot K$$
$$E_{act} = 8.2709 \times 10^4 \, J / mol$$

For 8 mol% Y$_2$O$_3$,

$$\sigma_0 = 2.94550 \times 10^7 \, S \cdot m^{-1} \cdot K$$
$$E_{act} = 7.7605 \times 10^4 \, J / mol$$

For 12 mol% Y$_2$O$_3$,

$$\sigma_0 = 5.87489 \times 10^7 \, S \cdot m^{-1} \cdot K$$
$$E_{act} = 8.9602 \times 10^4 \, J / mol$$

By applying the above curve fitting equations, YSZ ion conductivity for different Y$_2$O$_3$ doping compositions under different temperatures can be obtained as

<table>
<thead>
<tr>
<th>YSZ Ionic conductivity (Ω$^{-1}$·m$^{-1}$)</th>
<th>650°C</th>
<th>700°C</th>
<th>750°C</th>
<th>800°C</th>
<th>850°C</th>
<th>900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 mol% Y$_2$O$_3$</td>
<td>0.558</td>
<td>0.921</td>
<td>1.444</td>
<td>2.167</td>
<td>3.129</td>
<td>4.370</td>
</tr>
<tr>
<td>8 mol% Y$_2$O$_3$</td>
<td>1.294</td>
<td>2.064</td>
<td>3.138</td>
<td>4.577</td>
<td>6.441</td>
<td>8.789</td>
</tr>
<tr>
<td>12 mol% Y$_2$O$_3$</td>
<td>0.540</td>
<td>0.934</td>
<td>1.527</td>
<td>2.379</td>
<td>3.554</td>
<td>5.122</td>
</tr>
</tbody>
</table>

Next, the YSZ ion conductivity equation depends on both temperature and doping composition will be discussed. Eqn. (4.49) is the mathematical form.

$$\sigma = f(T,Y)$$

(4.49)
\( \sigma \) is the desired ion conductivity value (S/m); \( T \) is temperature (°C); \( Y \) is \( Y_2O_3 \) doping composition (mol %)

The function of \( \sigma \) is assumed to form a parabolic shape at both \( T-\sigma \) and \( Y-\sigma \) plane, thus the formula is built as

\[
\sigma = a_1 T^2 + a_2 Y^2 + a_3 TY + a_4 T + a_5 Y + a_6 
\] (4.50)

Here \( a_i \) are the coefficients that need to be calculated.

The least square algorithm is applied to fit function \( \sigma \). Based on Table 4, for each pair of \( T \) (temperature) and \( Y \) (\( Y_2O_3 \) doping composition), there is one corresponding ion conductivity value, \( g \). The purpose is to find one set of \( a_i \) that will make \( \sum_{i=1}^{n} (\sigma_i - g_i)^2 \) minimum. In order to do that, the gradient of \( \sum_{i=1}^{n} (\sigma_i - g_i)^2 \) must be equal to zero.

\[
\frac{\partial \sum_{i=1}^{n} (\sigma_i - g_i)^2}{\partial a_i} = 0, \ i = 1,2, ... 6 
\] (4.51)

After solving the above six equations, the value of each \( a_i \) can be calculated.

Then, the expression of conductivity can be expressed as

\[
\sigma = 6.046 \times 10^{-5} T^2 - 1.075 \times 10^{-1} Y^2 + 4.376 \times 10^{-4} TY - 7.610 \\
\times 10^{-2} T + 1.300 Y + 20.372 
\] (4.52)

which is plotted in the 3D contour below.
4.4 Relationships among volume fraction, number fraction and mass fraction

The relationship between volume fraction and number fraction is given by: (19)

\[
\varphi_e = \frac{n_e}{(1-n_e)\alpha^3 + n_e}
\]

(4.53)

\(\varphi\) is the volume fraction; \(n\) is the number fraction; \(\alpha\) is the radius ratio of ionic to electronic conductors. Subscript e represents electronic conductors.

The relations between volume fraction and mass fraction can be obtained by the following derivation.

\[
\begin{align*}
\varphi_e &= \frac{vol_e}{vol_e + vol_i} = \frac{m_e}{den_e} + \frac{m_i}{den_i} = \frac{m_e \cdot den_i}{m_e \cdot den_i + m_i \cdot den_e} \\
&= \frac{m_e}{m_e + m_i} \cdot \frac{den_i}{den_i} = \frac{\delta \cdot den_i}{\delta \cdot den_i + \delta \cdot den_e}
\end{align*}
\]

(4.54)
\( \phi \) is volume fraction; \( \text{vol} \) is volume; \( m \) is mass; \( \text{den} \) is density; \( \delta \) is mass fraction. Subscript \( e \) and \( i \) represent electronic and ionic conductors, respectively. It can be observed from the equation that if densities of the two materials are the same, their mass fraction is also identical.

4.5 Relationship between porosity and tortuosity
Since the materials in the model are assumed to be composed of binary spherical mixtures, the model proposed by Ricardo Dias [8] was adopted. His model is consistent with our assumption of treating the particles to be spheres. The tortuosity (\( \tau \)) is assumed to be inversely proportional to porosity (\( \varepsilon \)). The adjustable variable (n) in the correlation has been analyzed and determined so that it will fit most of the fuel cell cases.

\[
\tau = \frac{1}{\varepsilon^n} \tag{4.55}
\]

The following figure plots the data from the experiments of (51) for sphere mixtures. By applying eqn. (4.55) as the relationship, it can be observed from Fig. 17 that most of the data falls in the region where n value is in between 0.4 and 0.5.

![Figure 17 Dependence of the tortuosity on the packing porosity](image)

In order to further investigate the adjustable number, Ricardo (35) performed an experimental study for binary mixture spheres as shown in Fig. 18.
In the above figure, $D_l/D_s$ is the diameter ratio of large particle to small particle; $\Psi_D$ is volume fraction of large particles. It can be observed that for the particle size ratio less or equal to 3.33, the value of $n$ is approximately to be 0.5 regardless of the volume fraction. For most of the SOFCs, the sizes of ionic and electronic conductors are more or less the same, so it is reasonable to select the value of $n$ to be equal to 0.5 in the numerical model. However, if we happen to encounter large particle size ratio, the above plot will be used for selecting the appropriate $n$ value.

### 4.6 Relationship between porosity and particle size

#### 4.6.1 Relationship between mono-sized sphere particles and porosity

For mono-sized spherical particles, porosity has nothing to do with particle size. It only depends on the particle packing type. The following table lists porosity values under different particle packing types.

<table>
<thead>
<tr>
<th>packing type</th>
<th>coordination number</th>
<th>packing density</th>
<th>porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>face-centered cubic</td>
<td>12</td>
<td>0.7405</td>
<td>0.2595</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>0.7120</td>
<td>0.3880</td>
</tr>
<tr>
<td>tetragonal-prismoidal</td>
<td>10</td>
<td>0.7081</td>
<td>0.3819</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>0.6184</td>
<td>0.3866</td>
</tr>
<tr>
<td>body-centered cubic</td>
<td>8</td>
<td>0.6802</td>
<td>0.3198</td>
</tr>
<tr>
<td>orthorhombic</td>
<td>8</td>
<td>0.6046</td>
<td>0.3954</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>0.5612</td>
<td>0.4086</td>
</tr>
<tr>
<td>simple cubic</td>
<td>6</td>
<td>0.5296</td>
<td>0.4764</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.4031</td>
<td>0.5969</td>
</tr>
<tr>
<td>diamond</td>
<td>4</td>
<td>0.3401</td>
<td>0.6599</td>
</tr>
</tbody>
</table>
Porosity can also be calculated by the given coordination number. For example, if particles are packed in a simple unit cubic format, which means one particle is connected with 6 other particles, the porosity can be calculated as

\[ \varepsilon = 1 - \frac{4}{3} \pi \left( \frac{1}{2} \right)^3 = 0.4764 \]  

(4.56)

Figure 19 simple cubic packing

Another way to express porosity is to use packing density, which is the solid part in the porous structure, and can be calculated as \(1 - \varepsilon\).

**4.6.2 Relationship between bimodal mixtures of spherical particles and porosity**

For bimodal mixtures of spherical particles, S. Yerazunis (36) performed experimental study and plotted packing density vs. volume fraction as shown in Fig. 20.

Figure 20 packing density vs. composition for different particle size ratios

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The curve fitting equation of that experimental study is listed as

\[
1 - \varepsilon = \frac{0.64}{1 - \left(0.362 - 0.315 \left(\frac{D_s}{D_L}\right)^{0.7}\right) \varphi_L + 0.955 \left(\frac{D_s}{D_L}\right)^4 \left(\frac{\varphi_L^2}{1 - \varphi_L}\right)}
\]  

(4.57)

where \(\varphi\) is volume fraction. The subscript L means large particle size, S means small particle size.

Particle size ratio, number fraction, and porosity are the variables contained in eqn. (4.57). As long as two of them are provided, the last one can be calculated. This correlation is useful and can be used practical situations. For example, in the experimental study, once the volume fraction and particle sizes of electron conducting and ion conducting particles are determined, the porosity can be calculated using eqn. (4.57) without any measurement needed.

It can be deduced from the experimental data that the porosity value is trying to approach 0.36 as particle size ratio is getting closer to 1. Therefore, we assume that when ionic particle size is equal to electronic particle size, the porosity is set to be 0.36. It is obvious that under that particular circumstance bimodal mixtures turn into mono-sized particles. Table 5 lists the porosity range for different packing of mono-sized particles, which is from 0.26 to 0.66. The assumption we made is reasonable because 0.36 falls in between that range.
Chapter 5 Model Validation
In order to determine if the mathematical model and correlations of microstructure parameters have the potential to accurately describe the cell performance, model validation needs to be carried out. Three experiments are selected to facilitate the comparison between mathematical simulation and experimental data. All the selected experiments have different perspectives on investigating the cell performance. It will demonstrate a strong compatibility and proper selection of sub model correlations for our model if there is good agreement between the mathematical and experimental data.

There will be two types of inputs in the model: operational inputs and physical inputs. The operational inputs of the model include operating temperature and pressure, fuel gases composition, and current density. The physical inputs include exchange current density, thickness of anode, cathode and electrolyte, volume fraction (or mass fraction) of electronic and ionic conductors, particle size of electronic and ionic conductors, porosity, and tortuosity.

5.1 Case No.1
The first experimental data selected is from S.P. Jiang (52). The objective of the experiment is to investigate the effect of impregnation of different volume fractions of nano-sized YSZ particles into nickel anodes on the electrode behavior for the hydrogen oxidation reaction. The following table lists the parameters provided by the paper.
## Table 6 values of input parameters used in the model

<table>
<thead>
<tr>
<th>Parameter (provided by paper)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Temperature</td>
<td>1073K</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.0 atm</td>
</tr>
<tr>
<td>Anode thickness</td>
<td>30μm</td>
</tr>
<tr>
<td>Electrolyte thickness</td>
<td>1mm</td>
</tr>
<tr>
<td>Gas fuel in anode</td>
<td>97% H₂ (3% H₂O)</td>
</tr>
<tr>
<td>Volume fraction of NiO/YSZ</td>
<td>Ni: 100%/0%</td>
</tr>
<tr>
<td></td>
<td>Ni+2.7mg/cm² YSZ: 83%/17%</td>
</tr>
<tr>
<td></td>
<td>Ni+4.0mg/cm² YSZ: 79%/21%</td>
</tr>
<tr>
<td>Porosity</td>
<td>30%</td>
</tr>
<tr>
<td>YSZ particle size</td>
<td>0.1-0.3 μm</td>
</tr>
</tbody>
</table>

In order to solve this problem using the developed numerical model, Ni particle size, tortuosity, and anode exchange current density need to be determined.

Let us take Ni+4.0mg/cm² YSZ for example. The volume fraction of Ni/YSZ for Ni+4.0mg/cm² YSZ is given as 79%/21%. Combining the eqn. (4.10) - (4.13) from the coordination number model and volume fraction eqn. (4.53), the upper and lower bounds of particle size ratio and number fraction can be found in Table 7. The values within the two bounds will maintain the threshold of the same types of particles (electronic conductors and ionic conductors) connecting with each other through the electrodes and hence ensure good conductivity.
Table 7 upper and lower bounds for particle size ratio and electronic volume fraction

<table>
<thead>
<tr>
<th>$\varphi_e$ =0.79</th>
<th>Lower bound</th>
<th>Upper bound</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.13</td>
<td>0.53</td>
</tr>
<tr>
<td>$n_e$</td>
<td>0.09</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Substituting the porosity value and electronic volume fraction into eqn. (4.57) will give us particle size ratio $\alpha$=0.4. This number is within the range of particle size ratio calculated from coordination number model. By choosing the average YSZ particle size, which is 0.2 $\mu$m, Ni particle size can be derived as 0.5 $\mu$m. Note that the sensitivity study will be done to analyze the effect of the particle size in the next chapter. In addition, from eqn. (4.53) the number fraction of electronic conductors can also be calculated as $n_e$=0.19

Tortuosity can be obtained from eqn. (4.55). Since the particle ratio is less than 3.33, it is reasonable to set $n$ equals to 0.5.

$$\tau = \frac{1}{\varepsilon^n} = \frac{1}{0.3^{0.5}} = 1.826$$ (5.1)

The B-V equation can be simplified when activation overpotential is very small, for example, no external loads. The cell will be under this circumstance when the exchange current density is measured. A Taylor series expansion of exponential terms in B-V equations can be expressed as

$$\exp\left(\frac{nF\eta_{act}}{RT}\right) \approx 1 + \frac{nF\eta_{act}}{RT}$$ for small $\frac{nF\eta_{act}}{RT}$ value. Therefore, the B-V equation can be reduced as

$$J_0 = \frac{J}{\exp\left(\frac{nF\eta_{act}}{RT}\right) - \exp\left(\frac{(1-n)F\eta_{act}}{RT}\right)} = \frac{J}{1 + \frac{nF\eta_{act}}{RT} - (1 + \frac{(1-n)F\eta_{act}}{RT})}$$ (5.2)

$R_{ct}$ is charge transfer resistance due to electrochemical reactions and the paper mentioned that hydrogen oxidation on nickel anodes at high frequencies is most likely related to the charge-
transfer reaction at the TPB region. In contrast to the behavior of the high-frequency arc, impregnation of nano-YSZ phase has no effect on the characteristic frequency of the low-frequency arc.

Table 8 Fitted impedance parameters for hydrogen oxidation on Ni-YSZ anodes

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Temperature (°C)</th>
<th>Low-frequency arc $R_L$ (Ω cm²)</th>
<th>High-frequency arc $R_{H}$ (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>900</td>
<td>0.13</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.18</td>
<td>3.25</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>0.31</td>
<td>10.41</td>
</tr>
<tr>
<td>2.7 mg cm⁻² YSZ+Ni</td>
<td>900</td>
<td>0.34</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.61</td>
<td>2.02</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>1.26</td>
<td>6.81</td>
</tr>
<tr>
<td>4.0 mg cm⁻² YSZ+Ni</td>
<td>900</td>
<td>0.29</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>0.48</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>0.65</td>
<td>2.46</td>
</tr>
</tbody>
</table>

Therefore, based on Table 8 and Fig. 21 provided by the paper, the anode exchange current density at 800 °C can be expressed as

$$\begin{aligned}
J_{0,a} &= \frac{RT}{nF_{act}} = \frac{8.314 J \cdot K^{-1} \cdot mol^{-1} \times 1073K}{2 \times 96485C \cdot mol^{-1} \times 0.71 \Omega \cdot cm^2} = 0.0651A \cdot cm^{-2} \\
\end{aligned}$$

(5.3)

Since all the parameters applied in the model have been calculated, the mathematical simulation can be performed. From the figure below, it can be seen that the numerical results and experimental data agree reasonably well with each other.
5.2 Case No.2
The second experiment comes from Kim et al (53). The objective of this experiment was to investigate the performance and durability of Ni-coated YSZ anodes for intermediate temperature solid oxide fuel cells.
### Table 9 input parameters in the experiment

<table>
<thead>
<tr>
<th>Parameter (provided by paper)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Temperature</td>
<td>700°C / 800°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.0 atm</td>
</tr>
<tr>
<td>Anode thickness</td>
<td>1200μm</td>
</tr>
<tr>
<td>Electrolyte thickness</td>
<td>7μm</td>
</tr>
<tr>
<td>Cathode thickness</td>
<td>30μm</td>
</tr>
<tr>
<td>Gas fuel in anode</td>
<td>97% H₂ (3% H₂O)</td>
</tr>
<tr>
<td>Gas fuel in cathode</td>
<td>air</td>
</tr>
<tr>
<td>Volume fraction of NiO/YSZ</td>
<td>40%/60%</td>
</tr>
<tr>
<td>Mass fraction of LSM/YSZ</td>
<td>50%/50%</td>
</tr>
<tr>
<td>Porosity</td>
<td>40%</td>
</tr>
<tr>
<td>NiO particle size</td>
<td>20-30nm</td>
</tr>
<tr>
<td>YSZ particle size</td>
<td>&lt;300nm</td>
</tr>
</tbody>
</table>

LSM particle size, anode exchange current density, and cathode exchange current density will be calculated by using the sub model correlation and EIS plot from experimental measurement.

Let me take 700°C case as an example to show the procedure of calculation. The same approach will be used for the 800°C operating temperature case. Regarding the anode and cathode exchange current density, they can be figured by the EIS plots as shown in Fig. 23. For common SOFCs, the low frequency arc will represent the anode charge transfer resistance and high frequency arc will represent the cathode charge transfer resistance. Therefore, the anode and cathode exchange current can be approximate as follows.

\[
i_{0,a} = \frac{RT}{nFR_{ct,a}} = \frac{8.314 J \cdot K^{-1} \cdot mol^{-1} \times 973 K}{2 \times 96485 C \cdot mol^{-1} \times 0.07 \Omega \cdot cm^{2}} = 0.5989 A \cdot cm^{-2}
\]
\[
i_{0,c} = \frac{RT}{nF R_{\text{ct},c}} = \frac{8.314 J \cdot K^{-1} \cdot \text{mol}^{-1} \times 973 K}{2 \times 96485 \text{C} \cdot \text{mol}^{-1} \times 0.26 \Omega \cdot \text{cm}^2} = 0.1612 \text{A} \cdot \text{cm}^{-2}
\]

Figure 23 EIS plots of the SOFC at 700°C and 800°C

In the anode, the porosity is given and the particle size ratio and tortuosity can be calculated by submodel correlations. It turns out be that the particle size ratio is equal to 0.718 by applying eqn. (4.57) and this value falls within the upper and lower limits of the coordination number model. The tortuosity can also be calculated as 1.581 from eqn. (4.55). In cathode, the particle size ratio and tortuosity can be calculated as 0.71 and 1.581, respectively using the same approach as the anode.

The anode electron particle size is within 20 to 30 µm based on the information provided by the paper. Once we know the particle size ratio, the ionic particle, YSZ, can be obtained to be 39 µm by assuming the Ni particle size to be 25 µm, which is the average of the given bounds. Again the sensitivity study will be done to analyze the effect of the particle size. In the cathode, the particle size of LSM can be determined as 27.7 µm by the calculated particle size of YSZ from anode.
After that, the I-V curve can be calculated by applying the mathematical model. Again, a good consistency between mathematical results and experimental data can be seen from Fig. 24.

![Figure 24 Comparison between mathematical calculation and experimental data](image)

5.3 Case No.3
The last experiment data is from S. P. Jiang (12). The objective of his experiment is to examine the influence of sintering temperature on cell performance by using an anode half-cell.

Table 10 Input parameters provided by the paper

<table>
<thead>
<tr>
<th>Parameter (provided by paper)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Temperature</td>
<td>1273 K</td>
</tr>
<tr>
<td>Pressure</td>
<td>1.0 atm</td>
</tr>
<tr>
<td>Anode thickness</td>
<td>20-40μm</td>
</tr>
<tr>
<td>Electrolyte thickness</td>
<td>0.9±0.03mm</td>
</tr>
<tr>
<td>Gas fuel in anode</td>
<td>97% H₂ (3% H₂O)</td>
</tr>
<tr>
<td>Volume fraction of NiO/YSZ</td>
<td>50%/50%</td>
</tr>
<tr>
<td>NiO particle size</td>
<td>Approximate from SEM</td>
</tr>
<tr>
<td>YSZ particle size</td>
<td>Approximate from SEM</td>
</tr>
<tr>
<td>Anode exchange current density</td>
<td>Calculated based on charge transfer resistance</td>
</tr>
</tbody>
</table>
The paper provided SEM pictures of the anode micro structure at four different sintering temperatures. According to Fig. 25, the electronic and ionic particle size can be approximated by counting pixels from the SEM pictures. The green and red circles are used to denote Ni and YSZ particle size, respectively. For 1300°C, YSZ particle size can be approximate as 0.5μm, while Ni is about 2μm. Based on the coordination number model, the minimum particle size ratio of ion and electron particle in this volume fraction composition is 0.5. The model cannot predict the cell performance under this microstructure configuration because the percolation threshold will not be satisfied due to this extremely small particle size ratio. However, we can still use the limit particle size ratio to calculate and plot I-V curve just to compare with the experimental data. Theoretically, the mathematical results should not match the experimental data very well. Same conclusion can be drawn for 1350 °C sintering temperature because of the extreme particle size difference of two types of conductors (0.6μm for Ni, and 2μm for YSZ). For 1400 °C, the Ni and YSZ particle size can be estimated as 1.25μm and 1.5μm, respectively. For 1500 °C, both Ni and YSZ particle size can be estimated as 2μm. The particle size ratios are within the percolation threshold for 1400 and 1500 °C sintering temperature cases and numerical simulation can be applied.
Figure 25 SEM picture of Ni/8 mol% Y2O3-ZrO2 (Ni/TZ8Y) cermet anodes sintered at (a) 1300, (b) 1350, (c) 1400, (d) 1500 °C after fuel cell testing

Let us take 1400 °C sintering temperature as an example. Once the particle sizes of electronic and ionic conductors are figured out, the porosity can be obtained by using the sub model correlation, eqn. (4.57), which in this case is 0.401. The way of calculating tortuosity in this case is a little different from the previous ones. Since the paper provides the value of anode ohmic resistance, which is 1.03 Ωcm² for 1400°C sintering temperature, eqn. (3.5) can be applied to estimate tortuosity, and the tortuosity turns out to be 12.086. However, if we still insist to use the porosity and tortuosity correlation, the tortuosity would be estimated as 1.581. Use of this number will result in the calculated anode ohmic resistance to be one order of magnitude less the actual value measured by the author. It can be interpreted as: a large tortuosity value will cause ion particles take too many detours from electrode-electrolyte surface to reach the fuel channel. Therefore, it will reduce the effective ionic conductivity and result in a relative large ohmic resistance like this case.
Fig. 26 shows the comparison of model outcome vs. experimental data. It can be seen that for 1400 and 1500 °C sintering temperatures, the mathematical results matched reasonably well with experimental data. However, for the rest of the two sintering temperatures, there is a noticeable difference between model results and experimental data even with the limiting particle size ratio applied. This result is anticipated because the numerical model is trying to calculate the scenario that we artificially make particle size ratio to satisfy the percolation threshold. However, in reality the particle size ratio falls outside the percolation threshold range. Therefore, it is logical to see that the cell performance of experimental data is even worse than the one calculated from numerical model. Relatively low sintering temperature, such as 1300 and 1350 °C in this case will result in a larger particle size difference between ion and electron conductors after the sintering process. As mentioned before, the mathematical model is built based on a coordination number model, which ensures the connections of the two types of conductors are above the percolation threshold and hence provide smooth transportation of electrons and ions within the electrodes. If the particle ratio is outside the percolation limit, the percolation threshold will not be satisfied and the cell performance will be extremely poor due to bad connections of ion and electron conductors throughout the anode. As indicated from the experimental data, the terminal voltage drops rapidly and reaches zero at a very small current density value. This validation case also proves that applying the coordination number model, together with percolation threshold theory will facilitate the prediction of variation tendency of cell performance.
This sensitivity study is aimed at exploring the effect of micro structural parameters on model predictions. The ultimate goal is to be able to utilize a mathematical simulation to predict SOFC performance based on micro-scale cell structure. Therefore, it is imperative to understand which parameters play a significant role in the model predictions. For the parameters with noticeable sensitivity, they should be highlighted and noted for accurate measurement during experimental analysis. In contrast, for the parameters with trivial sensitivity the significance may be neglected and perhaps conventional values may be used in the analysis. In the end, a sensitivity table of each parameter will be provided so that model users can make their own judgment on which error range is affordable to them and then determine if the measurement is necessary for that particular parameter.

In order to perform the sensitivity studies, the first experiment in the model validation chapter is selected as a baseline. This is because the experiment has been tested and validated indicating a good consistency with the results from the mathematical model. Also, it is fabricated as an anode half-cell only, so there is no need to worry about differentiating effects between the anode and cathode. The desired variable will be varied to test the sensitivity and the rest of the parameters will be obtained from the experiment validation case.
6.1 Sub Model Correlations

6.1.1 Tortuosity vs. Porosity
There are two places containing the tortuosity parameter in the model. They are related to ohmic resistance in electrode and mass diffusion. First of all, based on eqn. (3.5), it can be found that increasing tortuosity will result in a growing of effective ionic resistivity and hence worsen the performance of SOFCs. Physically, if tortuosity increases, the transportation rate of ionic conductors will be reduced due to a relatively long and twisting path from one end of the electrode to the other end. Therefore, the effective ion resistivity is expected to increase. Since electronic conductivity is several orders of magnitude higher than the ionic conductivity, ohmic overpotential is primarily dominated by the resistance due to ionic conductors. That is why we are mainly interested in effective ionic resistivity. Secondly, the parameter of tortuosity also appears in the effective diffusivity to impact the gas diffusion process. From the eqn. (3.19), it can be seen that the increase of tortuosity will result in a decrease in effective diffusion coefficient. In that case, a larger tortuosity will lead to a lower concentration of fuel at electrode-electrolyte interface and hence increase the concentration overpotential. This is represented in the mathematical model as well. The concentration gradient will drop fast due to a large tortuosity in eqn. (3.31) and thus increase the concentration overpotential due to eqn. (1.6).

For this particular case, the porosity is given as 30%. The idea is to vary the unknown parameter n from eqn. (4.59) in order to find out how tortuosity impacts the model. Table 11, Table 12, and Fig. 28 show comparison among different tortuosity values. The n-value is chosen to vary from 0.01 to 1 for 79%/21% Ni/YSZ, and from 0.01 to 1.3 for 83%/17% Ni/YSZ, respectively. Tortuosity can be calculated by using eqn. (4.59). After that, each tortuosity value is applied into the model to calculate the overall overpotential. The last column in Table 11 and Table 12 is to compare the overpotential value calculated from the corresponding n values with experimental data for two different volume fractions of Ni and YSZ. In this case, the experiment data is represented by the mathematical model with n-value equal to 0.5. The purpose is to explore how the n-value affects the overall overpotential. As shown in Table 11 and Table 12, the range of n-value is proper selected so that the overall percentage difference is within around ±15%. After the range is determined, the domain will be averagely divided into 20 sections plus one additional point, the n-value equals to 0.5. And the same strategy will be applied for selecting the ranges and points for the rest of the testing variables. In addition, Fig. 28 converts the table into
an x-y plot, the dashed region indicates the range of ±5% difference of overpotential by compared with the experimental data. In order to maintain the change to be within 5% of the error bars, the range of n-value is approximately from 0.275 to 0.685 for 79%/21% Ni/YSZ, and from 0.08 to 0.79 for 83%/17% Ni/YSZ, respectively. Correspondingly, the tortuosity value and percentage range is about 1.4 - 2.25 (-23.3% - 33.7%) for 79%/21% Ni/YSZ, and 1.1 - 2.5 (-39.6% - 36.9%) for 83%/17% Ni/YSZ. It can be seen that the tortuosity value can vary over a relatively large range (~ +/-40%) while having a small impact on the predicted overpotential (+/- 5%). This indicates that the sensitivity of this factor is not that significant.
Table 11 comparison among different tortuosity for 79%/21% Ni/YSZ

<table>
<thead>
<tr>
<th>n-value</th>
<th>tortuosity</th>
<th>( \frac{\sum_{i=1}^{m} \text{overp@n_value} - \text{overp@n = 0.5}}{\text{overp@n = 0.5}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.010</td>
<td>1.012</td>
<td>-10.037%</td>
</tr>
<tr>
<td>0.062</td>
<td>1.078</td>
<td>-9.186%</td>
</tr>
<tr>
<td>0.114</td>
<td>1.147</td>
<td>-8.290%</td>
</tr>
<tr>
<td>0.166</td>
<td>1.222</td>
<td>-7.345%</td>
</tr>
<tr>
<td>0.218</td>
<td>1.301</td>
<td>-6.350%</td>
</tr>
<tr>
<td>0.271</td>
<td>1.385</td>
<td>-5.302%</td>
</tr>
<tr>
<td>0.323</td>
<td>1.475</td>
<td>-4.200%</td>
</tr>
<tr>
<td>0.375</td>
<td>1.570</td>
<td>-3.039%</td>
</tr>
<tr>
<td>0.427</td>
<td>1.672</td>
<td>-1.819%</td>
</tr>
<tr>
<td>0.479</td>
<td>1.780</td>
<td>-0.536%</td>
</tr>
<tr>
<td>0.500</td>
<td>1.826</td>
<td>0.000%</td>
</tr>
<tr>
<td>0.531</td>
<td>1.895</td>
<td>0.811%</td>
</tr>
<tr>
<td>0.583</td>
<td>2.018</td>
<td>2.226%</td>
</tr>
<tr>
<td>0.635</td>
<td>2.149</td>
<td>3.711%</td>
</tr>
<tr>
<td>0.687</td>
<td>2.288</td>
<td>5.268%</td>
</tr>
<tr>
<td>0.739</td>
<td>2.436</td>
<td>6.901%</td>
</tr>
<tr>
<td>0.792</td>
<td>2.594</td>
<td>8.612%</td>
</tr>
<tr>
<td>0.844</td>
<td>2.761</td>
<td>10.403%</td>
</tr>
<tr>
<td>0.896</td>
<td>2.940</td>
<td>12.278%</td>
</tr>
<tr>
<td>0.948</td>
<td>3.131</td>
<td>14.239%</td>
</tr>
<tr>
<td>1.000</td>
<td>3.333</td>
<td>16.288%</td>
</tr>
<tr>
<td>n value</td>
<td>tortuosity</td>
<td>$\sum_{i=1}^{n} \frac{\overline{r_p(n, value)} - \overline{r_p(n)} = 0.5}{\overline{r_p(n)} = 0.5}$</td>
</tr>
<tr>
<td>---------</td>
<td>-----------</td>
<td>--------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>0.010</td>
<td>1.012</td>
<td>-6.035%</td>
</tr>
<tr>
<td>0.078</td>
<td>1.098</td>
<td>-5.349%</td>
</tr>
<tr>
<td>0.146</td>
<td>1.192</td>
<td>-4.618%</td>
</tr>
<tr>
<td>0.214</td>
<td>1.293</td>
<td>-3.841%</td>
</tr>
<tr>
<td>0.282</td>
<td>1.404</td>
<td>-3.015%</td>
</tr>
<tr>
<td>0.349</td>
<td>1.523</td>
<td>-2.138%</td>
</tr>
<tr>
<td>0.417</td>
<td>1.653</td>
<td>-1.208%</td>
</tr>
<tr>
<td>0.485</td>
<td>1.794</td>
<td>-0.222%</td>
</tr>
<tr>
<td>0.500</td>
<td>1.826</td>
<td>0.000%</td>
</tr>
<tr>
<td>0.553</td>
<td>1.946</td>
<td>0.823%</td>
</tr>
<tr>
<td>0.621</td>
<td>2.112</td>
<td>1.930%</td>
</tr>
<tr>
<td>0.689</td>
<td>2.292</td>
<td>3.101%</td>
</tr>
<tr>
<td>0.757</td>
<td>2.487</td>
<td>4.340%</td>
</tr>
<tr>
<td>0.825</td>
<td>2.699</td>
<td>5.650%</td>
</tr>
<tr>
<td>0.893</td>
<td>2.929</td>
<td>7.036%</td>
</tr>
<tr>
<td>0.961</td>
<td>3.179</td>
<td>8.500%</td>
</tr>
<tr>
<td>1.028</td>
<td>3.449</td>
<td>10.047%</td>
</tr>
<tr>
<td>1.096</td>
<td>3.743</td>
<td>11.681%</td>
</tr>
<tr>
<td>1.164</td>
<td>4.062</td>
<td>13.407%</td>
</tr>
<tr>
<td>1.232</td>
<td>4.408</td>
<td>15.229%</td>
</tr>
<tr>
<td>1.300</td>
<td>4.783</td>
<td>17.151%</td>
</tr>
</tbody>
</table>
6.1.2 Particle size ratio vs. porosity

From the mass transfer governing equation and active surface area formula, it can be found that both mass diffusion and electrochemical reaction depend on the particle size ratio. Let us take 79%/21% Ni/YSZ as an example, the ion and electron particle size ratio need to be within 0.13 to 0.53 determined by coordination number model in order to maintain the threshold. Table 13 shows the proper range of particle size ratio. It can be found that as particle size ratio increases, the active surface area decreases and results in a growth of overpotential. It is because as particle size ratio gets smaller, the size difference of two types of conductors is expected to be more significant. Therefore, there will be more of the smaller particles falling in the porous space among large particles to increase the reaction sites at TPB region and hence improve the cell performance. The particle size ratio impact of gas diffusion is not significant due to a relative thin anode thickness. For both of the two volume fractions, the particle size ratio is strongly sensitive. As shown in Figure 29 if the overpotential difference is expected to be within 5% (dashed line region), the range of particle size ratio and its percentage needs to be 0.386 - 0.414 (-3.5% - 3.5%) for 79%/21% Ni/YSZ, and 0.376 - 0.385 (-1.3% - 1.1%) for 83%/17% Ni/YSZ.
Table 13 comparison among different particle size ratio for 79%/21% Ni/YSZ

<table>
<thead>
<tr>
<th>Particle size ratio $\alpha$</th>
<th>Active surface area</th>
<th>$\sum_{l=1}^m \frac{overp@\alpha_{value} - overp@\alpha = 0.4}{overp@\alpha = 0.4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.350</td>
<td>3.03E+05</td>
<td>-16.946%</td>
</tr>
<tr>
<td>0.355</td>
<td>2.96E+05</td>
<td>-15.544%</td>
</tr>
<tr>
<td>0.359</td>
<td>2.89E+05</td>
<td>-14.106%</td>
</tr>
<tr>
<td>0.364</td>
<td>2.82E+05</td>
<td>-12.631%</td>
</tr>
<tr>
<td>0.369</td>
<td>2.75E+05</td>
<td>-11.116%</td>
</tr>
<tr>
<td>0.374</td>
<td>2.68E+05</td>
<td>-9.559%</td>
</tr>
<tr>
<td>0.378</td>
<td>2.61E+05</td>
<td>-7.957%</td>
</tr>
<tr>
<td>0.383</td>
<td>2.55E+05</td>
<td>-6.307%</td>
</tr>
<tr>
<td>0.388</td>
<td>2.48E+05</td>
<td>-4.606%</td>
</tr>
<tr>
<td>0.393</td>
<td>2.42E+05</td>
<td>-2.850%</td>
</tr>
<tr>
<td>0.397</td>
<td>2.35E+05</td>
<td>-1.035%</td>
</tr>
<tr>
<td>0.400</td>
<td>2.32E+05</td>
<td>0.000%</td>
</tr>
<tr>
<td>0.402</td>
<td>2.29E+05</td>
<td>0.843%</td>
</tr>
<tr>
<td>0.407</td>
<td>2.23E+05</td>
<td>2.789%</td>
</tr>
<tr>
<td>0.412</td>
<td>2.17E+05</td>
<td>4.809%</td>
</tr>
<tr>
<td>0.416</td>
<td>2.11E+05</td>
<td>6.910%</td>
</tr>
<tr>
<td>0.421</td>
<td>2.05E+05</td>
<td>9.099%</td>
</tr>
<tr>
<td>0.426</td>
<td>1.99E+05</td>
<td>11.383%</td>
</tr>
<tr>
<td>0.431</td>
<td>1.93E+05</td>
<td>13.774%</td>
</tr>
<tr>
<td>0.435</td>
<td>1.87E+05</td>
<td>16.282%</td>
</tr>
<tr>
<td>0.440</td>
<td>1.81E+05</td>
<td>18.919%</td>
</tr>
</tbody>
</table>
Table 14 comparison among different particle size ratio for 83%/17% Ni/YSZ

<table>
<thead>
<tr>
<th>Particle size ratio $\alpha$</th>
<th>Active surface area</th>
<th>$\sum_{i=1}^{m} \frac{overp@\alpha_{-value} - overp@\alpha = 0.382}{overp@\alpha = 0.382}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.340</td>
<td>3.15E+05</td>
<td>-28.625%</td>
</tr>
<tr>
<td>0.343</td>
<td>3.06E+05</td>
<td>-27.160%</td>
</tr>
<tr>
<td>0.346</td>
<td>2.97E+05</td>
<td>-25.624%</td>
</tr>
<tr>
<td>0.349</td>
<td>2.88E+05</td>
<td>-24.008%</td>
</tr>
<tr>
<td>0.353</td>
<td>2.78E+05</td>
<td>-22.303%</td>
</tr>
<tr>
<td>0.356</td>
<td>2.69E+05</td>
<td>-20.498%</td>
</tr>
<tr>
<td>0.359</td>
<td>2.60E+05</td>
<td>-18.580%</td>
</tr>
<tr>
<td>0.362</td>
<td>2.51E+05</td>
<td>-16.534%</td>
</tr>
<tr>
<td>0.365</td>
<td>2.41E+05</td>
<td>-14.340%</td>
</tr>
<tr>
<td>0.368</td>
<td>2.32E+05</td>
<td>-11.974%</td>
</tr>
<tr>
<td>0.372</td>
<td>2.22E+05</td>
<td>-9.407%</td>
</tr>
<tr>
<td>0.375</td>
<td>2.12E+05</td>
<td>-6.600%</td>
</tr>
<tr>
<td>0.378</td>
<td>2.03E+05</td>
<td>-3.505%</td>
</tr>
<tr>
<td>0.381</td>
<td>1.92E+05</td>
<td>-0.055%</td>
</tr>
<tr>
<td>0.382</td>
<td>1.89E+05</td>
<td>0.000%</td>
</tr>
<tr>
<td>0.384</td>
<td>1.82E+05</td>
<td>3.841%</td>
</tr>
<tr>
<td>0.387</td>
<td>1.71E+05</td>
<td>8.312%</td>
</tr>
<tr>
<td>0.391</td>
<td>1.59E+05</td>
<td>13.552%</td>
</tr>
<tr>
<td>0.394</td>
<td>1.46E+05</td>
<td>19.865%</td>
</tr>
<tr>
<td>0.397</td>
<td>1.33E+05</td>
<td>27.774%</td>
</tr>
<tr>
<td>0.400</td>
<td>1.17E+05</td>
<td>38.283%</td>
</tr>
</tbody>
</table>
6.2 Direct Input Parameters

6.2.1 Particle Size

There are two places containing particle size in the model. The first one is related with the mass transfer process. Eqn. (3.16) indicates that the diffusivity is proportional to the particle size. After combining with Eqn. (3.16) and Eqn. (1.6), it can been determined that as particle size increases, fuel gas concentration gradient will drop slowly and hence improve the cell performance by reducing the concentration overpotential. This is because larger particle size will provide relative more vacant to fasten the gas diffusion. Another place in the model related with particle size is active surface area. As shown in eqn. (4.15), large particle size will reduce the active surface area so that activation overpotential will increase. In order to reduce the activation overpotential, the TPB region of reaction site is expected to get as large as possible. However, there will be less reaction surface area for a larger particle size as compared with small one. Correspondingly, it can be found that activation overpotential reduces as particle size decreases from Table 14. The effect of concentration overpotential in this case is subtle because of a thin anode thickness.

Table 15, Table 16, and Figure 30 show the results. After inputting different particle sizes into the model, it turns out that for 79%/21% volume fraction of Ni/YSZ, the best match with experimental data is when ion particle size is equal to 0.27µm after applying least square method. Similarly, the closet match is 0.17µm for 83%/17% volume fraction of Ni/YSZ. As indicated in
Figure 30, if the overpotential difference is considered to be within ±5% (as indicated within the dashed line), the change of range of particle size is within 0.02µm, which is from −7.4% to 7.4% in terms of percentage for 79%/21% volume fraction of Ni/YSZ. On the other hand, the ion particle size needs to be between from 0.156µm to 0.183µm (or −8.2% - 7.6%) for 83%/17% volume fraction of Ni/YSZ. This factor has a strong sensitivity in the model. Thus this parameter is extremely important in the model input and precise measurement is required. Also, the ion particle range provided by the paper, which varies from 0.1-0.3µm, is not good enough for a mathematical model to predict a solution within +/- 5%.

**Table 15 comparisons of particle sizes for two different composition of 79%/21% Ni/YSZ**

<table>
<thead>
<tr>
<th>Ionic particle size (µm)</th>
<th>∑_{i=1}^{m} \frac{overp@r - overp@r = 0.27}{overp@r = 0.27} m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.210</td>
<td>-15.958%</td>
</tr>
<tr>
<td>0.215</td>
<td>-14.670%</td>
</tr>
<tr>
<td>0.219</td>
<td>-13.388%</td>
</tr>
<tr>
<td>0.224</td>
<td>-12.110%</td>
</tr>
<tr>
<td>0.229</td>
<td>-10.837%</td>
</tr>
<tr>
<td>0.234</td>
<td>-9.569%</td>
</tr>
<tr>
<td>0.238</td>
<td>-8.306%</td>
</tr>
<tr>
<td>0.243</td>
<td>-7.047%</td>
</tr>
<tr>
<td>0.248</td>
<td>-5.793%</td>
</tr>
<tr>
<td>0.253</td>
<td>-4.543%</td>
</tr>
<tr>
<td>0.257</td>
<td>-3.298%</td>
</tr>
<tr>
<td>0.262</td>
<td>-2.058%</td>
</tr>
<tr>
<td>0.267</td>
<td>-0.822%</td>
</tr>
<tr>
<td>0.270</td>
<td>0.000%</td>
</tr>
<tr>
<td>0.272</td>
<td>0.410%</td>
</tr>
<tr>
<td>0.276</td>
<td>1.637%</td>
</tr>
<tr>
<td>0.281</td>
<td>2.860%</td>
</tr>
<tr>
<td>0.286</td>
<td>4.078%</td>
</tr>
<tr>
<td>0.291</td>
<td>5.292%</td>
</tr>
<tr>
<td>0.295</td>
<td>6.502%</td>
</tr>
<tr>
<td>0.300</td>
<td>7.707%</td>
</tr>
</tbody>
</table>
Table 16 comparisons of particle sizes for two different composition of 83%/17% Ni/YSZ

<table>
<thead>
<tr>
<th>Ionic particle size (μm)</th>
<th>$\sum_{i=1}^{m} \frac{\text{overlap} @ r \ - \ \text{overlap} @ r = 0.17}{\text{overlap} @ r = 0.17}$ m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.130</td>
<td>-16.634%</td>
</tr>
<tr>
<td>0.135</td>
<td>-14.580%</td>
</tr>
<tr>
<td>0.139</td>
<td>-12.550%</td>
</tr>
<tr>
<td>0.144</td>
<td>-10.543%</td>
</tr>
<tr>
<td>0.149</td>
<td>-8.558%</td>
</tr>
<tr>
<td>0.154</td>
<td>-6.595%</td>
</tr>
<tr>
<td>0.158</td>
<td>-4.655%</td>
</tr>
<tr>
<td>0.163</td>
<td>-2.735%</td>
</tr>
<tr>
<td>0.168</td>
<td>-0.837%</td>
</tr>
<tr>
<td>0.170</td>
<td>0.000%</td>
</tr>
<tr>
<td>0.173</td>
<td>1.041%</td>
</tr>
<tr>
<td>0.177</td>
<td>2.898%</td>
</tr>
<tr>
<td>0.182</td>
<td>4.736%</td>
</tr>
<tr>
<td>0.187</td>
<td>6.554%</td>
</tr>
<tr>
<td>0.192</td>
<td>8.353%</td>
</tr>
<tr>
<td>0.196</td>
<td>10.134%</td>
</tr>
<tr>
<td>0.201</td>
<td>11.896%</td>
</tr>
<tr>
<td>0.206</td>
<td>13.640%</td>
</tr>
<tr>
<td>0.211</td>
<td>15.367%</td>
</tr>
<tr>
<td>0.215</td>
<td>17.076%</td>
</tr>
<tr>
<td>0.220</td>
<td>18.768%</td>
</tr>
</tbody>
</table>
6.2.2 Porosity

All three different overpotentials are a function of porosity. Eqn. (3.5) indicates that the ohmic resistance within the electrodes will increase as porosity increases. On the other hand, it can be concluded from eqn. (3.15) that a larger porosity will make the effective diffusivity increase. Thus, fuel gas concentration gradient will drop slowly as indicated from eqn. (3.31) and result in a relatively larger concentration at TPB region. This will cause the concentration overpotential to reduce. Physically, increasing the porosity will reduce the solid parts in the electrodes, which is unfavorable for ion transport through particles. However, it will facilitate gas diffusion as more channels are available in a larger porous structure. Furthermore, eqn. (4.15) shows that active surface area will decrease with the increase of porosity. Therefore, a relative small porosity can enhance the electrochemical reaction by providing more reaction area and reduce the activation overpotential.

The porosity of 79%/21% Ni/YSZ is listed in Table 17 and Table 18 shows the comparison of porosity for 83%/17% Ni/YSZ. The selected porosity range has to maintain the threshold of same particles throughout the electrode connected with each other to form a good conductivity pathway. Therefore, for different compositions of Ni and YSZ, the porosity range need to be calculated by combining the coordination number model and porosity and particle size ratio sub model. It can be seen that the overpotential difference increases as porosity increases. This is because the activation overpotential is dominant as compared with ohmic and concentration
overpotential due to a thin anode thickness. The test results are consistent with the aforementioned physical analysis.

Table 17 comparison of porosity for 79%/21% Ni/YSZ

<table>
<thead>
<tr>
<th>Porosity (%)</th>
<th>( \sum_{i=1}^{m} \frac{\text{overp@} \varepsilon - \text{overp@} \varepsilon = 30%}{\text{overp@} \varepsilon = 30%} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.270</td>
<td>-17.651%</td>
</tr>
<tr>
<td>0.273</td>
<td>-15.926%</td>
</tr>
<tr>
<td>0.276</td>
<td>-14.175%</td>
</tr>
<tr>
<td>0.279</td>
<td>-12.394%</td>
</tr>
<tr>
<td>0.283</td>
<td>-10.584%</td>
</tr>
<tr>
<td>0.286</td>
<td>-8.742%</td>
</tr>
<tr>
<td>0.289</td>
<td>-6.866%</td>
</tr>
<tr>
<td>0.292</td>
<td>-4.953%</td>
</tr>
<tr>
<td>0.295</td>
<td>-3.003%</td>
</tr>
<tr>
<td>0.298</td>
<td>-1.012%</td>
</tr>
<tr>
<td>0.300</td>
<td>0.000%</td>
</tr>
<tr>
<td>0.302</td>
<td>1.023%</td>
</tr>
<tr>
<td>0.305</td>
<td>3.103%</td>
</tr>
<tr>
<td>0.308</td>
<td>5.233%</td>
</tr>
<tr>
<td>0.311</td>
<td>7.414%</td>
</tr>
<tr>
<td>0.314</td>
<td>9.652%</td>
</tr>
<tr>
<td>0.317</td>
<td>11.949%</td>
</tr>
<tr>
<td>0.321</td>
<td>14.309%</td>
</tr>
<tr>
<td>0.324</td>
<td>16.738%</td>
</tr>
<tr>
<td>0.327</td>
<td>19.241%</td>
</tr>
<tr>
<td>0.330</td>
<td>21.822%</td>
</tr>
</tbody>
</table>
### Table 18 comparison of porosity for 83%/17% Ni/YSZ

<table>
<thead>
<tr>
<th>Porosity (%)</th>
<th>( \sum_{i=1}^{m} \frac{\text{overp@}\varepsilon - \text{overp@}\varepsilon = 30%}{\text{overp@} \varepsilon = 30%} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.280</td>
<td>-21.617%</td>
</tr>
<tr>
<td>0.282</td>
<td>-20.293%</td>
</tr>
<tr>
<td>0.283</td>
<td>-18.922%</td>
</tr>
<tr>
<td>0.285</td>
<td>-17.501%</td>
</tr>
<tr>
<td>0.286</td>
<td>-16.026%</td>
</tr>
<tr>
<td>0.288</td>
<td>-14.491%</td>
</tr>
<tr>
<td>0.289</td>
<td>-12.892%</td>
</tr>
<tr>
<td>0.291</td>
<td>-11.222%</td>
</tr>
<tr>
<td>0.293</td>
<td>-9.474%</td>
</tr>
<tr>
<td>0.294</td>
<td>-7.640%</td>
</tr>
<tr>
<td>0.296</td>
<td>-5.710%</td>
</tr>
<tr>
<td>0.297</td>
<td>-3.672%</td>
</tr>
<tr>
<td>0.299</td>
<td>-1.514%</td>
</tr>
<tr>
<td>0.300</td>
<td>0.000%</td>
</tr>
<tr>
<td>0.301</td>
<td>0.781%</td>
</tr>
<tr>
<td>0.302</td>
<td>3.233%</td>
</tr>
<tr>
<td>0.304</td>
<td>5.864%</td>
</tr>
<tr>
<td>0.305</td>
<td>8.704%</td>
</tr>
<tr>
<td>0.307</td>
<td>11.790%</td>
</tr>
<tr>
<td>0.308</td>
<td>15.171%</td>
</tr>
<tr>
<td>0.310</td>
<td>18.908%</td>
</tr>
</tbody>
</table>

As shown in Figure 31, if a ±5% difference of overpotential needs to be satisfied (as indicated within the dashed line region), the porosity range is from 0.291 to 0.306 (or -3.0% - 2.0%) for 79%/21% Ni/YSZ, and from 0.296 to 0.303 (or -1.3% - 1.0%) for 83%/17% Ni/YSZ respectively. This indicates that this quantity is highly sensitive. Therefore, an accurate measurement may be needed to perform accurate predictions from the model.
6.2.3 Volume Fraction
First of all, volume fraction affects the ohmic overpotential. As indicated from eqn. (3.5), as ion volume fraction increases, ohmic overpotential decreases. Next, active surface area is a function of volume fraction as well. However, this quantity in active surface area formula is highly nonlinear and hence it is too complex to analyze the detailed influence. As shown in Fig. 32, if the overpotential difference is restricted to ±5%, the adjustable range of electron volume fraction is from 0.781 to 0.797 (or -1.1% - 0.8%) for 79%/21% volume fraction Ni/YSZ, and from 0.8275 to 0.832 (or -0.3% - 0.2%) for 83%/17% volume fraction Ni/YSZ respectively. Therefore, volume fraction value is extremely crucial for predicting SOFC performance.
Table 19 comparison of volume fraction for 79%/21% Ni/YSZ

<table>
<thead>
<tr>
<th>Electronic conductor $\psi_e$ volume fraction (%)</th>
<th>$\sum_{i=1}^{m} \frac{\text{overp@}$\psi_e$ - overp@$\psi_e = 79%}{m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>74.000</td>
<td>-18.521%</td>
</tr>
<tr>
<td>74.368</td>
<td>-17.701%</td>
</tr>
<tr>
<td>74.737</td>
<td>-16.819%</td>
</tr>
<tr>
<td>75.105</td>
<td>-15.873%</td>
</tr>
<tr>
<td>75.474</td>
<td>-14.856%</td>
</tr>
<tr>
<td>75.842</td>
<td>-13.763%</td>
</tr>
<tr>
<td>76.211</td>
<td>-12.588%</td>
</tr>
<tr>
<td>76.579</td>
<td>-11.324%</td>
</tr>
<tr>
<td>76.947</td>
<td>-9.962%</td>
</tr>
<tr>
<td>77.316</td>
<td>-8.491%</td>
</tr>
<tr>
<td>77.684</td>
<td>-6.901%</td>
</tr>
<tr>
<td>78.053</td>
<td>-5.177%</td>
</tr>
<tr>
<td>78.421</td>
<td>-3.302%</td>
</tr>
<tr>
<td>78.789</td>
<td>-1.256%</td>
</tr>
<tr>
<td>79.158</td>
<td>0.000%</td>
</tr>
<tr>
<td>79.526</td>
<td>0.987%</td>
</tr>
<tr>
<td>79.895</td>
<td>3.458%</td>
</tr>
<tr>
<td>80.263</td>
<td>6.196%</td>
</tr>
<tr>
<td>80.632</td>
<td>9.253%</td>
</tr>
<tr>
<td>81.000</td>
<td>12.698%</td>
</tr>
<tr>
<td>74.000</td>
<td>16.622%</td>
</tr>
</tbody>
</table>
Table 20 comparison of volume fraction for 83%/17% Ni/YSZ

<table>
<thead>
<tr>
<th>Electronic conductor $\psi_e$ volume fraction (%)</th>
<th>$\sum_{i=1}^{m} \frac{\text{overp}\psi_e - \text{overp}\psi_e = 83%}{m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>82.000</td>
<td>-16.303%</td>
</tr>
<tr>
<td>82.079</td>
<td>-15.381%</td>
</tr>
<tr>
<td>82.158</td>
<td>-14.415%</td>
</tr>
<tr>
<td>82.237</td>
<td>-13.403%</td>
</tr>
<tr>
<td>82.316</td>
<td>-12.340%</td>
</tr>
<tr>
<td>82.395</td>
<td>-11.221%</td>
</tr>
<tr>
<td>82.474</td>
<td>-10.041%</td>
</tr>
<tr>
<td>82.553</td>
<td>-8.793%</td>
</tr>
<tr>
<td>82.632</td>
<td>-7.470%</td>
</tr>
<tr>
<td>82.711</td>
<td>-6.063%</td>
</tr>
<tr>
<td>82.789</td>
<td>-4.562%</td>
</tr>
<tr>
<td>82.868</td>
<td>-2.955%</td>
</tr>
<tr>
<td>82.947</td>
<td>-1.227%</td>
</tr>
<tr>
<td>83.000</td>
<td>0.000%</td>
</tr>
<tr>
<td>83.026</td>
<td>0.639%</td>
</tr>
<tr>
<td>83.105</td>
<td>2.665%</td>
</tr>
<tr>
<td>83.184</td>
<td>4.877%</td>
</tr>
<tr>
<td>83.263</td>
<td>7.311%</td>
</tr>
<tr>
<td>83.342</td>
<td>10.009%</td>
</tr>
<tr>
<td>83.421</td>
<td>13.030%</td>
</tr>
<tr>
<td>83.500</td>
<td>16.451%</td>
</tr>
</tbody>
</table>
6.3 Summary
To sum up, Table 21 lists the results of sensitivity study for the microstructure parameters in the numerical model at two different volume fractions. It can be seen that the model is extremely sensitive to volume fraction, porosity and particle size ratio. These parameters can only be varied within a narrow range, which is within ±3.5% for all three in order to maintain a ±5% change in the predicted overpotential for both of the volume fractions. Furthermore, among those parameters, volume fraction is the most sensitive one. If the measurement has ±1% error, the error of the results will be ±5%. Therefore, a careful measurement is highly suggested for particle size ratio, porosity, and volume fraction. Next, as the variation of overpotential is within ±5%, the particle size changes at around ±8%. It is also a sensitive factor, but not as much as particle size ratio. As mentioned before, particle size ratio is strongly sensitive and needs to be measured. Since the only way to measure particle size ratio is to measure particle size, particle size also needs to be counted as a significant sensitive quantity and require careful measurement. However, the model does not seem to be very sensitive to tortuosity. For a small percent change of overpotential, ±5%, the model can allow the tortuosity to vary up to ±20% to ±30%. Besides, this factor is the most difficult parameter to perform a measurement of in an experiment. Therefore, the porosity-tortuosity correlation we adapt may be valid to approximate tortuosity depending on the accuracy requirement.
Table 21 Results of parameter sensitivity study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Percent change corresponding to +/- 5% change in predicted overpotential</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>79%Ni / 21% YSZ</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>-23.3% - 33.7%</td>
</tr>
<tr>
<td>Particle size ratio</td>
<td>-3.5% - 3.5%</td>
</tr>
<tr>
<td>Particle size</td>
<td>-7.4% - 7.4%</td>
</tr>
<tr>
<td>Porosity</td>
<td>-3% - 2%</td>
</tr>
<tr>
<td>Volume fraction</td>
<td>-1.1% - 0.8%</td>
</tr>
</tbody>
</table>
Chapter 7 Functionally Graded Electrodes

7.1 Boundary condition treatment
Another goal of our research is to implement and modify this model so that it can be applied in more complicated scenarios, such as FGEs. To accomplish this, the boundary conditions of our original model needed to be reconsidered. It required a more general treatment of boundary conditions so that they could fit the multiple layers and micro structural grading of electrodes. In the original model, the overall overpotential gradient at the EE interface is given as the product of effective resistivity at fuel channel and total current density. This is fine for conventional electrodes, since all the micro structural parameters are uniform throughout the electrode. However, it is incorrect for FGEs because the effective resistivity varies with different types of grading and the value at EE interface may not be the same as the one at fuel channel. In order to solve this problem, what we did is use an iterative method to adjust the overpotential value after each computing cycle until meet our requirement, which is to force electron current density equal to zero. Several linear-interpolation approaches can accomplish this job such as the Secant method (54).

7.2 Comparison between FGEs and non-FGEs SOFCs
In order to test if FGEs will provide better performance for SOFCs, a SOFC with FGEs will be studied and compared with conventional electrodes SOFC. Again, let us select the microstructure parameters from Jiang’s experimental data to do the analysis.

<table>
<thead>
<tr>
<th>Porosity (%)</th>
<th>Particle size ratio ($r_{ai}/r_{el}$)</th>
<th>Active surface area ($\text{m}^2/\text{m}^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.202</td>
<td>$6.65 \times 10^3$</td>
</tr>
<tr>
<td>30</td>
<td>0.396</td>
<td>$2.19 \times 10^3$</td>
</tr>
<tr>
<td>40</td>
<td>0.513</td>
<td>$0.64 \times 10^3$</td>
</tr>
</tbody>
</table>

The above table lists how the particle size ratio and active surface area changes with porosity. By applying porosity and particle size ratio correlation, it can be found out that as porosity gets bigger, particle size ratio also appears to be larger. Larger particle size ratio means the size difference between two types of conductors is becoming smaller. In addition, according to coordination number model, active surface area starts to drop with increasing of porosity. Physically, relative large porosity will be favorable for diffusion process because it will generate...
more channels for the mass transfer and hence reduce concentration overpotential. On the other hand, small porosity near the TPB region will enhance electrochemical reactions by providing more active reaction sites and reduce activation overpotential. For non-FGEs SOFCs, how to choose the value of porosity is a trade-off because larger porosity will be beneficial for diffusion but disadvantageous for electrochemical reaction, and vice versa. However, if FGEs can be employed to SOFC, all that need to be done is to apply larger porosity near fuel channel and smaller one near EE surface. In that case, both diffusion processes and the speed of the electrochemical reaction can be improved. In our study here, we will explore the effects of porosity grading which, due to the correlation between porosity and particle size, will result in changes to both the porosity and particle size. Another parameter which can be explored is grading the electrode composition, i.e. the ratio of ionic conducting material with electronic conducting material, but we do not explore that here.

![Figure 33 I-V curve of different porosity value at anode thickness equal to 30μm](image)

For a thin anode thickness like Jiang’s experimentation setup, a series of tests of porosity value is conducted. As shown in Fig. 33, five different cases are compared for an anode half-cell with thickness equal to 30μm. Case No. 1: we would like to test a relative coarse porous structure. Therefore porosity of the whole electrode is set to equal to 40%. Case No. 2: a finer porosity needs to be examined, and porosity of the whole electrode is set equal to 20%. Case No. 3: a two-layer electrode with two different porosity values is tested. In this case, anode is uniformly divided into two layers. Porosity is set to be 40% for the layer near the fuel channel, and 20% for
the other layer. Case No. 4: a linear change of porosity within the whole electrode will be considered. Thus, we would like to vary porosity starting from 40% in the fuel channel to 20% at EE interface. Case No. 5: Other than linearity, it is necessary to test a different curvature shape of porosity variation in the electrode such as exponential change. This time the porosity changes exponentially from 40% at fuel channel to 20% at EE interface. Due to the shape of an exponential function, most of the porosity value will be close to 20%. The plots of Fig. 3 indicate that overpotential depends on porosity mainly, and smaller porosity will result in better performance. This result is reasonable and can be interpreted from a detailed analysis in Fig. 34.

![Fig. 34 detailed plots of anode thickness=30μm and current density=0.4A/cm²](image)

Fig. 34 (c) shows the distribution of H₂ in the normalized anode. Since the anode thickness is extremely thin, there is almost no diffusion resistance in the whole electrode and that makes concentration of H₂ at EE surface remain almost the same as inlet condition. On other hand, it can be seen from Fig. 34 (a) that electrochemical reaction occurs throughout the whole anode and that makes activation overpotential dominate the whole overpotential. Since smaller porosity will provide larger active surface area and hence reduce activation overpotential, it can be found out from Fig. 34 (b) that, the electrode with 20% porosity has the minimum overpotential, while 40% has the maximum overpotential. Exponential change of porosity has the second minimum overpotential, and it is due to most of the porosity value is close to 20%. In this case, electrochemical reaction will be fastened at small porosity region. As a result, the two-layer electrode turns out showing better performance compared with a linear change porosity electrode.

In the previous tests, diffusion does not play an important role due to an extremely thin anode thickness. Next, we would like to take this factor into consideration and explore how the FGEs
will perform when anode thickness is getting thicker. The same tests will be run again but this
time the anode thickness is intentionally increased from 30μm to 300μm.

Figure 35 I-V curve of different porosity value at anode thickness equal to 300μm

Fig. 35 shows that all of the curves are clustered together and almost overlap with each other
except the 40% porosity case. This indicates that the effects of diffusion start coming into play.
Smaller porosity will not always provide best performance in this case, since diffusion is more
favorable to larger porosity.

Figure 36 detailed plots of anode thickness=300μm and current density=0.4A/cm²

Same conclusion can also be drawn from the detailed plots in Fig. 36. It can be seen from Fig.
36(a) that current density in electron conductor start to drop at around 0.8 of the normalized
anode thickness. As mentioned before, the slope of this quantity represents the rate of
electrochemical reactions. In the first 80% of the whole anode, the slope is almost zero indicating
that there is no electrochemical reaction occurs. After that, the slope drops significantly and 
electrochemical reaction starts to take place. Fig. 36(b) also proves that diffusion process is more 
dominant up to 80% of the whole anode and then takes over by electrochemical reactions. 
Moreover, compared with Fig. 34(c), the drop of H₂ molar concentration at EE interface is 
significant in Fig. 36(c). This is shows that diffusion process is expected to have more of an 
effect as thickness of electrode increases.

In the end, a typical anode-supported cell is tested as well. This time anode thickness is chosen to 
be equal to 1000μm. As shown in Fig. 37, the linear change porosity and two-layer porosity 
anode have lower overpotential than the uniform 20% and exponential distribution of porosity.

![Figure 37 I-V curve of different porosity value at anode thickness equal to 1000μm](image)

The results are anticipated and reasonable as it is consistent with the physics. Concentration 
overpotential due to diffusion process becomes more important as anode thickness gets thicker. 
Fig. 38 (a) shows that electrochemical reaction only takes place within about 10% of the whole 
anode near EE interface, elsewhere is dominated by mass transfer. Larger porosity will benefit 
diffusion and thus can reduce concentration overpotential. As indicated in Fig. 38 (c), the 
electrode with 40% porosity has the minimum concentration overpotential, since this porosity 
value will facilitate mass transfer and make molar concentration H₂ to be highest at EE interface. 
Same conclusion can also be found in Fig. 38 (b), which is the overpotential distribution in the
normalized anode. For almost 90% of anode starting from fuel channel, overall overpotential is governed by concentration overpotential and anode with 40% porosity has the minimum overall overpotential. As it approaches the EE surface, activation overpotential starts to climb dramatically. Anodes with smaller porosity have a higher slope representing a faster reaction rate.

From the above analysis, we can see that almost 90% of the anode is governed by mass transfer and the rest is dominated by electromechanical reactions. In order to further improve the cell performance, a two-layer porosity grading is proposed. In the first 90% of anode thickness, a larger porosity, 40%, will be applied to boost mass transfer process. On the other hand, for the rest of anode, a smaller porosity, 20%, is used to enhance electrochemical reactions. The black curve in Fig. 39 does show a best performance compared with the previous tests demonstrating a consistency of physical assumption and mathematical simulation.
Figure 39 an updated I-V curve of different porosity value

To sum up, for a thin anode, functionally grading is not really necessary. However, for an anode-supported cell, functionally grading will improve cell performance by reducing both concentration overpotential and activation overpotential.

7.3 Comparison between anode- and electrolyte-supported SOFCs
A comparison between anode- and electrolyte-supported SOFC is conducted. A cathode made of platinum is used as reference electrode. For an anode-supported cell, anode and electrolyte thicknesses are selected as 1000μm and 30μm, respectively. For electrolyte-supported cell, anode and electrolyte thicknesses are selected as 30μm and 1000μm, respectively. All other parameters are chosen to be the same values from the first model validation experiment. Four different temperatures are tested with an increment of 100 °C. As shown in Fig. 40, I-V and P-V curves both indicate that anode-supported cell has a better performance over electrolyte-supported cell. This is because ohmic resistance in the electrolyte for electrolyte-supported cell is five times larger than the combined concentration and activation overpotential in electrode for anode-supported cell at same operating temperature.
Figure 40 Comparison between anode- and electrolyte-supported SOFC
Chapter 8 Conclusions

In this study, SOFC performance has been investigated by a comprehensive mathematical model that can simulate both mass transfer and electrochemical reactions for both electrodes from a micro-scale level. The relationship of microstructure parameters such as the particle size of two types of conductors, tortuosity and porosity were explored. Two sub model correlations, i.e., porosity and tortuosity, particle size ratio and porosity are adopted and implemented in the model in order to mimic the SOFCs more closely to the practical situation. Next, three experiments that aimed to examine SOFCs from different perspectives selected from literature to perform the model validation. The numerical predictions agreed reasonably well with the experimental data indicating a strong reliability of mathematical model and proper selection of sub model correlations. After that, a sensitivity study of microstructure parameters and adopted sub model correlations were tested. We achieved the goal to provide a benchmark so that scientists can determine the precision of measurements required make reasonably accurate performance predictions from the model. Moreover, we illustrated that FGEs can be applied to SOFCs in order to achieve better cell efficiency when compared with uniform electrodes.
Works Cited


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