Florida State University Libraries

Electronic Theses, Treatises and Dissertations

The Graduate School

2011

Single Solid Oxide Fuel Cell Modeling and Optimization

Hang Wen

THE FLORIDA STATE UNIVERSITY
COLLEGE OF ENGINEERING

SINGLE SOLID OXIDE FUEL CELL MODELING AND OPTIMIZATION

By
HANG WEN

A Dissertation submitted to the
Department of Mechanical Engineering
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

Degree Awarded:
Fall Semester, 2011

Hang Wen defended this dissertation on November 1, 2011.

The members of the supervisory committee were:

Juan C. Ordóñez
Professor Directing Dissertation

Jim P. Zheng
University Representative

Helen Li
Committee Member

Chiang Shih
Committee Member

Patrick Hollis
Committee Member

The Graduate School has verified and approved the above-named committee members, and certifies that the dissertation has been approved in accordance with university requirements.

I dedicate this dissertation to
*My Mom Wuqiong Li, Dad Liang Wen, Wife Ning Ruan and My sister Jie Wen for their strong
and enduring support*

ACKNOWLEDGEMENTS

I would like to present my deepest appreciation to my advisor Dr. Juan Ordóñez, who gave me the opportunity to work on this dissertation by funding my research, serving as my major professor and providing valuable advice during my studies at Florida State University. Without his guidance and patience, I could not complete my graduate studies with success.

I would like to thank the members of my dissertation committee, Dr. Chiang Shih, Dr. Patrick Hollis, Dr. Helen Li and Dr. Jim P. Zheng. They were very supportive and provided me with valuable suggestions during my prospectus and encouraged me to continue further in my research. I appreciate their help and guidance.

I am thankful to Dr. J.V.C. Vargas who co-authored with me several publications during my doctoral work. I am also thankful to the other Thermal Management group members, Dr. J.V.C. Vargas, Dr. Rob Hovsapien, Dr. Thomas Brinson, Mr. Lauber Martins and Mr. Tom Tracy for intellectual discussions and valuable suggestions in research and dissertation.

I am also thankful to Ms. Nancy Rainey and Ms. Joann Jirak of the CAPS administrative staff for their help in issues related to human resources and management.

My special thanks would be presented to my mom, dad and sister for their continuous support in my study life. My wife, Ning Ruan's encouragement and warm care make me grateful and full of confidence.

TABLE OF CONTENTS

Nomenclature.....	vii
List of Figures.....	xiv
Abstract.....	xviii
1. INTRODUCTION.....	1
1.1 Introduction.....	1
1.2 Dissertation Objectives.....	3
1.3 Intellectual Merit.....	4
1.4 Literature Review.....	4
2. SINGLE SOFC MODELING.....	8
2.1 Thermal Model of the Single SOFC.....	9
2.1.1 Reactants Concentration in the Channels.....	9
2.1.2 Dimensionless Variables.....	11
2.1.3 Temperature Distribution across the SOFC.....	13
2.2 Electrochemical Model of the Single SOFC.....	20
2.2.1 Composite Electrodes Microstructure.....	20
2.2.2 Operating Potential and Losses.....	23
2.3 Model Validation.....	26
3. RESULTS AND DISCUSSION.....	28
3.1 Temperature Profile of the Single SOFC.....	28
3.2 Polarization Curves of the Single SOFC.....	29
3.3 Composite Electrodes Microstructure Discussion.....	31
3.4 Determination of Active TPB Regions at Two Electrodes.....	37
3.5 SOFC Operation Condition.....	39
3.5.1 Air Stoichiometric Ratio.....	39
3.5.2 Fuel Utilization Factor.....	40
3.6 Summary.....	41
4. SOFC INTERNAL STRUCTURE OPTIMIZATION.....	43
4.1 PEN Geometry Optimization under Fixed Operating Condition.....	43
4.2 Electrodes Geometry Optimization under Variable Operating Conditions.....	48
4.3 Summary.....	53
5. SOFC EXTERNAL CONFIGURATION OPTIMIZATION.....	54
5.1 External Configuration Optimization under Fixed Operating Condition.....	54
5.2 External Configuration Optimization under Variable Operating Conditions.....	63
5.3 Summary.....	69
6. CONCLUSIONS AND FUTURE WORK.....	71
6.1 Conclusions.....	71
6.2 Future Work.....	72

Table 1.....	74
References.....	76
Biographical Sketch.....	79
Publication List.....	80

NOMENCLATURE

A	area, m ²
A'_{opt}	area of the active TPB region, m ²
c	molar specific heat, J mol ⁻¹ K ⁻¹
c_v	specific heat capacity at constant volume, J mol ⁻¹ K ⁻¹
c_p	specific heat capacity at constant pressure, J kg ⁻¹ K ⁻¹
D	mass diffusivity, m ² s ⁻¹
D_h	gas channel hydraulic diameter, m
D_p	average diameter of the pore, m
D_w	width of a corrugation, m
E	activation energy, J mol ⁻¹
f	friction factor
F	Faraday's constant, C eq ⁻¹
h	heat transfer coefficient, W m ⁻² K ⁻¹
H	enthalpy, J mol ⁻¹
I	working current, A
i	current density, A m ⁻²
i_0	exchange current density, A m ⁻²
k	thermal conductivity, W m ⁻¹ K ⁻¹
L	length, m
L'	reaction region thickness, m
L'_{opt}	active TPB region thickness, m

M	molecular weight, kg mol ⁻¹
m	mass, kg
$\dot{m}$	mass flow rate, kg s ⁻¹
n	equivalent electron per mole of reactant, eq mol ⁻¹
$\dot{n}$	molar rate involved in the electrochemical reaction , mol s ⁻¹
$\dot{n}_{in}$	molar flow rate at the inlet , mol s ⁻¹
$\dot{n}_{out}$	molar flow rate at the outlet , mol s ⁻¹
n_{ch}	number of channels
$n_{m,i}$	number of moles of component i in the mixture
$n_{m,T}$	total number of moles in the mixture
N	heat capacity, J K ⁻¹
p	pressure, Pa
P	dimensionless pressure
p_{ref}	ambient pressure, Pa
Pr	Prandtl number
$\dot{W}$	power, W
$\dot{W}_E$	electric power, W
$\dot{W}_N$	net power, W
$\dot{W}_P$	pumping power, W
$\dot{Q}$	heat transfer rate, W
R	universal gas constant, J mol ⁻¹ K ⁻¹
R_j	specific gas constant, J kg ⁻¹ K ⁻¹

Re	Reynolds number
S^0	standard entropy, J mol ⁻¹ K ⁻¹
t	time, s
T	temperature, K
T_{ref}	ambient temperature, K
u	velocity, m s ⁻¹
V	operating potential, V
$V_{act,a}$	anode activation overpotential, V
$V_{act,c}$	cathode activation overpotential, V
$V_{conc,a}$	anode concentration overpotential, V
$V_{conc,c}$	cathode concentration overpotential, V
V_{offset}	offset overpotential, V
V_{ohm}	ohmic overpotential, V
V_T	total volume of the single SOFC, m ³
$\dot{w}_E$	electric power density, W cm ⁻²
$\dot{w}_N$	net power density, W cm ⁻²
$\dot{w}_P$	pumping power density, W cm ⁻²
X	molar fraction of component in the mixture
Zr	grain size, m

Greek symbols:

α	fraction of the reaction heat that is generated at the anode
α_c	charge transfer coefficient

α_t	anode thermal diffusivity, $\text{m}^2 \text{s}^{-1}$
β	ohmic resistance, Ω
χ	gas channel aspect ratio
δ	pre-exponential factor, $\Omega^{-1} \text{m}^{-2}$
ε	emissivity
ϕ	porosity
γ_f	fuel utilization factor
θ	dimensionless temperature
ξ	dimensionless length
τ	dimensionless time
λ_{air}	air stoichiometric ratio
μ	viscosity, Pa s
v	diffusion volume of simple molecules, cm^3
ρ	density, kg m^{-3}
σ	electrical conductivity, $\Omega^{-1} \text{m}^{-1}$
σ_{rad}	Stefan-Boltzmann Constant
ψ	tortuosity
κ	isentropic index

Subscript and superscript:

0	initial condition
1	bipolar plate (interconnect)
2	fuel channel or fuel

3	anode
4	electrolyte
5	cathode
6	air channel or air
~	dimensionless
a	anode
act	activation
actconc	activation and concentration
active	active reaction region
air	air
ambient	ambient condition
c	cathode
ch	channel
cnd	conduction
cnv	convection
conc	concentration
cross	cross section
eff	effective
f	fuel
h	hydraulic
H ₂	hydrogen
H ₂ O	water
i	substance or location in the fuel cell

in	inlet
limit	limit
loss	potential losses
m	one-way maximum
mm	two-way maximum
mmm	three-way maximum
mmmm	four-way maximum
mass	mass transfer
N ₂	nitrogen
n	nominal operating point
nernst	ideal Nernst
o	standard condition [gases at 1 atm, 298.15 K]
O ₂	oxygen
ocp	open circuit potential
offset	offset potential loss
ohm	ohmic
opt	optimal
out	outlet
rad	radiation
ref	reference
rct	reaction
TPB	Three-phase boundary
t	Channel shoulder

total	total
x	x direction
y	y direction
z	z direction

LIST OF FIGURES

1.1	Fuel cell unit	1
1.2	Christian Friedrich Schönbein	2
1.3	William Robert Grove	2
1.4	Project Gemini	2
1.5	Gemini fuel cell	2
1.6	Solid oxide fuel cell systems	3
2.1	The 3D configuration of a single planar cross- flow SOFC	8
2.2	Model of the positive electrode – electrolyte –negative electrode assembly (PEN) internal structure	21
2.3	Model for the composite microstructure of a SOFC anode.....	22
2.4	Comparison of single SOFC polarization curves simulated with the current model, with Aguiar’s model and the experimental data reported by Chick et al. [32].....	27
3.1	The temperature of each compartment in the single SOFC as functions of current.....	29
3.2	The polarization curves of the single SOFC.....	30
3.3	Polarization curves of the single SOFC with various anode reaction layer thicknesses	32
3.4	SOFC nominal net power density as a function of anode reaction layer thickness under various working temperatures	33
3.5	Polarization curves of the single SOFC with various cathode reaction layer thicknesses ...	34
3.6	SOFC nominal net power density as a function of cathode reaction layer thicknesses under various working temperatures	35
3.7	Polarization curves of the single SOFC with various electrodes porosities	36
3.8	The optimal reaction layer thicknesses in the two electrodes and the two-way maximized nominal net power density as functions of electrodes porosities	37

3.9	The total potential losses at the anode and electrical power and net power as functions of anode reaction region thickness under various working currents and anode thicknesses	38
3.10	The total potential losses at the cathode and electrical power as functions of cathode reaction region thickness under various working currents and cathode thicknesses	39
3.11	The working current, electrical power and electrolyte temperature at the nominal operating point as functions of air stoichiometric ratio	40
3.12	The electrolyte temperature, electrical power and net power at the nominal operating point as functions of fuel utilization factor	41
4.1	The electrical power at the nominal operating point as a function of anode reaction region thickness for various electrolyte thicknesses	44
4.2	The electrical power at the nominal operating point as a function of cathode reaction region thickness for various electrolyte thicknesses	44
4.3	The active TPB thickness at anode and cathode and the two-way maximized electrical power at the nominal operating point as functions of electrolyte thickness	45
4.4	The two-way maximized electrical power at the nominal operating point as a function of anode layer thickness under various electrolyte thicknesses	46
4.5	The optimal thickness distribution between the anode and cathode as well as the three-way maximized electrical power at the nominal operating point as functions of electrolyte thickness	47
4.6	The electrical power at the nominal operating point as a function of anode reaction region thickness under various fuel utilization factors	49
4.7	The electrical power at the nominal operating point as a function of cathode reaction region thickness under various fuel utilization factors	49
4.8	The active TPB regions thicknesses at the anode and cathode as functions of fuel utilization factor	50
4.9	The two-way maximized electrical power at the nominal operating point as a function of fuel utilization factor for various anode layer thicknesses	51
4.10	The optimal fuel utilization factor as a function of anode layer thickness	51
4.11	The active TPB regions thicknesses at the anode and cathode as functions of anode layer thickness	52

4.12	The three-way maximized electrical power at the nominal operating point as a function of anode layer thickness.....	53
5.1	The nominal temperature of each compartment in the single SOFC as functions of fuel cell cross section area.....	55
5.2	The convective heat transfer coefficients of air and fuel streams and convective heat transfer area between air and the single SOFC as functions of fuel cell cross section area.....	56
5.3	The polarization curves of the single SOFC with various cross section areas.....	58
5.4	The fuel cell actual operating potential as a function of working current density with various SOFC cross section areas	59
5.5	The working current density and working current at the nominal operating point as functions of SOFC cross section area.....	60
5.6	The SOFC net power at the nominal operating point as a function of anode reaction region thickness with various SOFC cross section areas.....	61
5.7	The SOFC net power at the nominal operating point as a function of cathode reaction region thickness with various SOFC cross section areas	61
5.8	The active TPB regions thicknesses at the anode and cathode as functions of SOFC cross section area	62
5.9	The two-way maximized SOFC net power, electrical power and pumping power at the nominal operating point as functions of SOFC cross section area.....	63
5.10	The SOFC net power at the nominal operating point as a function of anode reaction region thickness with various SOFC cross section areas and fuel utilization factors	64
5.11	The active TPB region thickness at the anode as a function of SOFC cross section area and fuel utilization factor	65
5.12	The SOFC net power at the nominal operating point as a function of cathode reaction region thickness with various SOFC cross section areas and fuel utilization factors	66
5.13	The active TPB region thickness at the cathode as a function of SOFC cross section area and fuel utilization factor.....	66
5.14	The two-way maximized net power at the nominal operating point as a function of fuel utilization factor with various SOFC cross section areas	68
5.15	The optimal fuel utilization factor as a function of SOFC cross section area.....	68

5.16	The three-way maximized net power, electrical power and pumping power at the nominal operating point as functions of SOFC cross section area	69
6.1	External configuration of a cross-flow planar SOFC stack.....	72
6.2	Internal structure of a cross-flow planar SOFC stack	73

ABSTRACT

This dissertation introduces a comprehensive model for a single solid oxide fuel cell (SOFC) as well as a procedure to optimize its configuration and operating condition, so that the net power is maximized. The model consists of coupled thermodynamic and electrochemical submodels to determine the SOFC performance under various configurations and operation conditions. The thermodynamic model is derived from physical laws (e.g., the first law of thermodynamics, Fick's law, Fourier's law) to obtain the temperature and reactants concentration distribution in the SOFC. The electrochemical model is integrated with a submodel for the microstructure of SOFC composite electrodes and allows the computation of the SOFC voltage, current, and power output. The electrochemical model is validated with experimental data and showed improved accuracy compared to previously published models. Based on the simulation results, the composite electrodes microstructure (porosities, active three phase boundaries), PEN (positive electrode-electrolyte-negative electrode assembly) internal structure and SOFC external structure, as well as the operating conditions such as fuel utilization factor and air stoichiometric ratio are investigated and their impact on the SOFC performance is discussed. Subjected to a fixed total volume, the optimal internal and external configuration and operating parameters are pursued so that the net power of the SOFC is maximized. The method used is general and the results are sharp, which shows the potential to use the model as a tool for future SOFC design, simulation and optimization.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Fuel cells are electrochemical devices that convert the chemical energy in the fuels directly to electricity. Unlike the conventional power generation methods, there are no intermediate steps such as burning fuels to generate thermal energy and then converting it to mechanical power with a heat engine. Thus, the fuel cells are not restricted by some thermodynamic limitations and have relatively high energy efficiency. Generally, the energy efficiency of a fuel cell is between 40-60%. If waste heat is captured, the energy efficiency could be further improved up to 85% [1]. Besides, fuel cells are also environmentally friendly. Except for the small amount of CO₂ emitted as the byproduct of hydrogen generation from hydrocarbon compounds, fuel cells exert minimum impact on the environment. Because of all these virtues, they are considered as one of the most attractive solutions for clean power systems and receive widespread attention from the automotive and power generation industry, as well as many research/academic organizations [2].

Figure 1.1 Fuel cell unit [3]

Fuel cells have a history of more than 170 years. The principle of fuel cell was first demonstrated by the German scientist Christian Friedrich Schönbein in 1838. In the next year, Welsh physicist William Grove developed the first crude fuel cells in the world.

Figure 1.2 Christian Friedrich Schönbein [4]

Figure 1.3 William Robert Grove [5]

In 1950s, two chemists in General Electric Company, W. Thomas Grubb and Leonard Niedrach modified the original fuel cell design and developed “Grubb-Niedrach fuel cell”, which was lately utilized in the NASA space program “Project Gemini”. It became the first commercial use of fuel cells in the history. Since then, fuel cells have been used in many other applications. i.e., they are used for primary and backup power for commercial, industrial and residential buildings and in remote or inaccessible areas. They are also used to power fuel cell vehicles, including automobiles, buses, forklifts, airplanes, boats, motorcycles and submarines [1].

Figure 1.4 Project Gemini [6]

Figure 1.5 Gemini fuel cell [7]

There are several types of fuel cells, such as Proton Exchange Membrane Fuel Cells (PEMFCs), Solid Oxide Fuel Cells (SOFCs), Alkaline Fuel Cells (AFCs) and etc. Among them, SOFCs are particularly attractive for their special features: great fuel flexibility, high energy conversion efficiency (55% - 60%), low emission and noise, and the potential application in highly efficient cogeneration power systems. Despite of all these virtues, there are some technical issues need to be addressed before their mass production and commercial application, which includes SOFCs operating condition control, configuration optimization and power density augmentation, etc.

Figure 1.6 Solid oxide fuel cell systems [8]

To analyze and solve these problems, in this dissertation, a comprehensive model for the single SOFC is developed from fundamental physical laws. Based on the model, the effects of single cell geometric configuration and operating conditions on its performance are studied. At last, by optimizing these configuration and operating parameters, SOFC power density is maximized. Both the methodology and conclusion presented in this dissertation could be served as guidance in the future SOFC design.

1.2 Dissertation Objectives

Based on the discussion above, there are two main objectives in this research. First, develop a comprehensive multiphysics model (composed of coupled thermodynamic and

electrochemical models) for the single SOFC. The model should capture all the dominant physical and electrochemical phenomena occurring in SOFC so that it depicts the performance of the SOFC accurately. In the meantime it should be relatively simple and require low computational time for each tested case. Second, based on the model, optimize fuel cell geometric configuration and operating condition to maximize the power output. The model and optimization result in this work would be integrated in the future design of the SOFC stack.

1.3 Intellectual Merit

The electrochemical aspects of the single SOFC have been studied widely in the scientific literature. They help us to understand the electrochemical phenomenon occurring in the fuel cell and identify key factors that influence its performance. However, how these factors depend on the fuel cell thermal environment and configuration, and correspondingly, lead to the change in the overall performance has not been fully discussed. This work supplements the electrochemical model with a thermodynamic model and a model for the porous electrodes structure. Based on the model, the impact of the single cell geometry configuration and operation condition on its thermal environment and electrochemical performance has been studied. These parameters are then further optimized to maximize fuel cell's power output. The optimal is sharp and could serve as the guidance in the fuel cell design and operation condition management, as well as assist the study of SOFC stack in the near future.

1.4 Literature Review

Many scientists and engineers engage in SOFC research and development. Among them, there is particular interest in understanding and describing the electrochemical mechanism of the fuel cell at micro-scale level. Virkar et al. [9] discussed the effect of SOFC electrodes microstructure on activation and concentration overpotential. They suggested that, due to the composite nature of the electrodes which comprise mixtures of electrocatalyst/electrolyte pair, the reaction region would spread out from the electrolyte/ electrode interface into the electrode. With the increase of the reaction area, the activation overpotential of the fuel cell would decrease dramatically. In addition, for small working current where activation overpotential can be approximated as being ohmic, the concept of effective charge transfer resistance was introduced

in the activation overpotential calculation. Tanner et al. [10] introduced a scanning electron micrograph (SEM) of a SOFC membrane, which is comprised of a thin electrolyte and two composite electrodes. Based on the SEM, a pore model for the composite electrodes was developed. Nam and Jeon [11] introduced a comprehensive model to account for the micro-scale transport and electrochemical reaction in SOFC, in which a random packing sphere sub-model of porous electrodes was introduced. The spatial distribution of transfer current density was obtained and based on the result, they further concluded that three phase boundaries (TPBs) at the electrode/electrolyte interface were most active. In the anode, most of electrochemical reaction took place within 10 μ m range from the electrolyte. Whereas in the cathode, there were significant amount of charge-transfer reactions which occurred at TPBs more than 10 μ m away from the electrolyte. Chan and Xia [12] developed a micro model for SOFC porous anode, in which the relationship between the transport phenomena (such as electrons, ions and gas molecules transport through the electrode) and the electrochemical reaction at the TPB was discussed. Based on the simulation result, one important conclusion was drawn in [12]: the active TPB sites where the reaction occurred were not chosen randomly, instead they were determined by the balance of effective electronic resistance, effective ionic resistance, and the effective gas resistance. The reactions took place where the total resistance reached minimum.

In engineering, research has been conducted to describe the electrochemical phenomena of the SOFC at macro-scale level. Chan et al. [13] presented a complete polarization model of SOFC that could work under different design and operating conditions. They used the universal Butler-Volmer equation to account for the activation overpotential in the fuel cells. The other two simplified equations: Tafel equation and linear current-potential equation which are also widely used in activation overpotential calculation, were compared with the Butler-Volmer equation and analyzed. The errors of the simplified equations relative to the Butler-Volmer equation as well as their application range were analyzed. When accounting for the concentration overpotential, both the ordinary diffusion and Knudsen diffusion of the reactants were considered for a wide range of porous electrode designs. In the end, the influence of cell component geometry on its performance was discussed and one important conclusion was drawn: given the same materials, same electrode kinetics and same operational constraints, the performance of anode-supported fuel cell is better than electrolyte-supported or cathode-supported fuel cell.

Some efforts are devoted to the study of the SOFC performance under different design and operation conditions. Sorrentino et al. [14] built a simplified 1-D model for the planar SOFC which accounted for the most important physical and electrochemical phenomena in SOFC, as well as internal reforming processes. The simulation result obtained with electrochemical model was validated with the experimental data from Pacific Northwest National Laboratory. Besides, based on the results obtained with numerical simulation, the effects of several operating parameters, such as fuel utilization factor, fuel cell operating temperature and pressure, on its performance were evaluated. Similarly, Aguiar et al. [15] built a 1-D model for the anode supported planar SOFC stack. The influence of reactants inlet temperature, fuel utilization factor, average current density and flow configuration on the SOFC performance was analyzed. In the paper authors further pointed out that, compared with SOFC with co-flow configuration of fuel and air gas channels, the SOFC with counter-flow configuration was shown to exert steeper temperature gradient with a consequent uneven current density distribution, leading to the conclusion that counter-flow configuration was not the best mode of operation.

Initiated by Bejan [16] in 1996, constructal principle has been used by many researchers for optimizing practical applications, including fuel cell geometry and structure. Vargas et al. [17] built a 1-D model for a PEM fuel cell, and used structured procedure to optimize the internal and external PEM configuration to maximize its net power. The model was further validated with the experiment data by Martins et al. [18]. Based on the model of the unit PEM fuel cell, Vargas et al. [19] developed a model for PEM fuel cell stack, and the effect of the stack internal and external configuration on the net power was discussed. For SOFCs, Ordóñez et al. [20] optimized the geometric features of a single SOFC based on a simplified model in 2007.

Young [21] and Ma et al. [22] recently reviewed the status of three-dimensional SOFC modeling. Young [21] discussed current thermo-fluid modeling capabilities for PEM fuel cell and SOFC, and highlighted key challenges such as gas diffusion in the porous layers, the internal fuel reforming rate and the transport of gas species, ions, and electrons accompanied with the electrochemical reaction. Ma et al. [22] reviewed the current computational fluid dynamics (CFD) modeling of fuel cells. Bove and Ubertini [23] developed a complete three-dimensional, time-dependent SOFC numerical model which accounted for various phenomena occurring in each component of the fuel cell. Janardhanan and Deutschmann [24] made CFD analysis of an

internally reforming anode supported SOFC button cell, which accounted for the heterogeneous fuel reforming chemistry, electrochemistry and porous media transport inside the fuel cell. In the paper the effect of steam content in the anode feed stream on the resulting potential losses and surface coverages of various species at the three-phase boundary were discussed. Furthermore, Janardhanan et al. [25] introduced a mathematical model to calculate the volume specific three-phase boundary length in the porous SOFC composite electrodes, which is of crucial importance to the SOFC performance.

Though very useful refined spatial information can be extracted from three-dimensional models, the computational time requirements prevent their use for optimization strategies in which multiple runs for different geometries and operating conditions are necessary. As a result, there is a need for an efficient computational methodology, which captures the dominant physical and electrochemical phenomena occurring in SOFC and is accurate enough to depict the response of the single SOFC under different design and operating conditions. Besides, no study that explores the effects of SOFC internal geometry on the electrochemical and thermal performance accounting for the porous nature of the electrodes was found. This is the goal of the current dissertation.

In this dissertation a one-dimensional single SOFC model based on the fundamental physical laws is developed. The single SOFC is divided into six lumped control volumes that correspond to the most representative parts of a single fuel cell. The phenomena such as heat and mass transfer, fluid flow, gas diffusion, electrochemical reaction, potential losses, power consumption and generation are taken into account, and the solutions include temperature and reactant concentration distribution in each control volume, fuel cell polarization curves and power generation under different conditions. Based on the simulation results obtained with the model, the effects of fuel cell operating parameters, such as air stoichiometric ratio and fuel utilization factor, as well as fuel cell configurations, such as composite electrodes microstructure, fuel cell internal and external structure on its performance are investigated. Finally, the optimal values for each investigated design and operating parameter are proposed for maximum fuel cell performance.

CHAPTER TWO

SINGLE SOFC MODELING

The configuration of a single planar cross-flow SOFC is shown in Figure 2.1. It consists of six control volumes: the solid bipolar plate--interconnect (CV1), the fuel channels (CV2), the anode layer (CV3), the electrolyte layer (CV4), the cathode layer (CV5), and the oxidant channels (CV6).

Figure 2.1 The 3D configuration of a single planar cross-flow SOFC

When SOFC operates, the fuel and oxidant that are fed into the fuel and oxidant channels diffuse through the anode layer and cathode layer respectively, where they react at the ionic conductor / electronic conductor / gas interface (Three Phase Boundaries, TPB). The bipolar plate (interconnect) provides a series of electrical connectors to the adjacent cells or to the

external circuit, and at the same time serves as a gas barrier between the fuel channels and oxidant channels of adjacent cells.

A wide range of fuels could be used in the electrochemical reaction of SOFC, including various hydrocarbon fuels. For simplicity, in the dissertation pure hydrogen and air are considered as fuel and oxidant, respectively.

Due to the heat and mass interaction inside the single SOFC, the thermal model includes mass and energy conservation equations for each control volume, as well as the electrochemical reaction equations at the two electrodes. The results obtained with the thermal model, which includes the temperature and reactant concentration distribution in the fuel cell, are used in the following electrochemical model to evaluate the overall performance of the single SOFC.

The electrochemical model contains the analysis and computation of ideal Nernst potential and various kinds of potential losses, such as the losses due to surface overpotentials (poor electrocatalysis), slow diffusion and all internal ohmic losses through the cell. The actual fuel cell potential results from the ideal Nernst potential by subtracting all the potential losses, most of which depends on the current density, reactant concentration, SOFC temperature and configuration. The computation of the actual electrical power generation within the SOFC and the power consumed to pump fuel and oxidant into the gas channels are also included in the model to obtain the net power output.

2.1 Thermal Model of the Single SOFC

2.1.1 Reactant Concentration in the Channels

In a single SOFC, electrochemical reactions take place in both the anode layer and the cathode layer. These reactions are expressed by:

The hydrogen in the anode layer and the oxygen in the cathode layer are supplied by the fuel and oxidant channels, respectively. Based on the electrochemical reaction equations, the molar flow rate of hydrogen at the inlet and outlet of fuel channels, as well as hydrogen consumed by the electrochemical reaction, are determined by the working current (I):

$$\dot{n}_{H_2,in} = \frac{I}{nF\gamma_f} = \frac{I}{2F\gamma_f}, \quad \dot{n}_{H_2,out} = \frac{I}{nF} \left(\frac{1}{\gamma_f} - 1 \right) = \frac{I}{2F} \left(\frac{1}{\gamma_f} - 1 \right), \quad \dot{n}_{H_2} = \frac{I}{nF} = \frac{I}{2F} \quad (3)$$

where n is the number of mols of electrons transferred per mol of reactant, for the hydrogen $n = 2$, and for the oxygen $n = 4$. F is the Faraday constant, 96500 C mol^{-1} , and γ_f ($\gamma_f \leq 1$) is the fuel utilization factor and defined as the ratio of the fuel consumed in the reaction and the fuel supplied to the fuel channels.

In the fuel channels, the average molar fractions $X_i = n_{m,i} / n_{m,T}$, defined as the average number of mols of component i divided by the total number of mols of the mixture, is approximated as:

$$X_{H_2O} = \frac{\gamma_f}{2}, \quad X_{H_2} = 1 - \frac{\gamma_f}{2} \quad (4)$$

Similarly, the molar flow rate of oxygen at the inlet and outlet of air channels and the oxygen consumed by the electrochemical reaction are:

$$\dot{n}_{O_2,in} = \frac{I}{nF} \lambda_{air} = \frac{I}{4F} \lambda_{air}, \quad \dot{n}_{O_2,out} = (\lambda_{air} - 1) \frac{I}{nF} = (\lambda_{air} - 1) \frac{I}{4F}, \quad \dot{n}_{O_2} = \frac{I}{nF} = \frac{I}{4F} \quad (5)$$

where λ_{air} is the air stoichiometric ratio, and defined as the air provided to the channels divided by the air consumed in the electrochemical reaction of interest.

In the present study, the oxidant provided in the oxidant channels is air, which is assumed to be composed of oxygen and nitrogen only. The molar flow rate of nitrogen at the inlet and outlet are obtained as:

$$\dot{n}_{N_2,in} = \dot{n}_{N_2,out} = \frac{I\lambda_{air}X_{N_2,in}}{nFX_{O_2,in}} = \frac{I\lambda_{air}X_{N_2,in}}{4FX_{O_2,in}} \quad (6)$$

The average molar fractions of oxygen and nitrogen in the oxidant channels are

$$X_{O_2} = \frac{2\lambda_{air}X_{O_2,in} - X_{O_2,in} - X_{O_2,in}^2}{2(\lambda_{air} - X_{O_2,in})}, \quad X_{N_2} = \frac{2\lambda_{air}X_{N_2,in} - X_{O_2,in}X_{N_2,in}}{2(\lambda_{air} - X_{O_2,in})} \quad (7)$$

2.1.2 Dimensionless Variables

By applying the first law of thermodynamics to every control volume of the single SOFC, a set of ordinary differential equations that account for the temperature across the fuel cell would be derived. To simplify these equations, they are written in dimensionless form and all the quantities in them are rescaled to values as close as possible to 1, which in turn simplifies the numerical calculations.

In a dimensionless model, all variables are directly proportional to the actual dimensional ones. Therefore, this allows for scaling up or down any system with similar characteristics to the system analyzed by the model. Another important aspect is that any dimensionless variable value used in the simulations could represent an entire and numerous set of dimensional values by varying appropriately the parameters in the dimensionless variables definition, which by itself stresses the generality of the dimensionless model. Physically, the set of results of a dimensionless model actually represents the expected system response to numerous combinations of system parameters (geometry, architecture) and operating conditions (e.g, ambient conditions, mass flow rates), without having to simulate each of them individually, as a dimensional model would require. Based on that reasoning, it is convenient to search for an alternative formulation that eliminates the physical dimensions of the problem.

For instance, all the actual lengths in the model are nondimensionalized in the following way, from which their corresponding dimensionless lengths are obtained:

$$\xi_i = \frac{L_i}{V_T^{1/3}}, \quad i = 1, 2, 3, 4, 5, 6, t, ch, x, y, z$$

where $V_T = L_x L_y L_z$ represents the total volume of the single SOFC.

Similarly, the dimensionless temperatures are defined as:

$$\theta_i = \frac{T_i}{T_{ref}}, \quad i = 1, 2, 3, 4, 5, 6$$

where T_{ref} is referenced to the ambient temperature. The dimensionless pressures are:

$$P_i = \frac{p_i}{p_{ref}}, \quad i = H_2, O_2, H_2O, N_2, air, f, TPB$$

where p_{ref} is referenced to the ambient pressure.

Other dimensionless quantities include:

The dimensionless time $\tau = t/t_{ref}$, where $t_{ref} = (4V_T^{2/3})/\alpha_t$. α_t refers to the thermal diffusivity of the anode and $\alpha_t = k_3/(\rho_3 c_{p,3})$.

The dimensionless area $\tilde{A}_i = A_i/(V_T^{2/3})$,

The dimensionless mass $\tilde{m}_i = m_i/m_{ref}$, where $m_{ref} = \rho_3 V_T$.

The dimensionless mass flow rate $\tilde{\dot{m}}_i = \dot{m}_i/\dot{m}_{ref}$, where $\dot{m}_{ref} = (\rho_3 V_T)/t_{ref}$.

The dimensionless thermal conductivity $\tilde{k}_i = (k_i V_T^{1/3})/(\dot{m}_{ref} c_{p,f})$.

The dimensionless convective heat transfer coefficient $\tilde{h}_i = (h_i V_T^{2/3})/(\dot{m}_{ref} c_{p,f})$.

The dimensionless Stefan-Boltzmann constant $\tilde{\sigma}_{rad} = (\sigma_{rad} V_T^{2/3} T_{ref}^3)/(\dot{m}_{ref} c_{p,f})$.

The dimensionless heat transfer rate and power $\tilde{\dot{Q}}_i = \dot{Q}_i/(\dot{m}_{ref} c_{p,f} T_{ref})$,
 $\tilde{\dot{W}}_i = \dot{W}_i/(\dot{m}_{ref} c_{p,f} T_{ref})$.

In all the equations above, the subscript i indicates a substance or a location in the fuel

cell.

2.1.3 Temperature Distribution across The SOFC

The temperature distribution across the SOFC is expressed by a set of ordinary differential equations, which are derived by applying the first law of thermodynamics to each control volume. In the present study the investigated single SOFC is considered to be an internal cell in a SOFC stack and has the interaction with its adjacent cells. It is also assumed that the adjacent cells have similar internal temperature profiles.

For CV1, energy conservation states that:

$$\frac{d\theta_1}{d\tau} = \frac{(\tilde{Q}_{rad,1-3} + \tilde{Q}_{rad,1-5} + \tilde{Q}_{cnv,1-2} + \tilde{Q}_{cnv,1-6} + \tilde{Q}_{ohm,1} + \tilde{Q}_{cnd,1-3} + \tilde{Q}_{cnd,1-5})}{\tilde{N}_1} \quad (8)$$

where the dimensionless heat capacities, $\tilde{N}_i$, are given as:

$$\tilde{N}_i = \frac{m_i c_{p,i}}{m_{ref} c_{p,f}}, \quad i = 1, 3, 4, 5 \quad (9)$$

where $m_1 = \rho_1 [L_1 L_y L_z + (L_y L_2 + L_6 L_z) L_t (n_{ch} + 1)]$ and $m_i = \rho_i L_y L_z L_i$, $i = 3, 4, 5$.

In Equation (8), the radiation heat transfer from the anode layer and cathode layer to the bipolar plate are:

$$\tilde{Q}_{rad,1-j} = \tilde{A}_{rad,j} \tilde{\sigma}_{rad} \varepsilon_{eff,j} (\theta_j^4 - \theta_1^4), \quad j = 3, 5 \quad (10)$$

where $\tilde{A}_{rad,3} = (n_{ch} L_{ch} L_y) / (V_T^{2/3})$ and $\tilde{A}_{rad,5} = (n_{ch} L_{ch} L_z) / (V_T^{2/3})$ are the dimensionless radiation heat transfer areas between the electrodes and the bipolar plate.

The effective emissivities are estimated by [26]:

$$\varepsilon_{eff,3} = \frac{1}{1/\varepsilon_3 + (L_{ch} / (L_{ch} + 2L_2))(1/\varepsilon_1 - 1)} \quad (11a)$$

$$\varepsilon_{eff,5} = \frac{1}{1/\varepsilon_5 + (L_{ch}/(L_{ch} + 2L_6))(1/\varepsilon_1 - 1)} \quad (11b)$$

In Equation (8), the heat conduction from the anode layer and the cathode layer to the bipolar plate are:

$$\tilde{Q}_{cnd,1-3} = \frac{2\tilde{A}_{cnd,3}(\theta_3 - \theta_1)\tilde{k}_3\tilde{k}_1}{(\xi_3\tilde{k}_1 + \xi_2\tilde{k}_3)} \quad (12a)$$

$$\tilde{Q}_{cnd,1-5} = \frac{2\tilde{A}_{cnd,5}(\theta_5 - \theta_1)\tilde{k}_5\tilde{k}_1}{(\xi_5\tilde{k}_1 + \xi_6\tilde{k}_5)} \quad (12b)$$

where $\tilde{A}_{cnd,3} = (1 - \varphi_3)(n_{ch} + 1)\xi_t\xi_y$ and $\tilde{A}_{cnd,5} = (1 - \varphi_5)(n_{ch} + 1)\xi_t\xi_z$ stand for the conduction heat transfer areas between bipolar plate and electrodes. φ_3 and φ_5 represent the anode and cathode porosities, respectively.

In addition, the dimensionless convective heat transfer from fuel channels and oxidant channels to the bipolar plate are expressed as:

$$\tilde{Q}_{cnv,1-j} = \tilde{h}_j\tilde{A}_{cnv,j}(\theta_j - \theta_1) \quad j = 2, 6 \quad (13)$$

where $\tilde{A}_{cnv,2} = n_{ch}(\xi_{ch} + 2\xi_2)\xi_y$ and $\tilde{A}_{cnv,6} = n_{ch}(\xi_{ch} + 2\xi_6)\xi_z$

The convective heat transfer coefficients h_j in the fuel and oxidant channels are estimated according to the flow regime. For the laminar flow ($Re_h < 2300$) [27]:

$$f_j Re_{h,j} = 24(1 - 1.3553\chi_j + 1.9467\chi_j^2 - 1.7012\chi_j^3 + 0.9564\chi_j^4 - 0.2537\chi_j^5), \quad j = 2, 6 \quad (14a)$$

$$\frac{h_j D_{h,j}}{k_j} = 7.541(1 - 2.610\chi_j + 4.970\chi_j^2 - 5.119\chi_j^3 + 2.702\chi_j^4 - 0.548\chi_j^5), \quad j = 2, 6 \quad (14b)$$

For the turbulent flow ($Re_h > 4000$) [28]:

$$f_j = 0.079 \text{Re}_{h,j}^{1/4}, \quad j = 2, 6 \quad (14c)$$

$$\frac{h_j D_{h,j}}{k_j} = \frac{(f_j / 2)(\text{Re}_{h,j} - 1000)Pr_j}{1 + 12.7(f_j / 2)^{1/2}(Pr_j^{2/3} - 1)}, \quad j = 2, 6 \quad (14d)$$

where $\chi_j = L_{ch} / L_j$, when $L_{ch} \leq L_j$ and $\chi_j = L_j / L_{ch}$, when $L_{ch} > L_j$; $D_{h,j} = 2L_{ch}L_j / (L_{ch} + L_j)$; Pr is the gas Prandtl number; and f is the friction factor.

The Reynolds number, $\text{Re}_{h,j}$, are functions of the average flow velocities in the channels u_j , which are approximated in terms of the molar flow rates:

$$u_2 = \frac{R[\dot{n}_{H_2,in}T_{f,in} + (\dot{n}_{H_2,out} + \dot{n}_{H_2O,out})T_2]}{2p_f L_{ch} L_2 n_{ch}} \quad (15a)$$

$$u_6 = \frac{R[(\dot{n}_{O_2,in} + \dot{n}_{N_2,in})T_{air,in} + (\dot{n}_{O_2,out} + \dot{n}_{N_2,out})T_6]}{2p_{air} L_{ch} L_6 n_{ch}} \quad (15b)$$

The heat generation due to ohmic potential losses and the heat generation due to activation and concentration potential losses are given as follows:

$$\tilde{Q}_{ohm,j} = \frac{V_{ohm,j}}{\dot{m}_{ref} c_{p,f} T_{ref}} I, \quad j = 1, 3, 4, 5 \quad (16a)$$

$$\tilde{Q}_{actconc,j} = \frac{V_{act,j} + V_{conc,j}}{\dot{m}_{ref} c_{p,f} T_{ref}} I, \quad j = 3, 5 \quad (16b)$$

where the activation, concentration and ohmic potential losses in each compartment, $(V_{act,j}, V_{conc,j}, V_{ohm,j})$, are discussed later in the electrochemical model.

In the present study, the fuel channels are open control volumes filled with hydrogen and its oxidation product, i.e., water. It is also assumed that the total pressure in the fuel channels and oxidant channels are known and constant. Applying the energy conservation law to CV2 yields:

$$\frac{d\theta_2}{d\tau} = \frac{[-\tilde{Q}_{cnv,1-2} + \tilde{Q}_{cnv,2-3} + \tilde{Q}_{mass,2}]}{\tilde{N}_2} \quad (17)$$

where the dimensionless heat capacity of CV2, $\tilde{N}_2$, is given as follows:

$$\tilde{N}_2 = \frac{p_f n_{ch} L_{ch} L_2 L_y (X_{H_2} c_{v,H_2} + X_{H_2O} c_{v,H_2O})}{RT_2 m_{ref} c_{p,f}} \quad (18)$$

$\tilde{Q}_{cnv,2-3}$ is the dimensionless convective heat transfer between the anode and the fuel channels and calculated by: $\tilde{Q}_{cnv,2-3} = \tilde{h}_2 n_{ch} \xi_{ch} \xi_y (1 - \phi_3)(\theta_3 - \theta_2)$, where the convective heat transfer coefficient, $\tilde{h}_2$, is computed with Equation (14). $\tilde{Q}_{mass,2}$ stands for the energy variation associated with the mass transfer (fuel and water vapor) in CV2 when they cross the boundaries:

$$\tilde{Q}_{mass,2} = \frac{\dot{n}_{H_2,in} (H_{H_2,f} - H_{H_2,2}) + \dot{n}_{H_2O} (H_{H_2O,3} - H_{H_2O,2})}{\dot{m}_{ref} c_{p,f} T_{ref}} \quad (19)$$

where $\dot{n}_{H_2O} = \dot{n}_{H_2}$.

Heat is generated when the electrochemical reactions expressed by Equations (1) and (2) take place. In the present study, it is assumed that the total thermal effect of the two semi-reactions on the SOFC temperature profile can be approximated as one overall electrochemical reaction: $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$, which takes place at the electrolyte temperature T_4 . The total heat generation of the overall reaction is given by [29]:

$$\tilde{Q}_{rct} = \frac{\dot{n}_{H_2} [-T_4 (S_{H_2O,4}^0 - S_{H_2,4}^0 - \frac{1}{2} S_{O_2,4}^0) + RT_4 \ln(\frac{P_{H_2O,TPB}}{P_{H_2,TPB} (P_{O_2,TPB})^{1/2}})]}{\dot{m}_{ref} c_{p,f} T_{ref}} \quad (20)$$

Part of the reaction heat, $\alpha \tilde{Q}_{rct}$, is generated at the anode ($0 < \alpha < 1$), and the rest, $(1 - \alpha) \tilde{Q}_{rct}$, is generated at the cathode.

According to the assumption, the standard entropy of formation S° in Equation (20), is evaluated at the electrolyte temperature T_4 . The three-phase boundaries pressures, P_{TPB} , refer to the partial pressures of reactants and products at the place where the electrochemical reaction actually take place. Equations for the three-phase boundaries pressures are given by Kim et al. [30] and Aguiar et al. [15] with the assumption that three-phase boundaries pressures are uniform within the reaction regions and approximated as the partial pressure at the electrode/electrolyte interface:

$$P_{H_2O,TPB} = p_f X_{H_2O} + \frac{RT_3 \psi_3}{2FD_3 \phi_3} \frac{L_3 I}{L_y L_z} \quad (21a)$$

$$P_{H_2,TPB} = p_f X_{H_2} - \frac{RT_3 \psi_3}{2FD_3 \phi_3} \frac{L_3 I}{L_y L_z} \quad (21b)$$

$$P_{O_2,TPB} = p_{air} - (p_{air} - X_{O_2} p_{air}) \exp\left(\frac{RT_5 \psi_5 L_5 I}{4FD_5 \phi_5 p_{air} L_y L_z}\right) \quad (21c)$$

where ψ is the tortuosity, D is the diffusivity, p_f is the total pressure in the fuel channels, p_{air} is the total pressure in the oxidant channels. According to Kim et al. [30], binary diffusion dominates the gas transport through the porous electrodes. The diffusivities, D_j , in the anode layer and the cathode layer are obtained from [31]:

$$D_3 = \frac{1.43 \times 10^{-7} T_3^{1.75} (M_{H_2} + M_{H_2O})^{1/2}}{P_f (2M_{H_2} M_{H_2O})^{1/2} (v_{H_2}^{1/3} + v_{H_2O}^{1/3})^2} \quad (22a)$$

$$D_5 = \frac{1.43 \times 10^{-7} T_5^{1.75} (M_{O_2} + M_{N_2})^{1/2}}{P_{air} (2M_{O_2} M_{N_2})^{1/2} (v_{O_2}^{1/3} + v_{N_2}^{1/3})^2} \quad (22b)$$

where v is the diffusion volume of simple molecules.

Therefore, for CV3, the energy balance accounts for energy change due to the heat transfer, potential losses heating, mass transfer, and the heat generated during the electrochemical reaction, as follows:

$$\frac{d\theta_3}{d\tau} = \frac{[-\tilde{Q}_{rad,1-3} - \tilde{Q}_{env,2-3} + \tilde{Q}_{ohm,3} + \tilde{Q}_{actconc,3} + \tilde{Q}_{cnd,3-4} - \tilde{Q}_{cnd,1-3} + \tilde{Q}_{mass,3} + \alpha\tilde{Q}_{rct}]}{\tilde{N}_3} \quad (23)$$

where $\tilde{Q}_{cnd,3-4}$ is the dimensionless conduction heat transfer from the electrolyte to the anode layer, and it is given by:

$$\tilde{Q}_{cnd,3-4} = \frac{2\tilde{k}_3\tilde{k}_4\tilde{A}_{cnd,3-4}(\theta_4 - \theta_3)}{\xi_4\tilde{k}_3 + \xi_3\tilde{k}_4} \quad (24)$$

The effective heat conduction area, $\tilde{A}_{cnd,3-4}$, in Equation (24) is given by $\tilde{A}_{cnd,3-4} = (1 - \varphi_3)\xi_y\xi_z$. Besides, $\tilde{Q}_{mass,3}$, the energy change of CV3 due to the mass flow across its boundaries, is given by:

$$\tilde{Q}_{mass,3} = \frac{\dot{n}_{H_2}(H_{H_2,2} - H_{H_2,3}) + \dot{n}_{H_2O}(H_{H_2O,4} - H_{H_2O,3})}{\dot{m}_{ref}c_{p,f}T_{ref}} \quad (25)$$

The energy equation for CV4, based on the first law of thermodynamics, is written as follows:

$$\frac{d\theta_4}{d\tau} = \frac{[-\tilde{Q}_{cnd,3-4} + \tilde{Q}_{cnd,4-5} + \tilde{Q}_{ohm,4} + \tilde{Q}_{mass,4}]}{\tilde{N}_4} \quad (26)$$

The dimensionless conduction heat transfer from the cathode layer to the electrolyte is written as:

$$\tilde{Q}_{cnd,4-5} = \frac{2\tilde{k}_4\tilde{k}_5\tilde{A}_{cnd,4-5}(\theta_5 - \theta_4)}{\xi_5\tilde{k}_4 + \xi_4\tilde{k}_5} \quad (27)$$

where the effective conduction heat transfer area is $\tilde{A}_{cnd,4-5} = (1 - \varphi_5)\xi_y\xi_z$.

The energy change due to mass transfer across the electrolyte boundaries is calculated as:

$$\tilde{\dot{Q}}_{mass,4} = \frac{\dot{n}_{H_2}(H_{H_2,3} - H_{H_2,4}) + \dot{n}_{O_2}(H_{O_2,5} - H_{O_2,4})}{\dot{m}_{ref} c_{p,f} T_{ref}} \quad (28)$$

Similarly to the anode layer, the transient variation of the cathode layer temperature is obtained based on the first law of thermodynamics as follows:

$$\frac{d\theta_5}{d\tau} = \frac{[-\tilde{\dot{Q}}_{rad,1-5} + \tilde{\dot{Q}}_{cnv,5-6} + \tilde{\dot{Q}}_{ohm,5} + \tilde{\dot{Q}}_{actconc,5} - \tilde{\dot{Q}}_{cnd,4-5} - \tilde{\dot{Q}}_{cnd,1-5} + \tilde{\dot{Q}}_{mass,5} + (1-\alpha)\tilde{\dot{Q}}_{rct}]}{\tilde{N}_5} \quad (29)$$

where the dimensionless convective heat transfer from the oxidant channels to the cathode layer is:

$$\tilde{\dot{Q}}_{cnv,5-6} = \tilde{h}_6 n_{ch} \xi_{ch} \xi_z (1-\phi_5)(\theta_6 - \theta_5) \quad (30)$$

And the energy change due to mass transfer across the cathode layer boundaries is:

$$\tilde{\dot{Q}}_{mass,5} = \frac{\dot{n}_{O_2}(H_{O_2,6} - H_{O_2,5}) + \dot{n}_{O_2} \frac{X_{N_2}}{X_{O_2}} (H_{N_2,6} - H_{N_2,5})}{\dot{m}_{ref} c_{p,f} T_{ref}} \quad (31)$$

The energy balance in the oxidant channels of CV6 yields:

$$\frac{d\theta_6}{d\tau} = \frac{[-\tilde{\dot{Q}}_{cnv,1-6} - \tilde{\dot{Q}}_{cnv,5-6} + \tilde{\dot{Q}}_{mass,6}]}{\tilde{N}_6} \quad (32)$$

where the energy change due to mass transfer across the oxidant channels boundaries is:

$$\tilde{\dot{Q}}_{mass,6} = \frac{\dot{n}_{O_2,in}(H_{O_2,air} - H_{O_2,6}) + \dot{n}_{N_2,in}(H_{N_2,air} - H_{N_2,6})}{\dot{m}_{ref} c_{p,f} T_{ref}} \quad (33)$$

The dimensionless heat capacity of CV6 is given by:

$$\tilde{N}_6 = \frac{p_{air} n_{ch} L_{ch} L_6 L_z (X_{O_2} c_{v,O_2} + X_{N_2} c_{v,N_2})}{RT_6 \dot{m}_{ref} c_{p,f}} \quad (34)$$

The pumping power consumed to supply fuel and oxidant streams to the single cell is calculated based on the assumption that the pumping process is adiabatic:

$$\dot{W}_p = \dot{m}_2 \frac{\kappa_2}{\kappa_2 - 1} R_2 T_2 \left[\left(\frac{p_f + \Delta p_2}{p_f} \right)^{\frac{\kappa_2 - 1}{\kappa_2}} - 1 \right] + \dot{m}_6 \frac{\kappa_6}{\kappa_6 - 1} R_6 T_6 \left[\left(\frac{p_{air} + \Delta p_6}{p_{air}} \right)^{\frac{\kappa_6 - 1}{\kappa_6}} - 1 \right] \quad (35)$$

where the pressure drop in the fuel and oxidant channels are:

$$\Delta p_2 = \frac{2 f_2 L_y \rho_2 u_2^2}{D_{h,2}}, \quad \Delta p_6 = \frac{2 f_6 L_z \rho_6 u_6^2}{D_{h,6}} \quad (36)$$

The average mass flow rates in the fuel and oxidant channels are given by:

$$\dot{m}_2 = \frac{1}{2} \left[M_{H_2} (\dot{n}_{H_2,in} + \dot{n}_{H_2,out}) + M_{H_2O} \dot{n}_{H_2O} \right] \quad (37a)$$

$$\dot{m}_6 = \frac{1}{2} \left[M_{O_2} (\dot{n}_{O_2,in} + \dot{n}_{O_2,out}) + M_{N_2} (\dot{n}_{N_2,in} + \dot{n}_{N_2,out}) \right] \quad (37b)$$

In Equation (35), κ_j is the specific heat ratio and given as $\kappa_j = c_{p,j} / c_{v,j}$, $j = 2, 6$. R_j is the specific gas constant and calculated by $R_j = c_{p,j} - c_{v,j}$. Note that the subscript j here indicates the gas mixture in the fuel and oxidant channels.

2.2 Electrochemical Model of the Single SOFC

To complete the model of the single SOFC, the thermal model needs to be coupled with the electrochemical counterpart before the SOFC performance can be evaluated.

2.2.1 Composite Electrode Microstructure

The fuel cell positive electrode – electrolyte – negative electrode assembly (PEN) microstructure has significant influence on its electrochemical performance. The electrodes of the single SOFC are a mixture of electronic and ionic conducting material (electrolyte material). In the present study, the ionic conducting material in the composite electrodes is modeled as regularly spaced corrugations, which protrude from the dense electrolyte surface, as shown in

Figure 2.2. The electronic conducting material is spread over the surface of ionic conducting material. The remaining space corresponds to the parallel tube-like pores used for the transport of gaseous species [10]. The interface of the ionic conducting material, electronic conducting material and reacting gases is called three-phase boundary (TPB), and it is the location where the electrochemical reaction is likely to take place. However, according to Nam and Jeon [11], the electrochemical reaction happens in only a small portion of the TPB. It is further concluded by Chan and Xia [12] that the electrochemical reactions take place where the total potential losses in each electrode reach a minimum. In the current study, the part of the TPB where the electrochemical reaction actually happens is called active TPB and labeled by $L'_{j,opt}$ in Figure 2.2.

Figure 2.2 Model of the positive electrode – electrolyte – negative electrode assembly (PEN) internal structure

Figure 2.3 illustrates in more detail the electrochemical reaction occurred in the composite electrodes and the path followed by ions and electrons during this process. The TPB

region in anode corresponds to the solid lines in Figure 2.3. Part of the TPB region where the electrochemical reaction actually take place is called active TPB and represented by the dashed lines. Oxygen ions transfer from the cathode through the electrolyte across the ionic conducting paths in anode to the active TPB, where they react with the incoming hydrogen molecules arriving through the pores. The reaction results in gaseous water product that diffuses back to the pores. The released electrons travel from the active TPB through the electronic conducting paths (dark regions) to the adjacent interconnect.

Figure 2.3 Model for the composite microstructure of a SOFC anode

The area of the active TPB regions in each electrode, $A'_{j,opt}$, is calculated with $A'_{j,opt} = (1 + 2L'_{j,opt}\phi_j / D_{p,j})L_yL_z$. Here, $D_{p,j}$ stands for the average diameter of the parallel pores in the electrodes and it is obtained with $D_{p,j} = D_{w,j}\phi_j / (1 - \phi_j)$. $D_{w,j}$ is the width of a corrugation with ionic conducting material as shown in Figure 2.2 and its value is given by Tanner et al. [10]. $L'_{j,opt}$ represents the thickness of active TPB region and its value will be discussed in the Chapter 3.

2.2.2 Operating potential and losses

The actual operating potential of the single SOFC, V , is derived from the ideal Nernst potential V_{nernst} , by taking into account various kinds of losses, i.e., the constant offset losses due to the contact electrical resistance, internal current and leaks, V_{offset} , the activation losses due to the energy consumption to activate the electrochemical reaction, $V_{act,j}$, the concentration losses due to the concentration gradient of reactants across the fuel cell, $V_{conc,j}$, as well as the ohmic losses in all the solid compartments of the fuel cell, $V_{ohm,j}$:

$$V = V_{nernst} - \left(\sum_j V_{ohm,j} + V_{conc,3} + V_{conc,5} + V_{act,3} + V_{act,5} + V_{offset} \right) \quad j = 1, 3, 4, 5 \quad (38)$$

The ideal Nernst potential of the single SOFC, V_{nernst} , is estimated by the difference of Gibbs free energy between the reactants and products of the electrochemical reactions, which are described by Equations (1) and (2). Its calculation is reported by Kim et al. [30] based on the assumption that both reactions occur at the electrolyte temperature, T_4 :

$$V_{nernst} = \frac{-\{(H_{H_2O,4} - H_{H_2,4} - 1/2 H_{O_2,4}) - T_4 (S_{H_2O,4}^0 - S_{H_2,4}^0 - 1/2 S_{O_2,4}^0) + RT_4 \ln[P_{H_2O} / (P_{H_2} (P_{O_2})^{1/2})]\}}{2F} \quad (39)$$

According to Chick et al. [32], the constant offset overpotential, V_{offset} , takes the value of 0.07 volt.

When electrochemical reactions take place rapidly, the concentrations of reactants at the reacting region would drop, which results in the so-called concentration losses. The concentration overpotentials in the anode layer and cathode layer are given by Aguiar et al. [15] as:

$$V_{conc,a} = \frac{RT_3}{2F} \ln \left(\frac{P_{H_2} P_{H_2O,TPB}}{P_{H_2,TPB} P_{H_2O}} \right) \quad (40a)$$

$$V_{conc,c} = \frac{RT_5}{4F} \ln \left(\frac{P_{O_2}}{P_{O_2,TPB}} \right) \quad (40b)$$

The ohmic losses, $V_{ohm,j}$, are obtained based on the Ohm's law as follows:

$$V_{ohm,j} = I \beta_j \quad j = 1, 4 \quad (41a)$$

$$V_{ohm,j} = \frac{I(A'_{j,opt} - L_y L_z) L'_{j,opt}}{2A'_{j,opt} L_y L_z (1 - \phi_j) \sigma_4} + \frac{I(L_j - L'_{j,opt})}{L_y L_z (1 - 1.8\phi_j) \sigma_j} \quad j = 3, 5 \quad (41b)$$

where the electrical resistances of the interconnect and electrolyte, β_1 and β_4 , are calculated according to their material and geometric features as follows [2]:

$$\beta_1 = \frac{L_1}{L_y L_z \sigma_1} + \frac{L_2}{(1 + n_{ch}) L_t L_y \sigma_1} + \frac{L_6}{(1 + n_{ch}) L_t L_z \sigma_1} \quad (42a)$$

$$\beta_4 = \frac{L_4}{L_y L_z \sigma_4} \quad (42b)$$

where σ_j is the electrical conductivity of each control volume.

In Equation 41 (b), the first term at the right side of the equation accounts for the ohmic losses in the active TPB regions where the ionic conducting resistance is dominant, the second term refers to the remaining regions of the electrodes where only electronic conducting resistance exists.

The activation losses, $V_{act,j}$, representing the energy needed to activate electrochemical reactions, are estimated by the Butler-Volmer equation [33] as follows:

$$i_j = i_{0,j} [\exp(\frac{\alpha_c n F}{RT_j} V_{act,j}) - \exp(-\frac{(1 - \alpha_c) n F}{RT_j} V_{act,j})], \quad j = 3, 5 \quad (43)$$

In Equation (43) n takes the value of 2, α_c stands for the charge transfer coefficient, and when it takes the typical value of 0.5, the explicit form for the activation overpotentials is given by:

$$V_{act,j} = \frac{RT_j}{\alpha_c n F} \sinh^{-1}(\frac{i_j}{2i_{0,j}}), \quad j = 3, 5 \quad (44)$$

where $i_{0,j}$ stand for the exchange current densities and are reported by Aguiar et al. [15] as follows:

$$i_{0,j} = \frac{RT_j}{nF} \delta_j \exp(-\frac{E_j}{RT_j}), \quad j = 3,5 \quad (45)$$

where δ_j and E_j are the pre-exponential factor and the activation energy, respectively. Their values are reported by Aguiar et al. [15].

In Equation (43) and (44), the working current densities at both electrodes, i_j , are defined as $i_j = I / A_{j,opt}$.

The total potential losses in each electrode, $V_{total,j}$, are defined as:

$$V_{total,j} = V_{act,j} + V_{ohm,j} + V_{conc,j} \quad j = 3,5 \quad (46)$$

With the knowledge of actual operating potential calculated by Equation (38), the electrical power of the single SOFC is obtained with:

$$\dot{W}_E = VI \quad (47)$$

And the net power (available for utilization) of the single SOFC is derived from its electrical power by subtracting the required pumping power:

$$\dot{W}_N = \dot{W}_E - \dot{W}_P \quad (48)$$

In the present work, fuel cell working current, potential and power are nondimensionalised as follows:

$$\tilde{I} = \frac{I}{I_{ref}} \quad (49)$$

where I_{ref} is a specified reference current and the value is listed in table 1.

$$\tilde{V}_j = \frac{V_j}{V_{ref}} \quad (50)$$

where $V_{ref} = (\dot{m}_{ref} c_{p,f} T_{ref}) / I_{ref}$ stands for the reference voltage. $\tilde{V}$ represents the dimensionless potential or potential losses.

$$\tilde{W}_j = \frac{\dot{W}_j}{\dot{W}_{ref}}, j = E, P, N \quad (51)$$

where $\dot{W}_{ref}$ is the reference power defined as $\dot{W}_{ref} = \dot{m}_{ref} c_{p,f} T_{ref}$. $\tilde{W}$ is the dimensionless power.

2.3 Model Validation

The current model improves the work of Aguiar et al. [15] by integrating a new pore model for the SOFC composite electrodes microstructure. In an effort to validate the model, we compare the electrochemical performance of the SOFC simulated using the current model with Aguiar's model [15] and with experimental data reported by Chick et al. [32]. The comparison is shown in Figure 2.4. Under the same SOFC geometric dimensions and operating condition defined in Chick et al. [32], the current model shows better agreement with the experimental data. In particular, for the current density ranging between 0.1-1.5 A cm⁻², the largest error of the current model is about 0.04 volt and the average error is 0.015 volt. The improvement with respect to [15] can be explained from the difference in the modeling of potential losses. In the present model: i) the composite electrodes are modeled as a mixture of electronic and ionic conductor; ii) the charge-transfer reaction happens at the active TPB regions expanding a small distance from the electrode/ electrolyte interface; iii) active TPB regions where the reactions actually happen are much larger than the electrode/ electrolyte interface which was simply taken as the reaction surface in Aguiar's model. As a result, the activation losses in the present model are smaller than the one in Aguiar's model. Besides, in the current model, the ohmic losses in the electrodes account for both the oxygen ion transfer which is in the region enclosed by the active TPB and electron transfer which is out of active TPB region.

Figure.2.4 Comparison of single SOFC polarization curves simulated with the current model, with Aguiar's model and the experimental data reported by Chick et al. [32]

CHAPTER THREE

RESULTS AND DISCUSSION

Figure 2.1 shows the main geometric features of the single SOFC under study, which include the external dimensions (L_x , L_y , and L_z), the individual layers thicknesses (L_i), the width (L_{ch}) and the shoulder thicknesses (L_t) of fuel and oxidant channels, and the number of channels embedded in the bipolar plate (n_{ch}). The inlet temperature and pressure of both fuel and oxidant streams are taken as 923.15 K ($T_{f,in}$, $T_{air,in}$) and 1 atm (p_f , p_{air}), respectively.

The values of the physical properties and parameters used in the equations of the present model are listed in Table 1. The thermo-fluid properties of the pure gas and their mixtures are obtained as temperature-dependent quantities according to Todd and Young [34].

As discussed in the previous chapter, the thermal model of the single SOFC consists of six ordinary differential equations to obtain the temperatures of each CV in SOFC. It also includes three algebraic equations to obtain the reactants partial pressures at the active TPB regions, i.e., Equations (21a), (21b), and (21c). The present work focuses on the SOFC performance at steady state. As a result, only steady state solutions of the model are considered, which are obtained by equating the time derivatives of each CV's temperature to zero and solving them with a quasi-Newton method [35]. The solutions obtained from the thermal model include temperature of each control volume, as well as the reactants concentration inside the fuel cell. These results are then used in the electrochemical model, from which the electrochemical performance of the single SOFC is evaluated.

3.1 Temperature Profile of the Single SOFC

Figure 3.1 shows the typical temperature profile across the single SOFC. It is observed that as working current increases, the temperature of all the control volumes increase as well. The reason is that the higher the current is, the more fuel is consumed in the electrochemical reaction. As a result, more reaction heat is generated in the single SOFC which drives the overall SOFC temperature to increase. Figure 3.1 also shows that there is significant temperature spatial gradient across the fuel cell, especially the temperature difference between the oxidant channels

(CV6) and the PEN (CV3, CV4, CV5) (positive electrode-electrolyte-negative electrode assembly). This is due to the poor thermal conductivity of air stream compared with the solid compartment of the SOFC, as well as relatively large heat capacity of air stream compared with fuel stream. The temperature spatial gradient has a direct impact on fuel cell performance, therefore the performance evaluation (featured by electrical power and polarization curves) should take all the spatial temperature gradients into consideration.

Figure 3.1 The temperature of each compartment in the single SOFC as functions of current

3.2 Polarization Curves of the Single SOFC

Figure 3.2 shows the polarization curves of the single SOFC obtained with the present model. When the working current increases, the overall temperature of the SOFC rises up, and the Gibbs free energy difference between the reactants and products of the electrochemical reactions drops down, which results in a reduced ideal Nernst potential, according to Equation (39). At the same time, the activation overpotential, concentration overpotential and ohmic overpotential increase monotonously, which, combined with the decrease of ideal Nernst

potential, results in the drop of the actual working potential, according to Equation (38). It is shown in Figure 3.2 that the constant offset overpotential is the dominant potential losses for small working current. As the working current increases, the activation overpotential and ohmic overpotential grow rapidly.

Figure 3.2 The polarization curves of the single SOFC

Fuel cells are normally designed to operate at a cell voltage between 0.6 and 0.7 V [36]. In this study, the nominal operating point is defined as the operating point with actual working potential of 0.7 V. The fuel cell temperature, working current and power at the nominal operating point are then taken as the nominal temperature, current and power of the fuel cell, respectively. For instance, under the operating condition and fuel cell geometry described by Figure 3.1 and 3.2, the dimensionless nominal working current is 1.124 and the dimensionless nominal PEN

temperature is about 3.832.

3.3 Composite Electrodes Microstructure Discussion

In this section, in order to highlight the influence of composite electrodes microstructure on fuel cell performance, it is assumed that a uniform and constant thermal environment corresponding to the typical SOFC operating condition is maintained throughout the cell. Uniform temperature distribution inside the SOFC is a good approximation when the heat transfer area and/or heat transfer coefficient between the PEN and the gas channels are sufficiently large to ignore the gradient across the fuel cell.

Figure 3.3 shows polarization curves of a single SOFC with different anode reaction layer thicknesses. For an operating temperature of $\theta = 3.6 (T = 1073\text{K})$, the cell with anode reaction layer of $\xi'_3 = 3.19 \times 10^{-4}$ ($L'_3 = 10\mu\text{m}$) has the best I - V performance. The nominal current densities of the single SOFC with anode reaction layers of $\xi'_3 = 3.19 \times 10^{-4}$, 12.77×10^{-4} and 22.36×10^{-4} ($L'_3 = 10\mu\text{m}$, $40\mu\text{m}$ and $70\mu\text{m}$) are $\tilde{i} = 0.108$, 0.0849 and 0.066 , respectively. The nominal power densities are $\tilde{w} = 0.109$, 0.086 and 0.067 , respectively.

Figure 3.3 Polarization curves of the single SOFC with various anode reaction layer thicknesses

Figure 3.4 shows how the nominal net power density changes with the fuel cell anode reaction layer thickness. The investigation is conducted under three working temperatures: $\theta=3.265, 3.60$ and 3.936 ($T = 973\text{K}, 1073\text{K}$ and 1173K). For each working temperature, there is a specific optimal reaction layer thickness that maximizes the fuel cell nominal net power density. By analysing the fuel cell polarization curve, it is concluded that optimal anode reaction layer thickness results from the trade-off between different potential losses in the anode.

Figure 3.4 SOFC nominal net power density as a function of anode reaction layer thickness under various working temperatures

In a similar way, the polarization curves of the single SOFC with different cathode reaction layer thicknesses are shown in Figure 3.5. Figure 3.6 shows how the fuel cell nominal net power density changes under different working temperatures as a function of cathode reaction layer thickness. For each investigated working temperature, $\theta = 3.265, 3.60$ and 3.936 ($T = 973\text{K}, 1073\text{K}$ and 1173K), there is a specific optimal reaction layer thickness in the cathode that maximizes the nominal net power density.

Figure 3.5 Polarization curves of the single SOFC with various cathode reaction layer thicknesses

Figure 3.6 SOFC nominal net power density as a function of cathode reaction layer thicknesses under various working temperatures

The fuel cell electrodes porosities also influence its performance. In the present study, the porosities of the two electrodes are assumed to be the same. The polarization curves of the current fuel cell with various electrodes porosities are shown in Figure 3.7. Besides, as the electrodes porosities change, the optimal reaction layer thicknesses in the two electrodes that maximize the fuel cell net power density change as well. This is illustrated in Figure 3.8 with the corresponding two-way maximized fuel cell net power density. It is concluded that neither very large nor very small porosity benefits fuel cell performance, and the fuel cell nominal net power density reaches a

maximum with electrodes porosities of 0.31. The optimal porosities are a result of the trade-off between different potential losses in the electrodes.

Figure 3.7 Polarization curves of the single SOFC with various electrodes porosities

Figure 3.8 The optimal reaction layer thicknesses in the two electrodes and the two-way maximized nominal net power density as functions of electrodes porosities

3.4 Determination of Active TPB Regions at Two Electrodes

Figure 3.9 shows the way to determine the active TPB region at the anode, $\xi'_{3,opt}$. According to [11], it corresponds to the optimal reaction layer thickness, ξ'_3 , that minimizes the total potential losses at the anode, $\tilde{V}_{total,3}$. Three anode thicknesses are considered, $\xi_3 = 6.4 \times 10^{-4}$ (dotted line), $\xi_3 = 16 \times 10^{-4}$ (dashed line) and $\xi_3 = 160 \times 10^{-4}$ (solid line) (the dotted and dashed lines overlap). As Figure 3.9 shows, for working currents of $\tilde{I} = 0.172, 0.344$ and 0.516 , the total potential losses at the anode reach a minimum at $\xi'_{3,opt} = 3.52 \times 10^{-4}, 3.2 \times 10^{-4}$ and 2.98×10^{-4} respectively, regardless of the total anode thickness ξ_3 . In other words, the optimal reaction layer thickness, $\xi'_{3,opt}$, is insensitive to the changes in the anode thickness. Figure 3.9 also shows that the active TPB region where the total potential losses in the anode reach a minimum

coincides with the optimal reaction layer thickness where the electrical and net power of SOFC reach a maximum. (e.g., $\xi'_{3,opt} = 2.98 \times 10^{-4}$ for a working current of $\tilde{I} = 0.516$). The electrical power and net power curves are parallel, since for the conditions of Figure 3.9, the pumping power is constant for each current level.

Figure 3.9 The total potential losses at the anode and electrical power and net power as functions of anode reaction region thickness under various working currents and anode thicknesses

Figure 3.10 shows the way to determine the active TPB region at the cathode, $\xi'_{5,opt}$. Similar conclusions to the anode side are obtained: the optimal ξ'_5 , is practically insensitive to the changes in the cathode thickness; the optimal ξ'_5 where the total potential losses in the cathode reach a minimum is also the optimal ξ'_5 where electrical and net power reach a maximum. When the working currents $\tilde{I}$ are 0.172, 0.344 and 0.516, the active TPB regions at the cathode, $\xi'_{5,opt}$, are 5.19×10^{-4} , 4.61×10^{-4} and 4.13×10^{-4} , respectively. Since the total

potential losses at the anode and cathode are computed separately and do not influence each other, $\xi'_{3,opt}$ and $\xi'_{5,opt}$ are independent of each other.

Figure 3.10 The total potential losses at the cathode and electrical power as functions of cathode reaction region thickness under various working currents and cathode thicknesses

3.5 SOFC Operation Condition

3.5.1 Air Stoichiometric Ratio

The effect of air stoichiometric ratio, λ_{air} , on the performance of the single SOFC is illustrated in Figure 3.11. It is observed that the nominal working current and electrical power decrease as the air stoichiometric ratio increases, which illustrates that large air stoichiometric ratio does not benefit SOFC performance. Such phenomenon can be explained physically: As the air stoichiometric ratio increases, more air with comparably low inlet temperature flows through the fuel cell, which drives SOFC temperature down, as shown in Figure 3.11. As the temperature of the single SOFC decreases, the cell's total potential losses increase rapidly and the actual operating potential drops down, ending up with small nominal current and electrical power.

Figure 3.11 The working current, electrical power and electrolyte temperature at the nominal operating point as functions of air stoichiometric ratio

3.5.2 Fuel Utilization Factor

Figure 3.12 illustrates the significant impact that the fuel utilization factor has on the performance of the single SOFC. The nominal electrical power reaches a maximum of 0.765 when $\gamma_f = 0.88$, which is approximately 110% higher than the nominal electrical power of 0.362 when $\gamma_f = 0.1$. Figure 3.12 also shows that very large or very small fuel utilization factor does not benefit the SOFC performance. This effect can be explained physically by analyzing two extremes: (i) for large fuel utilization factor, the fuel cell potential losses decrease due to the relatively high temperature in SOFC (less fuel with comparably low temperature at inlet flows through the fuel cell), as shown in Figure 3.12. However, due to the low concentration of hydrogen in the fuel channels, the ideal Nernst potential also decreases according to Equation (39), which leads to the drop of actual working potential and ends up with small nominal current and electrical power; (ii) for small fuel utilization factor, the ideal Nernst potential increases (due to the high concentration of hydrogen in the fuel channels), but the potential losses become

larger as well due to the low temperature in the fuel cell (more fuel with comparably low temperature at inlet flows through the single SOFC), so the actual working potential decreases at this extreme too, which leads to the low nominal current and electrical power.

Figure 3.12 The electrolyte temperature, electrical power and net power at the nominal operating point as functions of fuel utilization factor

3.6 Summary

In this chapter a typical temperature profile and polarization curves of the single SOFC are obtained. Several important parameters related to its performance are identified: the microstructure of the electrodes, the reaction layer thicknesses at the anode and cathode and the operating conditions (fuel utilization factor and air stoichiometric ratio). Based on the discussion several important conclusions are drawn: 1) a large air stoichiometric ratio does not benefit the fuel cell performance due to a decreased cell temperature. 2) The optimal fuel utilization factor results from the trade-off between SOFC operating temperature and fuel concentration. 3) The active TPB regions where the total potential losses in the electrodes reach a minimum coincide

with the optimal reaction layer thicknesses where the electrical and net power of SOFC reach a maximum. The active TPB regions are determined based on the trade-offs between all the potential losses in the electrodes. 4) The active TPB regions in the electrodes are insensitive to the variation of the electrodes thicknesses, and they are independent of each other.

CHAPTER FOUR

SOFC INTERNAL STRUCTURE OPTIMIZATION

4.1 PEN Geometry Optimization under Fixed Operating Condition

Under a constrained operating condition (fixed fuel utilization factor and air stoichiometric ratio), the optimization of the positive electrode-electrolyte-negative electrode assembly (PEN) internal structure consists of pursuing maximum nominal electrical power by optimizing the thicknesses of the anode layer, electrolyte and cathode layer subject to a fixed total thickness of PEN, i.e., $L_3 + L_4 + L_5 = \text{constant}$. Note that, for most single SOFCs produced currently, the minimum thicknesses of the anode layer, electrolyte and cathode layer are 50 μm , 5 μm and 50 μm , respectively, due to the limitation of fabrication techniques. The analysis and discussion about the PEN internal structure in this paper is based on a more extended range, and the conclusion from it could be used as reference in the future. The thicknesses ranges of the anode layer, electrolyte and cathode layer are 5 to 560 μm , 5 to 30 μm and 5 to 560 μm , respectively, and $L_3 + L_4 + L_5 = 570 \mu\text{m}$ ($\xi_3 + \xi_4 + \xi_5 = 182.4 \times 10^{-4}$).

Figure 4.1 shows that under a fixed operating condition, $\xi'_{3,opt}$, i.e., the optimal ξ'_3 in which the nominal electrical power reaches a maximum, is robust with respect to the changes in electrolyte thickness: $\xi'_{3,opt}$ is 2.399×10^{-4} , 2.415×10^{-4} and 2.431×10^{-4} when ξ_4 is 1.6×10^{-4} , 4.8×10^{-4} and 8×10^{-4} , respectively. Figure 4.2 shows the effect of electrolyte thickness on $\xi'_{5,opt}$: $\xi'_{5,opt}$ is 2.822×10^{-4} , 3.129×10^{-4} and 3.332×10^{-4} when ξ_4 is 1.6×10^{-4} , 4.8×10^{-4} and 8×10^{-4} .

Figure 4.1 The electrical power at the nominal operating point as a function of anode reaction region thickness for various electrolyte thicknesses

Figure 4.2 The electrical power at the nominal operating point as a function of cathode reaction region thickness for various electrolyte thicknesses

Figure 4.3 shows how $\xi'_{3,opt}$ and $\xi'_{5,opt}$ change as the electrolyte thickness varies. It is shown that within the selected thickness range of electrolyte, the active TPB region at the cathode, $\xi'_{5,opt}$, is larger than the counterpart at the anode; as the electrolyte increases, both $\xi'_{3,opt}$ and $\xi'_{5,opt}$ increase, though $\xi'_{3,opt}$ is practicably insensitive (i.e. robust) with respect to electrolyte thickness variation. The results of Figure 4.3 are used in the next discussion to set the values of $\xi'_{3,opt}$ and $\xi'_{5,opt}$, which are functions of electrolyte thickness. The two-way maximized electrical power at the nominal operating point is also reported in Figure 4.3.

Figure 4.3 The active TPB thickness at the anode and cathode and the two-way maximized electrical power at the nominal operating point as functions of electrolyte thickness

Figure 4.4 illustrates the impact of thickness distribution between two electrodes on the performance of the single SOFC, when the electrolyte thickness is fixed. For different electrolyte thicknesses, the nominal electrical power increases as the anode thickness increases at first, and then starts to drop after the anode thickness increases to an optimal value. The optimal thickness distribution between two electrodes is determined by the trade-off between the potential losses at the anode and cathode: (i) for small anode and large cathode, the potential losses at the anode,

primarily the concentration losses, would decrease, but the potential losses at the cathode would increase, mainly the ohmic losses; therefore, the total potential losses of the SOFC would increase, which leads to the drop of nominal electrical power; (ii) for the large anode and small cathode, the potential losses at the cathode would decrease, especially the ohmic losses, but the potential losses at the anode, mainly the concentration losses, would increase. In this way, the total potential losses of the SOFC would increase at this extreme too, leading to a drop of nominal electrical power.

Figure 4.4 The two-way maximized electrical power at the nominal operating point as a function of anode layer thickness under various electrolyte thicknesses

Figure 4.5 shows the optimal thickness distribution between the anode and cathode as a function of electrolyte thickness under a fixed operating condition. Within the selected thickness

range of electrolyte, $\xi_{3,opt}$ is much larger than $\xi_{5,opt}$, which suggests that under the fixed operating condition, an anode-supported SOFC would perform better than a cathode-supported SOFC. Figure 4.5 also shows that optimal anode and cathode thicknesses are essentially unchanged with variations in the electrolyte thickness. As the electrolyte thickness increases, the optimal anode thickness increases slightly and becomes stable when the electrolyte is larger than 8×10^{-4} . The opposite trend is observed for the optimal cathode thickness: as the electrolyte grows, the optimal cathode thickness decreases to some extent at first and becomes stable when the electrolyte is larger than 8×10^{-4} . These observations corroborate the robustness of the optimal internal structure.

Figure 4.5 The optimal thickness distribution between the anode and cathode as well as the three-way maximized electrical power at the nominal operating point as functions of electrolyte thickness

Figure 4.5 also shows the important impact the electrolyte has on the performance of the single SOFC. Under the fixed operating conditions, for the optimal electrodes thicknesses distribution and the active reaction regions at two electrodes, the three-way maximized nominal electrical power drops sharply as the electrolyte thickness increases, due to its large

ionic-conducting resistance and the consequent large ohmic losses. Therefore, the improvement of the ionic-conductivity of the electrolyte and the decrease of its thickness are key issues to improve SOFC performance.

4.2 Electrodes Geometry Optimization under Variable Operating Conditions

So far, the PEN internal structure optimization has been pursued at fixed operating conditions (i.e., $\gamma_f = 0.75$, $\lambda_{air} = 7$). It is concluded that a thin electrolyte would benefit fuel cell performance. In practice, the minimum thickness of the electrolyte is determined by the fabrication techniques. Therefore, in the following discussion, the electrolyte thickness is assumed to be constant. In contrast, the assumption of constant fuel utilization factor is relaxed. The optimization problem is simplified as follows: for a fixed electrolyte thickness and given total PEN thickness, the optimal fuel utilization factor and the optimal thickness distribution between the anode and cathode are pursued to achieve a maximum nominal electrical power. The four degrees of freedom are then the thicknesses of the active TPB regions in the anode and cathode, the anode and cathode thickness distribution, and the fuel utilization factor.

Figure 4.6 shows how the nominal electrical power changes with the thickness of anode reaction region thickness under various fuel utilization factors. $\xi'_{3,opt}$, the optimal ξ'_3 where the nominal electrical power reaches a maximum, changes slightly for different fuel utilization factors: $\xi'_{3,opt}$ is 3.11×10^{-4} , 2.59×10^{-4} and 2.39×10^{-4} for $\gamma_f = 0.1$, 0.5 and 0.9 , respectively. Similarly, Figure 4.7 shows that $\xi'_{5,opt}$ is 3.18×10^{-4} , 3.22×10^{-4} and 3.26×10^{-4} for $\gamma_f = 0.1$, 0.5 and 0.9 , respectively.

Figure 4.6 The electrical power at the nominal operating point as a function of anode reaction region thickness under various fuel utilization factors

Figure 4.7 The electrical power at the nominal operating point as a function of cathode reaction region thickness under various fuel utilization factors

Figure 4.8 shows how $\xi'_{3,opt}$ and $\xi'_{5,opt}$ change as the fuel utilization factor varies: as the fuel utilization factor increases, the active TPB region at the anode decreases, whereas the active TPB region at the cathode increases slightly. The results in Figure 4.8 are used in the next discussion to set the values of $\xi'_{3,opt}$ and $\xi'_{5,opt}$ as functions of the fuel utilization factor.

Figure 4.8 The active TPB regions thicknesses at the anode and cathode as functions of fuel utilization factor

Figure 4.9 shows how the two-way maximized nominal electrical power (e.g., corresponding to $\xi'_{3,opt}$ and $\xi'_{5,opt}$) changes with fuel utilization factor for different thickness distributions between the two electrodes. The optimal fuel utilization factor, $\gamma_{f,opt}$, is 0.844, 0.863 and 0.878 when ξ_3 is 1.6×10^{-4} , 64×10^{-4} and 160×10^{-4} , respectively. The consequent relationship between the optimal fuel utilization factor and the thickness distribution between the two electrodes is shown in Figure 4.10. It is observed that $\gamma_{f,opt}$, the optimal fuel utilization factor, increases as the anode layer thickness increases.

Figure 4.9 The two-way maximized electrical power at the nominal operating point as a function of fuel utilization factor for various anode layer thicknesses

Figure 4.10 The optimal fuel utilization factor as a function of anode layer thickness

Since $\xi'_{3,opt}$ and $\xi'_{5,opt}$ are functions of the fuel utilization factor (Figure 4.8) and the optimal fuel utilization factor is a function of the thickness distribution between the two electrodes (Figure 4.10), $\xi'_{3,opt}$ and $\xi'_{5,opt}$ are functions of the thickness distribution between two electrodes under optimal fuel utilization factor. This relationship is shown in Figure 4.11.

Figure 4.11 The active TPB regions thicknesses at the anode and cathode as functions of anode layer thickness

Figures 4.10 and 4.11 show that as the anode layer thickness increases, the optimal fuel utilization factor increases as well, and accordingly, $\xi'_{3,opt}$, the active TPB region at the anode, decreases slightly, and $\xi'_{5,opt}$, the active TPB region at cathode increases slightly.

The three-way maximized nominal electrical power (e.g., corresponding to $\gamma_{f,opt}$, $\xi'_{3,opt}$ and $\xi'_{5,opt}$) as a function of the thickness distribution between the two electrodes is shown in Figure 4.12. Within the selected thickness range of anode, the $\tilde{W}_{E,n,mm}$ increases as the anode thickness increases, which indicates that under flexible operating conditions, the

anode-supported SOFC exhibits better performance than the cathode-supported SOFC, when all the other parameters are the same.

Figure 4.12 The three-way maximized electrical power at the nominal operating point as a function of anode layer thickness

4.3 Summary

In this chapter the internal structure of the positive electrode – electrolyte – negative electrode assembly (PEN) is optimized so that several effects such as the open circuit potential and all kinds of losses are appropriately balanced to achieve maximum nominal electrical power. The optimization is conducted under fixed and variable working conditions and the same conclusion is drawn: under the same geometric constraints and operating conditions, the anode-supported SOFC exhibits better performance than the cathode-supported and electrolyte-supported SOFC.

CHAPTER FIVE

SOFC EXTERNAL CONFIGURATION OPTIMIZATION

5.1 External Configuration Optimization under Fixed Operating Condition

In chapter 4, the PEN internal structure is optimized to enhance the fuel cell power output. In this chapter, the same objective is achieved with another method of optimizing the fuel cell's external configuration as well as its working condition. As shown in Figure 2.1, L_x , L_y and L_z are the main external geometric parameters of the single fuel cell. L_x is composed of the dimensions of interconnect, fuel channels, anode, electrolyte, cathode and air channels, among which the thicknesses of fuel and air channels account for nearly 2/3 of the total L_x . The remaining parts (interconnect, anode, electrolyte, cathode) account for only 1/3 of the L_x dimension, and normally their sizes depend on the fabrication techniques.

In the procedure of optimizing fuel cell external shape (represented by L_x , L_y , L_z), we limit this study to fuel cells with square cross section, $L_y = L_z$. In this way, the total volume constraint can be written as $L_x \times A_{\text{cross}} = \text{constant}$ or $\left(\sum_{i=1,3,4,5} L_i + L_2 + L_6 \right) \times A_{\text{cross}} = \text{constant}$, where $A_{\text{cross}} = L_y \times L_z = L_y^2 = L_z^2$. In this study we fix the total PEN thickness, $\sum_{i=3,4,5} L_i$ and the interconnect thickness, L_1 , and assume the thicknesses of fuel channels and oxidant channels are the same, $L_2 = L_6$. We search for the optimal values of fuel cell cross section area that satisfy the constant total volume constraint and maximize its power output. The optimal cross section area values have a one – to – one correspondence to the fuel and oxidant channels thicknesses (L_2 , L_6) due to the assumption of fixed PEN and interconnect thicknesses.

Figure 5.1 shows how the SOFC temperature profile at the nominal operating point changes with fuel cell external configuration (represented by $\tilde{A}_{\text{cross}}$). Constrained by the fixed total volume, with the increase of fuel cell cross section area and the decrease of air and fuel channels thicknesses, the temperature of the air flow in the oxidant channels decreases at first till $\tilde{A}_{\text{cross}} = 8.26$, after that it starts to rise up. The temperature of the rest parts of the fuel cell -

interconnect, PEN and the fuel flow in the fuel channels - show an opposite trend, which increase till $\tilde{A}_{cross} = 8.26$, and then start to drop down.

Figure 5.1 The nominal temperature of each compartment in the single SOFC as functions of fuel cell cross section area

Figure 5.2 explains the results in Figure 5.1. Due to the high thermal conductivity between the solid parts of the fuel cell and the relatively low heat capacity of fuel stream, the temperature of interconnect, fuel channels and PEN are almost the same ($\theta_{1,n} \approx \theta_{2,n} \approx \theta_{3,n} \approx \theta_{4,n} \approx \theta_{5,n}$). The main heat interaction in the fuel cell is the convective heat transfer between the air flow in the oxidant channels and the rest parts of the fuel cell. As shown in Figure 5.2, with the increase of the fuel cell cross section area and the decrease of air channels thickness, the convective heat transfer coefficient as well as the convective heat transfer area in the air side decrease at first. Meanwhile, the fuel cell working current at the nominal operating point keeps increasing (shown in Figure 5.5). As a result, more heat is generated from the electrochemical reaction and from the potential losses. According to the energy conservation law,

at steady state, $\tilde{Q}_{rct} + \tilde{Q}_{loss} = \tilde{Q}_{cnv,6} + \tilde{Q}_{cnv,2} = \tilde{h}_6 \tilde{A}_{cnv,6} (T_5 - T_6) + \tilde{Q}_{cnv,2}$. In which $\tilde{Q}_{cnv,2}$ is far smaller than $\tilde{Q}_{cnv,6}$ and could be ignored. As $\tilde{Q}_{rct}$ and $\tilde{Q}_{loss}$ increase, and $\tilde{h}_6$ and $\tilde{A}_{cnv,6}$ decrease, the temperature of the air flow in the oxidant channels drops down and the remaining parts of the fuel cell heat up. When $\tilde{A}_{cross}$ is larger than 6.53, $\tilde{Q}_{rct}$ and $\tilde{Q}_{loss}$ keep increasing, but $\tilde{h}_6$ and $\tilde{A}_{cnv,6}$ start to increase as well. The combined effect leads the temperature difference between the oxidant channels and the remaining parts to keep increasing until $\tilde{A}_{cross} = 8.26$. After that, the temperature of the oxidant channels starts to grow, and the temperature of the remaining parts begin to decrease.

Figure 5.2 The convective heat transfer coefficients of air and fuel streams and convective heat transfer area between the air and the single SOFC as functions of fuel cell cross section area

Figure 5.3 shows the polarization curves of a single SOFC with different SOFC external

configurations (represented by $\tilde{A}_{cross} = 2.55, 5, 8.26, 12.34 \text{ and } 17.24$, which correspond to $L_y = L_z = 0.05, 0.07, 0.09, 0.11, 0.13 \text{ m}$). As discussed above, as the fuel cell cross section area increases, the temperature of PEN increases until $\tilde{A}_{cross} = 8.26$ and then drops down. Because the ideal Nernst potential, the activation overpotentials and ohmic overpotential decrease as the PEN temperature increases, and vice versa, the curves of the ideal Nernst potential, the activation overpotentials and the ohmic overpotential with $\tilde{A}_{cross} = 8.26$ are the lowest amongst all the curves. It is also shown in Figure 5.3 that the concentration overpotentials are relatively insensitive to the change of SOFC external configuration.

Figure 5.3 The polarization curves of the single SOFC with various cross section areas

Figure 5.4 shows the fuel cell actual operating potential as a function of the working current density with different SOFC external configurations. Among all the actual operating potential curves, the one with $\tilde{A}_{cross} = 8.26$ is the highest, corresponding to the highest PEN working temperature among all the external configurations. Figure 5.5 shows the nominal working current density and working current as functions of SOFC external structure. Following the same trend as the actual operating potential in Figure 5.4, the nominal working current density increases with $\tilde{A}_{cross}$ at first, and then starts to drop when $\tilde{A}_{cross}$ is larger than 8.26. The working current increases monotonously as the cross section area increases, but the increase rate begins to slow down when the cross section area is greater than 8.26.

Figure 5.4 The fuel cell actual operating potential as a function of working current density with various SOFC cross section areas

Figure 5.5 The working current density and working current at the nominal operating point as functions of SOFC cross section area

Figure 5.6 shows the way to determine the active TPB region at the anode with different SOFC external configurations. It is concluded in the previous chapter that the active TPB region in the anode, where the total potential losses in the anode reach a minimum, coincides with the optimal ξ_3' at which the SOFC electrical and net power reach a maximum. For the configurations with cross section area $\tilde{A}_{cross} = 5.0, 8.26$ and 12.34 , the SOFC nominal net power reach a maximum at $\xi_{3,opt}' = 2.62, 2.40$ and 2.52 , respectively. Similarly, Figure 5.7 shows the way to determine the active TPB region at the cathode with different SOFC configurations. For the configurations with cross section area $\tilde{A}_{cross} = 5.0, 8.26$ and 12.34 , the active TPB regions at the cathode are $\xi_{5,opt}' = 4.22, 3.93$ and 4.09 , respectively.

Figure 5.6 The SOFC net power at the nominal operating point as a function of anode reaction region thickness with various SOFC cross section areas

Figure 5.7 The SOFC net power at the nominal operating point as a function of cathode reaction region thickness with various SOFC cross section areas

Figure 5.8 shows the active TPB regions at both electrodes as functions of the SOFC cross section area. As the fuel cell cross section area increases, the active TPB regions at both electrodes decrease at first. When the cross section area is greater than 8.26, the active TPB regions at both sides start to increase, which show the opposite trend to the variation of PEN nominal temperature.

Figure 5.8 The active TPB regions thicknesses at the anode and cathode as functions of SOFC cross section area

Figure 5.9 shows the two-way maximized (i.e. active TPB regions at both electrodes) net power, electrical power and pumping power at the nominal operating point as functions of SOFC external configuration. Following the same trend as the nominal working current, the nominal electrical power increases monotonously with the increase of the SOFC cross section area, though the increase rate declines after $\tilde{A}_{cross}$ is greater than 8.26. A dramatic increase in the pumping power is also observed in Figure 5.9, which combined with the variation of electrical power, leads the two-way maximized net power to increase at first, and then drop down. A

maximum net power of 0.775 is obtained at $\tilde{A}_{cross} = 12.34$.

Figure 5.9 The two-way maximized SOFC net power, electrical power and pumping power at the nominal operating point as functions of SOFC cross section area

5.2 External Configuration Optimization under Variable Operating Conditions

In section 5.1, the optimal external configuration of SOFC is derived from the trade-off between the cross section area of SOFC and the thicknesses of fuel and air channels. The discussion is conducted under fixed operating conditions (fixed air stoichiometric ratio and fuel utilization factor). However, in practice, the fuel utilization factor is adjustable, and the discussion below addresses the optimization of SOFC external configuration under flexible fuel utilization factor.

Figure 5.10 shows the way to determine the active TPB region at the anode with different SOFC external configurations ($\tilde{A}_{cross} = 5.0, 8.26$ and 12.34) and fuel utilization factors

($\gamma_f = 0.5$ and 0.8). It is shown in the figure that for each combination of cross section area and fuel utilization factor, there is a specific $\xi'_{3,opt}$ which maximizes SOFC net power at the nominal operating point. The relationship between the active TPB region at the anode and the fuel cell cross section area and fuel utilization factor is illustrated in Figure 5.11.

Figure 5.10 The SOFC net power at the nominal operating point as a function of anode reaction region thickness with various SOFC cross section areas and fuel utilization factors

Figure 5.11 The active TPB region thickness at the anode as a function of SOFC cross section area and fuel utilization factor

Similarly, Figure 5.12 shows the way to determine the active TPB region at cathode with different SOFC external configurations ($\tilde{A}_{cross} = 5.0, 8.26$ and 12.34) and fuel utilization factors ($\gamma_f = 0.5$ and 0.8). Figure 5.13 illustrates the relationship between the active TPB region thickness in the cathode and the fuel cell external configuration (dictated by the cross section area) and fuel utilization factor.

Figure 5.12 The SOFC net power at the nominal operating point as a function of cathode reaction region thickness with various SOFC cross section areas and fuel utilization factors

Figure 5.13 The active TPB region thickness at the cathode as a function of SOFC cross section area and fuel utilization factor

Figure 5.14 shows the two-way maximized (active TPB regions at two electrodes) net power at nominal operating point as a function of fuel utilization factor with different SOFC external configurations ($\tilde{A}_{cross} = 5.0, 8.26, 12.34$ and 15.9). It is shown that neither very large nor very small fuel utilization factor benefits the SOFC performance. This effect can be explained physically by analyzing two extremes: (i) for large fuel utilization factor, less fuel with comparably low inlet temperature flows through the fuel cell, consequently, the potential losses and the required pumping power decrease, due to the relatively high temperature in SOFC and small mass flow rate of the fuel stream, respectively. However, due to the low concentration of fuel in the fuel channels, the ideal Nernst potential decreases according to Equation (39), which leads to the drop of actual operating potential and ends up with small nominal current and net power; (ii) for small fuel utilization factor, the ideal Nernst potential increases (due to the high concentration of fuel in the fuel channels), but the potential losses and the required pumping power become larger due to the low temperature in the fuel cell and increased fuel flow rate (more fuel with comparably low inlet temperature flows through the single SOFC), so the SOFC net power decreases at this extreme too. For each cross section area, an optimal fuel utilization factor and a three-way maximized net power are observed. The corresponding relationship between the optimal fuel utilization factor $\gamma_{f,opt}$ and the SOFC external configuration is described in Figure 5.15. It is observed that the optimal fuel utilization factor increases with the cross section area until $\tilde{A}_{cross} = 8.26$, after that it starts to drop down, following the same trend as PEN nominal temperature.

Figure 5.14 The two-way maximized net power at the nominal operating point as a function of fuel utilization factor with various SOFC cross section areas

Figure 5.15 The optimal fuel utilization factor as a function of SOFC cross section area

Figure 5.16 shows the three-way maximized (the active TPB regions at both electrodes and the optimal fuel utilization factor) net power as well as electrical power and pumping power at the nominal operating point as functions of SOFC external configuration. Compared to the two-way maximized nominal net power in Figure 5.9, there is an increase in the nominal net power with the three-way maximization condition, due to the optimal fuel utilization factor. Figure 5.16 also shows that in the whole range of SOFC configurations, the three-way maximized net power reaches another maximum when $\tilde{A}_{cross} = 11.2$. So for the fixed total volume ($\tilde{V}_T = 1$), the four-way maximized (the active TPB regions at both electrodes, the optimal fuel utilization factor and the optimal cross section area) net power is about 0.885.

Figure 5.16 The three-way maximized net power, electrical power and pumping power at the nominal operating point as functions of SOFC cross section area

5.3 Summary

In this chapter the SOFC external configuration optimization is conducted. It includes the

optimal dimension allocation between the cross section area of the single cell and the thicknesses of the gas channels so that SOFC nominal electrical power and pumping power are appropriately balanced to achieve maximum net power. As it is shown in Figure 5.16, the three-way maximized net power varies between 0.16-0.89 as the fuel cell cross section area changes from 2.6-16. It comes to the conclusion that the fuel cell external structure has a significant impact on the net power output.

CHAPTER SIX

CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

In this dissertation a comprehensive model for a single SOFC is developed. It addresses both thermal and electrochemical aspects of a single SOFC and captures all the major phenomena in the cell such as fluid flow, gas diffusion, electrochemical reactions and energy balance. Spatial temperature and concentration gradients across the single SOFC are also accounted in the model. A new submodel for the porous electrodes microstructure is proposed and integrated in the comprehensive model. The model is then validated with the experimental data reported by Chick et al. [32]. To enhance its generality, the model is nondimensionalized.

Based on the model, several important parameters that influence the SOFC performance are identified and investigated, including the microstructure of SOFC composite electrodes, the active three phase boundaries, fuel cell operating conditions, PEN internal structure and cell external structure. A few conclusions are drawn: (1) A large air stoichiometric ratio does not benefit the fuel cell performance due to a decreased cell temperature. (2) The optimal fuel utilization factor results from the trade-off between SOFC operating temperature and fuel concentration. (3) The active TPB regions in the electrodes are determined based on the trade-offs between all the potential losses in the electrodes. (4) The active TPB regions where the total potential losses in the electrodes reach a minimum coincide with the optimal reaction layer thicknesses where the electrical and net power of SOFC reach a maximum. (5) The active TPB regions in the electrodes are insensitive to the variation of the electrodes thicknesses, and they are independent of each other. (6) The fuel cell PEN internal structure has important effect on its performance. Within the discussion range of the PEN internal structure, the fuel cell dimensionless electric power varies between 0.66-0.87. (7) Under the same geometric constraints and operating conditions, the anode-supported SOFC exhibits better performance than the cathode-supported and electrolyte-supported SOFC. (8) The fuel cell external structure has significant impact on its net power output. Under the constraint of fixed total volume, the fuel

cell net power varies between 0.16-0.89 as its cross section area changes from 2.6-16. (9) The optimal fuel cell external structure that maximizes the SOFC net power results from the balance between its nominal electrical power generation and pumping power consumption.

6.2 Future Work

In order to produce a useful voltage, several single cells are often connected in series and / or in parallel and assembled as a stack. In the next step of the research, the fuel cell stack performance will be investigated with the procedure such as fuel cell stack modeling, analysis and optimization.

The external configuration and internal structure of a cross-flow SOFC stack are illustrated in Figure 6.1 and 6.2. The main components of the stack include input and output headers as well as the series of the single cells, which compose of fuel and air channels, PEN structure, and interconnectors. The fuel and air are fed by the input headers and then delivered to the fuel and oxidant channels of each single cell where they diffuse to the electrodes and take electrochemical reaction.

Figure 6.1 External configuration of a cross-flow planar SOFC stack

Figure 6.2 Internal structure of a cross-flow planar SOFC stack

In the future research, the temperature profile across the SOFC stack need to be addressed. Large temperature gradient could cause excessive stresses on the SOFC components and how to suppress it is a crucial problem in the stack design. The fuel and air pressure in the stack is another topic of the research. Except for the pressure drops in the gas channels of the single cells, the flow resistance in the input and output headers and the resulting pressure drop should be counted as well, which lead to a significant incline in the pumping power consumption. At last, taking all these factors into consideration, the external geometry and internal structure of the stack will be optimized to achieve the maximum net power.

Table 1 Properties and constant values used in the simulations

$B = 5.6697 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$	$k_1 = 25 \text{ W m}^{-1} \text{ K}^{-1}$
$c_{p,1} = 0.5 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$	$k_3 = k_5 = 2 \text{ W m}^{-1} \text{ K}^{-1}$
$c_{p,3} = 0.595 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$	$k_4 = 2 \text{ W m}^{-1} \text{ K}^{-1}$
$c_{p,4} = 0.606 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$	$n_{ch} = 10$
$c_{p,5} = 0.573 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$	$p_f = p_{air} = 0.1 \text{ MPa}$
$c_{p,f} = 14983 \text{ J kg}^{-1} \text{ K}^{-1}$	$p_{ref} = 0.1 \text{ MPa}$
$c_{v,H_2} = 21.718 \text{ J mol}^{-1} \text{ K}^{-1}$	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
$c_{v,H_2O} = 33.156 \text{ J mol}^{-1} \text{ K}^{-1}$	$T_{air,in} = 923.15 \text{ K}$
$c_{v,O_2} = 26.56 \text{ J mol}^{-1} \text{ K}^{-1}$	$T_{f,in} = 923.15 \text{ K}$
$c_{v,N_2} = 24.36 \text{ J mol}^{-1} \text{ K}^{-1}$	$T_{ref} = 298.15 \text{ K}$
$D_{w,3} = 14 \times 10^{-6} \text{ m}$	$V_T = 3.07 \times 10^{-5} \text{ m}^3$
$D_{w,5} = 14 \times 10^{-6} \text{ m}$	$Zr_3 = Zr_5 = 10^{-6} \text{ m}$
$E_3 = 140 \times 10^3 \text{ J mol}^{-1}$	$\alpha = 0.5$
$E_5 = 137 \times 10^3 \text{ J mol}^{-1}$	$\delta_3 = 6.54 \times 10^{11} \Omega^{-1} \text{ m}^{-2}$
$F = 96500 \text{ C mol}^{-1}$	$\delta_5 = 2.35 \times 10^{11} \Omega^{-1} \text{ m}^{-2}$
$I_{ref} = 116.58 \text{ A}$	$\varepsilon_1 = 0.1$
$k_f = k_2 = 0.43 \text{ W m}^{-1} \text{ K}^{-1}$	$\varepsilon_3 = \varepsilon_5 = 0.8$
$k_{air} = k_6 = 0.0717 \text{ W m}^{-1} \text{ K}^{-1}$	$v_{O_2} = 16.3 \text{ cm}^3$

(Table 1– Continued) Properties and constant values used in the simulations

$\nu_{N_2} = 18.5 \text{ cm}^3$	$\sigma_3 = 8.0 \times 10^4 \text{ } \Omega^{-1} \text{ m}^{-1}$
$\nu_{H_2} = 6.12 \text{ cm}^3$	$\sigma_4 = 33.4 \times 10^3 \exp(-10.3 \times 10^3 / T) \text{ } \Omega^{-1} \text{ m}^{-1}$
$\nu_{H_2O} = 13.1 \text{ cm}^3$	$\sigma_5 = 8.4 \times 10^3 \text{ } \Omega^{-1} \text{ m}^{-1}$
$\zeta_{ch} = 6.4 \times 10^{-2}$	$\phi_3 = 0.4$
$\zeta_t = 2.56 \times 10^{-1}$	$\phi_5 = 0.5$
$\rho_1 = 8000 \text{ kg m}^{-3}$	$\psi_3 = 9.5$
$\rho_3 = 6870 \text{ kg m}^{-3}$	$\psi_5 = 7.2$
$\rho_4 = 5900 \text{ kg m}^{-3}$	$\mu_f = 2.07 \times 10^{-5} \text{ Pa s}$
$\rho_5 = 6570 \text{ kg m}^{-3}$	$\mu_{air} = 4.18 \times 10^{-5} \text{ Pa s}$
$\sigma_1 = 1.5 \times 10^6 \text{ } \Omega^{-1} \text{ m}^{-1}$	

REFERENCES

- [1] Wikipedia contributors, "Fuel cell," Wikipedia, The Free Encyclopedia, [//en.wikipedia.org/w/index.php?title=Fuel_cell&oldid=454865725](http://en.wikipedia.org/w/index.php?title=Fuel_cell&oldid=454865725)
- [2] M. Sorrentino, C. Pianese, Y.G. Guezennec, "A hierarchical modeling approach to the simulation and control of planar solid oxide fuel cells," *J. Power Sources* 180 (2008) 380–392.
- [3] The American Ceramic Society, "Archive for Ceramic Fuel Cells," The American Ceramic Society, [//ceramics.org/ceramictechtoday/tag/ceramic-fuel-cells/](http://ceramics.org/ceramictechtoday/tag/ceramic-fuel-cells/)
- [4] Wikipedia contributors, "Christian Friedrich Schönbein," Wikipedia, The Free Encyclopedia, [//en.wikipedia.org/w/index.php?title=Christian_Friedrich_Sch%C3%B6nbein&oldid=450442875](http://en.wikipedia.org/w/index.php?title=Christian_Friedrich_Sch%C3%B6nbein&oldid=450442875)
- [5] Wikipedia contributors, "William Robert Grove," Wikipedia, The Free Encyclopedia, [//en.wikipedia.org/w/index.php?title=William_Robert_Grove&oldid=452605204](http://en.wikipedia.org/w/index.php?title=William_Robert_Grove&oldid=452605204)
- [6] Wikipedia contributors, "Project Gemini," Wikipedia, The Free Encyclopedia, [//en.wikipedia.org/w/index.php?title=Project_Gemini&oldid=454857590](http://en.wikipedia.org/w/index.php?title=Project_Gemini&oldid=454857590)
- [7] National Aeronautics and Space Administration, "Gemini fuel cell," Nasa, [//history.nasa.gov/SP-4203/ch7-4.htm](http://history.nasa.gov/SP-4203/ch7-4.htm)
- [8] Fuel Cell Technologies Ltd., "Solid Oxide Fuel Cell Systems," University of Toronto Mississauga, [//www.utm.utoronto.ca/index.php?id=5243](http://www.utm.utoronto.ca/index.php?id=5243)
- [9] A.V. Virkar, J. Chen, C.W. Tanner, J.W. Kim, "The role of electrode microstructure on activation and concentration polarizations in solid oxide fuel cells," *Solid State Ionics* 131 (2000) 189–198.
- [10] C.W. Tanner, K.Z. Fung, A.V. Virkar, "The effect of porous composite electrode structure on solid oxide fuel cell performance," *J. Electrochem. Soc.* 144(1) (1997) 21-30.
- [11] J.H. Nam, D.H. Jeon, "A comprehensive micro-scale model for transport and reaction in intermediate temperature solid oxide fuel cells," *Electrochim. Acta.* 51(2006) 3446-3460.
- [12] S.H. Chan, Z.T. Xia, "Anode micro model of Solid Oxide Fuel Cell," *J. Electrochem. Soc.* 148(4) (2001) A388-A394.
- [13] S.H. Chan, K.A. Khor, Z.T. Xia, "A complete polarization model of a solid oxide fuel cell and its sensitivity to the change of cell component thickness," *J. Power Sources* 93 (2001) 130–140.
- [14] M. Sorrentino, A. Mandourah, T.F. Petersen, Y.G. Guezennec, M.J. Moran, G.. Rizzoni, 2004. "A 1-D planar solid oxide fuel cell model for simulation of SOFC-based energy

- systems, IMECE2004-60927,” in : *Proceedings of the 2004 ASME International Mechanical Engineering Congress and Exposition*, November 13–20, Anaheim, CA, 2004.
- [15] P. Aguiar, C.S. Adjiman, N.P. Brandon, “Anode-supported intermediate temperature direct internal reforming solid oxide fuel cell. I: model-based steady-state performance,” *J. Power Sources* 138 (2004) 120-136.
 - [16] Bejan A. 1996. “Street Network theory of Organization in Nature.” *Journal of Advanced transportation* 30: 85-107
 - [17] J.V.C. Vargas, J.C. Ordóñez, A. Bejan, “Constructal flow structure for a PEM fuel cell,” *Int. J. Heat Mass Tran.* 47 (2004) 4177–4193.
 - [18] L.S. Martins, J.E.F.C. Gardolinski, J.V.C. Vargas, J.C. Ordóñez, S.C. Amico, M.M.C. Forte, “The experimental validation of a simplified PEMFC simulation model for design and optimization purposes,” *Appl. Therm. Eng.* 29 (2009) 3036–3048.
 - [19] J.V.C. Vargas, J.C. Ordóñez, A. Bejan, “Constructal PEM fuel cell stack design,” *Int. J. Heat Mass Tran.* 48 (2005) 4410–4427.
 - [20] J.C. Ordóñez, S. Chen, J.V.C. Vargas, F.G. Dias, J.E.F.C. Gardolinski, D. Vlassov, “Constructal flow structure for a single SOFC,” *Int. J. Energ. Res.* 31 (2007) 1337–1357.
 - [21] J.B. Young, “Thermofluid modeling of fuel cells, Annu. Rev.” *Fluid Mech.* 39 (2007) 193-215.
 - [22] L. Ma, D.B. Ingham, M. Pourkashanian, E. Carcadea, “Review of the computational fluid dynamics modeling of fuel cells,” *J. Fuel Cell Sci. Technol.* 2 (2005) 246-257.
 - [23] R. Bove, S. Ubertini, “Modeling solid oxide fuel cell operation: Approaches, techniques and results,” *J. Power Sources* 159 (2006) 543-559.
 - [24] V.M. Janardhanan, O. Deutschmann, “CFD analysis of a solid oxide fuel cell with internal reforming: Coupled interactions of transport, heterogeneous catalysis and electrochemical processes,” *J. Power Sources* 162 (2006) 1192-1202.
 - [25] V.M. Janardhanan, V. Heuveline, O. Deutschmann, “Three-phase boundary length in solid-oxide fuel cells: A mathematical model,” *J. Power Sources* 178 (2008) 368-372.
 - [26] A. Bejan, “Heat Transfer,” *Wiley*, New York, 1993.
 - [27] R.K. Shah, A.L. London, “Laminar flow forced convection in ducts, Supplement 1 to advances in heat transfer,” *Academic Press*, New York, 1978.
 - [28] A. Bejan, “Convection heat transfer,” second ed., *Wiley*, New York, 1995.

- [29] A. Bejan, "Advanced engineering thermodynamics," second ed., *Wiley*, New York, 1997.
- [30] J.W. Kim, A.V. Virkar, K.Z. Fung, K. Mehta, S.C. Singhal, "Polarization effects in intermediate temperature, anode-supported solid oxide fuel cell," *J. Electrochem. Soc.* 146(1) (1999) 69-78.
- [31] R.C. Reid, J.M. Prausnitz, B.E. Poling, "The properties of gases and liquids," fourth ed., *McGraw Hill*, New York, 1988.
- [32] L.A. Chick, R.E. Williford, J.W. Stevenson, 2003. "Spreadsheet Model of SOFC Electrochemical Performance," *SECA Modeling & Simulation Training Session* August 2003. (web-page: www.netl.doe.gov/publications/proceedings/03/seca-model/seca-model03.html).
- [33] A.J. Bard, L.R. Faulkner, "Electrochemical methods-fundamentals and applications," second ed., *Wiley*, New York, 2001.
- [34] B. Todd, J.B. Young, "Thermodynamic and transport properties of gases for use in solid oxide fuel cell modelling," *J. Power Sources* 110 (2002) 186-200.
- [35] D. Kincaid, W. Cheney, "Numerical Analysis Mathematics of Scientific Computing," first ed., *Wadsworth, Belmont*, 1991.
- [36] H.Y. Tu, U. Stimming, "Advances aging mechanisms and lifetime in solid-oxide fuel cells," *J. Power Sources* 127 (2004) 284-293.

BIOGRAPHICAL SKETCH

Hang Wen received his B.S. in Mechanical Engineering from Tianjin University, China in 2003. After that he attended Shanghai Jiao Tong University in China and got his M.S. degree in Mechanical Engineering in 2006. He is currently enrolled in the doctoral program in Mechanical Engineering department of Florida State University and working as a research assistant at the Center for Advanced Power Systems, Tallahassee, Florida, USA. His research is focused on the design, modeling, simulation and optimization of solid oxide fuel cells.

PUBLICATION LIST

- (1)H. Wen, J.C. Ordóñez and J.V.C. Vargas, “Single SOFC modeling and optimization”,
Journal of Power Sources, Vol. 196, No. 18, 2011, p7519-7532
- (2)H. Wen, J.C. Ordóñez and J.V.C. Vargas, “Optimization of Single SOFC External Shape for
Maximum Power”, Journal of Power Sources (submitted)
- (3)H. Wen, J.C. Ordóñez and J.V.C. Vargas, “Composite Electrode Modeling and Optimization
for Solid Oxide Fuel Cells”, International Journal of Heat and Mass Transfer (submitted)