

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**MODELING OF A SOLID OXIDE FUEL CELL
AND ITS INTEGRATION WITH A BIOMASS
GASIFICATION SYSTEM**

by
Anıl ERDOĞAN

December, 2022
İZMİR

MODELING OF A SOLID OXIDE FUEL CELL AND ITS INTEGRATION WITH A BIOMASS GASIFICATION SYSTEM

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**by
Anıl ERDOĞAN**

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Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**MODELING OF A SOLID OXIDE FUEL CELL AND ITS INTEGRATION WITH A BIOMASS GASIFICATION SYSTEM**” completed by **ANIL ERDOĞAN** under supervision of **PROF. DR. CAN ÖZGÜR ÇOLPAN** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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MODELING OF A SOLID OXIDE FUEL CELL AND ITS INTEGRATION WITH A BIOMASS GASIFICATION SYSTEM

ABSTRACT

The growth of the world population and the development of industry based on technologies relying on fossil fuels increases the carbon dioxide emitted into the atmosphere. This leads to generating greenhouse gas effects and as a consequence a significant global warming effect. The depletion of fossil fuels and the environmental problems connected with their use implies a change towards alternative energy sources and conversion technologies. Fuel cells, one of the alternative energy conversion technologies, are electrochemical devices that convert the chemical energy of a fuel (mostly hydrogen) into electricity. Fuel cells have gained considerable attention in recent years due to their high efficiency and lower emissions compared to well-established power generation technologies. In this thesis, an innovative 0-D mathematical model for anode recirculated SOFC fed with reformat gas mixture was developed. In this regard, a mathematical model was conducted using the parallel circuit approach to include the thermodynamic and electrochemical phenomena. On the other hand, the experimental studies on the SOFCs were performed to obtain the polarization curve and to determine the cell resistance through the electrochemical impedance spectroscopy method. Then, X-ray diffraction and scanning electron microscopy analyses were conducted to investigate the microstructure of the SOFC at the cell level. The developed model was validated through experimental studies conducted at Technical University of Denmark. Parametric studies were performed to assess the effect of operating parameters on the performance of the SOFC. After that, the developed innovative model was integrated with the biomass gasifier model in order to assess the performance of the system thermodynamic point of view. In addition, an optimization study, which is namely Taguchi method, was performed to find the optimum operating parameters of the integrated system in order to maximize the electrical and fuel utilization efficiencies of the integrated system. The results show that the maximum electrical and fuel utilization efficiencies are 0.1945 and 0.6693,

respectively. Taguchi method gives the dominant operating parameters as the operating temperature of the gasifier and pressure ratio of the blower.

Keywords: 0-D mathematical model, biomass gasifier, experimental studies, MATLAB, optimization, solid oxide fuel cell, syngas



KATI OKSİT YAKIT PİLİNİN MODELLENMESİ VE BİYOKÜTLE GAZLAŞTIRMA SİSTEMİ İLE ENTEGRASYONU

ÖZ

Dünya nüfusunun artması ve fosil yakıtlara dayalı teknolojilerle sanayinin gelişmesiyle birlikte atmosfere salınan karbondioksit miktarını artırmaktadır. Bu durum, sera gazı etkilerinin oluşmasına ve sonuç olarak önemli bir küresel ısınma etkisine yol açar. Fosil yakıtların tükenmesi ve bunların kullanımına bağlı çevre sorunları, alternatif enerji kaynaklarına ve dönüşüm teknolojilerine doğru bir değişimin gerektiğini ifade etmektedir. Alternatif enerji dönüştürme teknolojilerinden biri olan yakıt pilleri, bir yakıtın (çoğunlukla hidrojen) kimyasal enerjisini elektriğe çeviren elektrokimyasal cihazlardır. Yakıt pilleri, köklü enerji üretim teknolojilerine kıyasla yüksek verimlilikleri ve daha düşük emisyonları nedeniyle son yıllarda büyük ilgi görmüştür. Bu tezde, reformat gaz karışımı ile beslenen anot geri dönüşümlü SOFC için yenilikçi bir 0 boyutlu matematiksel model geliştirilmiştir. Bu bağlamda, termodinamik ve elektrokimyasal olayları içerecek şekilde paralel devre yaklaşımı kullanılarak bir model geliştirilmiştir. Öte yandan, polarizasyon eğrisi elde etmek ve elektrokimyasal empedans spektroskopisi yöntemi ile hücre direncini belirlemek için SOFC'ler üzerinde deneysel çalışmalar yapılmıştır. Ardından, hücre düzeyinde SOFC'nin mikro yapısını araştırmak için X-ışını kırınımı ve taramalı elektron mikroskopu analizleri yapılmıştır. Geliştirilen model, Danimarka Teknik Üniversitesi'nde yürütülen deneysel çalışmalarla doğrulanmıştır. Çalışma parametrelerinin SOFC'nin performansı üzerindeki etkisini değerlendirmek için parametrik çalışmalar yapılmıştır. Daha sonra geliştirilen yenilikçi yaklaşımlı model, sistemin performansını termodinamik açıdan değerlendirmek için biyokütle gazlaştırıcı modeli ile entegre edilmiştir. Buna ek olarak, entegre sistemin elektrik ve yakıt kullanım verimlerini en üst düzeye çıkarmak için entegre sistemin optimum çalışma parametrelerini Taguchi yöntemi yoluyla bir optimizasyon çalışması yapılmıştır. Sonuçlar, maksimum elektrik ve yakıt kullanım verimliliklerinin sırasıyla 0,1945 ve 0,6693 olduğunu göstermektedir. Taguchi yöntemi, gazlaştırıcının çalışma sıcaklığı ve üfleyicinin basınç oranı gibi baskın çalışma parametrelerini vermektedir.

Anahtar kelimeler: 0 boyutlu matematiksel model, biyokütle gazlaştırıcısı, deneysel çalışmalar, MATLAB, optimizasyon, katı oksit yakıt pili, sentez gazı



CONTENTS

	Page
Ph.D. THESIS EXAMINATION RESULT FORM.....	ii
ACKNOWLEDGMENTS.....	iii
ABSTRACT.....	v
ÖZ.....	vii
LIST OF FIGURES.....	xii
LIST OF TABLES.....	xv
LIST OF SYMBOLS.....	xvi
ABBREVIATIONS.....	xviii
 CHAPTER ONE - INTRODUCTION	1
1.1 Introduction.....	1
1.2 Motivation of the Thesis	2
1.3 Objective of the Thesis	2
1.4 Outline of the Thesis.....	3
 CHAPTER TWO - BACKGROUND AND LITERATURE REVIEW	4
2.1 Introduction.....	4
2.2 Fuel Cells	4
2.2.1 Types of Fuel Cells	5
2.2.1.1 Proton Electrolyte Membrane Fuel Cells (PEMFCs)	6
2.2.1.2 Phosphoric Acid Fuel Cells (PAFCs)	6
2.2.1.3 Alkaline Fuel Cell (AFC).....	7
2.2.1.4 Molten Carbonate Fuel Cells (MCFCs).....	7
2.2.1.5 Direct Methanol Fuel Cells (DMFCs)	8
2.2.1.6 Solid Oxide Fuel Cells (SOFCs)	8
2.2.2 Fuel Cell Applications.....	9
2.3 Solid Oxide Fuel Cells (SOFCs)	13
2.3.1 Classification of SOFCs	14

2.3.2 Material Types Used in the SOFCs.....	15
2.3.3 Carbon Deposition Problem in SOFCs	17
2.4 Literature Survey on SOFCs	18
2.4.1 Literature Survey on Modeling and Experimental Studies on SOFCs	18
2.4.1.1 Cell and Stack Level Modeling	18
2.4.1.2 Experimental Studies	24
2.4.1.3 System Level Modeling on SOFC based Integrated Systems.....	25
CHAPTER THREE - EXPERIMENTAL STUDY	30
3.1 Introduction.....	30
3.2 Performance Characterization of SOFC	30
3.3 Electrochemical Impedance Spectroscopy (EIS) Analysis of SOFC	36
3.4 X-Ray Diffraction Analysis (XRD).....	37
3.5 Visualization of SOFC Structure.....	38
CHAPTER FOUR - MATHEMATICAL MODELING.....	40
4.1 Introduction.....	40
4.2 Cell Level Modeling of SOFC	40
4.3 Mathematical Modeling of Integrated SOFC and Biomass Gasification System.....	49
4.4 Optimization of Integrated SOFC and Biomass Gasification System.....	52
CHAPTER FIVE - RESULTS AND DISCUSSION.....	54
5.1 Introduction.....	54
5.2 Experimental Studies on SOFC.....	54
5.3 Validation of the SOFC Model	60
5.4 Cell Level Modeling of SOFC Fed with Syngas.....	62
5.5 System Level Modeling of an Integrated SOFC and Biomass Gasification System.....	70

5.6 Optimization of Integrated SOFC and Biomass Gasifier	72
CHAPTER SIX - CONCLUSIONS.....	75
REFERENCES	78



LIST OF FIGURES

	Page
Figure 2.1 The basic schematic of fuel cell.....	4
Figure 2.2 The types of fuel cells including fuels and its ion carriers	5
Figure 2.3 The photograph of proof-of-concept (a) hydrogen capsulated concept car, NamX, (b) Volkswagen hydrogen car.	10
Figure 2.4 The photograph of (a) Karsan's e-ATA hydrogen bus (b) The hydrogen powered passenger train	11
Figure 2.5 The examples of fuel cells for combined heat and power applications	13
Figure 2.6 The schematics of SOFC	14
Figure 2.7 The image of YSZ material (a) molecular structure, (b) powder form	16
Figure 2.8 The SEM micrograph of anode surface of SOFC reformat as fuel (a) Ni- YSZ anode surface before carbon deposition experiment (b) SEM- micrograph of the anode surface after carbon deposition experiment (1 marked as Ni, 2 marked as YSZ 3 marked as Carbon).	18
Figure 3.1. The summary of the experimental studies conducted in SOFC	30
Figure 3.2 SOFC cell with bottom and top blocks	31
Figure 3.3. The photograph of placing the Ni meshes and Au sealing	32
Figure 3.4 The illustration of the SOFC layers used in the experimental tests (<i>blue arrows: air flow, orange arrows: fuel flow</i>).....	32
Figure 3.5 The photograph of (a) inside of the test house (b) gas and cable connections in the test house	33
Figure 3.6 C – H – O ternary diagram of SOFC according to the reference case, hydrogen excess case, and hydrocarbon excess case for (a) low S/C ratio and (b) high S/C ratio	35
Figure 3.7 The example of SOFC system (a) equivalent circuit and (b) Nyquist diagram of a SOFC system	37
Figure 3.8 The diffraction of X-Rays onto the material used.	38
Figure 3.9 The schematic of SEM and its structure.....	39
Figure 4.1 The schematic representation of the SOFC with anode off-gas recirculation and fed by simulated reformat	41
Figure 4.2 The equivalent circuit of the SOFC	44

Figure 4.3 The solution algorithm of the 0-D SOFC model developed in the Matlab environment.....	48
Figure 4.4 The layout of the integration of SOFC and biomass gasifier	49
Figure 5.1 The effect of the current density on the (a) cell voltage and (b) power produced by the SOFC through experimental studies (Conditions are given in Table 3.1).....	56
Figure 5.2 SEM cross-section micrograph taken in the center of the cell (From left to right Ni-YSZ support and active area (denser), YSZ electrolyte (denser layer), CGO barrier layer (white), and LSC/CGO oxygen electrode)	57
Figure 5.3 The Nyquist plot for SOFC fed with 4% hydrogen/steam, ...	58
Figure 5.4 The Nyquist plot of SOFC according to the different S/Cs at 850°C	59
Figure 5.5 XRD pattern for cell used in the experimental	59
Figure 5.6 The electrochemical performance curves: (a) polarization curve and (b) power curve for both modeling and experimental studies (T=850°C, Low S/C case: Anode gas composition: $x_{CH_4} = 9.19\%$, $x_{H_2} = 31.80\%$, $x_{CO} = 8.83\%$, $x_{CO_2} = 7.77\%$, $x_{H_2O} = 42.40\%$, air for cathode, Anode Flow Rate = 28.30 L/h, Cathode Flow Rate = 140 L/h; High S/C case: Anode gas composition: $x_{CH_4} = 9.3\%$, $x_{H_2} = 18.14\%$, $x_{CO} = 8.84\%$, $x_{CO_2} = 7.9\%$, $x_{H_2O} = 55.81\%$, air for cathode, Anode Flow Rate = 21.50 L/h, Cathode Flow Rate = 140 L/h; T=800°C, Low S/C case: Anode gas composition: $x_{CH_4} = 9.19\%$, $x_{H_2} = 31.80\%$, $x_{CO} = 8.83\%$, $x_{CO_2} = 7.77\%$, $x_{H_2O} = 42.40\%$, air for cathode, Anode Flow Rate = 32 L/h, Cathode Flow Rate = 141 L/h;).....	61
Figure 5.7 The effect of current density on the power obtained by the SOFC according to the different recirculation ratios.....	62
Figure 5.8 The effect of current density on the power obtained by the SOFC according to the different fuel utilization ratios	63
Figure 5.9 The effect of current density on the exergy destruction rate of SOFC according to the cases used in the experimental studies and low and high S/Cs at a temperature of 850°C.	64
Figure 5.10 The effect of current density on the exergy destruction of the SOFC according to the different fuel utilization ratios	65

Figure 5.11 The effect of current density on the exergy destruction of the SOFC according to the different recirculation ratios	66
Figure 5.12 The effect of current density on the exergy destruction rate according to the different S/Cs	67
Figure 5.13 The effect of current density on the exergy destruction rate according to the operating temperature of SOFC	68
Figure 5.14 The current density with respect to the cell voltage according to the different electrolyte thickness.....	69
Figure 5.15 The effect of the current density on the power produced by the SOFC according to the different electrolyte thickness.....	70
Figure 5.16 The effect of gasifier operating temperature on the molar fractions of the syngas composition.....	71
Figure 5.17 The effect of gasifier temperature on the electrical efficiency (left axis), and fuel utilization efficiency (right axis).	72
Figure 5.18 S/N plot for Taguchi method for the maximization of electrical and fuel utilization efficiencies.	74

LIST OF TABLES

	Page
Table 2.1 Classifications of SOFC according to the different parameters.....	15
Table 2.2 The SOFC based integrated system found in the literature and their performance results	27
Table 3.1 The experimental test conditions for SOFC	34
Table 4.1 The molar flow rates of each species at each state.....	43
Table 4.2. The reaction series occur in the gasification unit	50
Table 4.3 The properties of biomass.....	51
Table 5.1 The comparison of Nernst voltage values between experimental and modeling studies according to the different S/C ratios at 850°C	54
Table 5.2 The calculated area specific resistance values according to the S/C values for the cases	57
Table 5.3 Selection of factors and its levels used in Taguchi method.....	73
Table 5.4 L9 orthogonal array and electrical and fuel utilization efficiencies values for Taguchi method	73
Table 5.5 Standard deviation values and rank degrees for the integrated system studied	74

LIST OF SYMBOLS

a, b, c, d	: extent of reaction (mol/s)
A_{cell}	: active area of the cell (cm ²)
ASR	: area specific resistance (ohm·cm)
d	: distance between the atomic layers (nm)
$\overline{ex}_{\text{CH},k}$	: chemical flow exergy (J/mol)
$\overline{ex}_{\text{PH},k}$	: physical flow exergy (J/mol)
E^0	: equilibrium reaction potential (V)
$\dot{Ex}_D$	: exergy destruction rate (W)
$\dot{Ex}_Q$	: rate of exergy due to the work (W)
F	: Faraday's constant (C/mol)
FUE	: fuel utilization efficiency
$\bar{h}_i$	: molar enthalpy of the species (kJ/kmol)
HHV	: higher heating value (kJ/kmol)
HV	: heating value (kJ/kmol)
i	: current density (A/cm ²)
i_0	: exchange current density (A/cm ²)
i_{lim}	: limiting current density (A/cm ²)
K_{SMR}	: chemical equilibrium constant for SMR
K_{WGS}	: chemical equilibrium constant for WGS
L	: length (m)
LHV	: lower heating value (kJ/kmol)
$\dot{m}_f$	: mass flow rate of fuel (g/s)
MW_i	: molecular weight of species (kg/kmol)
n	: number of diffractions, number of experiments
$\dot{n}_i$	: molar flow rate of the species (mol/s)
P_i	: the partial pressure of the species (Pa)
P_{SOFC}	: SOFC pressure (Pa)
Q	: thermodynamic activity
$\dot{Q}_{\text{useful}}$	: useful heat rate (W)

$\bar{R}$	: universal gas constant (J/mol·K)
r_{circ}	: recirculation ratio
$r_{\text{S/C}}$	: steam to carbon ratio
$\bar{s}_i$	: molar entropy of the species (J/mol·K)
T	: temperature (K)
U_{O_2}	: oxygen utilization ratio
U_f	: fuel utilization ratio
V_{act}	: activation polarization (V)
V_{cell}	: cell voltage (V)
V_{conc}	: concentration polarization (V)
V_{Nernst}	: Nernst voltage (V)
V_{ohm}	: ohmic polarization (V)
$\dot{W}_{\text{SOFC}}$	: power produced by the SOFC (W)
x_i	: molar fraction of the species
y_i	: response (output parameter)
Z	: impedance (Ω)
Z_0	: impedance of free space (Ω)

Subscripts

ex	: exit
f	: fuel
i	: species
k	: component (anode, cathode, electrolyte)
0	: dead state

Greek Symbols

β	: surface factor
$\Delta\bar{g}$	: specific Gibbs free energy change (J/mol)
η_{el}	: electrical efficiency
θ	: incidence angle (rad)
λ	: wavelength
ρ_k	: electrical resistivity of cell components (ohm·cm)
φ	: phase angle (rad)

ABBREVIATIONS

AFC	: alkaline fuel cell
ARC	: absorption refrigeration cycle
CGO	: ceria gadolonia
DDMEFC	: direct dimethyl ether fuel cell
DIR	: direct internal reforming
DME	: dimethyl ether
DMFC	: direct methanol fuel cell
DTU	: technical university of Denmark
EIS	: electrochemical impedance spectroscopy
ER	: external reforming
FC	: fuel cell
FTIR	: Fourier transform infrared spectroscopy
GDC	: gadolinium doped ceria
GSHP	: ground source heat pump
GT	: gas turbine
HCCI	: homogenous charge compression ignition
HRSG	: heat recovery steam generator
HT	: high temperature
HUV	: hydrogen utility vehicle
ICE	: internal combustion engine
IIR	: indirect internal reforming
IT	: intermediate temperature
LSC	: lanthanum strontium cobaltite
LSCF	: lanthanum strontium cobalt ferrite
LSM	: lanthanum strontium manganite
LT	: low temperature
LVNG	: landesnahverkehrsgesellschaft niedersachsen
MCFC	: molten carbonate fuel cell
ORC	: organic Rankine cycle
ORR	: oxygen reduction reaction

PAFC	: phosphoric acid fuel cell
PEME	: proton exchange membrane electrolyzer
PEMFC	: proton exchange membrane fuel cell
RC	: Rankine cycle
S/C	: steam to carbon ratio
ScYSZ	: scandia and yttria stabilized zirconia
SEM	: scanning electron microscopy
SMR	: steam methane reforming
SOE	: solid oxide electrolyzer
SOFC	: solid oxide fuel cell
TEM	: transmission electron microscopy
VARs	: vapor absorption refrigeration cycle
WGS	: water gas shift
WHR	: waste heat recovery
XRD	: x-ray diffraction analysis
YSZ	: yttria stabilized zirconia

CHAPTER ONE

INTRODUCTION

1.1 Introduction

The increase in world population and growth of industry based on technologies relying on fossil fuels increases the carbon dioxide emitted into the atmosphere. This leads to generating greenhouse gas effect and as a consequence a significant global warming effect. The fossil fuel depletion and the environmental problems connected with their using implies a change towards alternative energy sources and conversion technologies. Fuel cells (FCs), as a promising of the alternative energy conversion devices, are electrochemical devices that can transform a fuel's chemical energy (mostly hydrogen) into electricity. Fuel cells have gained attention in recent years due to their high efficiency and lower emissions compared to well-established power generation technologies. Fuel cell-based systems mainly consist of three basic units: the fuel processing unit (if hydrogen is not used directly), the electrical power generation unit (e.g., FC and turbine), and the auxiliary components (e.g., heat exchanger and blower). Fuel cells can be classified according to their electrolyte material and the type of ions transferred between the electrodes. This classification can be given as Alkaline Fuel Cell (AFC), Proton Exchange Membrane Fuel Cell (PEMFC), Solid Oxide Fuel Cell (SOFC), Molten Carbonate Fuel Cell (MCFC), Direct Methanol Fuel Cell (DMFC), and Phosphoric Acid Fuel Cell (PAFC). Regarding the fuel cell types, various fuel types, e.g., hydrogen, natural gas, biogas, ammonia, methanol, and other higher hydrocarbons) can be used in various applications (e.g. stationary electricity and heat generation, transportation, and portable devices) (Choudhury et al., 2013; Dicks & Rand, 2018; O'Hayre et al., 2016). For stationary power and heat generation, integration of a SOFC with a biomass gasifier is a thermally efficient and environmentally friendly way to convert syngas into useful forms of energy.

1.2 Motivation of the Thesis

According to the literature, the motivation of the thesis can be listed as follows.

- 0-D SOFC modeling studies mostly lack the consideration of simultaneous carbon monoxide and hydrogen oxidation. According to the authors' knowledge, there is no study on the calculation of exergy destruction of a SOFC based on the parallel-circuit approach.
- To conduct a simple SOFC model, which is suitable to be used in a system-level model
- To the author's knowledge, there are very limited studies on the optimization of the integration of SOFC and biomass gasifier system in terms of thermodynamic point of view.

1.3 Objective of the Thesis

Objectives of the thesis can be given as follows.

- To develop a new mathematical model including carbon monoxide and hydrogen oxidations for anode recirculated solid oxide fuel cells fed with syngas mixture.
- To conduct experimental studies in order to validate the model and characterize the cell used in the experiments.
- To develop a mathematical model of a SOFC fed with syngas and examine the effect of some operating parameters (steam-to-carbon ratio, fuel utilization ratio, current density, operating temperature, and recirculation ratio) on the performance of SOFC (cell voltage and power obtained by the SOFC).
- To optimize the electrical and fuel utilization efficiencies using the system-level model with Taguchi method.

1.4 Outline of the Thesis

The structure of this thesis is as follows:

The following chapter emphasizes an overview of fuel cells and its types. In particular their advantages and disadvantages are discussed, and the literature survey on SOFC modeling including cell and stack levels, and carbon deposition problem, and system level modeling on SOFC based integrated systems is presented.

In Chapter 3, the performance characterization through experimental analyses including electrochemical impedance spectroscopy and visualization of SOFC structure are discussed.

The Chapter 4 emphasizes modeling techniques and equations for SOFC at various levels, such as from the cell level to the system level. Firstly, basic definitions and equations for SOFC systems in terms of thermodynamics and electrochemistry perspective are summarized. Secondly, a mathematical model for a SOFC operating with a reformat syngas mixture is clarified. Finally, modeling approaches for integrated SOFC and biomass gasifier systems are presented.

Section 5 presents results and discussion that are implemented using the mathematical model presented in Chapter 4. The validation of the SOFC model and also the results of the parametric study are given in this chapter.

The last section summarizes the significant achievements and gives recommendations and suggestions for future work.

CHAPTER TWO

BACKGROUND AND LITERATURE REVIEW

2.1. Introduction

This chapter emphasizes an introduction to the system studied in this thesis. An overview of fuel cells, types of fuel cells, particularly, SOFCs as well as their classifications are discussed in this section. In addition, the literature survey on modeling and experimental studies of SOFC including cell, stack and system levels are explained in detail.

2.2. Fuel Cells

In simple, fuel cells can be defined as follows. Fuel cells are electrochemical devices, which transform a fuel's energy into electricity through electrochemical reactions with a highly efficient and environmentally friendly way. A unit fuel cell, called cell, has three main parts, which are anode, electrolyte, and cathode. A simple schematic of the fuel cell is presented in Figure 2.1. The working principle of fuel cells is explained as follows. The air and fuel are fed to the cathode and anode sides, respectively. Ions, which occur through electrochemical reactions, are transmitted to the electrodes through electrolyte. An electrical current is produced by the flows of the electrons through the load. Thus, electricity can be obtained from the fuel cell.

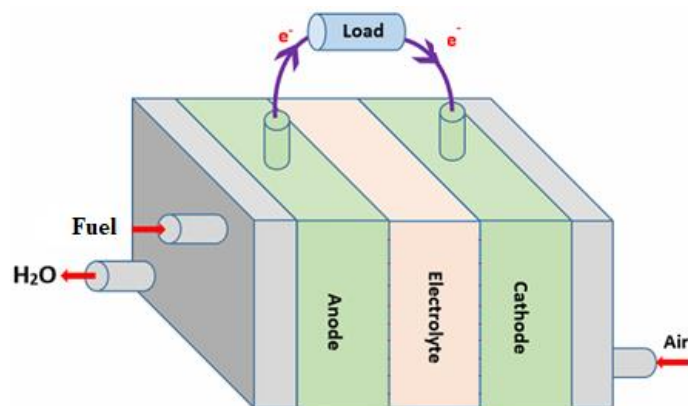


Figure 2.1 The basic schematic of fuel cell

A single cell provides production of little power. To produce desired amount or level of power, the cells are sandwiched with bipolar plates, called a fuel cell stack.

2.2.1 Types of Fuel Cells

There are many commercially available fuel cell types that are used for different purposes. Fuel cells can be classified by their operating temperature, type of catalyst used in the electrode, ion carrier, and fuel types. Therefore, the electrochemical reactions occurring at the interface between electrolyte-electrode and the ion type that are transmitted in electrolyte vary according to the type of fuel cell used. Figure 2.2 summarizes basic principles, carrier ion, and reactions in various fuel cell types.

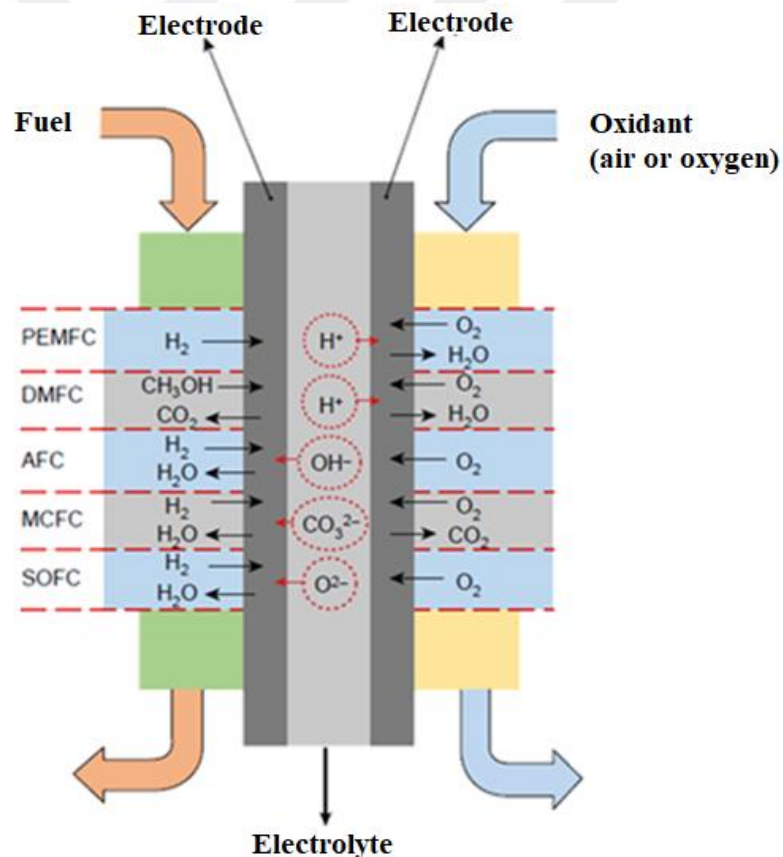
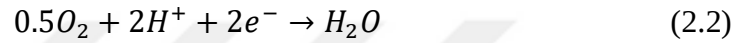


Figure 2.2 The types of fuel cells including fuels and its ion carriers (Colpan et al., 2018)

2.2.1.1 Proton Electrolyte Membrane Fuel Cells (PEMFCs)

This type of fuel cells is also called as proton exchange membrane fuel cells. It uses a thin polymer membrane (e.g., Nafion and PBI), which is proton conductive, as the electrolytes. The catalyst is generally platinum (Pt) supported carbon, and Pt-Ru (Ruthenium) alloy (for hydrogen (H₂) – carbon monoxide (CO) mixture applications).

The anode, cathode, and overall reactions are presented below.



There are some advantages for this type of fuel cells: (i) high hydrogen power density, (ii) higher efficiency levels, (iii) low temperature level operations, and (iv) rapid start-up.

The disadvantages are expensiveness of catalysts, intolerance to CO, thermal and water management problems due to low operating temperatures, and poor-quality waste heat.

2.2.1.2 Phosphoric Acid Fuel Cells (PAFCs)

It uses highly concentrated phosphoric acid (above 95% wt.) as electrolyte. The porous media used to hold the acid is usually SiC, and the electro-catalyst carbon-containing platinum in the anode and cathode sides. Air that contains CO₂ is used as oxidant, whereas hydrogen-rich gas mixture or pure hydrogen is used as fuel.

Main electrochemical reactions taking place at the anode and cathode sides and the overall reaction are given in Eqs. (2.1) – (2.3).

The advantages of this type of fuel cells are (i) CO-tolerant, (ii) good quality waste heat, (iii) favorable durability. The disadvantages are (i) low power density levels, (ii) expensive cost due to using Pt catalyst, (iii) slow start-up, and (iv) electrolyte loss.

2.2.1.3 Alkaline Fuel Cell (AFC)

Alkaline Fuel Cell (AFC) has a range of operating temperature from 60°C to 250°C. AFCs use high concentrated KOH (above 85% wt.) as the electrolyte for high-temperature operations and lesser concentrated (between 35-50% wt.) for low-temperature operations. Nickel (Ni), Silver (Ag), and noble metals are used as electro-catalyst in both anode and cathode sides.

The main reactions that occur in the anode and cathode sides are given as follows.

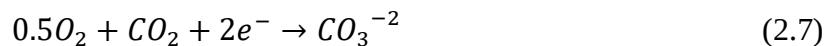
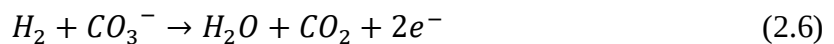


The main advantages of this type of fuel cells are (i) high efficiency and (ii) low oxygen reduction reaction (ORR) losses. Main disadvantage is that it should operate on pure oxygen without any contaminants.

2.2.1.4 Molten Carbonate Fuel Cells (MCFCs)

Molten Carbonate Fuel Cell (MCFC) operates at high-temperature levels (above 650°C). It uses alkali carbonates (e.g., Li, Na, and K) as the electrolytes. The electrolytes hold in a ceramic matrix of $LiAlO_2$. Molted salts are used for supporting the ionic conductions due to the high operating temperatures.

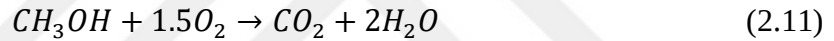
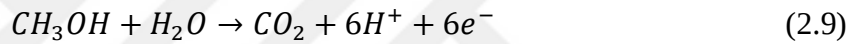
The anode, cathode and overall reactions are given below:



The advantages of these fuel cells are (i) good CO tolerant, (ii) use of wide range fuel types, (iii) high quality waste heat, (iv) use of inexpensive catalyst. There are some disadvantages: (i) electrolyte can be dissolved on the cathode catalyst, (ii) very long start-up time, (iii) electrolyte maintenance, and (iv) CO₂ must be fed to the cathode side.

2.2.1.5 Direct Methanol Fuel Cells (DMFCs)

Direct Methanol Fuel Cells (DMFCs) use proton conductive membrane as similar to the PEMFCs. The differences between DMFCs and PEMFCs is that the methanol is directly fed into the fuel cell without any reforming reactions. The reactions happen at the anode and cathode sides, and the overall reaction are presented as given below:



The advantages of this fuel cells are as follows: (i) methanol is an inexpensive fuel, (ii) it has high energy density, (iii) it is simple to use. On the other hand, there are some disadvantages for these types of fuel cells: (i) slow reaction kinetics, (ii) low-power density produced, (iii) fuel crossover, and (iv) toxicity and flammability of methanol.

2.2.1.6 Solid Oxide Fuel Cells (SOFCs)

Solid Oxide Fuel Cell (SOFC) is a high-temperature fuel cell type, which generally operates at temperature range between 600°C and 850°C. When SOFCs are compared with other fuel cell types (e.g. PEMFC and DMFC), there is no liquid phase inside the cell structure. Other advantages can be given as follows. SOFCs can be integrated with other energy systems such as waste heat recovery systems, Rankine cycles, Brayton cycles, gas turbines, and gasification systems. Other advantages are that wide range of fuel such as methane, hydrogen, ammonia, biomass derived syngas and other hydrocarbons can be fed to the fuel cell. More details on SOFCs are given in Section 2.3.

2.2.2 Fuel Cell Applications

Fuel cells can be used in various applications, which are generally categorized according to their power requirements. The main application areas include portable, transportation, and stationary power and heat generation.

For portable applications (e.g., laptops, phone chargers, and military equipments, and sensors), consumers prefer small, ergonomic and long-lasting devices. Portable fuel cells are lightweight and long-lasting that extend the usage time of devices without recharging from electricity. However, rechargeable batteries require an AC plug or DC chargers to be charged. These batteries might not be practical for some portable and military applications as they are heavy and do not adequately meet the power requirements (Kundu & Dutta, 2016).

Fuel cell vehicles are more efficient and quieter (since there are fewer vibrations) compared to internal combustion engines. In addition, hydrogen fuel allows vehicles to travel longer distances with less refueling due to its higher energy densities. Due to the energy demand and the increase in the use of clean energy resources in recent years, the use of hydrogen in vehicles is increasing day-by-day. For example, as shown in Figure 2.3a, NamX HUV, a new concept car designed by the Pininfarina design, which also designed TOGG. It aims to reinvent hydrogen fuel cell cars – by featuring removable fuel capsules. Two versions of this car is planned to be developed. An entry-level rear-drive version will offer 223 kW, a top speed of 124 mph (ca. 200 km/h), and a 0 to 62 mph time of 6.5 secs. Furthermore, the other version, an all-wheel-drive version, will boast 410 kW, with a limited maximum speed of 155 mph (ca. 250 km/h) and the ability to sprint from standing to 62 mph (ca. 100 km/h) in 4.5 s (*Autoevolution*, 2022). Another automotive company, Volkswagen is conducting a study on a new fuel cell (as given in Figure 2.3b), which is much cheaper than the other ones and promises hydrogen cars that could travel approximately 2000 km on a single tank (*Hydrogen Central*, 2022a). Volkswagen officers declared that the patent registration for the designed car has been applied. According to its creators, it gives cars up to 2000 km ranges no refueling needed.



(a)



(b)

Figure 2.3 The photograph of proof-of-concept (a) hydrogen capsulated concept car, NamX, (b) Volkswagen hydrogen car (*Autoevolution*, 2022).

Karsan, which is one of the heavy-duty vehicle companies launches e-ATA (as shown in Figure 2.4a) hydrogen vehicle in Germany. The CEO of the company announced that the 12-meter low-floor type e-ATA HYDROGEN, can meet the needs of users in many areas from high range to high passenger carrying capacity. It has 500 km of range under real conditions of use thanks to the 1560 liter of lightweight composite hydrogen tank. Furthermore, when the vehicle is full of passengers at the inside (approx. 95 passengers), it travels on stop-and-go line routes (*Hydrogen Central*, 2022b). The first hydrogen fueled train (as presented in Figure 2.4b) was established by Landesnahverkehrsgesellschaft Niedersachsen (LVNG), and Alstom. The trains are zero emissions, carbon-neutral, and low-noise, with only the mixture of steam and condensed water are emitted from the exhaust. These trains have a range of approximately 1000 km, meaning that they can run for an entire day on the route on a single tank of hydrogen (Buckley, 2022). Furthermore, the company has established hydrogen stations on the road in Germany.



(a)



(b)

Figure 2.4 The photograph of (a) Karsan's e-ATA hydrogen bus (*Hydrogen Central*, 2022b) (b) The hydrogen powered passenger train (Buckley, 2022)

Other application is the stationary power and heat generation. SOFCs and MCFCs are the most promising types of fuel cells on these applications due to their high operating temperature ranges. The most frequently used fuel type for these applications is natural gas. Other fuel types are propane, compressed hydrogen, biogas, methanol, petroleum-based fuels, town gas, biomass-derived syngas, digester gas, and landfill gas (Cigolotti et al., 2021). In the near future, green hydrogen-based systems should be expanded in order to comply with environmental solutions and zero-emission targets. Furthermore, in the use of carbon-containing fuels, these systems should be used together with carbon capture systems (*The 2030 Climate Target Plan*, 2020).

Among the fuel cell types, SOFCs can be integrated with various different systems. These are gasifiers, digesters, biogas reactors, gas and steam turbines, wastewater treatment systems. The main purpose of these integrated systems is to evaluate the high heat released from SOFC and increase efficiency (Corigliano et al., 2022). For example, the project called 'GREEN-FUEL-CELL' aims to develop a low-cost, reliable, up-scalable, tar decomposition and gas cleaning system that can be integrated with biomass gasifiers in order to produce a gas suitable for SOFC fuel cell applications (Broust, 2008). The overall electrical efficiency was achieved as 50%. In the project 'SOFCOM', SOFC combined cooling, heating, and power plant was used to generate useful energy forms from wood and 60% of electrical efficiency was achieved (European Commission, 2013). In the project, namely 'BIOCCHP', was on

the development of a trigeneration system consisting of a biomass gasifier, a solid oxide fuel cell stack, and a cooling system. As a result of the project, they found the electrical efficiency of the integrated system is in the range of 40.6-46.2%, and they achieved cooling power in the range of 1-2.3 MW (*Advanced Biomass CCHP Based on Gasification, SOFC and Cooling Machines*, n.d.). Another project, namely 'DEMOSOFC' was on the development of SOFC systems fed by biogas which is produced from wastewater treatment plant. As a result of the project, they obtained the electrical efficiency of the integrated system is in the range of 50-58%, and they found 45 kW of thermal power for the proposed integrated system (*DEMOSOFC Project*, 2020).

In recent years, there has been an increase in the building applications of fuel cells. Many companies are working on the area of the CHP systems. Bosch developed SOFC system for combined heat and power application. Their system is current in pilot-scale. It is possible to scale power outputs in MW ranges in home to business solution. They reported that the overall efficiency was achieved around 85% (*Bosch - SOFC*, 2022). Another company namely AVL developed SOFC system for combined heat and power applications for homes and industries. They declared that their products can be scaled from 5 kW to 200 kW and make it easy for grid connection and/or off-grid applications (*AVL - SOFC*, 2022). In a commercial product of SOLIDpower, it was reported that electrical efficiencies over 50% were achieved by utilizing natural gas in SOFCs for combined heat and power generation (SOLIDPower, 2022). Other products related on SOFC and combined heat and power generation systems are presented in Figure 2.5.

Elcore 2400	Dachs InnoGen	Cerapower FC10 Logapower FC10	Vitovalor	SteelGen	Galileo 1000 N	Vaillant G5+	PEMmCHP G5	BLUEGEN	ENGEN 2500	Inhouse 5000+
										
HT PEM 300W	LT PEM 700W	SOFC 700W	PEM 700W	LT SOFC 700W	SOFC 1kW	SOFC 1kW	LT PEM 2kW	SOFC 2kW	SOFC 2.5kW	LT PEM 5kW
Natural Gas	Natural Gas	Natural Gas, Gas	Natural Gas	Natural Gas	Natural gas+ Biogas	Natural Gas	Natural Gas + Biogas	Natural Gas	Natural Gas	Natural gas + Biogas + H2
Wall	Floor	Floor	Floor	Wall	Floor	Wall	Floor	Floor	Floor	Floor
Elcore	SenerTec	Bosch Thermotechnik	Viessmann	Ceres Power	Hexis	Vaillant	Ballard Power	Solid Power		RBZ

Figure 2.5 The examples of fuel cells for combined heat and power applications (Nielsen et al., 2019)

2.3 Solid Oxide Fuel Cells (SOFCs)

Solid oxide fuel cells are electrochemical devices, which can transform a fuel's chemical energy into heat and electricity. SOFCs contain ceramic materials that can withstand operating temperatures ranging between 600°C and 850°C. They are highly efficient for heat and electricity generation. Single SOFCs can be connected with bipolar layers and assembled into stacks to reach higher power densities. SOFCs are more advantageous over other fuel cell types (Bove & Ubertaini, 2008; Colpan et al., 2008; Ferrari et al., 2017; Huang & Goodenough, 2009) such as (1) no water management problems (because SOFCs operate at high temperatures); (2) cheap methods and materials can be used for cell and stack productions; (3) SOFCs can be thermally integrated with other systems thereby increasing the overall efficiency (e.g. Brayton cycle, gas turbine, biomass gasifiers, and Rankine cycle); (4) SOFCs can utilize many fuel types, such as hydrogen, ammonia, hydrocarbons, biomass produced gas mixtures, and methanol; (5) carbon-containing fuels undergo chemical transformation inside the fuel cell and are converted into hydrogen and CO, which are converted into electricity. The main challenges related to the development of SOFCs are: (1) the mechanical robustness of ceramics is limited, this has to be considered during manufacturing and for operative strategies; (2) in the case of carbon-containing fuels, the anode can be deactivated by carbon deposition that might occur and also by impurities like sulfur.

The working principle of SOFCs is simple. Figure 2.6 illustrates the simple working principle of SOFC. Oxygen (O_2) is reduced to oxide ions (O^{2-}) at cathode side and transferred to anode side by using an electrolyte. Water is produced by the reaction of hydrogen (H_2) and oxide ions, and the generated water leaves through the exhaust. The electrons formed in the anode are transferred to the cathode to reduce oxygen molecules.

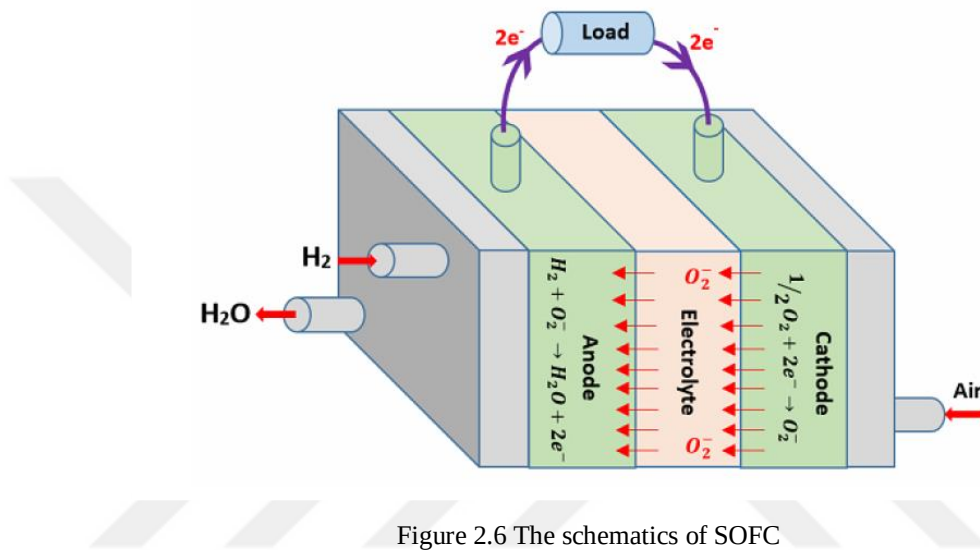


Figure 2.6 The schematics of SOFC

2.3.1 Classification of SOFCs

SOFCs are classified with respect to various parameters, e.g., operating temperature, anode and cathode flow designs, support type, gas spaces separation, electrolyte presence/absence, and cell design. These classifications are given in Table 2.1.

Table 2.1 Classifications of SOFC according to the different parameters (Kuterbekov et al., 2022)

Classification Parameters	Name
Operating Temperature	Low-Temperature SOFC (LT-SOFC): 550°C–650°C Intermediate-Temperature SOFC (IT-SOFC): 650°C–850°C High-Temperature SOFC (HT-SOFC): above 850°C
Flow Designs	Co-flow Counter-flow Cross-flow
Support Type	Anode Supported Cathode Supported Electrolyte Supported Substrate Supported Metallic Supported
Cell Design	Planar SOFC Tubular SOFC Flat-tube SOFC Monolithic SOFC
Gas Spaces Separation	Dual-chamber SOFC Single-chamber SOFC No-chamber SOFC
Electrolyte Presence/Absence	Oxygen-ion Conducting Electrolyte SOFC Proton-conducting Electrolyte SOFC Double-layer Fuel Cells Single-layer Fuel Cells
Fuel Reforming	External Reforming SOFC (ER-SOFC) Indirect Internal Reforming SOFC (IIR-SOFC) Direct Internal Reforming SOFC (DIR-SOFC)

2.3.2 Material Types Used in the SOFCs

In SOFCs, the cathode and anode layers are made of porous ceramic materials, while the electrolyte must be dense, and the material should possess high oxygen ion conductivity. Yttria Stabilized Zirconia (YSZ) is a widely adopted matter as electrolyte in SOFCs. It contains a ceramic based material where the cubic crystal structure of

zirconium dioxide is stabilized by the addition of yttrium oxide at room temperature. Those are referred to as "zirconia" (ZrO_2) and "yttria" (Y_2O_3). Doping with 8% yttria yields the highest conductivity (Kusnezoff, 2009; Mahapatra et al., 2013). Alternatively, ScYSZ (scandia and yttria stabilized zirconia) can be utilized as electrolyte material used in SOFCs. Typical electrode materials are LSC (Lanthanum Strontium Cobaltite), LSM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ - Lanthanum Strontium Manganite), and LSCF (lanthanum strontium cobalt ferrite- $(\text{La}_{0.60}\text{Sr}_{0.40})_{0.95}\text{Co}_{0.20}\text{Fe}_{0.80}\text{O}_{3-x}$) as oxygen electrode, often in combination with GDC (Gadolinium-Doped Ceria), while the fuel electrode is typically composed of Ni/8YSZ (Y_2O_3 (8 mol%)-doped ZrO_2) (Stolten & Samsun, 2016; Hagen, 2016).

Except for the application of SOFCs, YSZs have been used in various applications which are listed below. A molecular structure of YSZ and a real image for YSZ is given in Figure 2.7a and 2.7b, respectively. These are listed below.

- Dental applications
- Jet engines applications
- Thermal barrier coating in gas turbine systems
- Non-metallic type knife blades
- Optical fiber connector ferrules
- Jewelry industry

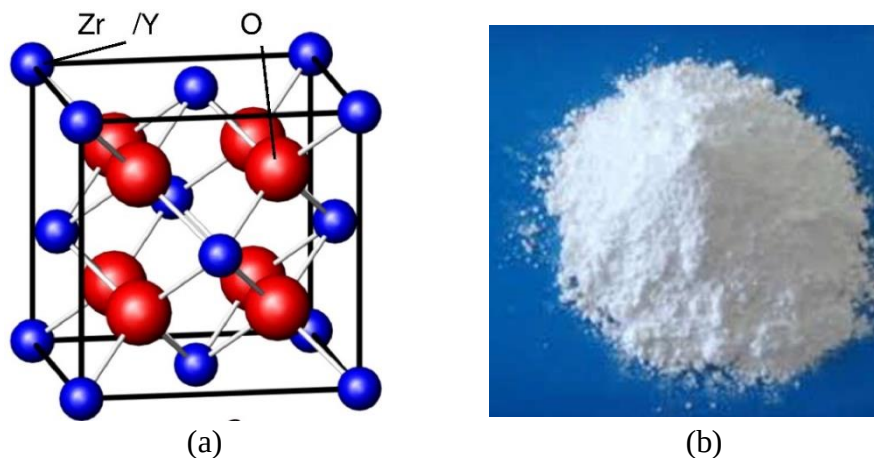


Figure 2.7 The image of YSZ material (a) molecular structure (Vonk et al., 2013), (b) powder form (Fuel Cell Store, n.d.)

The materials of bipolar plates in SOFCs should be stable and corrosion-resistant at high-temperature levels. The bipolar plate materials can be categorized according to the operating temperatures. The perovskite materials (e.g., lanthanum and yttrium chromites and its dopant such as Mg, Sr, Ca, Ca/Co) are used at temperature of above 850°C. The metallic alloys (e.g. steel, stainless steel, and titanium) are used at the temperature of 550°C to 850°C (Bhattacharya et al., 2018).

2.3.3 Carbon Deposition Problem in SOFCs

The main challenge in SOFCs due to the carbon-based gases used is carbon deposition when they are fed with hydrocarbon-based fuels. At the anode side, carbon deposition occurs on the active Ni particles, thereby deactivation of the electrode over time results with a decrease in the performance. Carbon deposition mainly occurs through the methane cracking reaction ($\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$) and/or the Boudouard reaction ($2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$). Carbon deposition is a function of various parameters such as steam to carbon (S/C) ratio, operating temperature, and current density. To avoid carbon deposition, operating temperature and S/C ratio can be increased while current density can be decreased. Furthermore, steam can be added to the gas mixture (Marcantonio et al., 2020; Ud Din & Zainal, 2016). To prevent carbon deposition in SOFC, the minimum S/C ratio is taken about 1.6. To understand the carbon deposition, SEM micrograph taken in the literature is given as follows. As can be seen in the figure, After the performed experiments, the Ni-YSZ surface was uniformly occupied with carbon particles and the growth of carbon on the anode surface can be seen. This effect is indicated as blockage and the SOFC performance decreases.

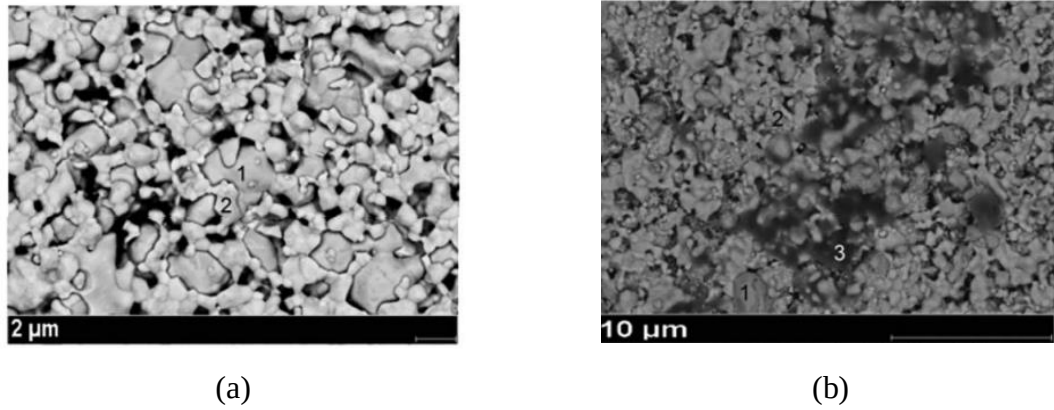


Figure 2.8 The SEM micrograph of anode surface of SOFC reformat as fuel (a) Ni-YSZ anode surface before carbon deposition experiment (b) SEM-micrograph of the anode surface after carbon deposition experiment (1 marked as Ni, 2 marked as YSZ 3 marked as Carbon).

2.4 Literature Survey on SOFCs

There are several studies on the SOFCs in terms of experimental and mathematical modeling point of view, and SOFC based integrated systems. Literature discussions on modeling of SOFCs and its integrated systems are presented in following subsections.

2.4.1 Literature Survey on Modeling and Experimental Studies on SOFCs

2.4.1.1. Cell and Stack Level Modeling

A system-level model for an integrated SOFC and biomass gasifier can be developed by combining the equations of SOFC, gasifier, and other components. There are 1-D (Cheddie & Munroe, 2007; Min et al., 2020), 2-D (Audasso et al., 2020; Ni, 2010), and 3-D (Peksen et al., 2013; Sezer et al., 2021) mathematical models for SOFCs in the literature. However, it is more complex to couple these models with the models of other energy systems and use them in the modeling of integrated energy systems. On the other hand, the 0-D modeling technique is advantageous in terms of coupling the equations and solution time; however, there is less accuracy in the results. However, the results are generally sufficient enough to estimate its performance as the main goal of the system-level modeling is mainly to estimate the value and trend of

the performance under various conditions. Hence, the 0-D modeling technique is generally preferred in the modeling of SOFC when the model is used as a sub-model in a system-level model of an integrated energy system. There are various 0-D mathematical modeling studies on SOFC in the literature. Colpan et al. (2007) proposed a mathematical model for an internal reforming SOFC to examine the system performance thermodynamically. They validated the model developed in the MathCad environment by comparing the results found in the literature. A parametric study was performed to assess the influence of fuel utilization factor and recirculation ratio on the SOFC efficiency. Results showed that the effect of the recirculation ratio on the performance is insignificant at low current densities, while it reduces the power obtained from the SOFC and the efficiency of the SOFC at higher current densities. De Lorenzo & Fragiaco (2015) performed 0-D mathematical modeling of a SOFC using synthesis gas as fuel. This model was developed using MATLAB software. In addition to this model, the amount of carbon produced on the anode was analytically calculated. They also assessed the effect of CO/H₂ ratio and recirculation ratio on the thermal efficiency and power obtained by the SOFC. The results illustrated that, when the recirculation ratio increases, carbon production risk at the anode decreases. Chan et al. (2002) developed a thermodynamic model for two different SOFCs that use hydrogen and methane as fuel. The internal resistance, anode-cathode current density, and flow diffusivity parameters of each component forming the SOFC were expressed as a function of temperature. In addition, each inlet and outlet point of the system was assessed in terms of exergy and energy point of views. The findings showed the energy and exergy efficiencies of the SOFC are found as 50.97% and 52.28%, respectively, when the fuel is H₂ under the operation of temperature, pressure, and fuel utilization of 873 K, 1 atm, and 75%. However, the exergy and energy efficiencies were estimated as 59.96% and 62.19%, respectively, when methane is used as the fuel. Chan et al. (2001) developed a mathematical model under different designs and working conditions of SOFC. In that model, the Butler-Volmer equation is used for defining the activation losses, while Knudsen and binary diffusions were taken into consideration for mass transport losses. In addition, a sensitivity analysis is conducted to examine the cell voltage drop effect on the thickness of each layer of the fuel cell. The results illustrated that the performance of an anode-supported cell is superior to

an electrolyte-supported cell or a cathode-supported cell for the same material, electrode kinetics, and operating parameters. Parhizkar & Roshandel (2017) presented an optimization study that incorporated a mathematical model of the SOFC. The aim function was to minimize the cost of electricity and minimize the deterioration caused by the long-term operation of the SOFC. The results showed that the optimum working conditions (e.g., fuel utilization of 40% and voltage of 0.60 V) can reduce the cost of electricity by 7.12%. Corigliano & Fragiaco (2020) analysed a SOFC fed with syngas in terms of energetic point of view. They used reaction rate equations for hydrogen carbon-monoxide transformation to find the outlet streams of SOFC. They assessed the performance of SOFC using electrochemical reactions. In addition, they conducted a carbon deposition analysis to indicate the favourable operating conditions that avoid the undesired issues.

There are several studies on SOFC modeling in various integrated systems. Ghaffarpour et al. (2018) proposed and investigated the biomass-based power system which includes SOFC, biomass, Rankine cycle, Brayton cycle, and gasifier. They developed a model for SOFC stack based on chemical equilibrium approach. Gholamian et al. (2018) developed models for integrated system. The models consisted of three cases which are gasifier, SOFC (case 1); gasifier, SOFC, gas turbine (case 2); gasifier, SOFC, gas turbine, and proton exchange membrane (PEM) electrolyser (case 3). Considering the SOFC model, chemical equilibrium method was used to identify the outlet conditions. In addition, they used electrochemical equations found from the literature easily to identify the performance of SOFC in terms of power and cell voltage. Habibollahzade et al. (2018) proposed and analysed three different integrated systems which are gasifier integrated with SOFC; gasifier integrated with SOFC and Stirling engine; and the combination of gasifier, SOFC, Stirling engine and PEM electrolyser. They used internal reforming type SOFC in the integrated system due to the lower cost and its higher potential for additional cooling of SOFC stack. They formed a model for the SOFC using chemical equilibrium method to find the exit streams of anode of SOFC. They considered hydrogen oxidation reaction at the anode side for indicating the performance of the SOFC. Hosseinpour et al. (2018) analysed a cogeneration system that consisting of biomass gasifier fed with wood as biomass

source, SOFC, and Goswami cycle. They conducted a model for SOFC using chemical equilibrium method to find the molar gas composition of exiting stream of SOFC anode. They solved the set of equations using iterative solver. In addition, they assumed that only hydrogen oxidation reaction occurs in the anode side of SOFC. Mojaver et al. (2018) performed thermodynamic analysis of SOFC combined with biomass gasifier. They developed a model for SOFC using chemical equilibrium constant to find the exit streams of the SOFC anode side. Bang-Møller & Rokni (2010) analysed biomass gasifier integrated with SOFC and gas turbine. Considering the SOFC model, they assumed that hydrogen is electrochemically converted in the anode side. In addition, their model took into account that CO produces extra one mole of hydrogen through WGS reaction, while four mole of hydrogen through reforming reaction including WGS produced from carbon-monoxide. Pierobon et al. (2013) conducted a thermodynamic assessment of integrated system that consists of a gasifier, a SOFC, and an ORC. The performance assessment was done using MATLAB software. Considering the SOFC model, modeling strategy is same with the study of Rokni, (2014b). Roy et al. (2019) assessed the hybrid electricity production system which includes an SOFC, an indirectly heated turbine, biomass gasifier, and a supercritical CO₂ power cycle. They used internal reforming type SOFC and they modeled using chemical equilibrium method and also assumed only hydrogen oxidation reaction occurs in the SOFC. Shayan et al. (2019) thermodynamically investigated the biomass fueled SOFC system. Considering the SOFC model, the chemical equilibrium concept was used to find the exit streams of SOFC. They solved equation sets to indicate the SOFC performance. Wang et al. (2020) analyzed a biogas fueled SOFC and gas turbine system with anode and combustor exhaust recirculation loops. Considering their SOFC model, only hydrogen enters an electrochemical reaction. In addition, reaction kinetics approach was used for methane reforming.

In SOFC modeling, some researchers have performed SOFC modeling in the integrated system using block based programs. For example, Jiang et al. (2021) assessed municipal solid waste-based power production system which consist of fluidized bed gasifier unit, HT-SOFC, chemical looping combustion, and heat recovery unit. Thermodynamic assessment performed by using ASPEN Plus program.

Regarding the SOFC model, anode and cathode sides were modeled based on RGibbs module, and Separator module, respectively in ASPEN Plus. In addition, they incorporated the calculator block to indicate the Nernst voltage, voltage losses due to the ohmic, activation, concentration, and also the power obtained by the SOFC. Li et al. (2020) analysed biomass based SOFC system integrated with ground source heat pump. Thermodynamic analyses were performed using ASPEN Plus. Considering the SOFC modeling, the internal reforming type SOFC was used in the integrated system. Hydrogen as fuel participated in the electrochemical reactions. In addition, RGibbs module was used for the anode side, while material separation module was used for the cathode side. Perna et al. (2018) investigated the performance of biomass downdraft gasifier hybridized with SOFC and gas turbine using ASPEN Plus software. Regarding the SOFC model, the anode side has two components which are RStoich reactor (electro-oxidation reactions occur), RGibbs reactor (the shifting and reforming reactions happen). However, Separator block, which transfers oxygen to anode side for the given utilization factor, was used for modeling cathode side. Recalde et al. (2019) analyzed a supercritical water gasification integrated with SOFC. They formed a model for SOFC using ASPEN Plus to find the exit streams using chemical equilibrium method. In addition, they assumed that only hydrogen reacts with oxygen ions for electrochemical reactions inside of the SOFC. Rokni (2014a) analysed an integrated system including a gasifier, a Stirling engine, and a SOFC for combined heat and power applications. They formed a model using Dynamic Network Analysis (DNA) tool which is a home-made and component-based program to assess the performance of the system. His model was based on chemical equilibrium method and assumed only hydrogen oxidation reaction. Toonssen et al. (2011) analyzed integrated system that consists of SOFC, gas turbine, and biomass gasification. They modeled SOFC using cycle-tempo which is block based program to identify the performance. Their SOFC model based on Gibbs minimization technique to find the electrical power output and cell voltage. Vecten et al. (2018) performed a performance study for SOFC integrated with microwave induced plasma gasifier. The performance assessment was done by using ASPEN Plus software. They modeled SOFC as block-based modeling technique. In this technique, the anode side of SOFC was modeled as RGibbs reactor; where the cathode side of SOFC was modeled as Separator which based on utilization

ratio. The electrochemical calculations which consider only hydrogen oxidation was done using Calculator block. Zhang et al. (2005) developed mathematical modeling of SOFC fed with natural gas through AspenPlus software. They validated the model with the test results of Siemens-Westinghouse tubular type SOFC. In addition, they analyzed the effect of fuel utilization on the cell voltage, SOFC efficiency, and gas composition at the anode outlet. Their results showed that when the fuel utilization ratio is 0.85, the electrical efficiency reaches a maximum value of 52%. In addition, when the fuel utilization ratio increases, the carbon dioxide amount at anode outlet increases.

The literature survey on the modeling strategies of SOFC shows that the internal reforming SOFC is generally used in integrated systems. Different equations can be used to calculate activation and concentration polarizations in a SOFC model. For calculating activation polarization, the mainly used equations are as follows: (1) Linearized Butler–Volmer, (2) Tafel Kinetics, and (3) Sinh Simplification. For calculating concentration polarization, the mainly used equations are as follows: (1) a relation as a function of the limiting current density, and (2) a relation including the mass transport effect. It has been also observed that only hydrogen is taken into account in the electrochemical reactions taking place in the SOFCs integrated with the biomass gasifier. In addition, since syngas produced from biomass is used as fuel in the SOFC, two different approaches, namely, reaction kinetics (e.g. (O. Corigliano & Fragiaco, 2020; Wang et al., 2020)) and chemical equilibrium method (e.g. (Gholamian et al., 2018; Perna et al., 2018)) have been used in the modeling studies for methane and carbon-monoxide conversions. Among these two approaches, the chemical equilibrium method is the mostly used one in the modeling of conversion reactions. An in-house code can be generated (e.g., (Pierobon et al., 2013; Roy et al., 2019a)) or commercial software such as Aspen Plus (e.g., (Jiang et al., 2021; Li et al., 2020)), and Cycle Tempo can be used (e.g., (Toonssen et al., 2011)) to solve the modeling equations.

2.4.1.2 Experimental Studies

The performance of SOFCs depends on the type of electrode catalysts for the electrochemical reactions, flow patterns, and operating parameters (e.g. temperature, pressure, fuel composition). There are several experimental studies on SOFCs in the literature that address the investigation of SOFCs and their system performance under variable operating conditions. For example, Subotić et al. (2019) conducted an experimental investigation of an industrial-scale SOFC fed with different gas mixtures produced from a biomass gasifier. In this context, they carried out experiments with the typical product gas compositions produced from downdraft biomass gasifier (with and without humidification) and fluidized bed gasifier (steam gasification agent). The results showed that it is possible to operate the SOFC at lower temperatures on wet producer gas, even though a higher cell temperature (800°C) and a dry product gas composition lead to higher efficiency. In addition, they observed that when the SOFC operates at low-temperature levels and contains low steam in the gas mixture, it becomes an alternative solution for combining these systems. Hagen et al. (2019) conducted a performance assessment of SOFC working with ammonia and biogas. In this context, two types of planar SOFCs were used. In the first case, the SOFC morphology was: Ni/YSZ in the anode support, electrolyte consisting of YSZ, and lanthanum-strontium zirconium (LSM)/YSZ containing cathode; in the second case, they used a barrier layer containing ceria gadolinia (CGO) and lanthanum strontium cobalt ferrite (LSCF) / CGO cathode. They reported that the use of pure ammonia and biogas as hydrogen carriers yields consistent results in terms of performance. Ammonia-fed SOFC demonstrated a usability with the operation of 1500 h, while biogas-fed SOFC over a period of ca. 130 h operation at lab scale. Hagen et al. (2014) experimentally investigated the hydrogen sulfide (H₂S) (0-100 ppm) impurity effects on Ni/ScYSZ containing planar SOFC electrochemical performance using methane fuel. The results showed that when the SOFC is operated with hydrogen fuel containing up to 100 ppm H₂S at 850 °C, the operation of SOFCs is feasible for methane-containing fuel and lower H₂S concentrations (ca. 20 ppm). In addition, they found that only moderate cell performance losses are observed at current densities up to 0.5 A/cm². Nielsen et al. (2010) conducted experimental studies on the single cell

anode supported SOFC with moistening of the anode inlet. The SOFCs considered were specified as Risø 2G and 2.5G. Risø 2G consists of a cell where the cathode is made with LSM / YSZ content, while Risø 2.5G consists of a cell with a cathode realized with LSCF / CGO content on the CGO protection layer. It was found that humidification has a significant effect on cathode polarization. In addition, Risø 2.5 G cells had a higher tolerance towards cathode humidification.

There are a lot of methods for materials imaging and characterization. In the literature, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR) are commonly used. The Fourier Transform Infrared Spectroscopy technique, also generally known as FTIR analysis, is a method used to define the polymeric, organic, and inorganic class materials. In FTIR analysis, infrared light is used to obtain properties of chemical and can test the samples. FTIR is used to identify the properties of unknown material, oxidation, decomposition in failure materials, and contamination in the material. Transmission electron microscopy (TEM) is another method for the characterization of materials. To indicate size and distribution of particle, as well as shape, TEM is used. In addition, TEM is used to provide better resolution compared to SEM method. TEM provides additional analytical capability measurements. In the literature, there are various studies through experimental by using SEM and TEM to investigate material characterization (e.g. oxide bonding, phase analysis, thermal stability, and electrochemical phenomena (e.g., oxygen vacancies, doped effect, and ionic conductivity) in recent years (Ghorbani-Moghadam et al., 2022; Iqbal et al., 2022; Irshad et al., 2021, 2022; Nouri et al., 2022).

2.4.1.3. System Level Modeling on SOFC based Integrated Systems

There are some studies on the integration of SOFC and biomass gasification systems. Maekinen et al., (1992) studied two different systems experimentally: a combined cycle process based on the gasification of wood with a pressurized fluidized bed and a natural gas combined cycle process. As a result of this study, the efficiency of the system based on the fuel cell and the pressurized gasification of the wood was

found to be approximately 10% higher compared to the case without the fuel cell. Alderucci et al., (1994) considered a fluidized bed gasifier using steam or CO₂ as the gasifying agent and the thermodynamic equilibrium calculations were used to estimate the conversion rates of species in the gasifier. The electrical efficiency of the SOFC was calculated under different gasifier operating temperatures. As a result of their study, at a gasifier operating temperature of 700°C, the electrical efficiency of SOFC was found as 47% and 51% when steam and CO₂ were used as the gasification agents, respectively. In the study conducted by Barchewitz & Palsson, (2000) they increased the thermal efficiency of SOFC integrated with gasifier by adding a gas turbine to the integrated system. However, they ignored the cracking of the tar formed inside the gasifier. Hutton et al. (2003) performed a feasibility study of an integrated biomass gasifier and SOFC system. In this study, the heat management of the integrated system was done using the heat obtained from SOFC in the gasifier. Gøbel et al. (2004) built a biomass gasifier called VIKING at the Technical University of Denmark (DTU). Since the pyrolysis and gasification processes took place in two different reactors in this gasifier, it was called a two-stage biomass gasifier. Between the pyrolysis and gasification zones, the volatiles from the pyrolysis is partially oxidized. In this way, most of the tars decompose into gas. Because of all these positive aspects, gas cleaning and its integration with SOFC was easier. Omosun et al., (2004) performed the thermodynamic modeling and cost evaluation of the integration of SOFC and biomass gasifier system using hot and cold gas cleaning systems.

As mentioned in Section 2.3, SOFCs are suitable for integration of other systems. For example, micro gas turbine (MGT) integrated gas turbine (GT) and externally fired gas turbine (EFGT) (Habibollahzade et al., 2018; Kumar & Singh, 2019; Ogorure et al., 2018; Ozgoli et al., 2017; Perna et al., 2018; Roy et al., 2019b; Roy & Samanta, 2021), Rankine (RC) and organic Rankine cycles (ORC) (Ghaffarpour et al., 2018; Kalina, 2019; Karimi et al., 2020; Kumar & Singh, 2019; Ogorure et al., 2018; Owebor et al., 2019; Ozcan & Dincer, 2015; Pierobon et al., 2013; Roy et al., 2019b; Yan et al., 2019), compression chiller, absorption (ARC) and vapor absorption (VARS) refrigeration cycles (E. Gholamian et al., 2016; Kumar & Singh, 2019b; Ogorure et al., 2018; Owebor et al., 2019; Ozcan & Dincer, 2015; Palomba et al., 2017), waste

heat recovery (WHR) and heat recovery steam generator (HRSG) (Borji et al., 2015; Jiang et al., 2021; Ozgoli et al., 2017; Roy & Samanta, 2021; Sadeghi et al., 2018; Wu et al., 2020), proton exchange membrane electrolyzer (PEME) (Ehsan Gholamian et al., 2018), solid oxide electrolyzer (SOE) (Habibollahzade et al., 2019), Goswami cycle (Hosseinpour et al., 2018), Stirling (Habibollahzade et al., 2018; Rokni, 2014b), ground source heat pump (GSHP) (Li et al., 2020), homogenous charge compression ignition (HCCI) (Wu et al., 2020), combustor and internal combustion engine (ICE) (Kalina, 2019; Vecten et al., 2018), in these integrated systems to generate only electricity (Ghaffarpour et al., 2018; Gholamian et al., 2018; Habibollahzade et al., 2019; Jiang et al., 2021; Ogorure et al., 2018; Owebor et al., 2019; Perna et al., 2018; Pierobon et al., 2013; Roy et al., 2019a, 2019b; Siefert & Litster, 2014; Vecten, et al., 2018; Yan et al., 2019), heat and electricity (Bang-Møller & Rokni, 2010; Borji et al., 2015; Doherty et al., 2010; Kalina, 2019; Karimi et al., 2020; Mojaver et al., 2018; Rokni, 2014b; Roy & Samanta, 2021; Sadeghi et al., 2018; Shayan et al. 2019; Toonssen et al., 2011; Wu et al., 2020), electricity and cooling (Ozcan & Dincer 2015) and heat, electricity, and cooling (Gholamian et al. 2016; Kumar & Singh 2019; Ozgoli et al., 2017; Palomba et al., 2017). The general summary of SOFC based integrated system studies is presented in Table 2.2.

Table 2.2 The SOFC based integrated system found in the literature and their performance results

Author(s)	Sub Systems	Analysis		Results	
		Energy	Exergy	Energy Eff.	Exergy Eff.
Bang-Møller & Rokni, (2010)	Biomass Gasifier, SOFC, MGT	✓	✓	79.7%	68.7%
Toonssen et al. (2011)	Biomass Gasifier + SOFC + Gas Turbine	✓	✓	-	49.4%
Pierobon et al. (2013)	Biomass Gasifier, SOFC, ORC	✓	X	56.4%	-
Rokni (2014a)	Biomass Gasifier, SOFC, Stirling Engine	✓	X	42.4%	-
Siefert & Litster (2014)	Biomass Gasifier, SOFC	✓	✓	-	~60%
Rokni (2014b)	Biomass Gasifier, SOFC, Stirling Engine	✓	X	42%	-
Ozcan & Dincer (2015)	Biomass Gasifier, SOFC, ORC, ARC	✓	✓	78%	50%
Gholamian et al. (2016)	Biomass Gasifier, SOFC, CCHP system	✓	✓	81%	39.35%
Perna et al. (2018)	Biomass Gasifier, SOFC, Micro Gas Turbine	✓	X	88%	-
Lv et al. (2019)	Biomass Gasifier, SOFC, gas turbine	✓	X	60.78%	-
Ghaffarpour et al. (2018)	Biomass Gasifier, SOFC, ORC, gas turbine, HRSG	✓	✓	22.4%	22.7%
Hosseinpour et al., (2018)	Biomass Gasifier, SOFC, Goswami Cycle	✓	✓	60.2%	34.7%
Sadeghi et al. (2018)	Biomass Gasifier, SOFC	✓	✓	69.47%	31.53%
Ogorure et al. (2018)	Biomass Gasifier, SOFC, GT, ARC, RC, ORC	✓	X	63.6%	-
Gholamian et al. (2018)	Biomass Gasifier, SOFC, PEME	✓	✓	-	33.22%
Habibollahzade et al. (2018)	Biomass Gasifier, SOFC, Stirling, PEME	✓	✓	67.38%	39.51%

Table 2.2 continue

Mojaver et al. (2018)	Biomass Gasifier, SOFC, HRSG	✓	✓	-	44.22%
Vecten et al. (2018)	Biomass Gasifier + SOFC	✓	X	70%	-
Recalde et al. (2019)	Biomass Gasifier + SOFC	✓	✓	50.3%	47.8%
Kalina (2019)	Biomass Gasifier, SOFC, cogeneration	✓	X	37-40%	-
Kumar & Singh (2019)	SOFC, gas turbine, VARS, ORC	✓	X	68.79%	-
Roy et al. (2019a)	Biomass Gasifier, SOFC, supercritical CO ₂ cycle	✓	✓	51%	45%
Shayan et al. (2019)	Biomass Gasifier, SOFC	✓	✓	-	39.85%
Yan et al. (2019)	Biomass Gasifier, SOFC	✓	✓	51.7%	-
Owebor et al. (2019)	Biomass Gasifier, SOFC, RC, ORC, Refrigeration Cycle	✓	✓	62.3%	55.5%
Roy et al. (2019b)	Biomass Gasifier, SOFC, ORC, Gas Turbine	✓	✓	41.172%	37.76%
Habibollahzade et al. (2019)	Biomass Gasifier, SOFC, SOE, Gas Turbine	✓	✓	-	45.25%
Mojaver et al. (2019)	Biomass Gasifier, SOFC	✓	✓	42.79%	32.5%
Li et al. (2020)	Biomass Gasifier, SOFC, GSHP	✓	✓	67.3%	29.2%
Wu et al. (2020)	Biomass Gasifier, SOFC, IC engine	✓	✓	68%	51%
Karimi et al. (2020)	Biomass Gasifier, SOFC, Micro Gas Turbine, ORC	✓	✓	55.2%	32.8%
Jiang et al. (2021)	Biomass Gasifier, SOFC, HRSG, Intercooling Compressor	✓	✓	40.9%	36.1%

CHAPTER THREE

EXPERIMENTAL STUDY

3.1 Introduction

This chapter gives information about the experimental studies conducted on SOFCs in this thesis. Information about the test setup, SOFC cell properties (material used), gas and electrical connections, and test cases used in the experiments are explained. In addition, SOFC structure imaging techniques and the determination of resistances in the SOFC structure through electrochemical impedance spectroscopy (EIS) are discussed in detail.

3.2 Performance Characterization of SOFC

In this section, the experimental studies performed in the Electrochemistry Laboratory of the Department of Energy Conversion and Storage at the Technical University of Denmark (DTU) are discussed. The tests using the state-of-the-art SOFC consisted of three main parts: mounting, start-up and reduction, and electrochemical characterization through the “fingerprint test protocol”. The experimental stages are summarized in the flowchart given in Figure 3.1.

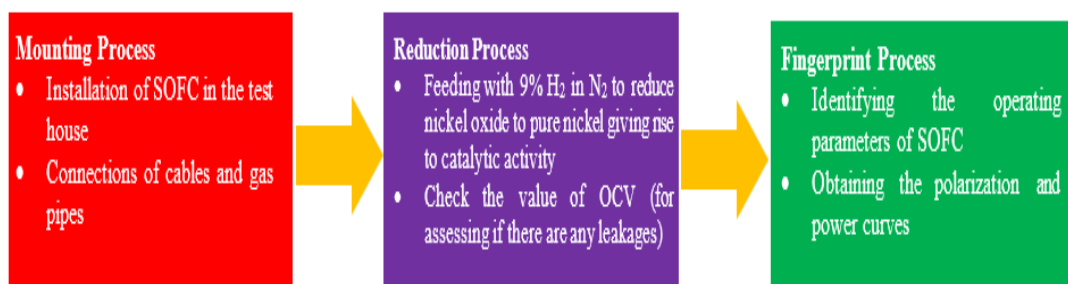


Figure 3.1 The summary of the experimental studies conducted in SOFC

The SOFC was placed in an alumina test house consisting of a bottom and top block as illustrated in Figure 3.2.



Figure 3.2 SOFC cell with bottom and top blocks

Fine and porous Ni meshes were used for providing gas transport and electrical contact on the anode side. A gold frame was used as the sealant of the anode compartment to prevent fuel leakages outside. The photograph of the Ni meshes and gold sealant frame is shown in Figure 3.3.

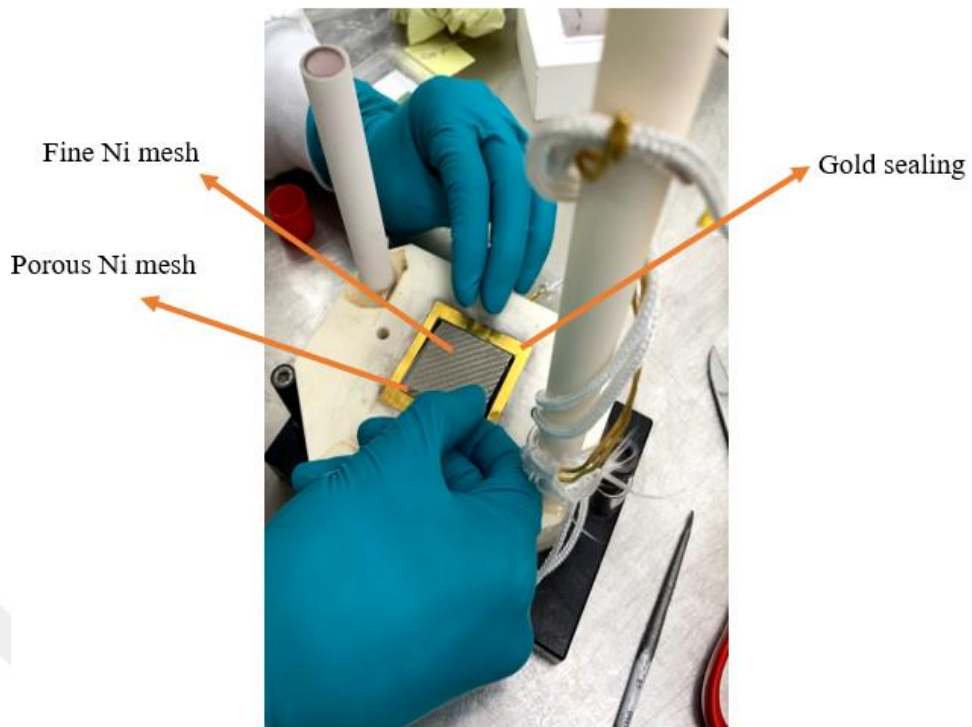


Figure 3.3 The photograph of placing the Ni meshes and Au sealing

On the other side, a gold porous mesh was used as the gas transport layer and for electrical contacting at the cathode side. The cell was finally sandwiched between Ni and gold current collectors thanks to the application of weights on top (see Figure 3.2). The gas mixtures were distributed horizontally at the anode side and from the center at the cathode side. To understand easily of assemble system, the illustration of the test housing assembly is shown in Figure 3.4.

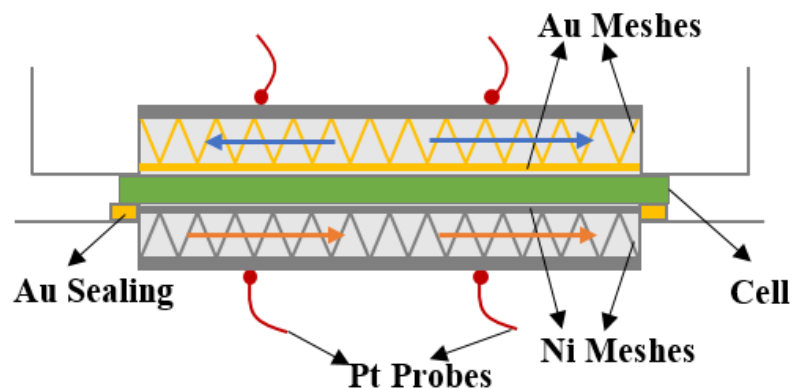
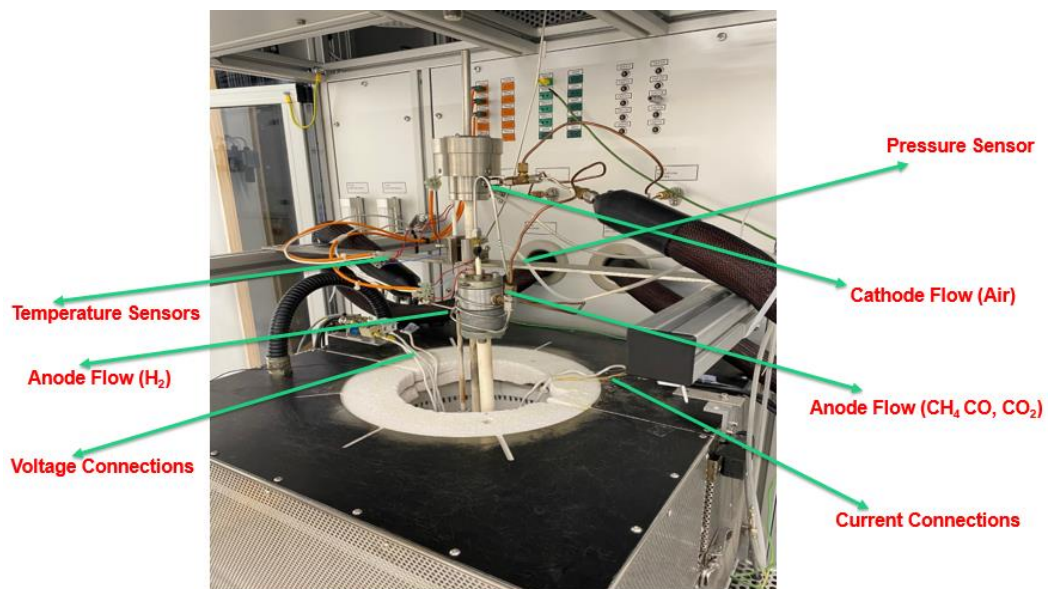


Figure 3.4 The illustration of the SOFC layers used in the experimental tests (blue arrows: air flow, orange arrows: fuel flow)

The cell in the alumina test house was placed in a Fuelcon Evaluator S brand test rig, where the performance tests were carried out. The photograph of test house is presented in Figure 3.5.



(a)



(b)

Figure 3.5 The photograph of (a) inside of the test house and (b) gas and cable connections in the test house

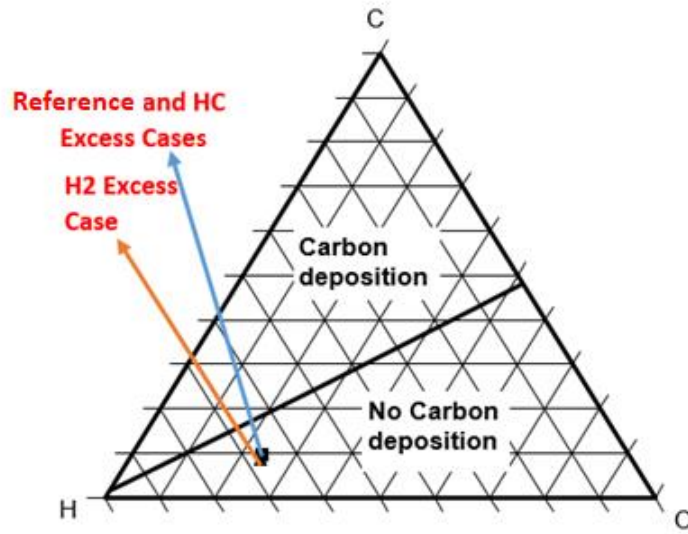
The cell was heated to 850°C feeding with pure nitrogen at the anode side and air at the cathode. After that, NiO in the fuel electrode was reduced feeding a mixture of 9% H₂ in nitrogen for two hours, before starting to apply pure hydrogen. An initial characterization following a standardized fingerprint protocol was carried out at 850°C, consisting of a set of i-V curves and electrochemical impedance measurements in different steam/H₂ ratios (4, 20, 50, 90% steam in hydrogen), followed by a specific characterization with the conditions relevant for the modeling. The conditions are given in Table 3.1. A reference gas mixture was chosen for two different S/C ratios (low S/C ratio of 1.64 and high S/C ratio of 2.14) and hydrogen excess and hydrocarbon excess mixtures, with respect to the references, were obtained by increasing hydrogen and hydrocarbons contents, respectively. Such characterization was then repeated at 800°C. After that, the cell was tested at lower temperatures and in different conditions for other studies.

Table 3.1 The experimental test conditions for SOFC

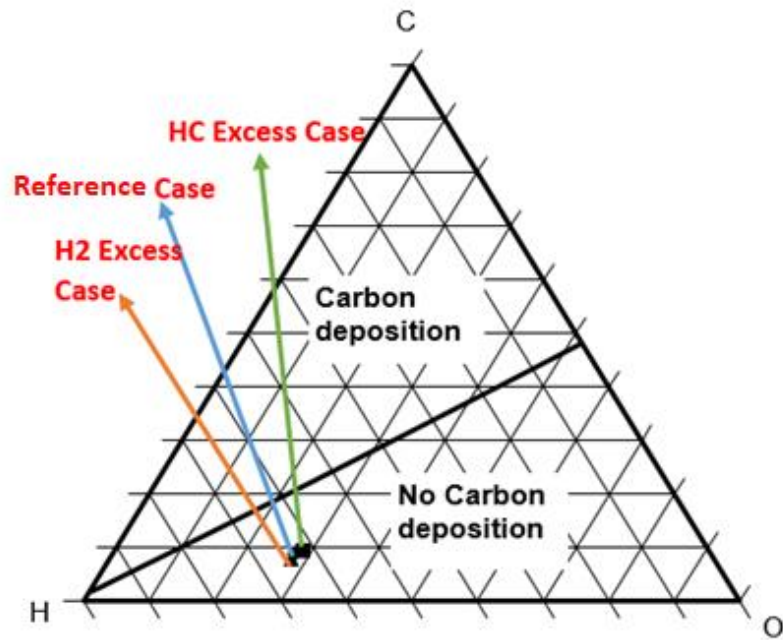
REFERENCE CASE					HYDROGEN EXCESS CASE				HYDROCARBON EXCESS CASE			
Species	Molar Fraction (%)		Flow Rate (L/h)		Molar Fraction (%)		Flow Rate (L/h)		Molar Fraction (%)		Flow Rate (L/h)	
	S/C	S/C	S/C	S/C	S/C	S/C	S/C	S/C	S/C	S/C	S/C	S/C
	1.6	2.1	1.6	2.1	1.9	2.6	1.9	2.6	1.5	2.1	1.5	2.1
Methane	9.2	9.3	2.6	2.0	8.4	8.4	2.3	1.7	9.6	9.9	2.9	2.0
Hydrogen	31.8	18.1	9.0	3.9	32.7	17.7	9.0	3.6	33.1	13.3	22	2.7
Carbon monoxide	8.8	8.8	2.5	1.9	8.0	7.9	2.2	1.6	9.3	9.4	2.8	1.9
Carbon dioxide	7.8	7.9	2.2	1.7	7.3	6.9	2.0	1.4	8.3	8.4	2.5	1.7
Steam	42.4	55.8	12.0	12.0	43.6	59.1	12.0	12.0	39.7	59.1	12.0	6.0

As mentioned in Section 2.4.1.2, carbon deposition is the most challenging issue in SOFCs. Depending on the type of gas used, a carbon deposition analysis using ternary diagrams is required to prevent breakage and damage to cells. Before starting the experiments, it was analyzed whether the carbon deposition window was reached for the specific conditions since carbon-containing species were used. In this regard, the carbon, hydrogen, and oxygen atom ratios in the reformate syngas mixture entering the SOFC were calculated and shown in the ternary diagram given in Figure 3.6. According to this diagram, it was found that there is no carbon deposition to be

expected for all three cases (reference, hydrogen excess, and hydrocarbon excess cases) and all S/C ratios shown in Table 3.1.



(a)



(b)

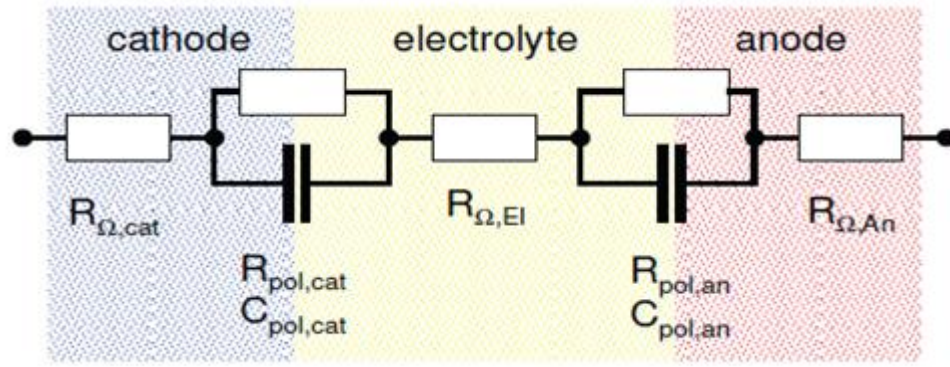
Figure 3.6 C – H – O ternary diagram of SOFC according to the reference case, hydrogen excess case, and hydrocarbon excess case for (a) low S/C ratio and (b) high S/C ratio

3.3 Electrochemical Impedance Spectroscopy (EIS) Analysis of SOFC

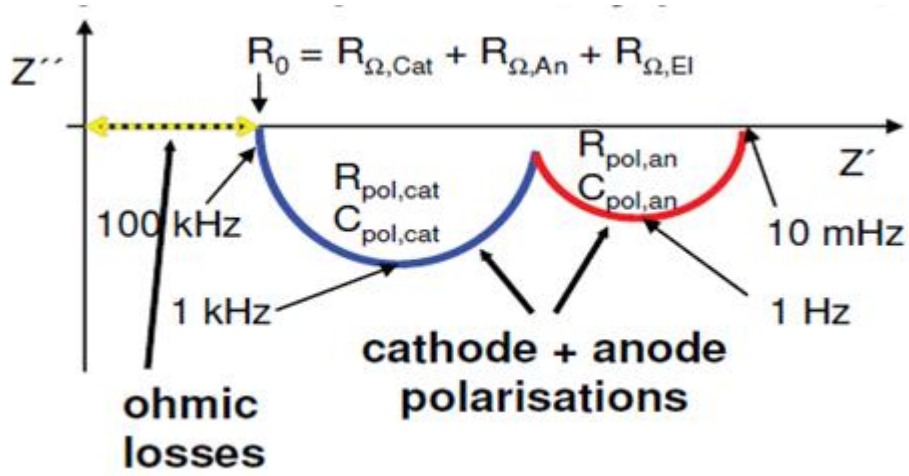
Electrochemical impedance spectroscopy (EIS) is a method to find the losses in a SOFC or other electrochemical devices. Furthermore, this method provides which process or component is decayed during the operation. In this technique, the impedance of SOFC electrodes is first studied with diagrams consisting of a series of suppressed semicircles. Each resulting semicircle is then usually attributed to the reactions or process that takes place within the SOFC. SOFC electrodes consist of deep ionic and electronically conductive networks in order to increase the reaction area and thus decrease the resistance of polarization. Generally, the impedance of an electrochemical systems can be determined following relations given in Eq. (3.1).

$$Z = Z_0 \cdot \cos \varphi - i \cdot Z_0 \cdot \sin \varphi \quad (3.1)$$

EIS can be basically explained as follows. The components of the electrochemical system are determined and the equivalent circuit is drawn. Then impedance spectra are determined using Nyquist plots. The example of an equivalent circuit and Nyquist diagram can be illustrated in Figure 3.7.



(a)



(b)

Figure 3.7 The example of SOFC system (a) equivalent circuit and (b) Nyquist diagram of a SOFC system (Mücke, 2011)

3.4. X-Ray Diffraction Analysis (XRD)

X-Ray diffraction analysis (XRD) is a non-destructive method which provides information about the structure of crystallographic, physical and chemical properties of a sample. XRD is one of the microstructural analysis used for indication of phases and its orientations. This technique is based on the constructive interference of a crystalline sample and monochromatic X-rays. In XRD technique, the produced X-rays are applied and directed to the sample; wherein the incident rays' interactions with the sample produces a diffracted beam which is determined. The refracted intensity rays dispersed at the material's angle is plotted to show a diffraction pattern.

Basically, the XRD technique is explained by the Bragg's equation shown in Eq. (3.2).

$$n \cdot \lambda = 2 \cdot d \sin \theta \quad (3.2)$$

where, n indicates the number of diffraction, λ refers wavelength, d is the vertical distance between the atomic layers, and θ is the incident angle. The schematic of X-ray diffracted on a material is shown below.

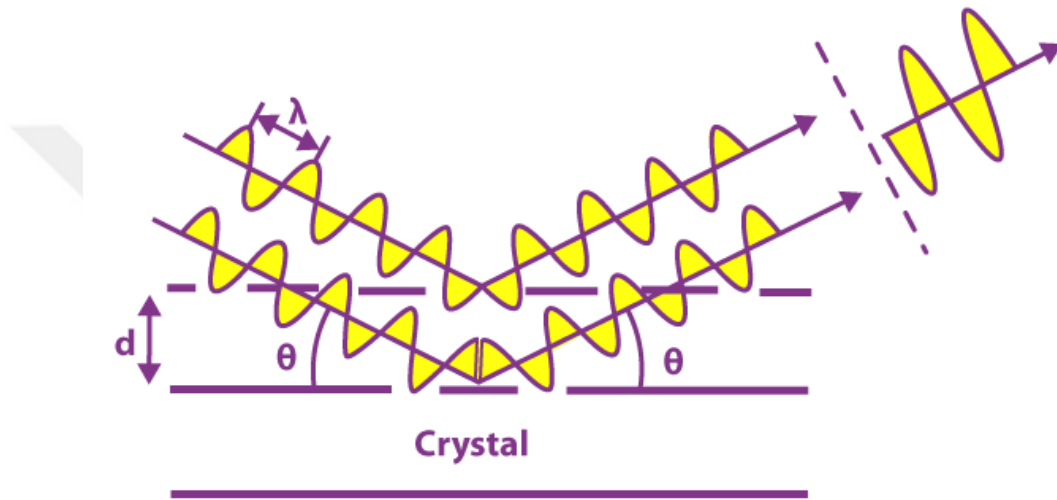


Figure 3.8 The diffraction of X-Rays onto the material used (Byju's, n.d.).

3.5 Visualization of SOFC Structure

Scanning electron microscopy (SEM) uses a focused beam of high-energy electrons to produce different type signals on the samples surface. SEM gives mechanical and chemical properties such as the chemical composition and the crystal structure and material atomic orientation. In addition, data are gathered over the sample selected surface area. Two-dimensional images are derived showing the changes in these properties used in most applications. The schematic of SEM and its components is presented in Figure 3.9.

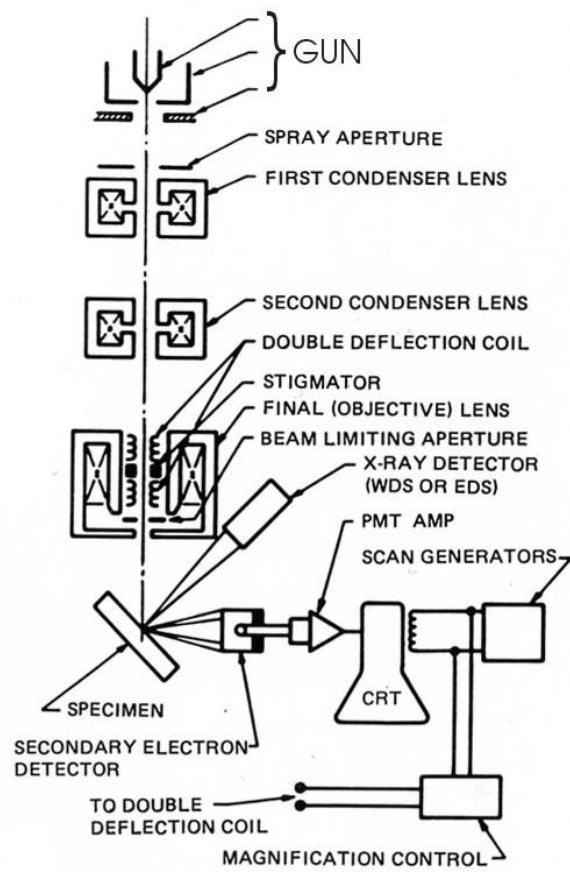


Figure 3.9 The schematic of SEM and its structure (Swap, n.d.)

CHAPTER FOUR

MATHEMATICAL MODELING

4.1 Introduction

This chapter gives information on the mathematical modeling of SOFC at the cell level, and the integrated SOFC and biomass gasification system at the system-level. The mathematical relations using thermodynamics and electrochemistry phenomena are discussed in detail. The solution procedure is presented and discussed. Furthermore, the optimization method is presented.

4.2. Cell Level Modeling of SOFC

In this section, the mathematical modeling equations for SOFC are given and discussed. The modeling equations are solved under the following assumptions and simplifications:

- SOFC operates under steady-state conditions.
- Contact resistances are negligible.
- SOFC is thermally insulated, which means that there is no heat transfer between the SOFC unit and the environment.
- The species at the exit of the anode channel are considered to be in chemical equilibrium.
- The air used at the cathode inlet consists of 21% oxygen and 79% nitrogen

The schematic of the SOFC considered is presented in Figure 4.1. The working principle of the system can be depicted as follows. The fuel mixture (namely syngas mixture), which consists of methane, hydrogen, carbon monoxide, carbon dioxide, and water vapor, enters the anode channel. At the anode side, steam-methane reforming (Eq. (4.1)), water gas shift reaction (Eq. (4.2)), and hydrogen and carbon-monoxide oxidation reactions (Eqs. (4.3)-(4.4)) occur. Here, the fuel mixture reacts with the catalytically active sites and leaves the anode with a different composition. A part of

the leaving fuel gas is extracted and diverted (State 4) to the anode again (anode off-gas recirculation) in order to utilize the depleted anode stream more effectively and combine with the reformat gas (State 1). On the other side, the air enters the cathode side of SOFC (State 6). Oxygen molecules are reduced to oxide ions (Eq. 4.3), which travel through the electrolyte to oxidize the species at the anode side, whereas nitrogen is an inert gas. The electrons formed at the anode side pass to the cathode side through an external circuit after passing the load.

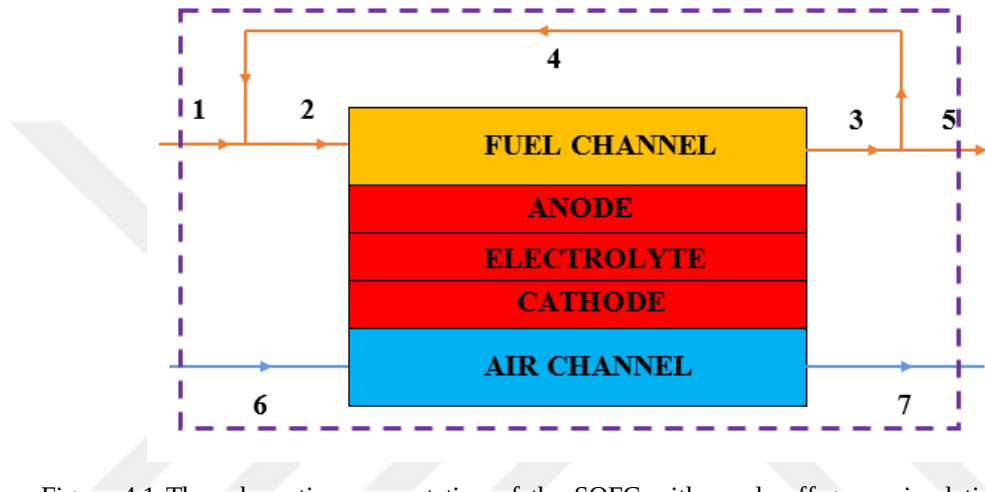


Figure 4.1 The schematic representation of the SOFC with anode off-gas recirculation and fed by simulated reformat

Methane and carbon-monoxide can convert hydrogen-rich gas mixtures with steam-methane reforming (SMR) and water-gas shifting (WGS) reactions. These reactions are given in Eqs. (4.1) and (4.2), respectively.

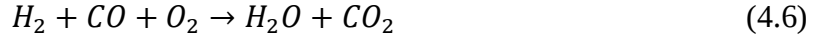


Electrochemical reactions occur in both anode (Eqs. (4.3)-(4.4)) and cathode (Eq. (4.5)) sides as given below.





The overall electrochemical reaction is presented in Eq. (4.6).



The chemical equilibrium constants for SMR and WGS reactions are given in Eqs. (4.7) and (4.8), respectively.

$$K_{SMR} = \exp\left(\frac{-\Delta\bar{g}}{\bar{R} \cdot T_{anode,ex}}\right) = \frac{x_{CO} \cdot x_{H_2}^3}{x_{CH_4} \cdot x_{H_2O}} \cdot P_{SOFC}^2 \quad (4.7)$$

$$K_{WGS} = \exp\left(\frac{-\Delta\bar{g}}{\bar{R} \cdot T_{anode,ex}}\right) = \frac{x_{CO_2} \cdot x_{H_2}}{x_{CO} \cdot x_{H_2O}} \quad (4.8)$$

where, $\Delta\bar{g}$ is the Gibbs free energy, $\bar{R}$ is the universal gas constant, $T_{anode,ex}$ is the anode exit temperature, x_{CO} , x_{H_2} , x_{CO_2} , and x_{H_2O} are the molar fractions of carbon monoxide, hydrogen, carbon dioxide, and water, respectively, at the anode outlet (State 3).

Steam to Carbon Ratio at the anode inlet is presented in Eq. (4.9).

$$r_{S/C} = \frac{\dot{n}_{H_2O,2}}{\dot{n}_{CH_4,2} + \dot{n}_{CO_2,2} + \dot{n}_{CO,2}} \quad (4.9)$$

In this equation $\dot{n}_{H_2O,2}$, $\dot{n}_{CH_4,2}$, $\dot{n}_{CO_2,2}$ and $\dot{n}_{CO,2}$ are molar flow rates of steam, methane, carbon dioxide, and carbon monoxide, respectively. The recirculation ratio can be determined using Eq. (4.10).

$$r_{circ} = \frac{\dot{n}_4}{\dot{n}_3} \quad (4.10)$$

Fuel utilization ratios for hydrogen and carbon monoxide can be given as follows.

$$U_{f,H_2} = \frac{a}{\dot{n}_{H_2,2} + 3c + d} \quad (4.11)$$

$$U_{f,CO} = \frac{b}{\dot{n}_{CO,2} + c - d} \quad (4.12)$$

Five equations, which are Eqs. (4.7), (4.8), (4.9), (4.11), and (4.12), are solved iteratively in order to find the extents of reactions (a, b, c, and d) and mass flow rate fuel ($\dot{m}_f$). The molar flow rates of each species at each state are given in Table 4.1. It should be noted that a, b, c, and d are the extents for hydrogen oxidation reaction, carbon monoxide oxidation reaction, steam methane reforming reaction, and water gas shift reaction, respectively.

Table 4.1 The molar flow rates of each species at each state

State Number	Equations
1	$\dot{n}_{1,i} = x_{1,i} \frac{\dot{m}_f}{\sum_i (x_{1,i} \cdot MW_i)}$
2	$\dot{n}_{2,i} = \dot{n}_{1,i} + r_{circ} \cdot \dot{n}_{3,i}$
3	$\dot{n}_{3,CH_4} = \dot{n}_{2,CH_4} - c$ $\dot{n}_{3,H_2} = \dot{n}_{2,H_2} - a + 3c + d$ $\dot{n}_{3,CO} = \dot{n}_{2,CO} - b + c - d$ $\dot{n}_{3,CO_2} = \dot{n}_{2,CO_2} + b + d$ $\dot{n}_{3,H_2O} = \dot{n}_{2,H_2O} + a - c - d$
4	$\dot{n}_{4,i} = r_{circ} \cdot \dot{n}_{3,i}$
5	$\dot{n}_{5,i} = (1 - r_{circ}) \cdot \dot{n}_{3,i}$
6	$\dot{n}_{6,O_2} = \frac{a+b}{2 \cdot U_{O_2}}$ $\dot{n}_{6,N_2} = \frac{79}{21} \cdot \dot{n}_{6,O_2}$
7	$\dot{n}_{7,O_2} = \dot{n}_{6,O_2} \cdot (1 - U_{O_2})$ $\dot{n}_{7,N_2} = \dot{n}_{7,O_2} \cdot \frac{79}{21}$

The parallel circuit approach model is used, as depicted in Figure 4.2. In this approach, the oxidations of hydrogen and carbon monoxide are considered separately. The cell current is equal to the summation of the cell current due to the hydrogen oxidation (I_{H_2}) and cell current due to the carbon monoxide oxidation (I_{CO}); whereas the cell voltages in each branch are equal to each other. Furthermore, polarizations can be assessed separately for hydrogen and carbon-monoxide oxidation. The equations used in this approach are given below (Aicart et al., 2014, Aicart et al., 2015).

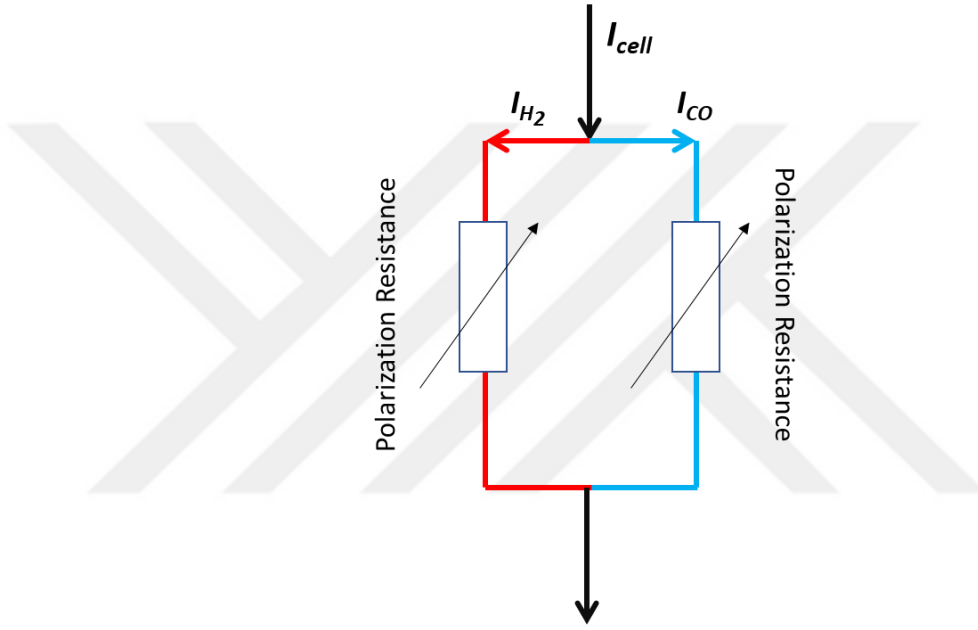


Figure 4.2 The equivalent circuit of the SOFC (adapted from (Aicart et al., 2014))

The Nernst voltage is obtained using the equations reported below. It should be noted that Nernst voltage is calculated for both hydrogen and carbon monoxide oxidations separately (Aicart et al., 2014).

$$V_{Nernst,H_2} = 1.253 - 0.00024516 \cdot T_{anode,ex} + \frac{\bar{R} \cdot T_{anode,ex}}{2 \cdot F} \cdot \ln \left(\frac{P_{H_2} \cdot P_{O_2}^{0.5}}{P_{H_2O}} \right) \quad (4.13)$$

$$V_{Nernst,CO} = 1.46713 - 0.0004527 \cdot T_{anode,ex} + \frac{\bar{R} \cdot T_{anode,ex}}{2 \cdot F} \cdot \ln \left(\frac{P_{CO} \cdot P_{O_2}^{0.5}}{P_{CO_2}} \right) \quad (4.14)$$

There are three types of polarizations, which are ohmic, activation, and concentration polarizations, calculated and found using equations below. Ohmic polarization is caused due to the flow of oxide ions through the electrolyte and the resistance due to electron flow. Activation polarization is the voltage drop due to the slowness of the reactions occurring at the electrode electrolyte interfaces. Concentration polarization occurs due to the mass transport limitations. Regarding the calculation of activation and concentration polarizations, Butler–Volmer equation with identical charge transfer coefficients ($\alpha_a = \alpha_c$) called sinh simplification, and mass-limiting current density approaches are used, respectively (Mench, 2008).

$$V_{ohm}(i_{H_2}) = \sum_k (\rho_k \cdot L_k) \cdot i_{H_2} \quad (4.15)$$

$$V_{ohm}(i_{CO}) = \sum_k (\rho_k \cdot L_k) \cdot i_{CO} \quad (4.16)$$

$$V_{act}(i_{H_2}) = \frac{\bar{R} \cdot T}{F} \cdot \sinh^{-1} \left(\frac{i_{H_2}}{i_{0,H_2}} \right) + \frac{\bar{R} \cdot T}{F} \cdot \sinh^{-1} \left(\frac{i_{H_2}}{i_{0,O_2}} \right) \quad (4.17)$$

$$V_{act}(i_{CO}) = \frac{\bar{R} \cdot T}{F} \cdot \sinh^{-1} \left(\frac{i_{CO}}{i_{0,CO}} \right) + \frac{\bar{R} \cdot T}{F} \cdot \sinh^{-1} \left(\frac{i_{CO}}{i_{0,O_2}} \right) \quad (4.18)$$

$$V_{conc}(i_{H_2}) = \frac{\bar{R} \cdot T}{2 \cdot F} \cdot \ln \left(\frac{i_{H_2}}{i_{lim,H_2}} \right) \quad (4.19)$$

$$V_{conc}(i_{CO}) = \frac{\bar{R} \cdot T}{2 \cdot F} \cdot \ln \left(\frac{i_{CO}}{i_{lim,CO}} \right) \quad (4.20)$$

The cell voltage for hydrogen and carbon monoxide sides and the power developed by the SOFC can be found using the equations below.

$$V_{cell,H_2} = V_{Nernst,H_2} - V_{ohm}(i_{H_2}) - V_{act}(i_{H_2}) - V_{conc}(i_{H_2}) \quad (4.21)$$

$$V_{cell,CO} = V_{Nernst,CO} - V_{ohm}(i_{CO}) - V_{act}(i_{CO}) - V_{conc}(i_{CO}) \quad (4.22)$$

$$\dot{W}_{SOFC} = i_{cell} \cdot A_{cell} \cdot V_{cell} \quad (4.23)$$

According to the parallel circuit law, voltage equality can be given in Eq. (4.24).

$$V_{cell,H_2} = V_{cell,CO} = V_{cell} \quad (4.24)$$

The cell current density due to the carbon monoxide oxidation can be found using Eq. (4.25) (Aicart et al., 2014, 2015).

$$i_{CO} = \frac{i_{cell} - (\beta \cdot i_{H_2})}{1 - \beta} \quad (4.25)$$

Here, i_{H_2} is the current density due to the hydrogen oxidation and β is the surface factor which can be found using Eq. (4.26) (Aicart et al., 2014, 2015).

$$\beta = \frac{x_{H_2,3}}{x_{H_2,3} + x_{CO,3}} \quad (4.26)$$

The steady-state open-system energy balance equation for the control volume enclosing the SOFC, which is shown with the purple dashed line in Figure 4.1, can be applied (Eq. (4.27)) to find the oxygen utilization (U_{O_2}) iteratively (Moran, M. J., Shapiro, H. N., Boettner, D. D., & Bailey, 2010).

$$0 = -\dot{W}_{SOFC} + (\dot{n}_1 \cdot \bar{h}_1 + \dot{n}_6 \cdot \bar{h}_6) - (\dot{n}_5 \cdot \bar{h}_5 + \dot{n}_7 \cdot \bar{h}_7) \quad (4.27)$$

After finding the unknown properties of SOFC after solving the equations shown above, exergy analysis is conducted to find the exergy destruction rate of the SOFC. The open-system exergy rate balance equation for the control volume enclosing the SOFC is given in Eq. (28) (Moran, M. J., Shapiro, H. N., Boettner, D. D., & Bailey, 2010).

$$0 = -E\dot{x}_W + \left(\dot{n}_1 \cdot (\bar{e}x_{PH,1} + \bar{e}x_{CH,1}) + \dot{n}_6 \cdot (\bar{e}x_{PH,6} + \bar{e}x_{CH,6}) \right) - \left(\dot{n}_5 \cdot (\bar{e}x_{PH,5} + \bar{e}x_{CH,5}) + \dot{n}_7 \cdot (\bar{e}x_{PH,7} + \bar{e}x_{CH,7}) \right) - E\dot{x}_D \quad (4.28)$$

Here, $E\dot{x}_W$ is the exergy rate due to the work, $\bar{e}x_{PH}$ and $\bar{e}x_{CH}$ are physical and chemical flow exergies, respectively. These parameters can be found using Eqs. (4.29) and (4.30), respectively.

$$\bar{e}x_{PH} = (\bar{h} - \bar{h}_0) - T_0 \cdot (\bar{s} - \bar{s}_0) \quad (4.29)$$

$$\bar{e}x_{CH} = \sum_k (x_k \cdot \bar{e}x_{k,CH}) + \bar{R} \cdot T_0 \cdot (x_k \cdot \ln x_k) \quad (4.30)$$

where, $\bar{h}$ is the molar enthalpy, $\bar{s}$ is the molar entropy, x_k is the molar fraction, $\bar{R}$ is the universal gas constant, T_0 is the environmental temperature, $\bar{e}x_{k,CH}$ is the standard chemical exergy, k denotes the species, and 0 denotes the dead state. Standard chemical exergy values for each species can be found in Refs (Cengel et al., 2002; Moran, M. J., Shapiro, H. N., Boettner, D. D., & Bailey, 2010).

For the solution of the equations discussed above, a solution algorithm is presented as displayed in Figure 4.3. The algorithm begins with identifying the input parameters. Then, initial guess values for a , b , c , d , and $\dot{m}_f$ given in Table 4.1 are set. The non-linear equations (Eqs. (4.7-4.12)) are solved using the iterative solver (FSolve of MATLAB). If the convergence criteria (the error of 10^{-5}) are satisfied, the algorithm gives the molar flow rates and molar fractions for each state. In the second step of the algorithm, the initial values for the current densities regarding the hydrogen and carbon monoxide oxidations are set. The algorithm then solves the system of non-linear equations (Eqs. (4.13-4.27)). If the error between the initial values and the results is equal to or less than 10^{-5} , the algorithm gives the current density regarding the hydrogen and carbon monoxide oxidations, the cell voltage, and the power output.

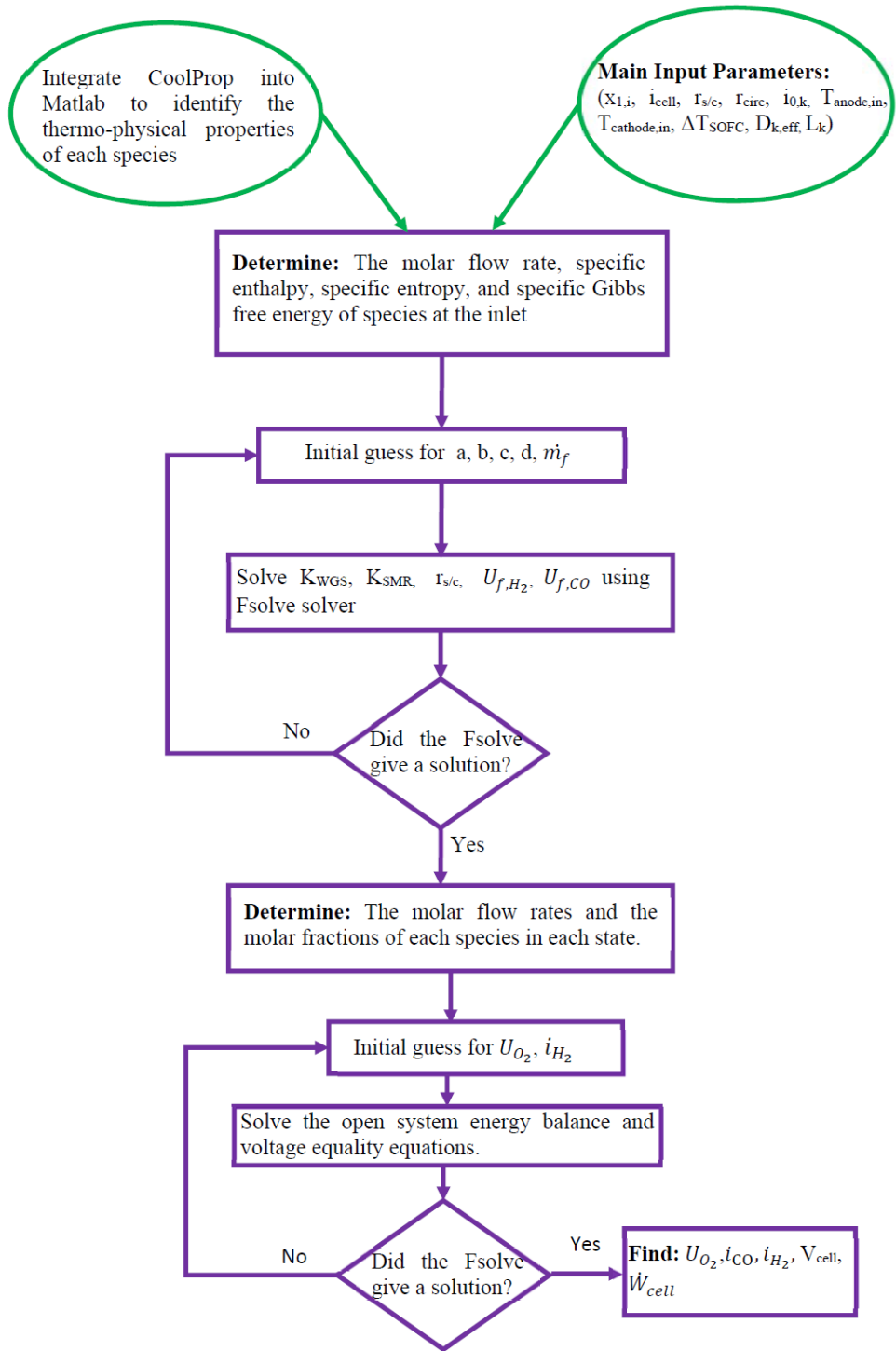


Figure 4.3 The solution algorithm of the 0-D SOFC model developed in the Matlab environment

4.3 Mathematical Modeling of Integrated SOFC and Biomass Gasification System

In this chapter, the modeling equations for integrated system are illustrated. The schematic diagram of the integration of SOFC and biomass gasifier are shown in Figure 4.4.

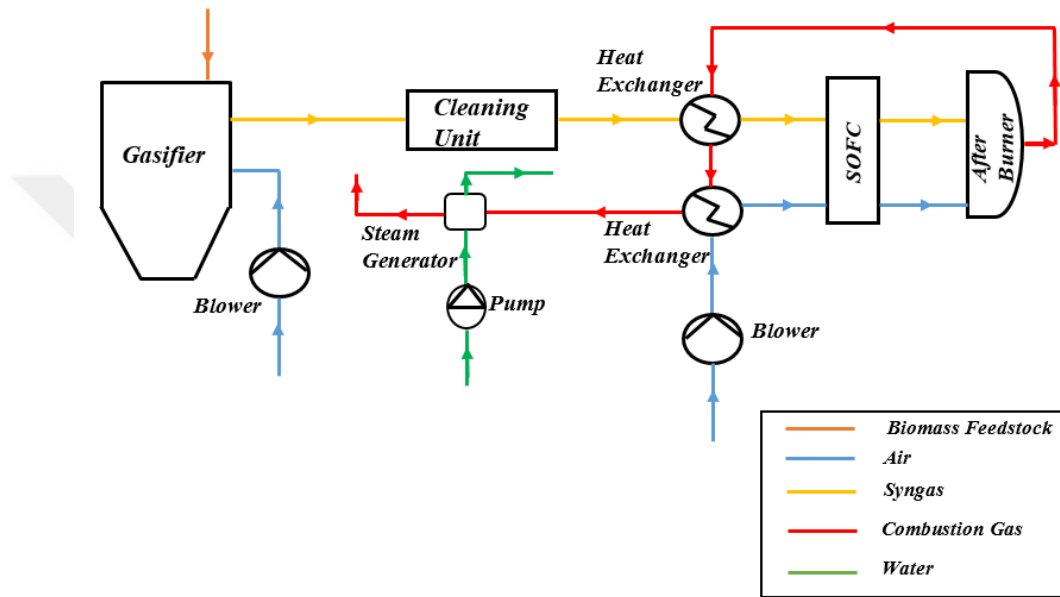


Figure 4.4 The layout of the integration of SOFC and biomass gasifier

The working principle of the integrated system can be explained in detail as follows. The biomass feedstock enters into the gasifier while air is entered to the gasifier as the gasification agent for reactions to take place. A synthesis gas mixture is formed as a result of a series of reactions (as presented in Table 4.2). Since the synthesis gas mixture formed contains harmful gases such as NO_x and SO_x , it should be sent to the cleaning unit. The cleaned syngas mixture passes through the preheater where the temperature is up and is sent to the SOFC. On the other hand, air is used for the SOFC cathode side as oxidant. Here, power and heat are produced by undergoing electrochemical reactions (as mentioned in Section 3.2.). Then, the gas mixture coming out of the SOFC enters the afterburner and complete combustion is performed. The combusted gas mixture is used for increasing syngas temperature, air, and water (to produce steam) by passing through a series of heat exchangers.

Table 4.2. The reaction series occur in the gasification unit (Koido & Iwasaki, 2018; Kushwah et al., 2022)

Reaction Type	Reaction Formula	Enthalpy of Reaction (kJ/mol)
Oxidation	$C_{(s)} + O_2 \leftrightarrow CO_2$	-392.5
	$C_{(s)} + \frac{1}{2}O_2 \leftrightarrow CO$	-110.5
	$CH_4 + \frac{1}{2}O_2 \leftrightarrow CO + 2H_2$	-35.7
	$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$	-802.3
	$H + \frac{1}{2}O_2 \leftrightarrow H_2O$	-242
Boudouard	$C_{(s)} + CO_2 \leftrightarrow 2CO$	172
Water –Gas	$C_{(s)} + H_2O \leftrightarrow CO + H_2$	131.4
	$C_{(s)} + 2H_2O \leftrightarrow CO_2 + 2H_2$	90.4
Water-Gas Shifting	$CO + H_2O \leftrightarrow CO_2 + H_2$	-41
Steam Reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	205.9
	$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$	164.7
	$C_nH_m + nH_2O \leftrightarrow nCO + \left(\frac{n+m}{2}\right)H_2$	210.1
	$C_nH_m + \frac{n}{2}H_2O \leftrightarrow \frac{n}{2}CO + (m-n)H_2 + \frac{n}{2}CH_4$	4.2
CO₂ Reforming	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	247
	$C_nH_m + nCO_2 \leftrightarrow 2nCO + \left(\frac{m}{2}\right)H_2$	292.4
	$C_nH_m + \left(\frac{n}{4}\right)CO_2 \leftrightarrow \left(\frac{n}{2}\right)CO + \left(\frac{m-3n}{2}\right)H_2 + \left(\frac{3n}{4}\right)CH_4$	45.3
Methanation	$C_{(s)} + 2H_2 \leftrightarrow CH_4$	-74.6
	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-205.9
	$2CO + 2H_2 \leftrightarrow CH_4 + CO_2$	-247.3
	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	-164.9
Decomposition	$pC_xH_y \leftrightarrow qC_nH_m + rH_2$	
	$C_nH_m \leftrightarrow nC + \left(\frac{m}{2}\right)H_2$	

Regarding the gasifier modeling, in order to find the syngas composition an iterative solution method is performed by using chemical equilibrium constant (steam-methane reforming, water-gas shifting, and methane production reaction), atom balance, and energy balance equations (Colpan, 2009). Studies on gasifier modeling found in the literature have obtained that the methane formation reaction, steam-reforming and water-gas shifting reactions are handled in the calculation of syngas mixture obtained. In addition, undesirable solids such as ash and tar are not considered in the calculations. The properties of the biomass type used in the modeling are presented in Table 4.3.

Table 4.3 The properties of biomass (Colpan et al., 2010)

Biomass Type	Wood
Ultimate Analysis of Biomass [wt% dry basis]	50% C, 6% H, 44%O
Moisture Content in Biomass [wt %]	40%
Proximate Analysis	
Ash	3.38%
Fixed Carbon	12.68%
Volatiles	80.87%

Generally, mathematical relations used in the integrated system are presented as follows. The open system energy balance and mass balance equations enclosing the integrated system's components are applied in order to find the state properties is shown in Eqs. (4.31) and (4.32), respectively.

$$0 = \sum_i \dot{m}_i - \sum_e \dot{m}_e \quad (4.31)$$

$$0 = \dot{Q}_{CV} - \dot{W}_{CV} + \sum(\dot{n}_i \cdot \bar{h}_i) - \sum(\dot{n}_e \cdot \bar{h}_e) \quad (4.32)$$

Here, $\dot{Q}_{CV}$ indicates the heat transfer of the components, $\dot{W}_{CV}$ is the power, $\dot{m}$, $\dot{n}$, and $\bar{h}$ are the mass flow rate, molar flow rate and molar enthalpy of species, respectively.

The performance of the developed system-level model can be assessed in terms of a thermodynamic point of view (energy and exergy). As a result of the energy analysis, electrical efficiency, η_{el} (Eq. (4.33)), and fuel utilization efficiency, FUE (Eq. (4.34)), can be found as follows.

$$\eta_{el} = \frac{\dot{W}_{net}}{\dot{n}_{biomass} \cdot HV_{biomass}} \quad (4.33)$$

$$FUE = \frac{\dot{W}_{net} + \dot{Q}_{useful}}{\dot{n}_{biomass} \cdot HV_{biomass}} \quad (4.34)$$

In the equations given above, the heating value (HV) [kJ/kmol] can be given as the lower heating value (LHV) or the higher heating value (HHV). $\dot{n}$ is the molar flow rate [kmol/s].

4.4 Optimization of Integrated SOFC and Biomass Gasification System

After performing thermodynamic analysis of integrated systems, optimization studies can be carried out to maximize the thermodynamic performance. In literature, many methods are applied in the optimization of energy systems. Commonly used optimization tools include General Algebraic Modeling System (GAMS), MATLAB Optimization Toolbox, Microsoft Excel, LINDO, Taguchi and SolvOpt (Ahmed et al., 2012). Optimization methods can be divided into three main groups: deterministic, stochastic, and meta-heuristic. Mixed Integer Linear Program (a deterministic approach), Pareto Optimal (a stochastic approach), and Genetic Algorithm (a meta-heuristic approach) are mostly used as optimization methods in the integrated SOFC and biomass gasifier systems (Ramadhani et al., 2017).

Taguchi method is an effective and simple method based on statistical tools sophisticated by Genichi Taguchi (Meena et al., 2018). This approach is one of the well-known experimental methodologies used to obtain the minimum experiment numbers to be conducted within the level boundaries. This method gives called orthogonal arrays experiments with optimum control parameters settings. Therefore,

this method combines experiment design with the optimization of variable parameters to reach the best results. Orthogonal Arrays (OA) can be determined as an experimental set. Signal-to-Noise ratio is a measure of quality and helps in data analysis. It also supports in estimating dominant parameters.

The Taguchi method offers two different options for the objective function. If the value of your objective function needs to be maximized, the "Larger is Better" condition should be selected, whereas if your objective function value needs to be minimized, the "Smaller is Better" state should be selected. The signal-to-noise ratios for these states are given below (Karazi et al., 2019). .

$$S/N_L = -10 \cdot \log \left(\frac{1}{n} \cdot \sum_{i=1}^n \frac{1}{y_i^2} \right) \quad (4.35)$$

$$S/N_S = -10 \cdot \log \left(\frac{1}{n} \cdot \sum_{i=1}^n y_i^2 \right) \quad (4.36)$$

Here, n is the number of experiments and y_i is the response (output) parameter.

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Introduction

This chapter gives information about the results and discussion on the experimental studies on SOFC including polarization curves, area specific resistance values, SEM micrograph of SOFC structure, and EIS results, cell level modeling of SOFC fed with syngas, and system level modeling results of integrated SOFC and biomass gasification. Furthermore, the validation of the developed SOFC model with experimental results is presented. In addition, optimization study results for integrated system are presented.

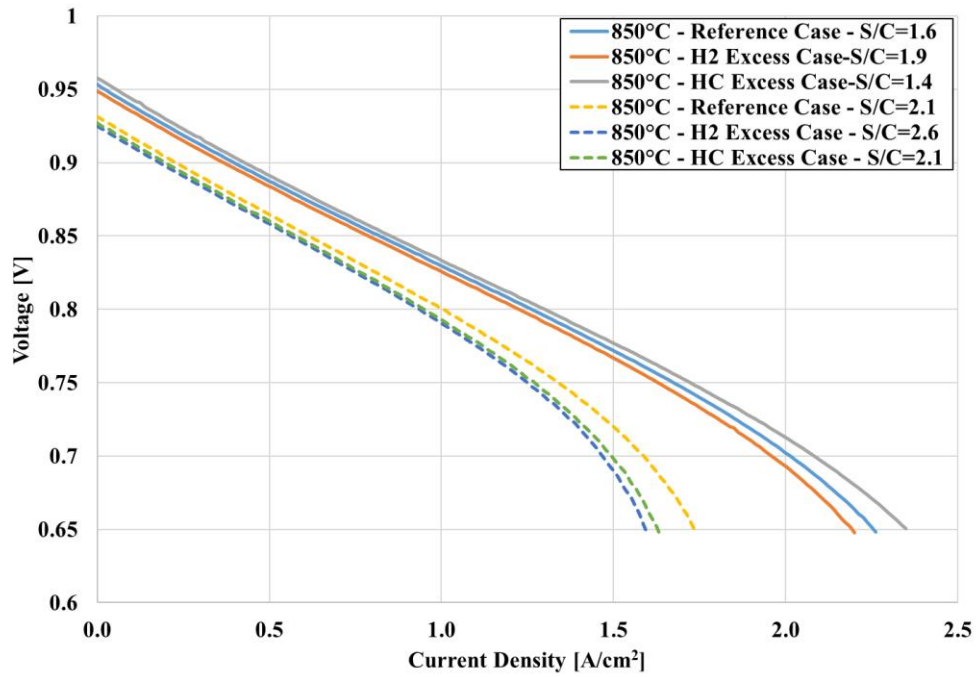
5.2 Experimental Studies on SOFC

In this section, the results for experimental studies are given and discussed. The Nernst voltage values obtained from the experimental study and the modeling study are compared in Table 5.1 according to the cases studied and the different S/C ratio values. As can be seen from the table that the differences between the experimental and modeling are acceptable with low error rates. For each case, it was obtained that Nernst voltage is higher under the low S/C ratios. In addition, it can be observed that the Nernst voltage values obtained by the experimental studies are a bit lower due to the irreversibilities inside of the SOFC.

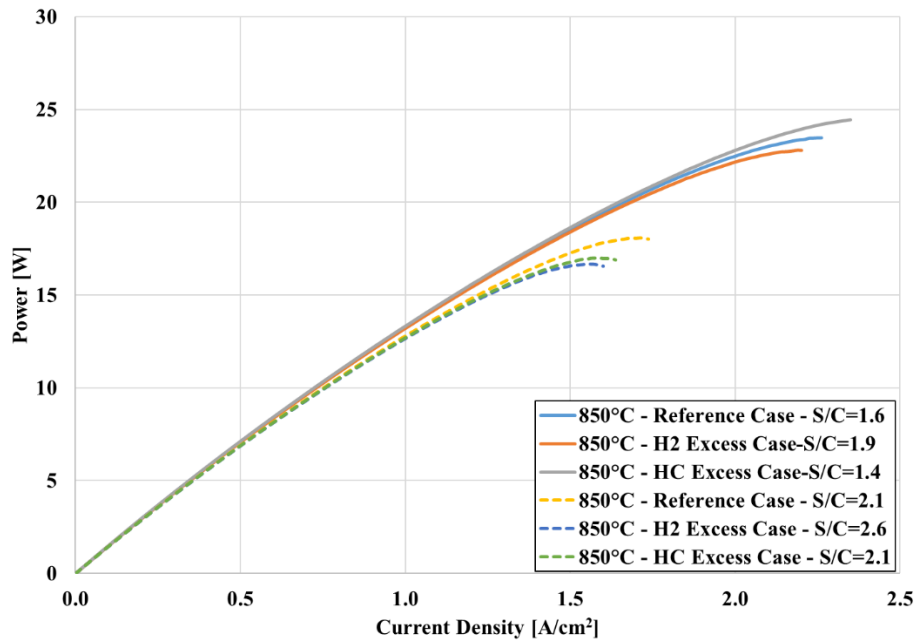
Table 5.1 The comparison of Nernst voltage values between experimental and modeling studies according to the different S/C ratios at 850°C

	REFERENCE CASE		HYDROGEN EXCESS CASE		HYDROCARBON EXCESS CASE	
	S/C=1.6	S/C=2.1	S/C=1.9	S/C=2.6	S/C=1.5	S/C=2.1
Experimental (V)	0.9532	0.9312	0.9489	0.9250	0.9576	0.9270
Model (V)	0.9701	0.9427	0.9608	0.9472	0.9759	0.9366
Error (%)	1.77	1.24	2.08	2.40	1.92	1.04

Figure 5.1(a) shows the experimental i-V curves obtained at 850°C, adding a change in the feed gas mixture (H₂ excess and hydrocarbon excess cases). As the current density increases, the cell voltage decreases with a slope corresponding to the cell resistance. This trend is due to ohmic and polarization resistances combined. Among the three cases, the reference case for high S/C ratio and the hydrocarbon excess case for low S/C ratio has the highest cell voltage values due to the higher hydrogen flow rates and Nernst values for a given current density. In addition, the area specific resistances (ASR) for reference, hydrogen excess, and hydrocarbon excess cases according to the different S/C ratios are presented in Table 5.2. Area specific resistance is the slope of the polarization curve for a certain current value. As can be seen from the table that while the ASR values are similar under low and medium current densities, they differ under high current density. At higher current densities, fuel starvation occurs, expressed by a bending down of the i-V curve due to the higher flow rates. Under the higher S/C ratios, higher current densities are reached. Furthermore, it was observed that high performance is obtained when SOFC is operated at low S/C ratios. However, it should be noted that this ratio should be determined by taking into account the carbon deposition. On the other hand, Figure 5.1(b) shows the effect of current density on the power obtained by the SOFC. When the current density increases, the power increases up to a certain point. While high power is obtained in Hydrocarbon Excess case for low S/C ratio; High power is achieved in the Reference Case for high S/C ratio. Those values are calculated as 18.1 W and 24.5 W, respectively.



(a)



(b)

Figure 5.1 The effect of the current density on the (a) cell voltage and (b) power produced by the SOFC through experimental studies (Conditions are given in Table 3.1).

Table 5.2 The calculated area specific resistance values according to the S/C values for the cases

Current Density (A/cm ²)	ASR ($\Omega \cdot \text{cm}^2$)					
	REFERENCE CASE		HYDROGEN EXCESS CASE		HYDROCARBON EXCESS CASE	
	S/C = 1.6	S/C = 2.1	S/C = 1.9	S/C = 2.6	S/C = 1.5	S/C = 2.1
0.25	0.139	0.137	0.135	0.136	0.139	0.137
0.50	0.132	0.134	0.130	0.131	0.133	0.134
1.50	0.121	0.141	0.121	0.157	0.120	0.153

In order to see the structure of SOFC used in the experiments, the SEM cross-section micrograph is shown in Figure 5.2. In the image, the cell is slightly oxidized (oxides visible as a darker gray surface in the support structure) since it was taken at the end of the test. The white spots are epoxy resin surface impurities/irregularities.

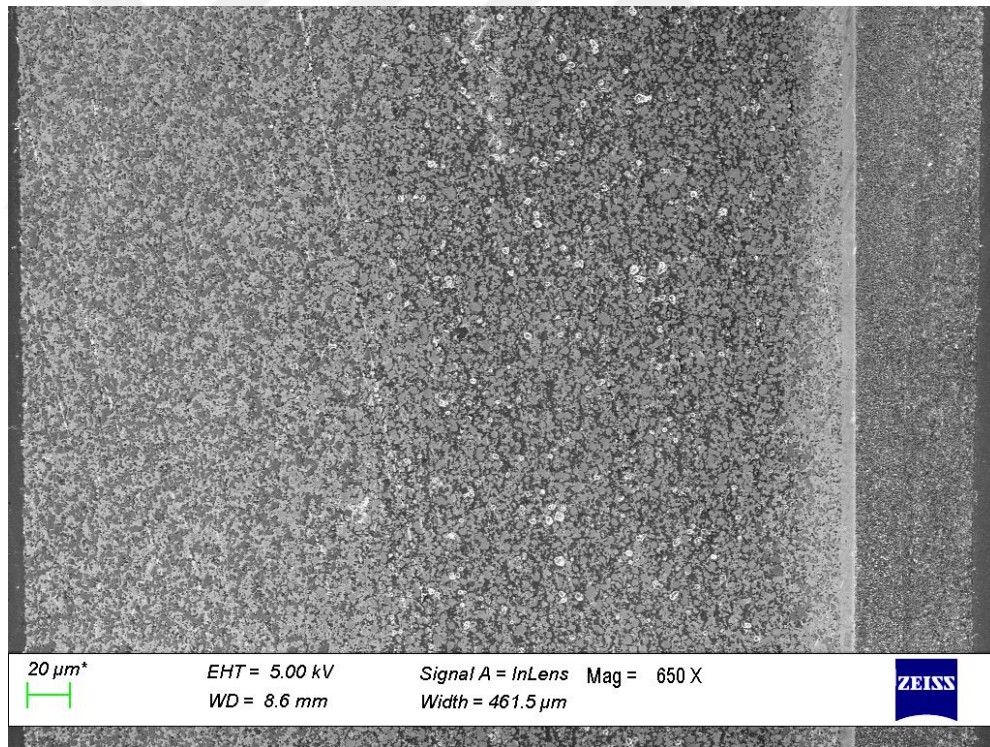


Figure 5.2 SEM cross-section micrograph taken in the center of the cell (From left to right Ni-YSZ support and active area (denser), YSZ electrolyte (denser layer), CGO barrier layer (white), and LSC/CGO oxygen electrode)

Figure 5.3 shows the Nyquist diagram for 4% H₂O/H₂ ratio according to the different operating temperature values. As can be seen in the figure, there are two hills

which are anode side (large one) and the cathode side (small one). On the other hand, as the temperature increases, the total ohmic resistance (anode, electrolyte, and cathode) decreases. It can be observed that the total ohmic resistances are found as $0.35 \Omega \cdot \text{cm}^2$ for 620°C , $0.22 \Omega \cdot \text{cm}^2$ for 650°C , $0.18 \Omega \cdot \text{cm}^2$ for 700°C , and $0.11 \Omega \cdot \text{cm}^2$ for 750°C .

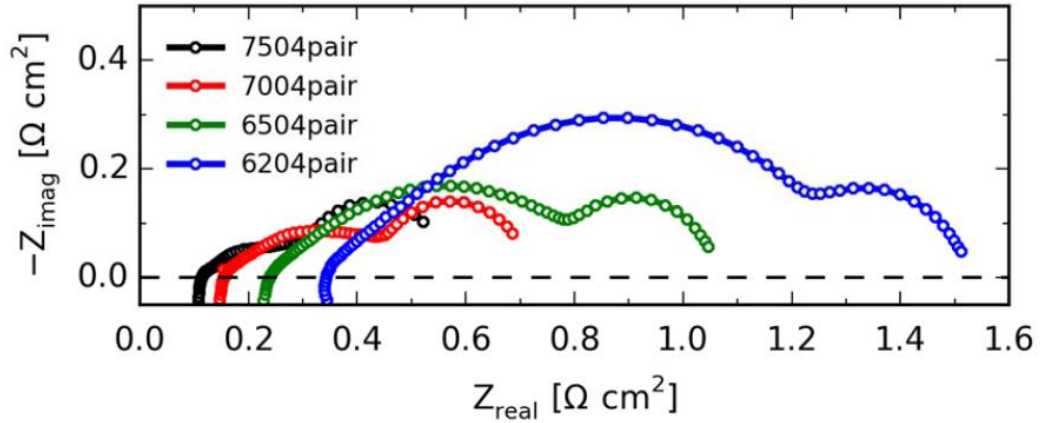


Figure 5.3 The Nyquist plot for SOFC fed with 4% hydrogen/steam,

Figure 5.4 demonstrates the EIS results according as function of the S/C ratios for syngas mixture as fuel for SOFC. As the S/C ratio increases, the polarization resistance, as well as the total cell resistance decreases. This happens because steam enhances the catalytic activity on Nickel (Ni). It was found from the EIS that there is an important presence of Ni, and indeed the polarization resistance is affected by the steam/carbon ratio considerably.

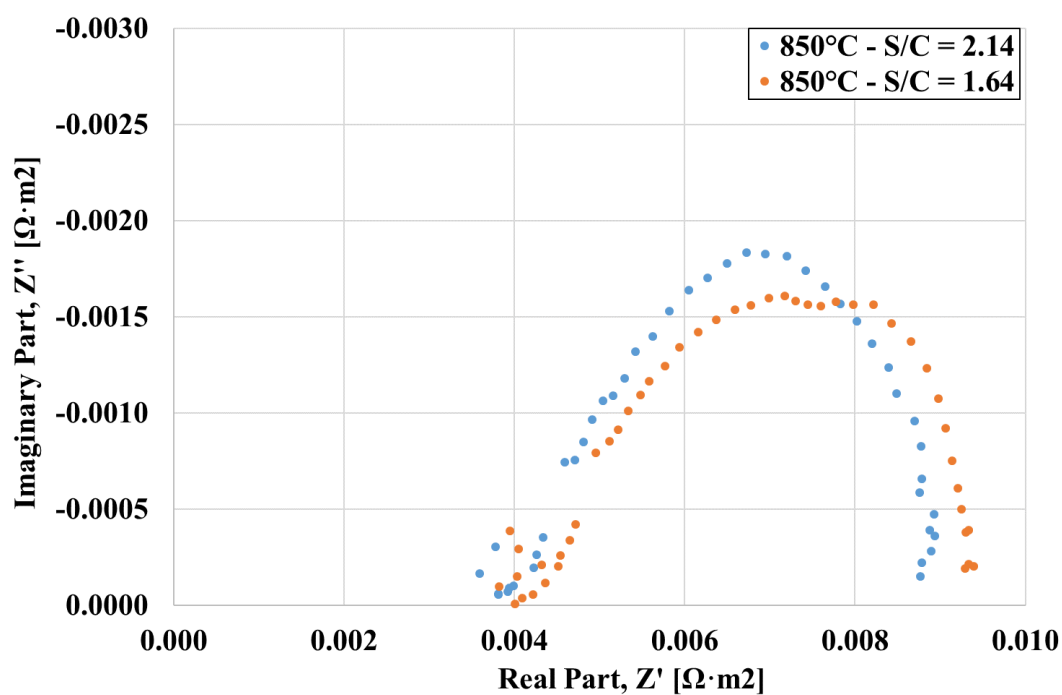


Figure 5.4 The Nyquist plot of SOFC according to the different S/Cs at $850^\circ C$

XRD results for cell testing in order to analyze the structure of crystalline materials, and its phases are presented in Figure 5.5

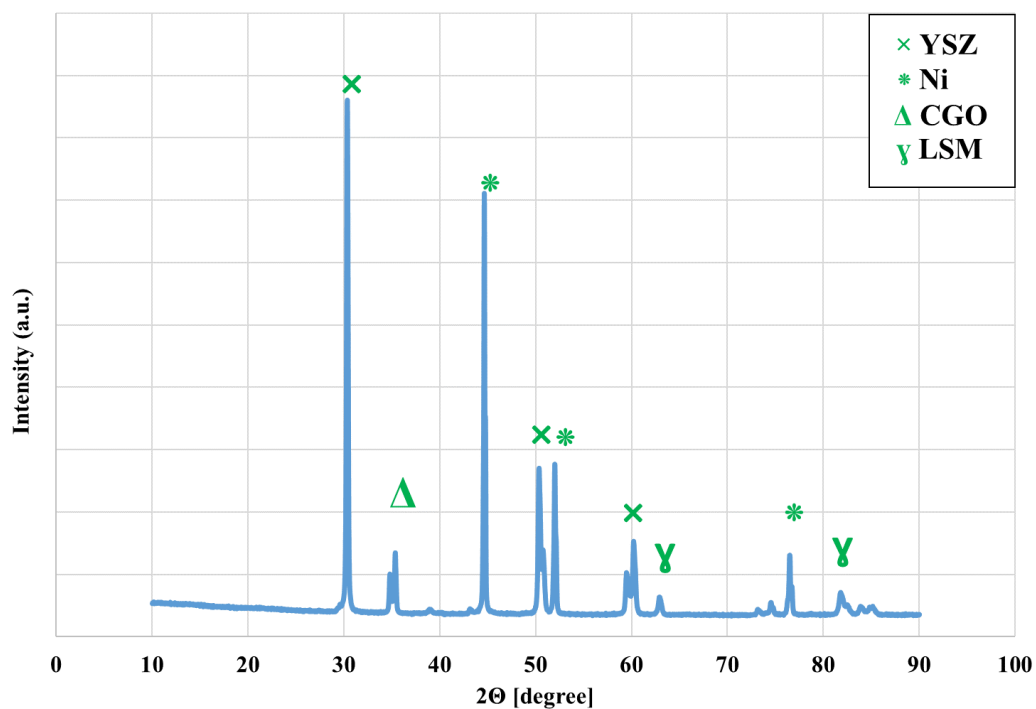
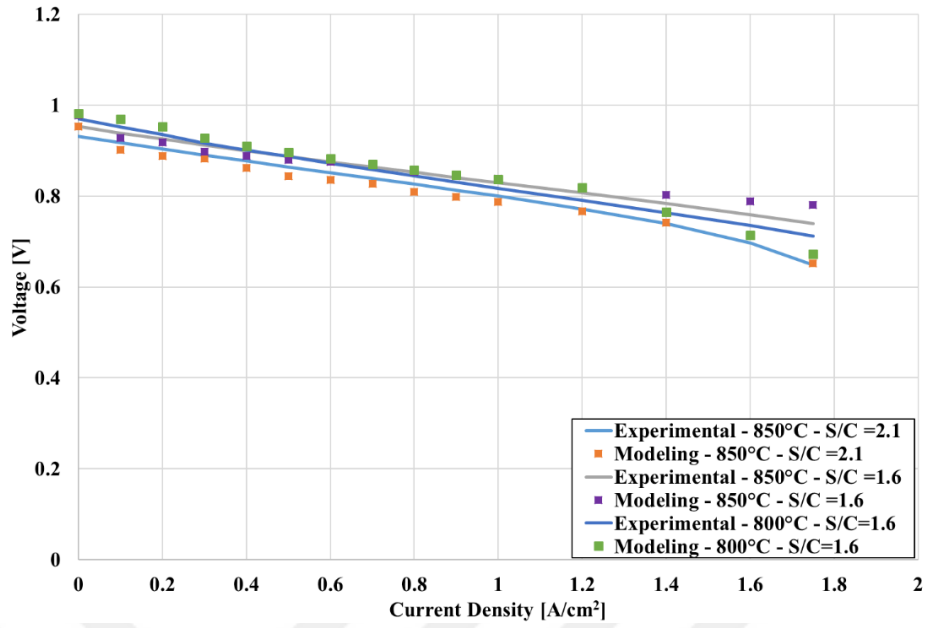


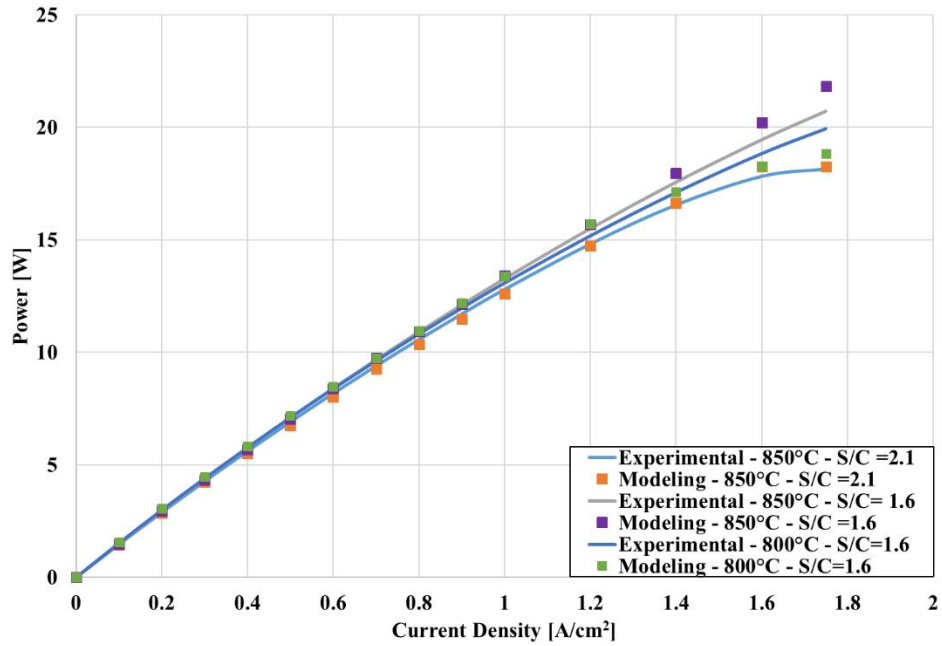
Figure 5.5 XRD pattern for cell used in the experimental (compounds were labeled according to the Ref. (Tong et al., 2020))

5.3 Validation of the SOFC Model

The proposed model discussed in Section 4.2 is validated through experimental data. The validation study is performed for the reference case under the low and high steam to carbon ratios at 850°C and with the low steam-to-carbon ratio at 850 °C and 800 °C to highlight the strength of the model by changing both feed composition and operative temperature. The results obtained from the experimental study and mathematical modeling are compared to each other. Figures 5.6(a) and 5.6(b) show the polarization and power curves obtained by the SOFC modeling compared with the experimental study according to low ($S/C=1.6$) and high S/C ratios ($S/C=2.1$) at 850°C and low S/C ratio at 800°C. The figures show that the cell voltage and power values are very agreeable with the experimental study for all conditions. The local maximum error rates for the low and high S/C s are obtained as 5.6%, 3.5%, and 6.8% (800°C), respectively. At low current densities, the performance is better for the 800°C because of a higher theoretical Nernst potential, while at higher current densities the performances are better for 850°C as a consequence of the lower area specific resistance (ASR) mainly given by a higher electrolyte ionic conductivity.



(a)



(b)

Figure 5.6 The electrochemical performance curves: (a) polarization curve and (b) power curve for both modeling and experimental studies ($T=850^{\circ}\text{C}$, **Low S/C case:** Anode gas composition: $x_{\text{CH}_4} = 9.19\%$, $x_{\text{H}_2} = 31.80\%$, $x_{\text{CO}} = 8.83\%$, $x_{\text{CO}_2} = 7.77\%$, $x_{\text{H}_2\text{O}} = 42.40\%$, air for cathode, Anode Flow Rate = 28.30 L/h, Cathode Flow Rate = 140 L/h; **High S/C case:** Anode gas composition: $x_{\text{CH}_4} = 9.3\%$, $x_{\text{H}_2} = 18.14\%$, $x_{\text{CO}} = 8.84\%$, $x_{\text{CO}_2} = 7.9\%$, $x_{\text{H}_2\text{O}} = 55.81\%$, air for cathode, Anode Flow Rate = 21.50 L/h, Cathode Flow Rate = 140 L/h; $T=800^{\circ}\text{C}$, **Low S/C case:** Anode gas composition: $x_{\text{CH}_4} = 9.19\%$, $x_{\text{H}_2} = 31.80\%$, $x_{\text{CO}} = 8.83\%$, $x_{\text{CO}_2} = 7.77\%$, $x_{\text{H}_2\text{O}} = 42.40\%$, air for cathode, Anode Flow Rate = 32 L/h, Cathode Flow Rate = 141 L/h;)

5.4 Cell Level Modeling of SOFC Fed with Syngas

Figure 5.7 shows the effect of current density on the power produced by the SOFC according to the different anode off-gas recirculation ratios. It can be seen from the figure that as the current density increases, the power increases for all recirculation ratios. It was observed that SOFC reaches higher current density values when the recirculation ratio is 0.1. In addition, the recirculation ratio does not have a significant effect on the SOFC performance at low current density values (up to 0.8 A/cm^2). When the recirculation ratio was changed from 0.1 to 0.4 under the same current density (0.6 A/cm^2), the power obtained by the SOFC was decreased by 4.58%.

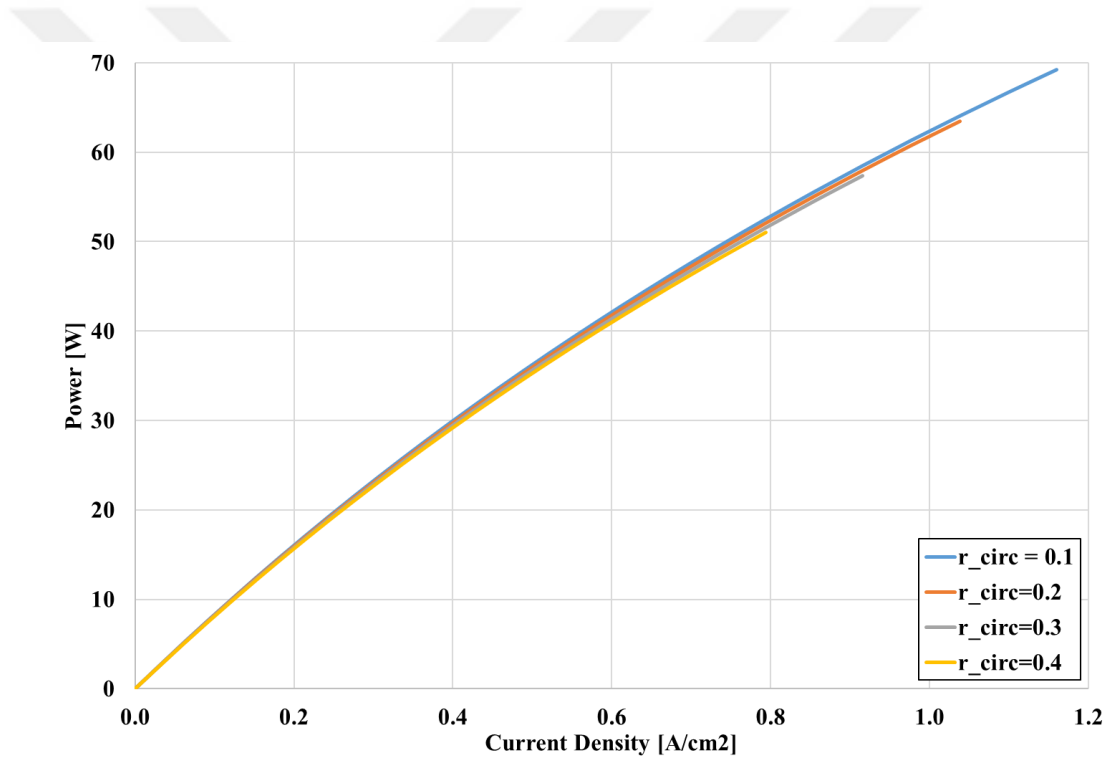


Figure 5.7. The effect of current density on the power obtained by the SOFC according to the different recirculation ratios

Figure 5.8 demonstrates the effect of current density on the power produced by the SOFC according to the different fuel utilization ratios. As the current density increases, the power increases for all fuel utilization ratios. When the fuel utilization is 0.75, more power is produced by the SOFC. In addition, it was observed that the performance of the SOFC decreases as the fuel utilization ratio increases.

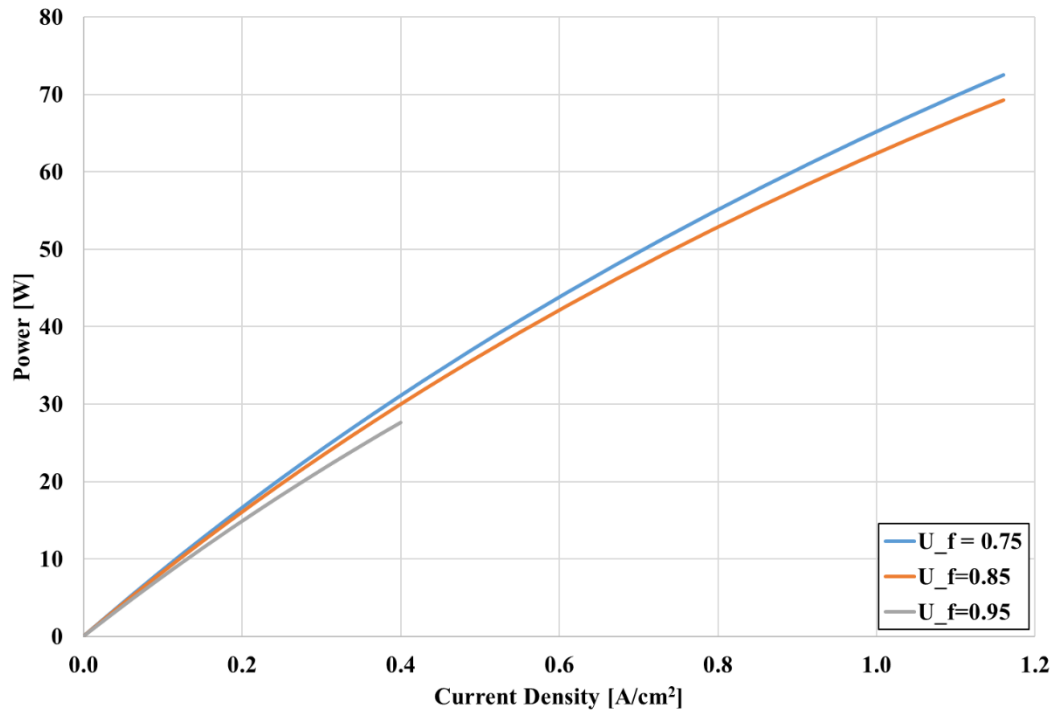


Figure 5.8 The effect of current density on the power obtained by the SOFC according to the different fuel utilization ratios

Exergy analysis is a type of thermodynamic analysis based on the combination of the First and Second Laws of Thermodynamics, which provides a tool to assess and compare systems in more detail than classical energy analysis. In particular, the exergy analysis allows for determining the positions and magnitudes of irreversibility within a system (Dincer & Rosen, 2021). The conditions used in the experimental studies for SOFC (presented in Table 3.1) are assessed and the exergy destruction rates are calculated for each case. Figure 5.8 shows the effect of current density on the exergy destruction rate of SOFC according to the three different cases and low and high S/C ratios. As the current density increases, the exergy destruction rate increases for all cases. This trend is mainly due to the fact that when the current density increases, the hydrogen and carbon monoxide consumptions increase, and, as a consequence, the entropy production related to the reforming reactions increases. Thus, according to the exergy balance enclosing the SOFC, the rate of exergy destruction increases. According to Figure 5.8, it was found that the case “Hydrocarbon Excess” with S/C of 1.5 has the highest exergy destruction rates. On the other hand, the lowest exergy

destruction rates are observed in the case “Hydrocarbon Excess” with S/C of 2.1. Furthermore, the results showed that feeding more steam or hydrogen into the SOFC appears to have a reducing effect on the irreversibility of the system.

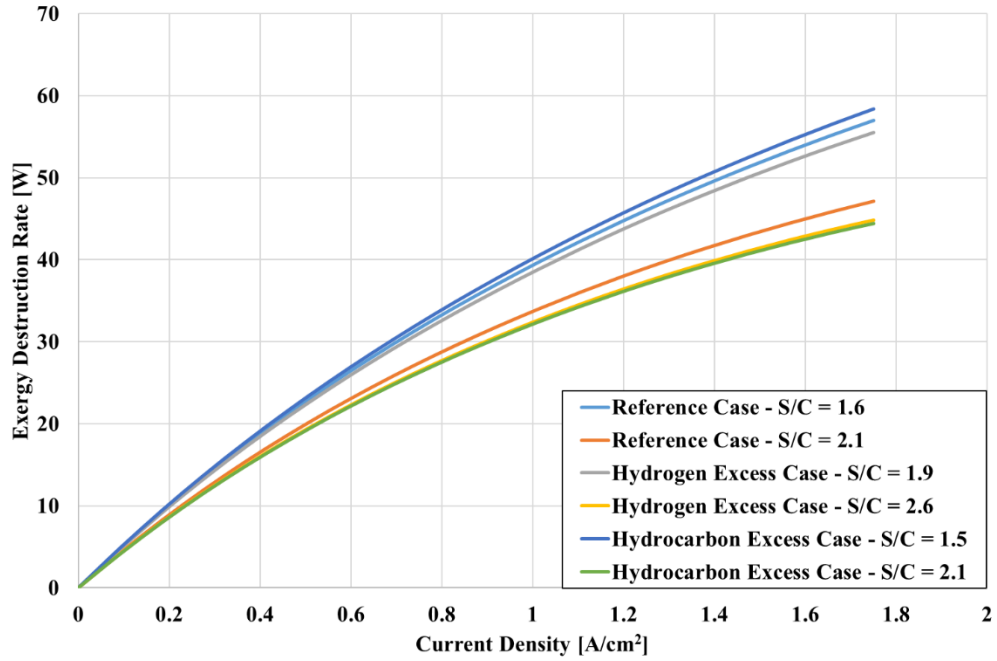


Figure 5.9 The effect of current density on the exergy destruction rate of SOFC according to the cases used in the experimental studies and low and high S/Cs at a temperature of 850°C.

In addition, the effect of operating parameters of SOFC (e.g., fuel utilization ratio and recirculation ratio) on the exergy destruction rate is investigated by using the SOFC model. Figure 5.9 illustrates the effect of current density on the rate of exergy destruction for different fuel utilization ratios. As the current density increases, the exergy destruction rate increases for all ratios. When the fuel utilization increases from 0.75 to 0.95, the exergy destruction also increases. In addition, under the same current density (1.2 A/cm²), the maximum change of exergy destruction is found as 27.5%. It can be interpreted from the figure that reducing the fuel utilization ratio leads to a decrease in the irreversibility of SOFC.

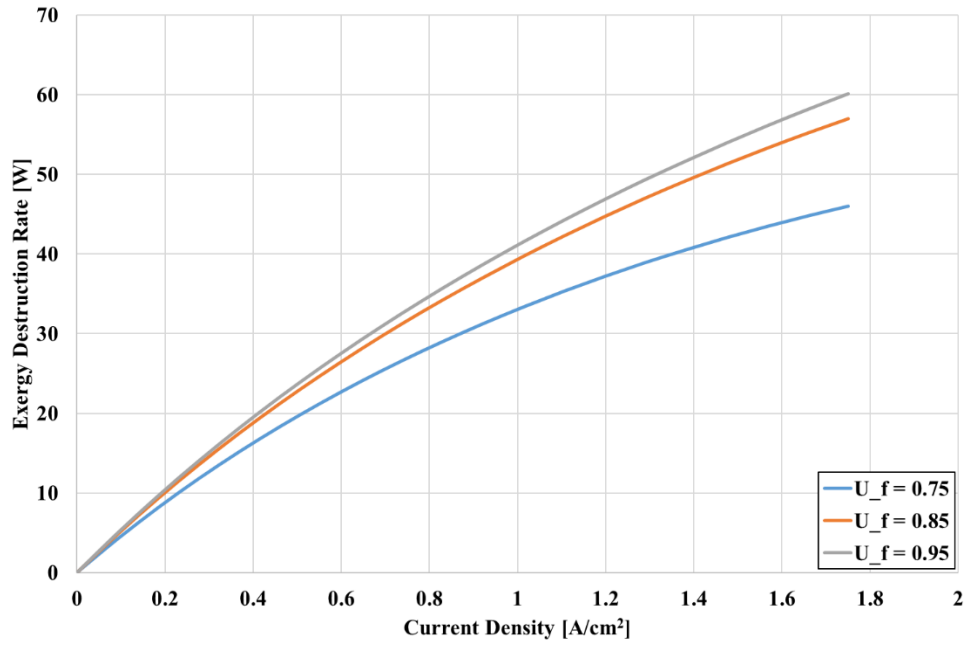


Figure 5.10 The effect of current density on the exergy destruction of the SOFC according to the different fuel utilization ratios

Figure 5.11 shows the effect of current density on the exergy destruction rate of SOFC according to the different recirculation ratios. When the recirculation ratio varies from 0.1 to 0.4, the rate of exergy destruction slightly increases. It was found that the recirculation ratio does not have a significant effect on the irreversibility of the SOFC operating at low current densities. However, under the high current densities (1.6 A/cm²), the change of maximum exergy destruction rate is obtained as 3.46%.

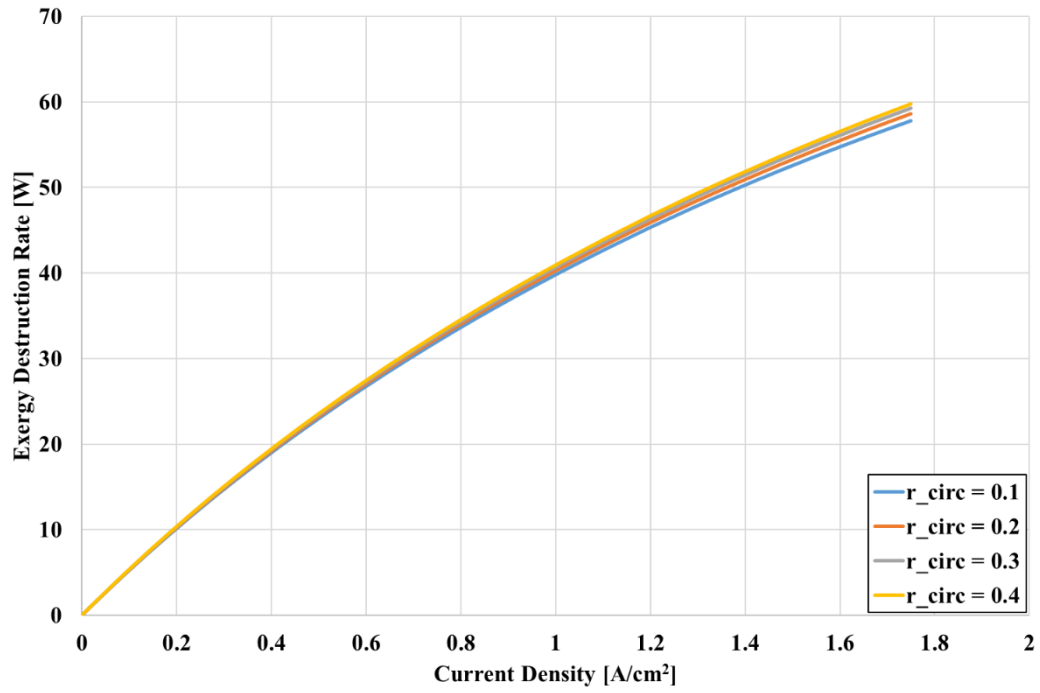


Figure 5.11 The effect of current density on the exergy destruction of the SOFC according to the different recirculation ratios

The effect of the current density on the exergy destruction rate according to the different S/C ratios is shown in Figure 5.12. Increasing the S/C ratio has a positive effect on the SOFC performance. It was obtained that under the same current density (e.g. 1.6 A/cm²), the exergy destruction rate decreases by 19.71% when the S/C changes from 1.5 to 2.5.

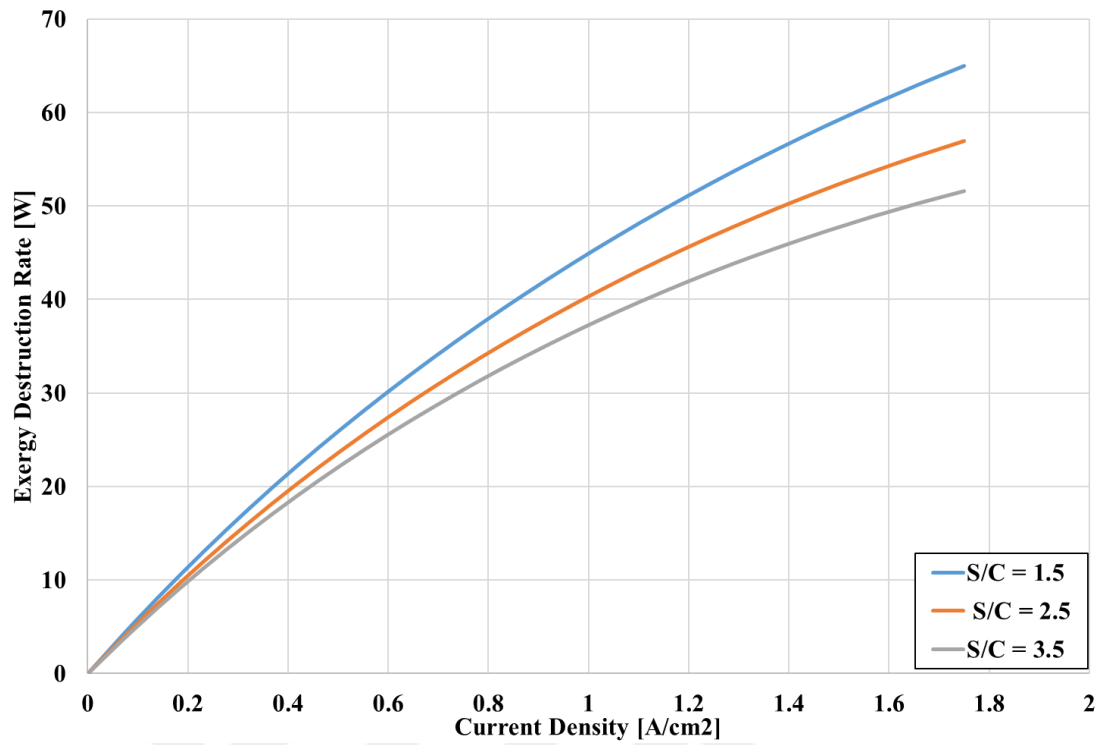


Figure 5.12 The effect of current density on the exergy destruction rate according to the different S/Cs

Figure 5.13 shows the effect of current density on the exergy destruction rate of SOFC according to the different operating temperatures. When the operating temperature varies between 750°C to 850°C, the exergy destruction rate decreases for all current densities.

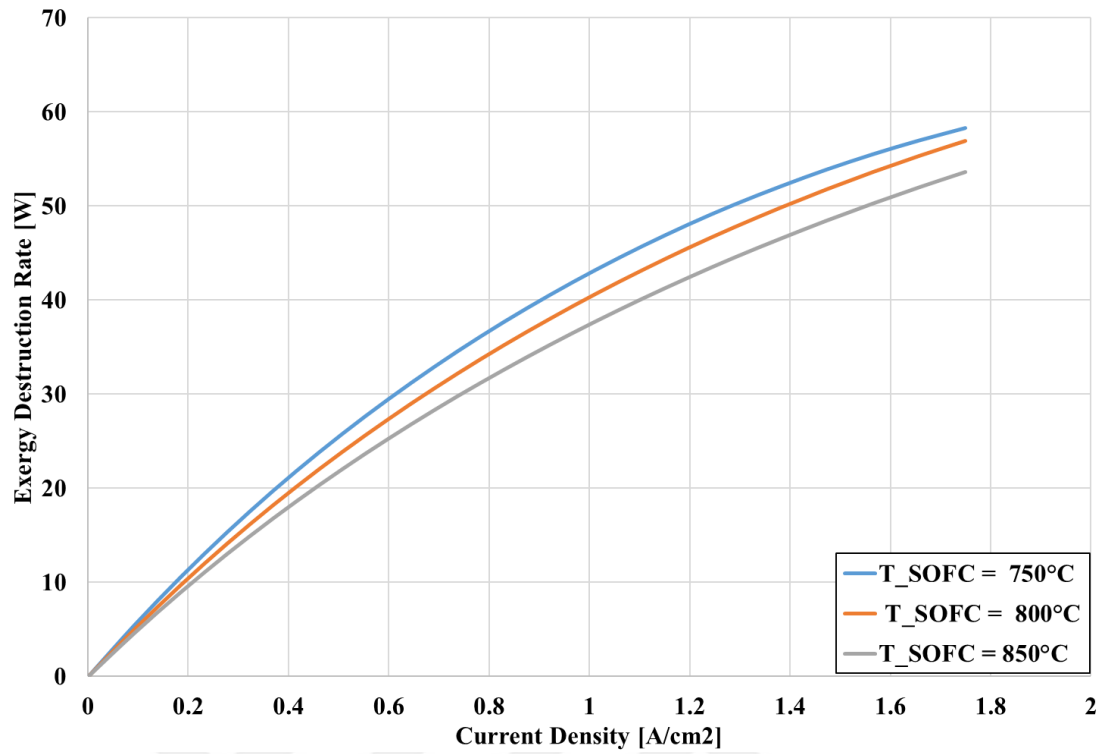


Figure 5.13 The effect of current density on the exergy destruction rate according to the operating temperature of SOFC

Figure 5.14 shows the current density – cell voltage curve (e.g. polarization curve) according to the different electrolyte thickness. As the current density increases, the cell voltage decreases for all the electrolyte thicknesses. The main reason of this trend can be explained as follows. If the current density increases, the polarization terms (e.g. ohmic, activation, and concentration) increases. Hence the cell voltage decreases. On the other hand, when the electrolyte thickness increases the cell voltage decreases. It can be seen from the figure that under the same current density (0.4 A/cm^2) when the electrolyte thickness increases from $10 \text{ }\mu\text{m}$ to $40 \text{ }\mu\text{m}$, the cell voltage reduced by 41.24%.

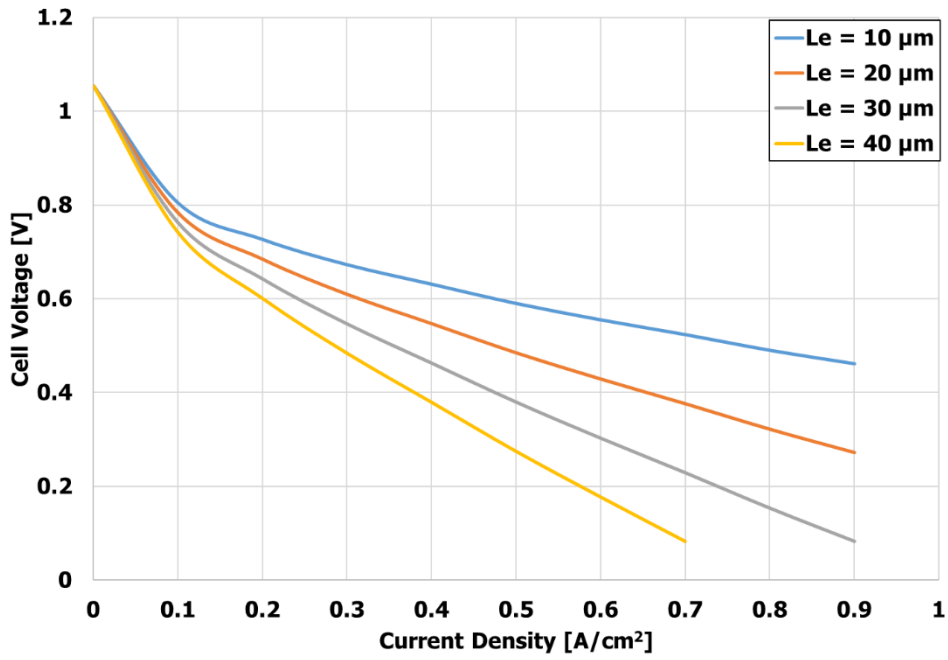


Figure 5.14 The current density with respect to the cell voltage according to the different electrolyte thickness

Figure 5.15 demonstrates the effect of current density on the power produced from the SOFC. It was observed that as the current density increases the power first increases up to a certain value and then decreases. This trend mainly due to the fact that the activation polarization gets higher at high current densities. It can be obtained from the figure that when the current density is about 0.7 A/cm^2 for electrolyte thickness of 10 μm , the power gets its maximum value and found as 36.6 W . On the other hand, the electrolyte thickness increases the power decreases due to the ohmic polarizations. When the electrolyte thickness is changed from 10 μm to 40 μm , the power decreases by 39.96% .

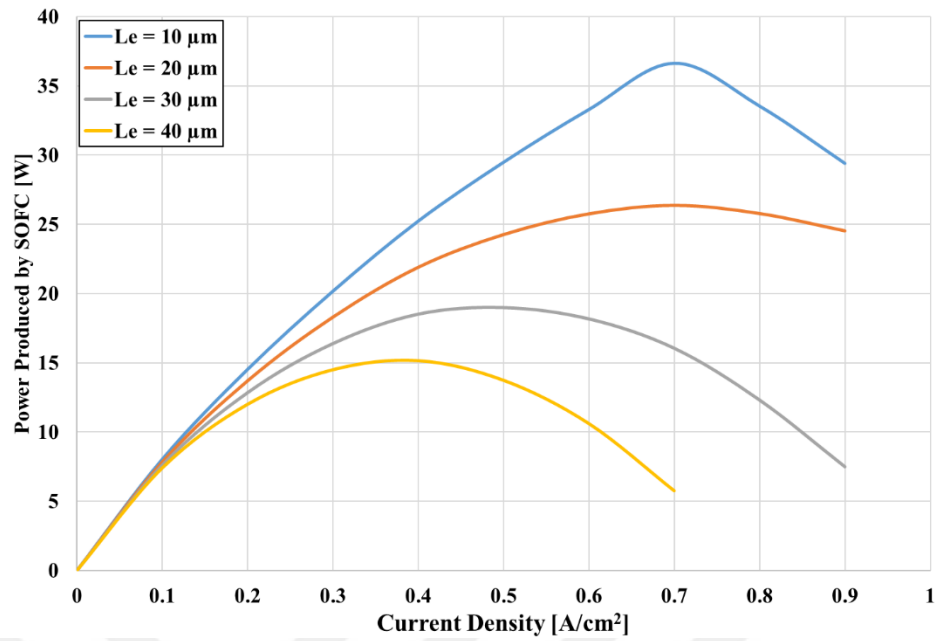


Figure 5.15 The effect of the current density on the power produced by the SOFC according to the different electrolyte thickness

5.5 System Level Modeling of an Integrated SOFC and Biomass Gasification System

In this section, the results derived from the integrated system study are presented and discussed. Figure 5.16 illustrates the effect of gasifier temperature on the molar gas composition of the syngas mixture. As the gasifier temperature increases, the molar fraction of nitrogen, carbon dioxide slightly decreases; whereas the molar fraction of carbon monoxide, and water vapor slightly increases. It should be noted that the molar composition of the methane seems to be keeps stable at the temperature ranges studied. Furthermore, the molar composition of the hydrogen first slightly increases then decreases. For this reason, it was obtained that if the gasifier operates at high temperature, the conversion rate of hydrogen decreases.

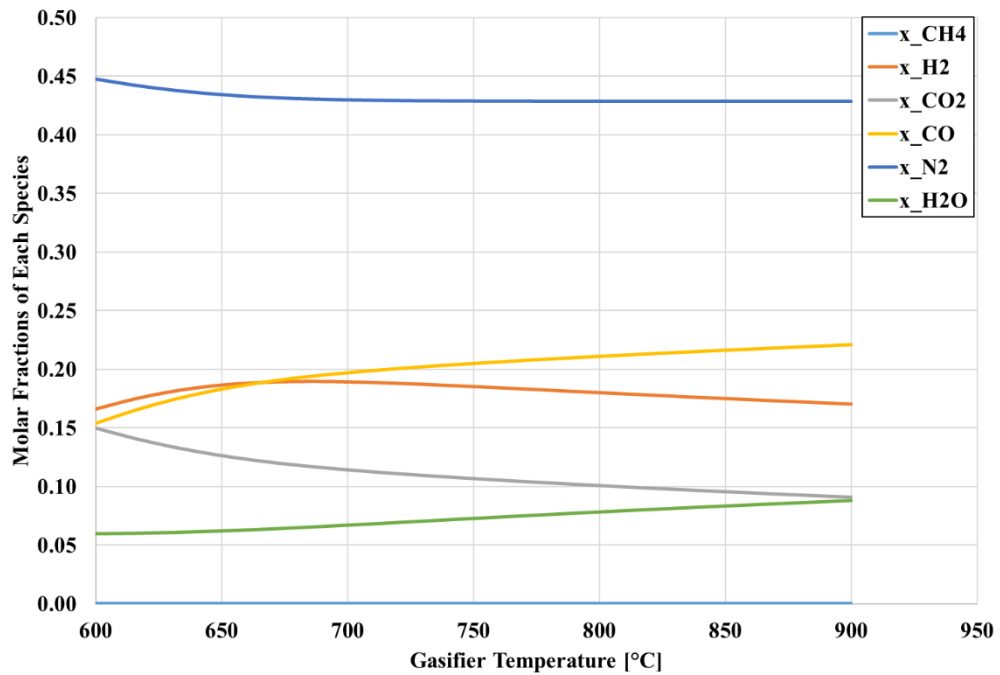


Figure 5.16 The effect of gasifier operating temperature on the molar fractions of the syngas composition

Figure 5.17 shows that the effect of gasifier temperature on the electrical efficiency and fuel utilization. As the gasifier temperature increases, the electrical efficiency increases. This trend mainly due to the slightly increase of net power output of the integrated system. On the other hand, when the gasifier temperature increases, the fuel utilization efficiency decreases due to the decrease of useful heat from the steam. In addition, it can be observed that if the gasifier temperature increases from 800°C to 980°C, the electrical efficiency increases by 7.69%; whereas FUE decreases by 22.5%.

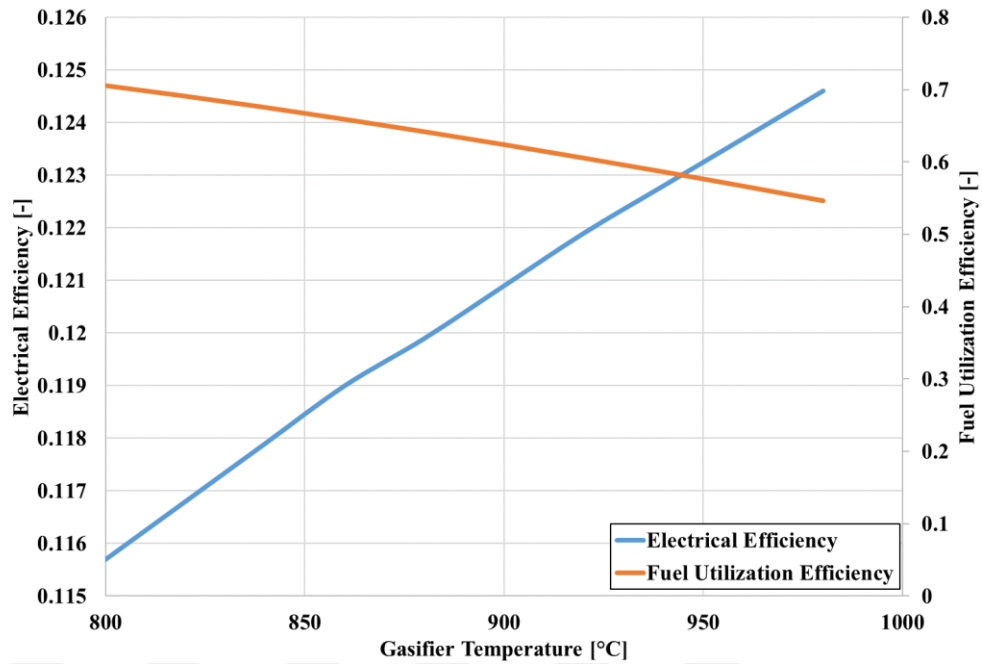


Figure 5.17 The effect of gasifier temperature on the electrical efficiency (left axis), and fuel utilization efficiency (right axis).

5.6 Optimization of Integrated SOFC and Biomass Gasifier

In the parametric analyses presented in Sections 5.4 and 5.5 for both SOFC and integrated SOFC and gasifier system, the effect of one of the operating parameters in the integrated system is studied while taking other operating parameters as fixed. However, to obtain the maximum electrical efficiency and fuel utilization efficiency (FUE), the impact of multiple parameters on the output parameters should be evaluated simultaneously. Thus, this type of evaluation could be performed using Taguchi method which is explained in Section 4.4. Regarding this method, four different operating parameters which are gasifier temperature, pressure ratio of blowers, pressure ratio of pump, and fuel utilization efficiency of SOFC, and 3-level design are selected as presented in Table 5.2. Standard L-9 orthogonal array is selected as shown in the Table 5.3.

Table 5.2 Selection of factors and its levels used in Taguchi method

Factors	Level - 1	Level - 2	Level – 3
Gasifier Temperature	750	850	950
Fuel Utilization Ratio of SOFC	0.75	0.85	0.95
Pressure Ratio of Blowers	1.2	1.5	1.8
Pressure Ratio of Pump	1.2	1.5	1.8

Table 5.3 L9 orthogonal array and electrical and fuel utilization efficiencies values for Taguchi method

No	Gasifier Temperature (°C)	Fuel Utilization Ratio	Pressure Ratio of Blower	Pressure Ratio of Pump	Electrical Efficiency	Fuel Utilization Efficiency
1	750	0.75	1.2	1.2	0.1790	0.6283
2	750	0.85	1.5	1.5	0.1194	0.6147
3	750	0.95	1.8	1.8	0.0610	0.6016
4	850	0.75	1.5	1.8	0.1209	0.6241
5	850	0.85	1.8	1.2	0.0615	0.6106
6	850	0.95	1.2	1.5	0.1814	0.6380
7	950	0.75	1.8	1.5	0.0618	0.6164
8	950	0.85	1.2	1.8	0.1830	0.6444
9	950	0.95	1.5	1.2	0.1219	0.6302

The change of S/N ratios for each factor is presented in Figure 5.18. According to Taguchi method, increasing the S/N ratio increases the quality. When the gasifier temperature is 950°C, the fuel utilization ratio of SOFC is 0.95, the pressure ratio of blower is 1.2, and the pressure ratio of pump is 1.5, the electrical and the fuel utilization efficiencies for the integrated system studied can be obtained as 0.1945 and 0.6693, respectively.

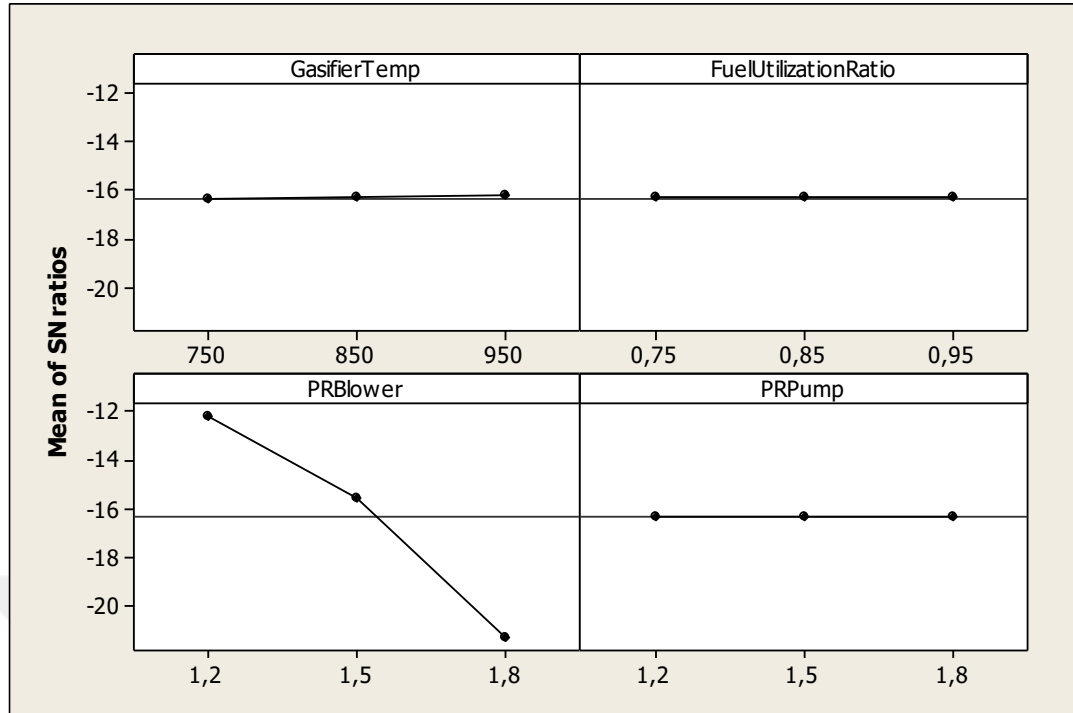


Figure 5.18 S/N plot for Taguchi method for the maximization of electrical and fuel utilization efficiencies.

In addition, to determine the dominated parameters of integrated system, means of response table is used as shown in Table 5.4. In the Taguchi method, the minimum rank value of the parameter has the most dominant parameter. According to Table 5.4, pressure ratio of blower and gasifier temperature are the most dominant parameters among the other parameters studied.

Table 5.4 Standard deviation values and rank degrees for the integrated system studied

Standard Deviation Values				
Level	Gasifier Temperature (°C)	Fuel Utilization Ratio	Pressure Ratio of Blower	Pressure Ratio of Pump
1	0.3673	0.3718	0.4090	0.3719
2	0.3728	0.3723	0.3719	0.3720
3	0.3763	0.3724	0.3355	0.3725
Delta	0.0089	0.0006	0.0735	0.0006
Rank	2	3	1	4

CHAPTER SIX

CONCLUSIONS

In this thesis, an innovative 0-D mathematical model for anode recirculated SOFC fed with reformat gas mixture is developed. In this regard, a mathematical model is conducted using the parallel circuit approach to include the thermodynamic and electrochemical phenomena. On the other hand, the experimental studies on the SOFCs are performed to obtain the polarization curve and to determine the cell resistance through the electrochemical impedance spectroscopy method. Then, X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses are performed to investigate the microstructure of the SOFC cell used in the experiments. The proposed model is validated by experimental studies. Parametric studies are conducted to assess the impact of operating parameters on the performance of the SOFC. After that, the developed innovative model is integrated with the biomass gasifier model in order to assess the performance of the system thermodynamic point of view. In addition, an optimization study, which is namely Taguchi method, is performed to find the optimum working parameters of the integrated system in order to maximize the electrical and fuel utilization efficiencies of the integrated system. Furthermore, the dominant operating parameters for the integrated system are found through Taguchi method. The results derived from the thesis conducted are given as follows.

- Experimental study results show that as the S/C increases, the SOFC performance decreases. However, in order to prevent carbon deposition in SOFCs fed with reformat gases, the S/C ratio should be kept at an optimum value. The case namely "Hydrocarbon Excess" yields the highest performance operating under low S/C ratios; whereas the case namely "Reference" gives the highest performance operating under the high S/C ratios. EIS analysis shows that increasing the S/C ratio decreases the total cell resistance.

- The modeling results showed that at low current densities, the anode-off-gas recirculation rate does not have a significant effect on SOFC performance. However, at higher current densities, SOFC performance decreases as the recirculation ratio

increases. The variation of the fuel utilization ratio has a significant effect on the SOFC performance. Higher fuel utilization ratio (e.g., greater than 90%) reduces the SOFC operating current density range, thus reducing its performance. In addition, as the current density of SOFC increases, the cell voltage decreases for all the electrolyte thicknesses. Regarding the validation of the model, the proposed model is consistent with the experimental studies. The highest error rate found in the validated model is 6.8%. Considering the exergy analysis of the SOFC, the rate of exergy destruction increases when the SOFC is operated at high current densities. The case "Hydrocarbon Excess with S/C of 1.5" yields the highest exergy destruction rate for SOFC. The fuel utilization ratio has a significant effect on the exergy destruction of SOFC, whereas the recirculation ratio does not have a significant effect under the low current densities. In addition, as the S/C ratio increases, the exergy destruction rate of SOFC decreases. As the operating temperature of SOFC increases, the exergy destruction rate of SOFC decreases.

- Regarding the integration of SOFC and biomass gasification system, when the gasifier temperature increases, the molar fraction of nitrogen, carbon dioxide slightly decreases, whereas the molar fraction of carbon monoxide, and water vapor slightly increases. In addition, the molar composition of the methane seems to be kept stable at the temperature ranges studied. Furthermore, the molar composition of the hydrogen first slightly increases then decreases. For this reason, it was found that if the gasifier operates at high temperature, the conversion rate of hydrogen decreases. In addition, it can be observed that if the gasifier temperature increases from 800°C to 980°C, the electrical efficiency increases by 7.69%; whereas FUE decreases by 22.5%. Considering the optimization study using Taguchi method, if the gasifier temperature is 950°C, fuel utilization ratio of SOFC is 0.95, pressure ratio of blower is 1.2, and the pressure ratio of pump is 1.5, the electrical efficiency and the fuel utilization efficiency of the integrated system can be calculated as 0.1945 and 0.6693, respectively. In addition, Taguchi method gives us that among the parameters studied, the most dominant parameters are blower pressure ratio and gasifier temperature, respectively.

This thesis guides researchers working on hybrid SOFC modeling to develop an accurate enough SOFC model to be used in the exergy analysis of the integrated system. As a future study, the developed model is planned to be used in an integrated SOFC-based energy system and to conduct performance (through energy and exergy analyses), economic, and environmental assessment analyses.



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