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Dynamic modeling and analysis of multiple SOFC system configurations

Andrew J. Slippey

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Dynamic Modeling and Analysis of Multiple SOFC System Configurations

by

Andrew J. Slippey

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Mechanical Engineering

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Dynamic Modeling and Analysis of Multiple SOFC System Configurations

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Abstract

Solid oxide fuel cells (SOFC) are a variety of high temperature fuel cells with particular advantages such as fuel flexibility, internal fuel reforming capability, and combined heat and power (CHP) applications. To aid in the advancement of this technology, this work develops dynamic, computer-based, mathematical models of two SOFC configurations employing different SOFC and reformer technologies. Starting from an existing recirculation-based tubular SOFC system with a steam reformer, new component models are developed for a planar SOFC stack and a partial oxidation (POX) reformer. Both the new and existing component models were updated and improved by including new pressure dynamics and current distribution schemes. A structured method for model development and management through hierarchical libraries developed herein allows easy modification of the models on multiple levels for simulation of various SOFC system configurations. The pertinent physical phenomena are captured, including temperature, pressure, chemical, and electrochemical dynamics.

Analysis of the simulation results provides insights into the varied time scales and lays the ground work for future development of hybrid control schemes. Simulation also shows the interconnection of individual physical phenomena, giving a complex and rich dynamical behavior to SOFC systems. Model-based analysis of the two configurations reveals multiple common behaviors of SOFC systems, valid across configurational variations. Of particular interest for control is the performance parameter, fuel utilization. A generalized approach for generating closed-form expressions for fuel utilization is developed to accurately predict steady-state conditions as a function of input conditions. The closed-form solutions obtained by this approach for different configurations demonstrate fuel utilization as an invariance property that can be exploited in feedback control of SOFC systems where knowledge of the system and sensing capabilities are limited.
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Nomenclature

\begin{itemize}
\item \( A \) Area, \( m^2 \)
\item \( C \) Specific heat, \( J/(kg\cdot K) \)
\item \( C_v \) Specific heat at constant volume, \( J/(kg\cdot K) \)
\item \( F \) Faraday’s constant, 96485.34 Coulombs/mol
\item \( F_{body}, F_{surface} \) Body and surface forces acting on a control volume, \( N \)
\item \( G \) Gibbs free energy, \( J \)
\item \( G^o \) Gibbs free energy at standard pressure, \( J \)
\item \( h \) Molar enthalpy, \( J/mol \)
\item \( h_{conv} \) Coefficient of convection, \( W/(m^2\cdot K) \)
\item \( h_{react} \) Enthalpy of formation, \( J/mol \)
\item \( i \) Current draw, \( A \)
\item \( i_{cell} \) Current demand for particular cell, \( A \)
\item \( J_o \) Exchange current density, \( A/m^2 \)
\item \( J_{lim} \) Limiting current density, \( A/m^2 \)
\item \( k \) Anode recirculation fraction
\item \( k_{cond} \) Coefficient of conduction
\item \( k_f \) flow rate constant, \( m/s \)
\item \( L \) Length, \( m \)
\item \( m \) Mass, \( kg \)
\item \( \dot{m} \) Mass flow rate, \( kg/s \)
\item \( MW \) Molecular weight, \( kg/mol \)
\item \( n \) Number of electrons participating in electrochemical reaction
\item \( N \) Number of moles, \( mol \)
\end{itemize}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{N}_{\text{air}}$</td>
<td>Molar flow rate of air, $\text{mol/s}$</td>
</tr>
<tr>
<td>$\dot{N}_{\text{enter}}$</td>
<td>Molar flow rate entering combustor, $\text{mol/s}$</td>
</tr>
<tr>
<td>$\dot{N}_{\text{exhaust}}$</td>
<td>Molar flow rate exhausted from combustor, $\text{mol/s}$</td>
</tr>
<tr>
<td>$\dot{N}_{\text{f}}$</td>
<td>Molar flow rate of fuel, $\text{mol/s}$</td>
</tr>
<tr>
<td>$\dot{N}_{\text{in}}$</td>
<td>Anode inlet flow rate, $\text{mol/s}$</td>
</tr>
<tr>
<td>$\dot{N}_{\text{inlet}}$</td>
<td>Cathode inlet flow rate, $\text{mol/s}$</td>
</tr>
<tr>
<td>$\dot{N}_{\text{o}}$</td>
<td>Anode exit flow rate, $\text{mol/s}$</td>
</tr>
<tr>
<td>$\dot{N}_{\text{outlet}}$</td>
<td>Cathode exit flow rate, $\text{mol/s}$</td>
</tr>
<tr>
<td>$N_{\text{cell}}$</td>
<td>Number of cells</td>
</tr>
<tr>
<td>$N_{\text{element}}$</td>
<td>Number of elements</td>
</tr>
<tr>
<td>$O2C$</td>
<td>Ratio of oxygen molecules to carbon atoms in the fuel</td>
</tr>
<tr>
<td>$p$</td>
<td>Partial pressure, $\text{Pa}$</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure, $\text{Pa}$</td>
</tr>
<tr>
<td>$\dot{Q}$</td>
<td>Net rate of heat transfer into a solid or gaseous volume, $\text{W}$</td>
</tr>
<tr>
<td>$\dot{q}_{\text{cond}}$</td>
<td>Rate of heat transfer into a solid volume via conduction, $\text{W}$</td>
</tr>
<tr>
<td>$\dot{q}_{\text{conv}}$</td>
<td>Rate of heat transfer into a solid volume via convection, $\text{W}$</td>
</tr>
<tr>
<td>$r_a$</td>
<td>Reaction rate for a particular reaction, $a = a, b, c, d, e, f, g, h, \text{mol/s}$</td>
</tr>
<tr>
<td>$r_{\text{anode}}$</td>
<td>Area specific resistance of anode, $\Omega/\text{m}^2$</td>
</tr>
<tr>
<td>$r_{\text{cathode}}$</td>
<td>Area specific resistance of cathode, $\Omega/\text{m}^2$</td>
</tr>
<tr>
<td>$r_{\text{electrolyte}}$</td>
<td>Area specific resistance of electrolyte, $\Omega/\text{m}^2$</td>
</tr>
<tr>
<td>$r_{\text{interconnect}}$</td>
<td>Area specific resistance of interconnect, $\Omega/\text{m}^2$</td>
</tr>
<tr>
<td>$R_u$</td>
<td>Universal Gas Constant, $8.314 \text{J/(mol-K)}$</td>
</tr>
<tr>
<td>$\mathcal{R}$</td>
<td>Species rate of formation, $\text{mol/s}$</td>
</tr>
<tr>
<td>$t$</td>
<td>Time $\text{s}$</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature, $\text{K}$</td>
</tr>
<tr>
<td>$u$</td>
<td>Internal energy, $\text{J}$</td>
</tr>
<tr>
<td>$U$</td>
<td>Utilization</td>
</tr>
<tr>
<td>$v$</td>
<td>Specific volume, $\text{m}^3/\text{kg}$</td>
</tr>
</tbody>
</table>
\( V \) Velocity, m/s
\( V \) Volume, m\(^3\)
\( V \) Voltage, V
\( V_{\text{act}} \) Activation loss, V
\( V_{\text{conc}} \) Concentration loss, V
\( V_{\text{Nernst}} \) Nernst potential, V
\( V_{\text{ohm}} \) Ohmic loss, V
\( \dot{W} \) Rate of work done on a control volume, W
\( x_{j.g} \) Species mass fraction, kg/kg
\( x \) Selectivity for partial vs. total oxidation
\( X \) Species mole fraction, mol/mol
\( \alpha \) Selectivity for hydrogen oxidation
\( \dot{n} \) Generic molar flow rate, mol/s
\( \mu \) Dynamic viscosity, (N\( \cdot \)s)/m\(^2\)
\( \rho \) Density, kg/m\(^3\)

**Subscripts**
- \( a \): Anode control volume
- \( c \): Cathode control volume
- \( ex \): Exit condition of control volume
- \( g \): Generic gas control volume
- \( in \): Inlet condition of control volume
- \( j \): Values of 1 - 7 represent species \( CH_4, CO, CO_2, H_2, H_2O, N_2, \) and \( O_2 \)
- \( m \): Element number
- \( r \): Reformate control volume
- \( s \): Solid volume
- \( ss \): Steady-state
- \( t \): Time step
- \( tot \): Sum of all species values
Chapter 1

Introduction

1.1 Motivation

An ever-increasing demand for energy, along with depleting reserves of fossil fuels and environmental considerations, have triggered renewed interest in the development of alternative energy sources in the United States [1]. In recent years, alternative energy technologies have become a dominant area of research and innovation. One such technology that is deemed promising is fuel cells. Fuel cell research, development, and commercialization have expanded significantly in recent years. Several types of fuel cells such as Polymer Electrolyte Membrane Fuel Cells (PEMFC), Solid Oxide Fuel Cells (SOFC), Molten Carbonate Fuel Cells (MCFC), Phosphoric Acid Fuel Cells (PAFC), Direct Methanol Fuel Cells (DMFC), and, more recently, bio- and micro-fuel cells are being studied by researchers all over the world [2].

Among different fuel cell technologies, the SOFC technology has attracted significant research interest in recent years. This is evident in the initiatives taken by the Department of Energy such as the formation of the Solid-state Energy Conversion Alliance (SECA) [3]. SECA was created within the National Energy Technology Laboratory’s fuel cells program, exclusively for accelerated development of SOFC technology and rapid deployment to market as an affordable alternate energy option.

There are multiple advantages of SOFC systems. They are solid state devices that are simpler in concept than other fuel cell technologies. High temperature operating conditions
(800 to 1000°C) in SOFCs are conducive to internal reforming of fuels and hot exhaust gases from SOFC systems are excellent means for sustaining on-board fuel reforming. SOFCs are not only tolerant to carbon monoxide but can also use it as fuel as opposed to other fuel cell types. These properties substantially simplify fuel reforming in SOFC systems and make them well poised for use with a variety of fuels. Furthermore, high operating temperatures makes SOFC-GT (Gas-Turbine) hybrids excellent combined heat and power (CHP) systems that can achieve system efficiencies that surpass normal Carnot limitations of GT systems.

The high temperatures do, however, cause some difficulties regarding thermal stress of materials and significant start-up times which have precluded SOFC systems from most automotive applications. Possible applications of SOFC systems include stationary power plants and auxiliary power generators for buildings, ships, or other military equipment. SOFCs have the potential to provide efficient power, as well as quieter power than combustion engines, increasing audio stealth.

1.2 Generic Description of SOFC Systems

Fuel cells directly utilize electrochemical reactions to generate electricity. For the SOFC, the particular electrochemical reaction employed is illustrated in Fig. 1.1. Fuel and air flow through the anode and cathode, respectively. Electrons are collected in the anode, pass through a load, and are deposited back in the cathode. Oxygen ions are able to pass through the solid oxide electrolyte from the cathode to the anode in order to complete the circuit. The electrolyte is not a thin membrane, as in other types of fuel cells where molecules or atoms are passing through it. Rather it is a pure ionic conductor allowing only the oxygen ions to pass through, but only at elevated temperatures [4].

SOFCs use hydrogen as the primary fuel for generating electricity, but do not require pure hydrogen as the fuel. Due to the high operating temperatures (800 to 1000°C) and the presence of catalysts, hydrogen can be generated through internal reforming within
the anode chamber of an SOFC from hydrocarbon fuels, [2, 5]. In addition, hydrogen is also generated through external reforming in reformers placed upstream of fuel cell. Some reforming processes are endothermic and so the hot gases exhausted from the fuel cell can serve as a means of providing heat to sustain those reformers.

A final note on generic SOFC systems relates to their size. The demonstrated SOFC stacks have been constructed on relatively large geometric scales, avoiding the inherent difficulties of micro-channel flow. Typical flow channels for SOFCs have diameters on the order of centimeters [2].

1.3 The State of the Art

1.3.1 SOFC stacks and Models

There are two basic types of SOFCs which can be found in the literature, namely the planar and the tubular, [2, 4, 5]. These titles describe the physical geometry of the cells, each of which creates a variety of challenges in terms of design, fabrication, and operation. Tubular SOFC stacks, pioneered by Siemens Westinghouse Power Corporation [6], have been the staple of SOFC technology for some time. The advantage of tubular geometry over planar stacks is in eliminating the need for high temperature gas seals. There are many inherent technical problems because of the huge range of temperatures the materials must withstand...
that are eliminated by the tubular geometry. However, planar technologies have developed as well and provide many other significant advantages. Power density is much greater in planar stacks, as there is less void space when the cells are placed together, and fabrication requires simpler, and therefore cheaper, technology than tubular stacks. The electrical connections between cells in a planar stack are also significantly shorter, reducing ohmic losses and increasing overall performance. Multi-cell planar stacks have been constructed, though generally on much smaller power scales than current tubular stacks (less than 1 kW versus 100 kW) [2].

The commercial availability of this technology is still very limited. While a number of industrial entities have developed and demonstrated the SOFC technology, their production has been primarily limited to prototypes for research and experimentation, and they are not marketed commercially.

Present research on SOFC systems is largely centered around fuel reforming and materials selection. [7]. The study of SOFC system dynamics is in nascent stages. This is primarily because sufficient experimental data on fuel reforming has appeared in the literature only in the last few years. The recent abundance of such information has now set the stage for detailed dynamic analysis. System level dynamic analysis can be used to address a primary objective in the development of the SOFC technology, which is optimal performance. This can be achieved through accurate control over performance variables such as fuel utilization, stack temperature, etc. However, control design poses multiple challenges since SOFC systems are complex, nonlinear, and exhibit coupled physical phenomena. This interdependence of physical phenomena also leads to rich system dynamics. An analytical study of its dynamic behavior is thus crucial in enhancing the competitiveness of the SOFC technology and in ultimately achieving the desired efficiency and longevity for SOFC systems.

Dynamic models are valuable as stand-alone tools used in industry and scientific research to provide predictive results, transient analysis, optimization studies, and to develop
control systems. Characterizing the transient and steady-state response of a fuel cell system is an essential step to allow for future control designs that will allow the system to follow changing loads. Some published analyses of SOFC system responses to load variations and fuel appear in [8–10]. In [11], the authors study the detrimental effects of load transients due to differences in the response times of the SOFC, power electronics, and balance-of-plant components.

Dynamic mathematical models of planar SOFCs appear in [12–14], but they do not include any of the additional balance-of-plant components which greatly affect the system dynamics. Also [13] uses an iterative approach to model two dimensions, which greatly increases computational burden. In [15] a more complete system is modeled that includes a combustor and heat exchangers, but still does not include any external fuel reformer. Models of tubular SOFCs appear in [16–21]. Several of these include steam reformers as a part of the modeled system, but thermal and pressure dynamics are often limited or not existent. For a comprehensive review of mathematical models of SOFC systems see [22]. Overall, while the existing models are useful, they are highly specific to particular test cases, lack important system components, or use computationally burdensome iterative methods.

1.3.2 External Reformers

External reformers significantly contribute to the total system dynamics of an SOFC system. The reforming process can be carried out using a variety of procedures. Among them, thermo-chemical conversion of fuels to hydrogen remains the most prevalent means. Electrolysis is also attractive given its zero carbon-dioxide emission. However, the process is inefficient due to its high electrical energy requirement [23]. The use of bio-reactors for hydrogen production has also been explored in recent years. The technology is still in early stages with severe technical difficulties and is far from industrial applications [23]. There are three primary methods for thermo-chemical production of hydrogen, namely Steam Reforming (SR), Catalytic Partial Oxidation (POX), and Auto-Thermal Reforming
In SR, a mixture of hydrocarbon fuel and steam is catalytically reformed to produce molecular hydrogen. The process is endothermic and external heat is required to maintain the necessary yield-rate of hydrogen. POX involves catalytic partial oxidation of fuel (flameless) to generate hydrogen as well as the heat and the steam required to sustain further SR downstream. ATR employs SR, but first burns part of the fuel with a sub-stoichiometric amount of oxygen to provide the heat necessary to sustain the reaction.

While traditional SR may be suitable for fixed power applications, its slow start-up and endothermic operation are hindrances to efficient mobile applications [27]. Catalytic POX requires shorter contact times, on the order of milliseconds with Rh-based catalysts, and provides over 90% fuel conversion and over 80% hydrogen selectivity for large alkanes and diesel fuel [27]. In addition to the above advantages, thermodynamic analyses have shown that POX and ATR can be more efficient than SR alone [27, 28].

The above mentioned existing processes for hydrogen production are catalytic in nature where thermal energy plays a vital role. In recent years there has been vigorous research in this area, aimed at identifying the optimum catalyst composition and operating conditions for enhanced hydrogen production [25, 29]. In spite of certain inherent drawbacks of these processes, such as catalyst deactivation and sulfur poisoning [29], catalysis-based thermochemical reforming processes for hydrogen production are still predominantly used for hydrogen production due to their simplicity and applicability across different fuels [24, 25, 30, 31].

Despite its prominence, limited experimental results and numerical simulations of POX reforming appear in literature. Most of the models that do appear do not include dynamic effects. In [32, 33], the authors carry out steady-state simulations of POX reforming of surrogate jet fuels. In [34], a POX reformer model is developed with methane (CH$_4$) as fuel. The model uses thermodynamic equilibrium analysis presented in [35]. In [36], the authors assume a single reaction and instantaneous fuel oxidation. Ibrahim develops kinetic rate expressions for POX reforming of gasoline in Ni-CeO$_2$ catalyst through experiments
and analysis in [37]. The approach in this paper involves modeling detailed reaction pathways that can result in computationally burdensome models. Thus, a sufficiently simple dynamic POX model does not exist in the literature. Comprehensive experimental results from a POX reformer are reported in [38–41], which clearly show the existence of two distinct regimes within a POX reformer, namely an exothermic oxidation regime and an endothermic SR regime. This phenomena is also not captured in any existing models.

1.4 Objectives

This thesis presents a structured model development effort and a model based analytical approach to the study of the dynamic behavior of SOFC systems. Adopting a systems perspective, the research develops a comprehensive mathematical model that captures the essential physical phenomena including thermodynamics, heat transfer, chemical kinetics, pressure dynamics, and electrochemistry. The characteristics of the system are studied through a model-based analytical approach. The research reveals common characteristics of SOFC systems that are valid across different stack and reformer types. This leads to generalized approaches for analysis and control of SOFC systems. The research has been conducted in the Hybrid Sustainable Energy Systems (HySES) Laboratory in the Mechanical Engineering Department at Rochester Institute of Technology.

The model development efforts at the HySES laboratory are aimed to generate a detailed understanding of the system dynamics of SOFCs leading to predictive tools for control. In addition, the models are directly integrated into a hybrid energy system experimental infrastructure being developed in the laboratory also called a Hardware-In-the-Loop (HIL) environment. To this end, the fuel cell system models developed in this research will be executed on real-time processing platforms and, in conjunction with a programmable power supply, will serve as virtual fuel cells in future work. A tubular SOFC model with SR and methane as fuel was previously developed at the HySES laboratory. Most of the major physical phenomena that affect the operation of the SOFC system, such as heat
and mass transfer, chemical kinetics, and electrochemistry, were modeled in detail. In the present research a planar SOFC stack is also considered, which requires a new model to deal with different directions and forms of gas flow and heat transfer. Next, a POX reforming scheme is modeled. Reformer modeling is an important component of this research. Previous models developed at the HySES lab have implemented SR of methane, which consists of equilibrium endothermic reactions. The chemical kinetics of SR were modeled based partly on experimental results and observations presented in [42, 43]. In contrast, this thesis develops a dynamic model of POX reforming of methane with Rh-based catalysts, based on experimental data in [38–41]. The model developed in this research combines the reaction scheme and data reported in these papers with a parameterized rate formulation for steam reforming of methane in [42] to complete the overall dynamic model of the POX reformer. The final major contribution of the present work to the modeling effort is the inclusion of phenomena such as the internal pressure dynamics and spatial current density variations of the stack which had not previously been modeled in depth. The SR-tubular model is modified with these newly modeled phenomena and a brand new POX-planar model is assembled.

These configurations are explained in more detail in Chapter 2. The details of the model development efforts, including generic control volume models, discretization method and component models are discussed in Chapter 3 and model management using a hierarchical arrangement of libraries is discussed in Chapter 4. In addition to the modeling effort, analytical study of dynamic behavior is performed on both the SR-tubular and POX-planar configurations. Of particular interest is the performance characteristic, fuel utilization. Steady-state forms are derived and work on generalization is begun and presented in Chapter 5. Simulations and model-based analysis make it possible to determine which phenomena dominate others, as well as to determine if and when some transients can be neglected with minimal loss of accuracy. Simulation results are presented in Chapter 6 and concluding remarks are made Chapter 7.
Chapter 2

System Description

An SOFC system typically consists of three main components: reformer, stack, and combustor. The reformer converts the fuel into a hydrogen rich gas. Methane is chosen as the fuel for the following systems, but other hydrocarbons could be modeled and analyzed with the same approach. Because of the high temperatures in SOFCs pure hydrogen fuel is not necessary and reforming is included as part of the system. The reformed fuel flows into the stack, a set of interconnected fuel cells, in which the electrochemical reactions occur to generate electricity. In the combustor, the remaining fuel is burned to produce heat useful for preheating the incoming air flow. Figure 2.1 shows both system configurations examined in this paper.

2.1 SR-tubular Configuration

The SR-tubular configuration, shown in Fig.2.1(a), features a tubular cell geometry coupled with a steam reformer. The fuel enters the system with an incoming molar flow rate of $\dot{N}_f$ and is mixed with the recirculated flow containing $H_2O$. This flow then passes through the reformer catalyst where an endothermic reaction occurs to generate hydrogen rich gas. Heat must be added to sustain this reaction and is done so by passing the hot exhaust and recirculated flow around the reformer. Hydrogen rich gas then proceeds from the reformer to the anode of the fuel cell stack with a molar flow rate of $\dot{N}_{in}$. An exothermic electrochemical reaction occurs here based on an electrical current demand. Steam rich gas
leaves the anode at $\dot{N}_o$ mol/s and a fraction, $k$, of this is recirculated back to the reformer, providing necessary $H_2O$ and heat. The recirculation is achieved by intentionally leaving the seals imperfect, [2]. The remaining flow enters the combustion chamber with air from the cathode and is burned there. Heat from the combustion preheats the incoming air flow, $\dot{N}_{air}$, which is used as a source of oxygen in the cathode for the electrochemical reaction. Exhaust from the combustor is sent back to heat the reformer as mentioned previously.

### 2.2 POX-planar Configuration

The POX-planar configuration, shown in Fig.2.1(b), features a planar cell geometry coupled with a partial oxidation (POX) reformer. The fuel flowing into the POX reformer at a
molar flow rate of \(\dot{N}_f\) is a known mixture of methane and air quantified by the ratio of oxygen molecules to carbon atoms, called the \(O2C\) ratio \([34]\). An exothermic reaction occurs within the catalyst bed of the reformer, generating a hydrogen rich gas which flows into the anode of the fuel cell stack at a molar flow rate of \(\dot{N}_{in}\). The same electrochemical reaction occurs in planar SOFC as in the tubular. Flow leaves the anode at a rate of \(\dot{N}_o\) mol/s and high temperature seals contain the flow, sending it all to the combustor with the air from the cathode, where it is burned. As in configuration A, the incoming air is preheated by the combustor before supplying oxygen to the cathode of the fuel cell stack.

### 2.3 Control Issues

Several factors differentiate the two configurations. First is the geometry of the stacks. Next, the SR-tubular configuration recirculates a known fraction of the unused fuel, which does not occur in the POX-planar configuration. The steam reforming reaction in the SR-tubular is endothermic while the POX reforming reaction in the POX-planar is exothermic, which changes the need for heat exchangers. The kinetics of the reforming reactions also vary. Additionally, the incoming fuel flow in the SR-tubular is pure methane, while in the POX-planar the fuel flow is a mixture of methane and air at a known \(O2C\) ratio.

For both configurations there are two primary controllable inputs: the inlet fuel flow, \(\dot{N}_f\), and the inlet air flow, \(\dot{N}_{air}\). During the course of operation these inputs can be adjusted to maintain healthy operation of the system. The fuel flow must be increased to prevent fuel starvation in the anode under high load conditions and should be decreased to avoid wasting fuel when power demand is low. Similarly, the air flow must be high enough preclude oxygen starvation in the cathode. Both types of starvation cause irreparable damage to their respective electrodes. However, the oxygen comes from atmospheric air, so unused oxygen does not have a cost associated with it like unused fuel does. The air flow is therefore kept well in excess of the starvation point and serves as a coolant. \(\dot{N}_{air}\) is controlled in order to maintain constant temperature in the stack.
Secondary control options include the $O2C$ ratio of the fuel flow in the POX-planar configuration and the recirculation fraction, $k$, in the SR-tubular configuration. For models developed in this research, these input conditions are considered to be design parameters that may be optimized but are not employed for active control.
Chapter 3

Modeling Methods

The models developed in this section are to accurately capture the transient behavior of the SOFC systems described in Chapter 2. The goal for the models is to be useful for control development in real-time simulations, and the approach should allow predictive analysis for evaluating newly proposed SOFC configurations. The thermal, electrical, chemical, and flow rate characteristics are the primary effects being modeled.

For processing speed while capturing transients, a lumped model approach is chosen. This is opposed to using a computational, finite-element model where a system of equations must be solved iteratively at each time step. The iterative approach could provide additional details regarding some of the internal flows or species distribution, and it could be helpful to resolve specific system design challenges. However, running real-time simulations with this type of model would prove impossible, and for the desired system level analysis finite elements would be more cumbersome than helpful. This non-iterative approach does not preclude it from all the benefits of a discretized model. A 1-dimensional discretization scheme can be applied as described in Section 3.2.

The following assumptions are made during the model development. They are noted and justified where appropriate in the derivations that follow.

- Lumped solid control volumes with uniform properties
- Homogeneous gas mixtures with uniform properties
- Known and constant heat transfer and current density coefficients
Neglect radiation heat transfer

No phase changes

One-dimensional flow

No body forces (gravity) in flow direction

Neglect local changes in kinetic energy

Darcy’s law for frictional effects

Ideal gas equation of state

Constant specific heats

Constant selectivities for POX reactions

Electrochemical reactions occur at electrode surface

Always sufficient \( \text{O}_2 \) in cathode air

No fuel or air leakage through or around electrolyte

Equipotential condition

Combustion reactions are instantaneous

\( \text{O}_2 \) has equal affinity to all fuels in combustor

\section*{3.1 Control Volumes}

The lumped model approach is realized using Eulerian control volumes where a volume is fixed in space, and the flow of material and energy are seen passing through it. There are two primary types of volumes: solid and gas.
3.1.1 Solid Control Volume

Solid control volumes represent the solid physical structures of the system that contain the gas flows. In the model they serve primarily to capture the thermal characteristics of the system. The following fundamental energy balance equation is employed,

\[ \dot{Q}_s = \dot{T}_s m_s C_s \]  \( (3.1) \)

The total heat flux, \( \dot{Q}_s \), into the volume is the sum of both convective and conductive heat transfer. Heat transfer via radiation is neglected due to small cross section of the flow channels relative to their length [13]. Figure 3.1 shows a typical solid control volume. Where the solid control volume boarders gas control volumes convection is modeled while conduction equations are employed along boundaries with other solid control volumes.

Newton’s law of cooling is used to model convection,

\[ \dot{q}_{conv} = h_{conv} A_{conv}(T_s - T_g) \]  \( (3.2) \)
where $A_{\text{conv}}$ is the surface area of the solid where convection is occurring and $h_{\text{conv}}$ is the convection coefficient. Both of these are considered to be known constants and are not calculated dynamically, [14, 15].

For conduction Fourier’s law of conduction is used to model the heat transfer.

$$\dot{q}_{\text{cond}} = k_{\text{cond}} A_{\text{cond}} \frac{(T_s - T_{s+1})}{L_{\text{cond}}}$$  \hspace{1cm} (3.3)

where $A_{\text{cond}}$ is the cross sectional area across which conduction is occurring, $L_{\text{cond}}$ is the length of the volume across which conduction is occurring, $T_{s+1}$ is the temperature of the neighboring solid control volume, and $k_{\text{cond}}$ is a known constant material property.

After combining Eqs.(3.2) and (3.3) to obtain $\dot{Q}_s$, the temperature can be found using Eq.(3.1).

### 3.1.2 Gas Control Volume

Gas control volumes represent the flow of fuel, air, and water vapor through the system. Because of the high temperatures in the SOFC system all the fluids are in a gaseous state and therefore phase changes can be neglected. Each molecular species is tracked separately, as the composition of an incoming gas may change due to chemical reactions within the volume. The gas mixture within the volume is considered homogeneous with uniform properties; therefore, the flow leaving the volume exhibits the same values for these properties as the flow within the volume.

The total mass, momentum, and energy must be conserved within each volume. A complete derivation for obtaining the mass, momentum, and energy balances is provided below.

#### 3.1.2.1 Conservation of Mass

The generic conservation of mass for a one-dimensional compressible flow is given by, [44],

$$\frac{\partial}{\partial t} \int_{CV} \rho \, dV + \int_{CS} \rho \vec{V} \cdot d\vec{A} = 0$$  \hspace{1cm} (3.4)
Performing the integrations for a particular species yields,

$$\frac{\partial}{\partial t} \rho_g V g x_{j,g} - \mathcal{R}_{j,g} MW_j + (-\rho_{in} V_{in} A) x_{j,in} + (-\rho_g V_{ex} A) x_{j,g} = 0$$  \hspace{1cm} (3.5)$$

where specific values of subscripts $j, j=1,2,\cdots,7$, correspond to the species $\text{CH}_4, \text{CO}, \text{CO}_2, \text{H}_2, \text{H}_2\text{O}, \text{N}_2,$ and $\text{O}_2$ respectively and $\mathcal{R}$ is the molar reaction rate, meaning it is the rate at which moles of the species are being generated. Note that the mass fraction and the density terms describing the gas exiting the volume, $x_{j,g}$ and $\rho_g$, use the subscript $g$ rather than $ex$ because of the homogeneous nature of volume mentioned previously.

Next, Eq.(3.5) is re-written in terms of mass and mass flow,

$$\frac{\partial}{\partial t} m_g x_{j,g} - \mathcal{R}_{j,g} MW_j - \dot{m}_{in} x_{j,in} + \dot{m}_{ex} x_{j,g} = 0$$  \hspace{1cm} (3.6)$$

Because chemical reactions deal with amount rather than mass of a species, it is easier for everything to be in terms of moles. Therefore, Eq.(3.6) is divided by the molecular weight of the species, $MW_j$, and re-written in terms of moles and molar flow,

$$\frac{\partial}{\partial t} N_g X_{j,g} - \mathcal{R}_{j,g} - \dot{n}_{in} X_{j,in} + \dot{n}_{ex} X_{j,g} = 0$$  \hspace{1cm} (3.7)$$

Some simple rearranging and expansion of the derivative yields the mass balance equation for an individual species as employed in the model,

$$\dot{N}_g X_{j,g} + N_g \dot{X}_{j,g} = \dot{n}_{in} X_{j,in} - \dot{n}_{ex} X_{j,g} + \mathcal{R}_{j,g}$$  \hspace{1cm} (3.8)$$

Additionally it should be noted that by definition of the mole fraction, $X_j$,

$$\sum_{j=1}^{7} X_{j,in} = \sum_{j=1}^{7} X_{j,g} = 1$$  \hspace{1cm} (3.9)$$

therefore,

$$\sum_{j=1}^{7} \dot{X}_{j,g} = 0$$  \hspace{1cm} (3.10)$$

For other variables summing them gives a total for which the notation used here is the subscript $\text{tot}$. So, summing Eq.(3.8) for all species gives,

$$\dot{N}_g = \dot{n}_{in} - \dot{n}_{ex} + \mathcal{R}_{\text{tot},g}$$  \hspace{1cm} (3.11)$$
3.1.2.2 Conservation of Momentum

The generic conservation of momentum for a compressible fluid control volume with one-dimensional flow is given by, [44],

\[ F_{\text{surface}} + F_{\text{body}} = \frac{\partial}{\partial t} \int_{CV} V \rho \, dV + \int_{CS} V \rho \bar{V} \cdot d\bar{A} \]  

(3.12)

Assuming no body forces in the flow direction, \( F_{\text{body}} = 0 \). Performing the integration for an individual species yields,

\[ F_{\text{surface},j} = \frac{\partial}{\partial t} \bar{V} m_{j,g} x_{j,g} - \bar{V} R_{j,g} MW_j + V_{in} (- \rho_{in} V_{in} A) x_{j,in} + V_{ex} (\rho_{ex} V_{ex} A) x_{j,g} \]  

(3.13)

Re-writing in terms of mass gives,

\[ F_{\text{surface},j} = \frac{\partial}{\partial t} \bar{V} m_{j,g} x_{j,g} - \bar{V} R_{j,g} MW_j - V_{in} \dot{m}_{in,x_{j,in}} + V_{ex} \dot{m}_{ex,x_{j,g}} \]  

(3.14)

Dividing through by \( MW_j \) to convert to moles yields,

\[ F_{\text{surface},j}/MW_j = \frac{\partial}{\partial t} \bar{V} N_{j,g} x_{j,g} - \bar{V} R_{j,g} - V_{in} \dot{n}_{in,x_{j,in}} + V_{ex} \dot{n}_{ex,x_{j,g}} \]  

(3.15)

Keeping in mind Eqs.(3.9) and (3.10), Eq.(3.15) can be summed for all species to get,

\[ F_{\text{surface},g}/MW_g = \frac{\partial}{\partial t} \bar{V} N_g - \bar{V} R_{tot,g} - V_{in} \dot{n}_{in} + V_{ex} \dot{n}_{ex} \]  

(3.16)

The assumption is made that the velocity of the gas does not vary significantly across the control volume or over time. Therefore, \( V_{in} \approx V_{ex} \approx \bar{V} \) and \( \bar{V} = \text{const} \). So, expanding the derivative and factoring out the velocities makes Eq.(3.16) look like,

\[ F_{\text{surface},g}/MW_g = \bar{V} N_g + \bar{V} \left[ \dot{N}_g - R_{tot,g} - \dot{n}_{in} + \dot{n}_{ex} \right] \]  

(3.17)

From the conservation of mass in Eq.(3.11) the term inside the brackets equals zero, and because of the assumption \( \bar{V} = \text{const} \), \( \bar{V} \) also equals zero. So, the entire right hand side of the equation goes to zero, leaving only,

\[ F_{\text{surface},g} = 0 \]  

(3.18)
Surface forces acting on the control volume in the flow direction include the pressures acting on the inlet and outlet areas of the control volume and the friction along the walls. Any pressure exerted by the wall boundaries is orthogonal to the flow direction and so does not affect the flow. So, the surfaces forces are given by,

$$F_{surface,g} = A(P_{in} - P_g) - F_{fric} \quad (3.19)$$

Combining Eqs.(3.18) and (3.19) the force balance can be represented as,

$$A(P_{in} - P_g) = F_{fric} \quad (3.20)$$

To contend with the complexities of fluid friction, Eq.(3.20) is replaced with Darcy’s law, [44], which can be written for either the inlet or exit flow,

$$\dot{m}_{in} = k_f(P_{in} - P_g) \quad (3.21)$$
$$\dot{m}_{ex} = k_f(P_g - P_{ex})$$

where $k_f$ is a flow rate constant determined from experimental data, but based on physical properties of the fluid and geometry. Equation(3.21) is then divided by the molecular weight, $MW_g$, to obtain molar flow rate, $\dot{\eta}$,

$$\dot{\eta}_{in} = k_f(P_{in} - P_g)/MW_g$$
$$\dot{\eta}_{ex} = k_f(P_g - P_{ex})/MW_g \quad (3.22)$$

In previous models, pressure drops between control volumes were assumed at fixed, experimentally determined values, [45]. To incorporate dynamics resulting from pressure and density changes in the system the assumption of an ideal gas is made. Thus, the pressure in each volume is calculated by,

$$P_g = N_gR_uT_g/V_g \quad (3.23)$$

where $P$, $N$, and $T$ are all functions of time. The ideal gas assumption is accurate for either low pressures or high temperatures. Within the fuel cell system, temperatures are well above the critical point of the gases involved and validate the assumption.
The coupling of Eqs.(3.22) and (3.23) generates a dynamic response in the system referred to as pressure dynamics.

A special case exists for the gas volumes used in the POX reformer. The flow there passes through a porous ceramic catalyst, and non-Darcian effects become relatively significant. Moreira studies the flow through these types of catalyst beds and proposes this correlation in [46] to obtain the pressure drop across a unit length,

\[
\frac{(P_g - P_{ex})}{L} = \frac{\mu MW_g}{B_1 \rho A} \eta_{ex} + \frac{MW_g}{\rho A^2 B_2} \eta_{ex}^2
\]  

(3.24)

where,

\[
B_1 = \frac{\epsilon^3 \rho_{pore}^{0.264}}{1.36 \times 10^8 (1 - \epsilon)^2}
\]

(3.25)

\[
B_2 = \frac{\epsilon^3 \rho_{pore}^{-0.24}}{1.8 \times 10^4 (1 - \epsilon)}
\]

(3.26)

and where, \(\epsilon\) is the porosity of the ceramic, and \(d_{pore}\) is the average pore diameter.

Using the quadratic formula, Eq.(3.24) is solved for \(\dot{\eta}\) and used in place of Eq.(3.22) in gas control volumes with flow through a porous ceramic.

### 3.1.2.3 Conservation of Energy

The generic conservation of energy for a compressible fluid control volume with one-dimensional flow is given by, [44],

\[
\dot{Q} - \dot{W}_s - \dot{W}_{shear} - \dot{W}_{other} = \frac{\partial}{\partial t} \int_{CV} e \rho \, dV + \int_{CS} (e + P v) \rho \vec{V} \cdot d\vec{A}
\]

(3.27)

where \(v\) is the specific volume given by, \(v = 1/\rho\). Neglecting gravity, the energy of the system, \(e\) is given by \(e = u + V^2/2\). Also, there is no work being done on or by the control volume, so those terms drop out and Eq.(3.27) becomes,

\[
\dot{Q} = \frac{\partial}{\partial t} \int_{CV} (u + V^2/2) \rho \, dV + \int_{CS} (u + P v + V^2/2) \rho \vec{V} \cdot d\vec{A}
\]

(3.28)

Performing the integration for an individual species and re-writing in terms of mass
\[
\dot{Q} = \frac{\partial}{\partial t} \left( u_{j,g} + \frac{V^2}{2} \right) m_g x_{j,g} - \left( h_{\text{react},j} + \frac{V^2}{2} \right) R_{j,g} MW_j \\
- \left( u_{j,in} + P_{in} v_{in} + \frac{V^2_{in}}{2} \right) \dot{m}_{in} x_{j,in} + \left( u_{j,g} + P_g v_g + \frac{V^2_{ex}}{2} \right) \dot{m}_{ex} x_{j,g}
\] (3.29)

where \(h_{\text{react},j}\) is enthalpy of formation of the species, meaning it is the energy released when this species is created in a chemical reaction. Dividing through by molecular weight, \(MW_j\), to convert to moles and substituting in enthalpy for internal energy and flow energy using \(h \equiv u + Pv\), yields,

\[
\dot{Q}/MW_j = \frac{\partial}{\partial t} \left( u_{j,g} + \frac{V^2}{2} \right) N_g \chi_{j,g} - \left( h_{\text{react},j} + \frac{V^2}{2} \right) R_{j,g} \\
- \left( h_{j,in} + \frac{V^2_{in}}{2} \right) \dot{\eta}_{in} \chi_{j,in} + \left( h_{j,g} + \frac{V^2_{ex}}{2} \right) \dot{\eta}_{ex} \chi_{j,g}
\] (3.30)

Summing Eq.(3.30) for all species and simplifying the result with Eqs.(3.9) and (3.10) gives,

\[
\dot{Q}/MW_g = \frac{\partial}{\partial t} \left( u_g + \frac{V^2}{2} \right) N_g - \left( h_{\text{react}} - \frac{V^2}{2} \right) R_{\text{tot},g} \\
- \left( h_{in} + \frac{V^2_{in}}{2} \right) \dot{\eta}_{in} + \left( h_g + \frac{V^2_{ex}}{2} \right) \dot{\eta}_{ex}
\] (3.31)

The same assumption used to acquire Eq.(3.17) is applied here. Namely, the kinetic energy is assumed to vary insignificantly across the control volume and over time. Therefore, \(V_{in} \approx V_{ex} \approx \bar{V}\) and \(\bar{V} = \text{const.}\) So, expanding the derivative and factoring out the velocities makes Eq.(3.31) look like,

\[
\dot{Q}/MW_g = \frac{\partial}{\partial t} (u_g N_g) - R_{\text{tot},g} h_{\text{react}} - h_{in} \dot{\eta}_{in} + h_g \dot{\eta}_{ex} \\
+ \frac{N_g}{2} \frac{\partial}{\partial t} (\bar{V}^2) + \frac{\bar{V}^2}{2} \left[ \dot{N}_g - R_{\text{tot},g} - \dot{\eta}_{in} + \dot{\eta}_{ex} \right]
\] (3.32)

From the conservation of mass in Eq.(3.11) the term inside the brackets equals zero, and because of the assumption \(\bar{V} = \text{const.}\) \(\frac{\partial}{\partial t} (\bar{V}^2)\) also equals zero, therefore,

\[
\dot{Q}/MW_g = \frac{\partial}{\partial t} (u_g N_g) - R_g h_{\text{react},g} - h_{in} \dot{\eta}_{in} + h_g \dot{\eta}_{ex}
\] (3.33)
The practical use of conservation of energy is to find the temperature of the control volume, which is accomplished by assuming constant specific heats and setting \( \partial u = C_v \partial T \).

Expanding the remaining derivative and making this substitution yields,

\[
\dot{Q}/MW_g = \frac{\partial N_g}{\partial t} u_g + \frac{\partial T_g}{\partial t} N_g C_{v,g} - R_g h_{react,g} - h_{in} \dot{\eta}_{in} + h_g \dot{\eta}_{ex} \tag{3.34}
\]

Two more substitutions are made for convenience of calculation. First, it is easier to determine a gas’s enthalpy than internal energy, so from ideal gas relationships internal energy, \( u_g \), is replaced with \((h_g - R_u T_g)\). Second, the only heat transfer into or out of the gas control volume is via convection from the neighboring solid control volume, so the \( \dot{Q} \) term can be replaced with \( \dot{q}_{conv} \) from Eq.(3.2). Making these substitutions and rearranging the terms yields the final complete form of the conservation of energy,

\[
\frac{\partial T_g}{\partial t} N_g C_{v,g} = h_{in} \dot{\eta}_{in} - h_g \dot{\eta}_{ex} + R_g h_{react,g} - \dot{q}_{conv} - \frac{\partial N_g}{\partial t} (h_g - R_u T_g) \tag{3.35}
\]

### 3.2 1-D Discretization

Many material properties such as \( C_v \) and \( h \) are found as functions of temperature, and because heat is being generated and transferred in various places in the system, there are often significant temperature gradients from one point to another. The lumped control volume approach, assumes that properties such as temperature and pressure are uniform throughout the volume. While knowing all the details of the internal temperature distribution is not necessary for the desired analysis, neglecting these gradients can have a negative affect on the overall accuracy of the model. To improve the accuracy of the model then, a one dimensional discretization scheme can be applied to the the control volume method.

The system is discretized only in the direction of flow, which itself has been modeled as a 1-D flow. To implement this change requires only minor modification of the generic control volume equations developed in Section 3.1.

For the solid control volume the overall energy balance in Eq.(3.1) remains the same, but \( \dot{Q}_s \) includes two conduction terms. Based on Eq.(3.3) and Fig. 3.2 the total \( \dot{q}_{cond} \) can
be written as,

\[ \sum q_{\text{cond}} = k_{\text{cond}}A_{\text{cond}} \frac{2T_s - T_{s+1} - T_{s-1}}{L_s} \]  

(3.36)

where the cross-sectional area, \( A_{\text{cond}} \), and the length, \( L_s \), of each element is the same. Also the surface area for convection, \( A_{\text{conv}} \), in Eq.(3.2), is scaled based on the length of the element.

For the gas control volume, conservation of mass, Darcy’s law, and conservation of energy remain the same. The volumes are simply linked together so that the outlet conditions of one volume become the inlet conditions of the next volume downstream. To actually perform the calculations, however both the inlet flow rate and the outlet flow rate are required. The inlet flow rate can simply be the outlet flow rate from the upstream volume, but the outlet flow rate must be calculated using Darcy’s law, Eq.(3.22), which requires knowing the downstream pressure. So while most information propagates downstream through the discretized elements from the inlet conditions, the pressure information propagates upstream from the outlet condition. Both system configurations analyzed here ultimately exhaust into atmospheric conditions, so the final outlet condition is atmospheric pressure.

Using the notation introduced in Fig 3.3 the pertinent gas control volume equations are reproduced here.
Conservation of mass from Eq.(3.8),

$$\dot{N}_g \dot{X}_{j.g} + N_g \dot{X}_{j.g} = \dot{n}_{g-1} X_{j,g-1} - \dot{n}_g X_{j,g} + R_{j,g} \tag{3.37}$$

Darcy’s law from Eq.(3.22),

$$\dot{n}_g = k_f (P_g - P_{g+1}) / MW_g \tag{3.38}$$

Ideal gas law from Eq.(3.23)

$$P_g = N_g R_u T_g / V_g \tag{3.39}$$

And conservation of energy from Eq.(3.35)

$$\frac{\partial T_g}{\partial t} N_g C_v.g = h_{g-1} \dot{h}_{g-1} - h_g \dot{h}_g + R_g h_{\text{react},g} + q_{\text{conv}} - \frac{\partial N_g}{\partial t} (h_g - R_u T_g) \tag{3.40}$$

### 3.3 Component Models

Several different versions of the generic gas control volume are required to model the entire system. The primary differences between each type are the chemical reactions occurring in the volume and how the reaction rates are calculated. There are different schemes employed for the steam reformer, POX reformer, fuel cell anode, fuel cell cathode, and combustor. These modified gas volumes are combined with parameterized solid volumes to create each component in the system.
3.3.1 Reformers

The goal of a reformer is to convert the fuel into a hydrogen rich gas for use in the fuel cell. There are multiple technologies available to do this. As described in Chapter 2, the SR-tubular configuration employs a steam reformer while the POX-tubular configuration uses a POX reformer. In both cases the fuel is methane, but the same methods could be employed for modeling higher hydrocarbons as the fuel.

3.3.1.1 Steam Reformer

Figure 3.4 shows a schematic of a tubular packed-bed steam reformer, [47].

To model this component three gas control volumes and one solid control volume are required. The exhaust flow and recirculated flow volumes are generic gas control volumes with no chemical reactions. Their main purpose is to transfer heat into the system which is consumed by the chemical reactions in the reformate flow volume. Figure 3.5 demonstrates how the heat transfer network is connected. The heat transfer rates, $\dot{q}_1$, $\dot{q}_2$, and $\dot{q}_3$ are calculated by Eq.(3.2) using the convective heat coefficients, $h_1$, $h_2$, and $h_3$, as shown in the figure. For the discretized model, the heat transfer network is increased to include the conduction terms as shown in Fig. 3.6. Equation 3.36 is used to model these two additional heat transfers, with conduction coefficients $k_1$ and $k_2$. 

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The actual purpose of the steam reformer is carried out in the reformate gas control volume where chemical reactions occur to produce hydrogen rich gas. The three main chemical reactions for the steam reforming of methane are \[42\],

\[
\begin{align*}
(I) & \quad CH_4 + H_2O & \leftrightarrow & CO + 3H_2 \\
(II) & \quad CO + H_2O & \leftrightarrow & CO_2 + H_2 \\
(III) & \quad CH_4 + 2H_2O & \leftrightarrow & CO_2 + 4H_2
\end{align*}
\]

The mass balance equations for a lumped steam reformer model derived from Eq.(3.8) and Fig.2.1(a) are shown here, where \( r_a, r_b, \) and \( r_c \) are the reaction rates of the chemical reactions (I), (II), and (III) in Eq.(3.41), respectively,

\[
\begin{align*}
\frac{d}{dt}(N_{r}\dot{X}_1) &= k\dot{N}_o\dot{X}_{1a} - \dot{N}_{in}\dot{X}_{1r} + \dot{N}_f - r_a - r_c \\
\frac{d}{dt}(N_{r}\dot{X}_2) &= k\dot{N}_o\dot{X}_{2a} - \dot{N}_{in}\dot{X}_{2r} + r_a - r_b \\
\frac{d}{dt}(N_{r}\dot{X}_3) &= k\dot{N}_o\dot{X}_{3a} - \dot{N}_{in}\dot{X}_{3r} + r_b + r_c \\
\frac{d}{dt}(N_{r}\dot{X}_4) &= k\dot{N}_o\dot{X}_{4a} - \dot{N}_{in}\dot{X}_{4r} + 3r_a + r_b + 4r_c \\
\frac{d}{dt}(N_{r}\dot{X}_5) &= k\dot{N}_o\dot{X}_{5a} - \dot{N}_{in}\dot{X}_{5r} - r_a - r_b - 2r_c \\
\frac{d}{dt}(N_{r}\dot{X}_6) &= k\dot{N}_o\dot{X}_{6a} - \dot{N}_{in}\dot{X}_{6r} + 0 \\
\frac{d}{dt}(N_{r}\dot{X}_7) &= k\dot{N}_o\dot{X}_{7a} - \dot{N}_{in}\dot{X}_{7r} + 0
\end{align*}
\]
Remembering from Eq.(3.9) that the mole fractions always add up to one, summing Eqs.(3.42) gives,

\[ \dot{N}_r = k \dot{N}_o - \dot{N}_{in} + \dot{N}_f + 2r_a + 2r_c \]  

(3.43)

Note that \(- (r_a + r_c)\) is the reaction rate of \(CH_4\) in the reformer, \(R_{1r}\). Making this substitution, the total mass balance for the steam reformer can be written as,

\[ \dot{N}_r = k \dot{N}_o - \dot{N}_{in} + \dot{N}_f - 2R_{1r} \]  

(3.44)

The following reaction rate expressions, given in [42], are used to model the kinetics of steam reforming reactions in Eq.(3.41). The equations below are written for a generic gas control volume. These equations apply for the reactions in the steam reforming control volume as well as the reforming reactions in the anode control volume to be discussed in
Section 3.3.2.3.

\[ r_a = \frac{M_{\text{cat}} \kappa_a}{p_{H_2}^{2.5}} \left( p_{CH_4}p_{H_2O} - \frac{p_{H_2}^3p_{CO}}{K_a} \right) / \delta^2 \]  
(3.45)

\[ r_b = \frac{M_{\text{cat}} \kappa_b}{p_{H_2}} \left( p_{CO}p_{H_2O} - \frac{p_{H_2}p_{PCO_2}}{K_b} \right) / \delta^2 \]  
(3.46)

\[ r_c = \frac{M_{\text{cat}} \kappa_c}{p_{H_2}^{2.5}} \left( p_{CH_4}^2p_{H_2O} - \frac{p_{H_2}^2p_{CO_2}}{K_c} \right) / \delta^2 \]  
(3.47)

where

\[ \delta = 1 + K_{CO}p_{CO} + K_{H_2}p_{H_2} + K_{CH_4}p_{CH_4} \]

\[ + K_{H_2O}p_{H_2O}p_{H_2} \]  
(3.48)

In Eqs. (3.45), (3.46) and (3.47), the rate coefficients \( \kappa_a, \kappa_b, \) and \( \kappa_c \) are given by

\[ \kappa_f = \kappa_{f,T_{ref}} \exp \left[ -\frac{E_f}{R_a} \left( \frac{1}{T_g} - \frac{1}{T_{ref,f}} \right) \right], f = a, b, c \]  
(3.49)

and the adsorption constants \( K_{CO}, K_{H_2}, K_{CH_4}, K_{H_2O} \) are given as follows

\[ K_q = K_{q,T_{ref}} \exp \left[ -\frac{\Delta H_q}{R_a} \left( \frac{1}{T_g} - \frac{1}{T_{ref,q}} \right) \right], \]

\[ q = CO, H_2, CH_4, H_2O \]  
(3.50)

where the values of \( E_f, T_{ref,f}, \kappa_{f,T_{ref}}, \) with \( f = a, b, c, \) and \( \Delta H_q, T_{ref,q}, K_{q,T_{ref}}, \) with \( q = CO, H_2, CH_4, H_2O, \) are given in [42].

### 3.3.1.2 POX Reformer

Because the oxidation reactions in a POX reformer are highly exothermic, the heat exchanges with the hot exhaust and recirculated gases seen in the steam reformer are unnecessary. Therefore, only a single gas control volume and a single solid control volume are required to model an element of the POX reformer. The heat transfer network is much simpler as shown in Fig. 3.7. The convection and conduction heat transfer rates are again calculated by Eqs. (3.2) and (3.3), respectively.

Within a catalytic partial oxide reformer there are two primary reaction regimes. Oxidation occurs first and dominates until all the oxygen is depleted. Steam reforming reactions begin occurring as soon as \( H_2O \) becomes available and continue through the rest of the
reactor. For a typical one centimeter length POX reformer, the oxidation regime generally ends within the first millimeter of the reactor, after which steam reforming dominates, [35, 38]. The model developed here is discretized along the direction of flow. In the discretized model, each element checks for the presence of oxygen within the volume and in the incoming flow and then chooses which reaction regime to follow. If oxygen is available then the POX regime is chosen, however, if a minimum quantity of oxygen is not met then the steam reforming regime is chosen. For the simplest model two unequally sized elements are used. The first corresponds to the 1mm zone of partial oxidation and the second to the remaining 9mm of steam reforming.

**Partial Oxidation Regime** Three reactions are used to describe the oxidation regime: partial oxidation, total oxidation, and hydrogen oxidation [38].

\[
\begin{align*}
(I) & \quad (x) \quad [CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2] \\
(II) & \quad (1 - x) \quad [CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O] \\
(III) & \quad (2x\alpha) \quad [H_2 + \frac{1}{2}O_2 \rightarrow H_2O]
\end{align*}
\]
The selectivities, $x$ and $\alpha$, are determined by the ratio of oxygen molecules to methane molecules, $O2C$ ratio, in the incoming gas. From the published results it was determined that $x$ and $\alpha$ can be assumed constant for $O2C$ ratios in the range of 0.833 to 0.357 [38]. Using $x = 0.85$ and $\alpha = 0.33$ Eq.(3.51) reduces to:

$$CH_4 + 1.0055O_2 \rightarrow 0.85CO + 0.15CO_2 + 1.139H_2 + 0.861H_2O$$  \hspace{1cm} (3.52)

The rate of this reaction is modeled as a function of the gas temperature. From the Arrhenius plots published in [38] the following equation for the hydrogen production rate can be obtained,

$$\mathcal{R}_{4,g} = 2.9771 \times 10^{-9} \mathcal{V}_g e^{(-1125/T_g - 1.9)}$$  \hspace{1cm} (3.53)

The reaction rates for the other species are then obtained using $\mathcal{R}_{4,r}$ and ratios of the coefficients from Eq.(3.52).

$$\mathcal{R}_{1,g} = \mathcal{R}_{4,g}[-1/1.139]$$  \hspace{1cm} (3.54) \\
$$\mathcal{R}_{2,g} = \mathcal{R}_{4,g}[0.85/1.139]$$  \hspace{1cm} (3.54) \\
$$\mathcal{R}_{3,g} = \mathcal{R}_{4,g}[0.15/1.139]$$  \hspace{1cm} (3.54) \\
$$\mathcal{R}_{5,g} = \mathcal{R}_{4,g}[0.861/1.139]$$  \hspace{1cm} (3.54) \\
$$\mathcal{R}_{7,g} = \mathcal{R}_{4,g}[-1.0055/1.139]$$

If $-\mathcal{R}_{7,g} > \dot{\eta}_{in}x_{7,in}$ and $N_r x_{7,g} = 0$, then the reaction rates must be adjusted keeping the same proportions but setting $-\mathcal{R}_{7,g} = \dot{\eta}_{in}x_{7,in}$, because the amount of oxygen within the control volume cannot become a negative value.

**Steam Reforming Regime**  Recall the chemical reactions of steam reforming shown in Eq.(3.41). From experimental results in [39, 40], it can be seen that negligible $CO_2$ is generated in the the POX reformer, this means that reactions (II) and (III), which generate $CO_2$ can be considered insignificant in this region. Only reaction (I) is applied in this regime, using the method presented in Section 3.3.1.1 to calculate the reaction rate.

**Conservation of Mass**  The conservation of mass for each species can be written for the entire POX reformer based on Eq.(3.8), incorporating $r_d$ as the reaction rate of Eq.(3.52)
and \( r_a \) as the rate for reaction (I) in Eq.(3.41).

\[
\begin{align*}
\frac{d}{dt} (N_r X_1) &= \dot{N}_f X_{1f} - \dot{N}_{in} X_{1r} - r_d - r_a \\
\frac{d}{dt} (N_r X_2) &= \dot{N}_f X_{2f} - \dot{N}_{in} X_{2r} + 0.85 r_d + r_a \\
\frac{d}{dt} (N_r X_3) &= \dot{N}_f X_{3f} - \dot{N}_{in} X_{3r} + 0.15 r_d \\
\frac{d}{dt} (N_r X_4) &= \dot{N}_f X_{4f} - \dot{N}_{in} X_{4r} + 1.139 r_d + 3 r_a \\
\frac{d}{dt} (N_r X_5) &= \dot{N}_f X_{5f} - \dot{N}_{in} X_{5r} + 0.861 r_d - r_a \\
\frac{d}{dt} (N_r X_6) &= \dot{N}_f X_{6f} - \dot{N}_{in} X_{6r} + 0 \\
\frac{d}{dt} (N_r X_7) &= \dot{N}_f X_{7f} - \dot{N}_{in} X_{7r} - 1.0055 r_d
\end{align*}
\]

(3.55)

When these equations are added together the mole fractions, \( X_j \), always sum to 1 giving,

\[
\dot{N}_r = \dot{N}_f - \dot{N}_{in} - 2( - r_d - r_a ) - 1.0055 r_d
\]

(3.56)

Note that \( - r_d - r_a \) is the reaction rate of \( CH_4 \) in the reformer, \( \mathcal{R}_{1r} \), and \( - 1.0055 r_d \) is the reaction rate of \( O_2 \) in the reformer, \( \mathcal{R}_{7r} \). Making this substitution, the total mass balance for the POX reformer can be written as,

\[
\dot{N}_r = \dot{N}_f - \dot{N}_{in} - 2 \mathcal{R}_{1r} + \mathcal{R}_{7r}
\]

(3.57)

### 3.3.2 SOFC Stack

The SOFC stack uses the hydrogen rich gas from the reformer and air that has been pre-heated in the combustor to generate electricity. It is a collection of individual cells connected electrically in series. The models developed here are for individual cells. To model the entire stack the flow data is simply divided by the number of cells when going into the stack and multiplied by the number of cells when leaving the stack. The voltage output of the cell is also multiplied by the number of cells to obtain the voltage output of the stack.

Different methods can be used to physically build an SOFC which will result in varying geometries that will affect some system characteristics, particularly the heat transfer. As described in Chapter 2, the SR-tubular configuration has a tubular SOFC stack and the POX-planar configuration has a planar SOFC stack. Fortunately, the chemical and electrochemical reactions that occur in the anode and cathode do not change with geometry, so
the method of calculating those reaction rates can be applied to gas control volumes in both configurations. In addition the voltage being produced by the cell can be modeled in the same way for both configurations, though some parameters may be dependent on geometry.

### 3.3.2.1 Tubular SOFC

The tubular cell consists of several annular regions as shown in Figure 3.8. The preheated air enters in the center from the right, then reverses direction and flows back through the cathode contained by the electrolyte. The hydrogen rich gas from the reformer enters from the left and flows around the outside electrolyte in the anode.

![Figure 3.8: Schematic of Tubular SOFC](image)

Three gas control volumes and two solid control volumes are required to model this component. A generic gas control volume with no reactions rates serves as the inlet air flow, while the anode and cathode are modeled by gas control volumes with different reaction schemes. One solid control volume represents the electrolyte and catalyst beds while the other is the structure between the air flow and the cathode flow. The heat transfer between the volumes is illustrated in Fig. 3.9 for a discretized model. The convective and conductive heat transfer rates, \( \dot{q}_{\text{conv}} \) and \( \dot{q}_{\text{cond}} \), are found using Eqs. (3.2) and (3.3), respectively.
3.3.2.2 Planar SOFC

The planar cell modeled here is a co-flow model where the anode and cathode gases flow parallel as illustrated in Fig. 3.10. In a wholly lumped model the relative directions do not matter, but for the 1-D discretized model, only parallel and anti-parallel can be modeled accurately. A discretized model for cross flow, where the flows move perpendicular to each other, would require two dimensions.

Two gas control volumes and one solid control volume are required to model each
Figure 3.10: Schematic of Planar SOFC

element of a planar cell. The gas control volumes represent the anode and the cathode and the solid control volume serves in place of the electrolyte. The parameters of the electrolyte control volume also include the effects of other connected solids such as catalyst beds or structural material that can store heat. Figure 3.11 shows how the control volumes are connected in terms of heat transfer.

Figure 3.11: Heat Transfer Network in the Planar SOFC
3.3.2.3 Anode Reactions

The same steam reforming reactions given in Eq. (3.41) occur in the anode along with this electrochemical reaction,

\[ H_2 + O^{2-} \rightarrow H_2O + 2e \quad (3.58) \]

Using \( r_a, r_b, \) and \( r_c \) as before for the rates for each reaction in Eq. (3.41) and with \( r_e \) as the rate for the electrochemical reaction in Eq. (3.58) the mass balance can be constructed for each species based on Eq. (3.8),

\[
\begin{align*}
\frac{d}{dt}(N_aX_{1a}) &= \dot{N}_{in}X_{1in} - \dot{N}_oX_{1a} - r_a - r_c \\
\frac{d}{dt}(N_aX_{2a}) &= \dot{N}_{in}X_{2in} - \dot{N}_oX_{2a} + r_a - r_b \\
\frac{d}{dt}(N_aX_{3a}) &= \dot{N}_{in}X_{3in} - \dot{N}_oX_{3a} + r_b + r_c \\
\frac{d}{dt}(N_aX_{4a}) &= \dot{N}_{in}X_{4in} - \dot{N}_oX_{4a} + 3r_a + r_b + 4r_c - r_e \\
\frac{d}{dt}(N_aX_{5a}) &= \dot{N}_{in}X_{5in} - \dot{N}_oX_{5a} - r_a - r_b - 2r_c + r_e \\
\frac{d}{dt}(N_aX_{6a}) &= \dot{N}_{in}X_{6in} - \dot{N}_oX_{6a} + 0 \\
\frac{d}{dt}(N_aX_{7a}) &= \dot{N}_{in}X_{7in} - \dot{N}_oX_{7a} + 0 \\
\end{align*}
\]

(3.59)

Summing the elemental equations gives,

\[ \dot{N}_a = \dot{N}_{in} - \dot{N}_o + 2r_a + 2r_c \quad (3.60) \]

which can be simplified as in the steam reformer by noting \(- (r_a + r_c)\) is the reaction rate of \( CH_4 \) in the anode, \( \mathcal{R}_{1a} \). Making this substitution yields,

\[ \dot{N}_a = \dot{N}_{in} - \dot{N}_o - 2\mathcal{R}_{1a} \quad (3.61) \]

Note that the oxygen ions in Eq. (3.58) are not the oxygen molecules represented by \( X_7 \), so \( r_e \) is not applied to the seventh mass balance in Eq. (3.59). The ions themselves enter the anode through the electrolyte and are assumed to react with the hydrogen at the surface. The rate that they are reacting, and thus \( r_e \) is driven by the current draw by, [2],

\[ r_e = \frac{iN_{cell}}{nF} \quad (3.62) \]

35
where \( n \) is the number of electrons involved in the electrochemical reaction, which from Eq.(3.58) is 2.

An assumption is made here that there will always be enough oxygen in the cathode to be ionized and sent through to the anode. Because air in the cathode is being used to cool the system the flow rate is high enough that there is no danger of depleting the oxygen. Also, at the high operating temperatures the electrolyte is sufficiently conductive to not limit the supply of oxygen ions to the anode.

3.3.2.4 Cathode Reactions

In the cathode control volume the only the following electrochemical reaction occurs,

\[
\frac{1}{2}O_2 + 2e \rightarrow O^{2-}
\]  

(3.63)

this reaction is coupled with the electrochemical reaction in Eq.(3.58), so that both progress at the same rate, \( r_e \), which is driven by the current draw as given in Eq.(3.62).

The only species this effects is \( O_2 \) so the mass balance for it, found using Eq.(3.8) is,

\[
\frac{d}{dt}(N_cX_{7c}) = \dot{N}_{\text{inlet}}X_{7\text{inlet}} - \dot{N}_{\text{outlet}}X_{7c} + \frac{1}{2}r_e
\]  

(3.64)

When summed with the other species,

\[
\dot{N}_c = \dot{N}_{\text{inlet}} - \dot{N}_{\text{outlet}} - \frac{1}{2}r_e
\]  

(3.65)

3.3.2.5 Voltage Calculation

The voltage produced by the fuel cell is computed by first finding the ideal open circuit voltage called the Nernst potential and then subtracting several loss factors, [2, 5]. The major types of loss that affect the operational voltage of an SOFC are called activation loss, ohmic loss, and concentration loss. A fourth category of loss which affects some fuel cell systems, fuel crossover and internal current losses, is minimal in SOFCs and can be neglected [2]. The cell voltage is given by,

\[
\nu_{\text{cell}} = \nu_{\text{Nernst}} - \nu_{\text{act}} - \nu_{\text{ohm}} - \nu_{\text{conc}}
\]  

(3.66)
To begin finding the Nernst potential the electrochemical reactions Eq.(3.58) and Eq.(3.63) are combined to show the basic overall reaction of the fuel cell,

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O
\]  

(3.67)

The Nernst potential is based on the total change in Gibbs free energy, \(\Delta G\), caused by the overall reaction,

\[
\mathcal{V}_{\text{Nernst}} = -\frac{\Delta G}{nF}
\]

(3.68)

where \(n\) is the number of electrons involved in the reaction, and \(F\) is Faraday’s constant. The total change in Gibbs free energy from this reaction gives the amount of energy released. At standard pressure the Gibbs free energy is only a function of temperature and the change can be found by subtracting the energy of the reactants from the products,

\[
\Delta G^o = G^o_{H_2O} - G^o_{H_2} - \frac{1}{2}G^o_{O_2}
\]

(3.69)

where \(G^o_{H_2O}, G^o_{H_2}\), and \(G^o_{O_2}\) are all functions of temperature, [48]. When not at standard pressure the activity of the reactants, as determined by the partial pressures, also has an effect on the total change in Gibbs free energy,

\[
\Delta G = \Delta G^o - RT \ln \left( \frac{p_{H_2}p_{O_2}^{\frac{1}{2}}}{p_{H_2O}} \right)
\]

(3.70)

Note that the partial pressures are given by \(p_{H_2} = P_a \chi_{4,a}\), \(p_{O_2} = P_c \chi_{7,c}\), and \(p_{H_2O} = P_a \chi_{5,a}\). Substituting these and Eq.(3.70) into Eq.(3.68) gives the Nernst potential as,

\[
\mathcal{V}_{\text{Nernst}} = -\frac{\Delta G^o}{nF} + \frac{R_u T_a}{nF} \ln \left( \frac{\chi_{4,a}^{\frac{1}{2}}}{\chi_{5,a}^{\frac{1}{2}} P_c^{\frac{1}{2}}} \right)
\]

(3.71)

The activation loss is the energy consumed to drive the chemical reactions at the surface of the electrode. It is highly non-linear but can be approximated by, [5],

\[
\mathcal{V}_{\text{act}} = \frac{R_u T_c}{nF} \arcsinh \left( \frac{i_{\text{cell}}/A_{\text{cell}}}{J_o} \right)
\]

(3.72)

where the exchange current density, \(J_o\), is considered to be a known constant. The area, \(A_{\text{cell}}\), is not surface or cross-sectional area, but the total length and width of the cell. In a
discretized element $A_{cell}$ is the area of the element and $i_{cell}$ is the current draw from that element.

The ohmic loss, or resistance loss, comes from the resistance to the flow of electrons through the electrode materials and interconnections as well as the resistance to the flow of ions through the electrolyte. As suggested by its name, the voltage drop is found simply summing the area specific resistances in Ohm’s law,

$$V_{ohm} = \frac{i_{cell}}{A_{cell}} (r_{anode} + r_{cathode} + r_{electrolyte} + r_{interconnect})$$  \hspace{1cm} (3.73)

The resistance of each component is found from the geometry and resistivity, which is a function of temperature given in [5]. The solid control volume temperature, $T_s$, is used when finding the resistivity.

The concentration losses result from the reduction of the concentration of reactants near the electrode as they are used up by the reaction. The voltage reduction from these losses is given by,

$$V_{conc} = -\frac{R_u T_a}{nF} \ln \left( 1 - \frac{i_{cell}/A_{cell}}{J_{lim}} \right)$$  \hspace{1cm} (3.74)

where $J_{lim}$ is assumed to be a known constant that represents the theoretical limiting current density achieved if the fuel is consumed at the maximum rate.

Plugging Eqs.(3.71), (3.72), (3.73), and (3.74) back into Eq.(3.66), the cell voltage can be easily calculated. In a discretized model, however, there is one other consideration to be made. All three loss factors are dependent on the local current density, $i_m/A_m$, which varies along a cell because of variations in temperature and reactant concentrations. If the input current demand for the cell is simply divided evenly across all the elements then each one will produce a different voltage, but since they are connected in parallel the differences must be reconciled. Many models impose an equipotential assumption and calculate the local current densities ahead of time so that each element produces the same voltage, [20, 49]. To avoid this up front iterative calculation, the current is adjusted on the fly using Ohm’s law and the results from the previous time step. Based on the circuit diagram for a discretized section of the fuel cell shown in Figure 3.12 the local current
demand is calculated by,

\[ i_{m,t} = \frac{i_{cell,t} - i_{cell,t-1}}{N_{element}} + i_{m,t-1} + \frac{V_{m,t-1} - V'_{m+1,t-1}}{R_{cc}} + \frac{V'_{m,t-1} - V'_{m-1,t-1}}{R_{cc}} \]  

(3.75)

where the resistance, \( R_{cc} \), is the transverse resistance of the current collectors in the electrodes. These are generally made of gold or some other highly conductive material, so \( R_{cc} \) is close to zero. With such a low value of \( R_{cc} \) the voltages of neighboring elements are brought to near equality extremely fast, having virtually the same effect as an equipotential assumption without the added up front computation.

### 3.3.3 Combustor

In the combustor excess fuel from the anode is combusted with the excess oxygen from the cathode. The combustion produces extra heat which is utilized to pre-heat the air supply for the cathode. Two gas control volumes and one solid control volume are required to model this. One gas control volume is a simple non-reactive volume with air passing through it, the other is the afterburner, or combustion chamber where anode and cathode exhausts mix and oxidation reactions take place. The solid control volume models the structure separating the two flows and through which heat is transfered. Figure 3.13 shows how heat is transfered through the combustor. The \( q_{conv} \) terms are calculated in the solid control volume using Eq.(3.2) as in previous components.

The combustor model is not discretized as the details of its internal design are not
a significant portion of the analysis. The mixture of the anode and cathode exhausts is assumed to be uniform and complete so that the molar flow rate of the mixture entering the combustor is given by the following,

for SR-tubular:
\[ \dot{N}_{\text{enter}} \chi_{j,\text{enter}} = \dot{N}_{\text{outlet}} \chi_{j,c} + (1 - k) \dot{N}_o \chi_{j,a} \]  
(3.76)

for POX-planar:
\[ \dot{N}_{\text{enter}} \chi_{j,\text{enter}} = \dot{N}_{\text{outlet}} \chi_{j,c} + \dot{N}_o \chi_{j,a} \]  
(3.77)

The combustion reactions are assumed to happen instantaneously, the rate being defined by the incoming rate of the reactants. The three species that can be oxidized in the combustion chamber are \( CH_4, CO, \) and \( H_2 \) via the following total oxidation reactions,

(I) \( CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 \)

(II) \( CO + \frac{1}{2}O_2 \rightarrow CO_2 \)  
(3.78)

(III) \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \)
Assigning the $r_f$, $r_g$, and $r_h$ as the reaction rates for (I), (II), and (III) in Eq.(3.78), respectively, the species mass balance can be constructed as follows from Eq.(3.8),

\[
\begin{align*}
\frac{d}{dt}(N_bX_{1b}) &= \dot{N}_{\text{enter}}X_{1\text{enter}} - \dot{N}_{\text{exhaust}}X_{1b} - r_f \\
\frac{d}{dt}(N_bX_{2b}) &= \dot{N}_{\text{enter}}X_{2\text{enter}} - \dot{N}_{\text{exhaust}}X_{2b} - r_g \\
\frac{d}{dt}(N_bX_{3b}) &= \dot{N}_{\text{enter}}X_{3\text{enter}} - \dot{N}_{\text{exhaust}}X_{3b} + r_f + r_g \\
\frac{d}{dt}(N_bX_{4b}) &= \dot{N}_{\text{enter}}X_{4\text{enter}} - \dot{N}_{\text{exhaust}}X_{4b} - r_h \\
\frac{d}{dt}(N_bX_{5b}) &= \dot{N}_{\text{enter}}X_{5\text{enter}} - \dot{N}_{\text{exhaust}}X_{5b} + 2r_f + r_h \\
\frac{d}{dt}(N_bX_{6b}) &= \dot{N}_{\text{enter}}X_{6\text{enter}} - \dot{N}_{\text{exhaust}}X_{6b} + 0 \\
\frac{d}{dt}(N_bX_{7b}) &= \dot{N}_{\text{enter}}X_{7\text{enter}} - \dot{N}_{\text{exhaust}}X_{7b} - 2r_f - \frac{1}{2}r_g - \frac{1}{2}r_h
\end{align*}
\]

(3.79)

The reaction rates are set so that all the $CH_4$, $CO$, and $H_2$ molecules entering the chamber are consumed by the reactions, if that is stoichiometrically possible. So the reaction rates are given by,

\[
\begin{align*}
    r_f &= \dot{N}_{\text{enter}}X_{1\text{enter}} \\
    r_g &= \dot{N}_{\text{enter}}X_{2\text{enter}} \\
    r_h &= \dot{N}_{\text{enter}}X_{4\text{enter}}
\end{align*}
\]

(3.80)

if there is sufficient $O_2$ available in the incoming flow, which means, if,

\[
X_{7\text{enter}} \geq 2X_{1\text{enter}} + \frac{1}{2}X_{2\text{enter}} + \frac{1}{2}X_{4\text{enter}}
\]

(3.81)

If this condition is not met then an assumption is made that $O_2$ has equal affinity to each of the reactions in Eq.(3.78) and the reaction rates are each reduced by the same fraction of the $O_2$ available in the inlet flow to the total $O_2$ needed to fully oxidize the fuels. For this case the reaction rates are given by,

\[
\begin{align*}
    r_f &= \dot{N}_{\text{enter}}X_{1\text{enter}} \frac{X_{7\text{enter}}}{(2X_{1\text{enter}} + \frac{1}{2}X_{2\text{enter}} + \frac{1}{2}X_{4\text{enter}})} \\
    r_g &= \dot{N}_{\text{enter}}X_{2\text{enter}} \frac{X_{7\text{enter}}}{(2X_{1\text{enter}} + \frac{1}{2}X_{2\text{enter}} + \frac{1}{2}X_{4\text{enter}})} \\
    r_h &= \dot{N}_{\text{enter}}X_{4\text{enter}} \frac{X_{7\text{enter}}}{(2X_{1\text{enter}} + \frac{1}{2}X_{2\text{enter}} + \frac{1}{2}X_{4\text{enter}})}
\end{align*}
\]

(3.82)
Chapter 4

Implementation

The mathematical models developed for describing the SOFC systems are far too complex to solve by hand in a timely fashion. To implement the model in a usable form it must be programmed into a computer based solver which can run simulations of the system with various inputs over time and provide the dynamic results for later analysis. Also, to facilitate future growth of the research program and allow more versatile use of the models, a model management scheme has been developed to organize the implementation and development.

4.1 Model Management

A broad goal of the research program of which this thesis is a part is to develop predictive capabilities for a variety of energy systems that will be incorporated into novel system level control paradigms. These predictive capabilities will be built through model-based analysis. In particular, high resolution control-oriented models will form the basis of such analysis. Over time, the research aims to encompass a broad range of distributed energy resources. Therefore, the modeling effort is expected to be significant, giving rise to a plethora of models for energy systems such as fuel cells, wind turbines, photovoltaic systems, gas power cycles such as Sterling engines, micro-turbines, CHP systems, etc. With this forethought, a structured approach to model development has been adopted. Specifically, in contrast to building isolated models of individual energy systems, the approach
develops an architecture comprising of a hierarchical arrangement of model libraries. On a smaller scale, looking only at SOFC systems the architecture supports simulations with multiple fuels, varying fuel quality and air contaminants, different reformer and stack technologies, different component layouts, and varying physical properties and dimensions; while minimizing the effort required to switch between the different scenarios mentioned above.

The salient features of this structured approach for modeling SOFC systems are explained below and illustrated in Fig. 4.1.

Figure 4.1: Approach to Hierarchical Library Development
4.1.1 Hierarchical Libraries

As shown in Fig. 4.1, at each level of the hierarchy, models are built by instantiating models from lower levels. Fundamental mathematical calculations are carried out at the lower levels of the hierarchy, and at higher levels, assembly models are predominant. Higher level models (such as those in the unit-reformer library in Fig. 4.1) have a greater physical significance since they represent physical components.

4.1.2 Model Reuse

This feature allows multiple instantiations of the same model at different locations within the model hierarchy. Model reuse is enhanced by parameterization. For example, a non-reactive gas control volume model can be used at multiple locations within a model with different parameter values at different instantiations. Another example is shown in Fig. 4.2, which is a snapshot of a reactive control volume model. Here, species enthalpies are calculated in parameterized instantiations of one generic enthalpy computation subroutine.

4.1.3 Modularity

This feature implies that a dynamic behavior in a model is realized by an assembly of interconnected modules, each of which performs specific operations. Modularity is pervasive in the model architecture. At any hierarchical level, a module is essentially a model that has been instantiated from a lower level library, as indicated in Fig. 4.2. Modularity is particularly useful in model organization and simplifies structural complexity. For instance, the only difference between a reactive and a non-reactive gas control volume model is that a reaction kinetics subsystem is replaced by a null-vector in the non-reactive volume, Fig. 4.2.
4.1.4 Uniform Bus Structure

In the higher level libraries the modules transmit data relating to mixed gas flows via a multi-element vector signal, wherein each element represents a different molecule type. Operations can be performed element-wise on an entire vector, or as shown in the enthalpy calculation in Fig. 4.2, a lower level module may break up the vector to perform a parameterized operation on each element individually. The content and signal sequence of the bus is maintained uniformly throughout the model to allow simple integration of various modules.
4.1.5 Resolution and Flexibility

Spatial resolution of simulation results can be conveniently increased by switching between lumped and discretized models at the component levels of the hierarchy, as indicated in Fig. 4.1. Discretized models consist of multiple interconnected instantiations of lumped models. The model architecture also allows flexibility of simulations by permitting easy switching between different versions of the same model. For instance, one could use a simplified version of a non-reactive control volume model where individual species mass balance equations are excluded, Fig. 4.1. Such flexibility can be useful when the reduction of computational load is of paramount importance.

4.1.6 Expedient Storage

The model hierarchy results in efficient model storage since model instantiations are stored as library links only. In addition, model management is facilitated by maintaining four distinct storage categories, namely,

- **Model libraries**, where the model hierarchy is stored,
- **Data Storage**, where parameter values, physical property data, etc. are stored in separate databases, each corresponding to specific component models,
- **Initialization scripts**, where conditions for initialization of the model are managed,
- **Test models**, where model compilation and simulations are carried out.

4.2 MATLAB® / Simulink®

MATLAB® / Simulink® provides a convenient way to implement the models and the model management structure described above. The approach, by design, incorporates several concepts of Object Oriented Programming, which can be implemented utilizing features available in the MATLAB® / Simulink® modeling environment. In particular, user-created
libraries and subsystems lend themselves to the hierarchical library approach. MATLAB® m-files are used to store parameters and initialization scripts separate from the models. The graphical Simulink® interface allows component subsystems to be assembled into full systems in an intuitive way, that is simple to rearrange without disturbing the rest of the model.

The environment is also versatile as it allows embedding programs written in other languages such as C, C++, FORTRAN, etc. into Simulink® using S-functions. Additionally, a system model can be compiled and run with constant time steps on a real-time processor to provide a simulation that interfaces with physical hardware components.
Chapter 5

System Characteristics and Performance

5.1 Fuel Utilization

Fuel utilization, $U$, is a commonly referenced parameter when characterizing the performance of SOFC systems. It represents how completely the system uses all the fuel provided to it. In generic terms, utilization is the mass of fuel reacted in the cell divided by the mass of fuel input to the cell, [2]. Fuel utilization is a critical indicator of the performance of an SOFC system. On one hand, low fuel utilization implies inefficient performance and ineffective use of fuel. On the other hand very high fuel utilization leads to significant drop in cell voltage due to reduced hydrogen pressure and makes the anode susceptible to oxidation [20]. Typically, it is preferred to maintain $U$ within a range of 80% to 90% during the operation [18, 50]. The reason for this target range is discussed further in Section 5.2.

Fuel utilization has been formulated in various ways in the literature. In [51, 52], the authors express $U$ mathematically as a function of fuel enthalpy, Eq.(5.1).

$$U = 1 - \frac{\dot{m}_{f, out} \Delta h_{out}}{\dot{m}_{f, in} \Delta h_{in}}$$  \hspace{1cm} (5.1)

where, $\dot{m}_{f, in}$ and $\dot{m}_{f, out}$ are the anode inlet and exit fuel mass flow rates. In [20], two formulations are shown. The first formulation, based on current, is given by

$$U = \frac{i N_{cell}}{n F N_{in} \left(4 \chi_{1r} + \chi_{2r} + \chi_{4r}\right)}$$  \hspace{1cm} (5.2)
The second formulation incorporates the full dynamics, given by,

\[ U = 1 - \frac{\dot{N}_o (4x_{1o} + x_{2o} + x_{4o})}{\dot{N}_{in} (4x_{1r} + x_{2r} + x_{4r})} \]  

Equation (5.3) represents a more generalized expression from which Eq.(5.2) can be derived under steady-state conditions. The formulation in Eq.(5.1) can be reduced to Eq. (5.3) with certain assumptions regarding the specific heats and constituents of the fuel flow. In [53], the authors use a simplified version of Eq.(5.2). Among the three formulations given in Eqs.(5.1), (5.2), and (5.3), it is Eq.(5.3) that is chosen to serve in this analysis by virtue of its direct connection to the concept of fuel utilization and its incorporation of the dynamics of the system. The formulation in Eq.(5.3) is based on the steam reforming reactions in Eq.(3.41) where a single molecule of \( CH_4 \) can at most produce four \( H_2 \) molecules, \( CO \) can produce one \( H_2 \) molecule and \( H_2 \) is obviously already one \( H_2 \) molecule. In Eq.(5.3) \( \dot{N}_{in} (4x_{1r} + x_{2r} + x_{4r}) \) essentially represents the effective hydrogen flow rate into the anode and \( \dot{N}_o (4x_{1a} + x_{2a} + x_{4a}) \) represents the effective hydrogen flow rate out of the anode. Equation (5.3) is rewritten with the following coordinate transformation,

\[ \zeta_a = 4x_{1a} + x_{2a} + x_{4a} \] 
\[ \zeta_r = 4x_{1r} + x_{2r} + x_{4r} \]  

therefore,

\[ U = 1 - \frac{\dot{N}_o \zeta_a}{\dot{N}_{in} \zeta_r} \]  

From the species conservation of mass in the stack, Eq.(3.59), the states \( x_{1r}, x_{1a}, x_{2r}, \) \( x_{2a}, x_{4r} \) and \( x_{4a} \) can be combined and written in terms of \( \zeta_r \) and \( \zeta_a \) which yields,

\[ \dot{N}_a \zeta_a + \dot{N}_o \dot{\zeta_a} = \dot{N}_{in} \zeta_r - \dot{N}_o \zeta_a - \gamma_e \]  

The same is done with the species conservation of mass equations for the reformer. For the POX-planar configuration, the mass balance in the POX reformer are given by, Eq.(3.55). Two additional conditions are necessary, namely

1. All oxygen molecules are consumed in the POX reformer. Therefore,

\[ r_d = \frac{1}{1.0055} \dot{N}_f x_{7f} \]  

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2. There is no $CO$ or $H_2$ in the incoming fuel flow.

Both the above conditions can be justified as follows. The first condition is valid due to the choice of a specific range of $O2C$ ratios in the POX reformer that allow the reactions to be sustained. If $O2C$ ratios are large enough for $O_2$ to be left over, then the fuel would be completely consumed in total combustion rather than reformed by partial oxidation and steam reforming. Additionally the reformer would overheat causing physical damage to the system. The second condition is valid since we consider $CH_4$ as the fuel and a mixture of $CH_4$ and air are supplied to the POX reformer. Applying these conditions in conjunction with Eq.(3.55) leads to,

$$\dot{N}_r\zeta_a + N_r\dot{\zeta}_r = -\dot{N}_{in}\zeta_r + \dot{N}_f[4\chi_{1f} - 2\chi_{7f}]$$  \hspace{1cm} (5.8)

Recalling the definition of the $O2C$ ratio,

$$O2C = \frac{\chi_{7f}}{\chi_{1f}}$$  \hspace{1cm} (5.9)

and noting from Eq.(3.62) that $r_e = iN_{cell}/nF$, Eqs.(5.6) and (5.8) can be written in state-space form as follows:

$$\dot{Z} = A_1Z + B_1$$

$$Z = \begin{bmatrix} \zeta_r \\ \zeta_a \end{bmatrix}$$

$$A_1 = \begin{bmatrix} -(\dot{N}_{in} + \dot{N}_r)/N_r & 0 \\ \dot{N}_{in}/N_a & -(\dot{N}_o + \dot{N}_a)/N_a \end{bmatrix}$$  \hspace{1cm} (5.10)

$$B_1 = \begin{bmatrix} \dot{N}_f\chi_{1f}[2 - O2C]/N_r \\ iN_{cell}/2nFN_a \end{bmatrix}$$

The following expression for the steady-state utilization can be obtained by setting
$\dot{\zeta}_r = \dot{\zeta}_a = \dot{N}_r = \dot{N}_a = 0$ and combining Eqs.(5.10) and (5.5)

$$U_{ss} = \frac{iN_{\text{cell}}}{2nF\dot{N}_fX_1[2 - O2C]}$$ (5.11)

It is interesting to note that Eq.(5.11) contains only known constants and input parameters. It can therefore be used to exactly predict the steady-state fuel utilization for any set of input conditions.

A similar analysis has been performed for the SR-tubular configuration, [54]. Using the same definition for $U$ given in Eq.(5.3), and using the steam reformer and stack equations in Eqs.(3.42) and (3.59), the following state-space model is obtained:

$$\dot{Z} = A_2 Z + B_2$$

$$Z = \begin{bmatrix} \zeta_r \\ \zeta_a \end{bmatrix}$$

$$A_2 = \begin{bmatrix} -(\dot{N}_in + \dot{N}_r)/N_r & k\dot{N}_o/N_r \\ \dot{N}_in/N_a & -(\dot{N}_o + \dot{N}_a)/N_a \end{bmatrix}$$ (5.12)

$$B_2 = \begin{bmatrix} 4\dot{N}_f/N_r \\ -iN_{\text{cell}}/nFN_a \end{bmatrix}$$

By setting $\dot{\zeta}_r = \dot{\zeta}_a = \dot{N}_r = \dot{N}_a = 0$, the steady-state utilization calculated from Eqs.(5.12) and (5.5) is,

$$U_{ss} = \frac{1 - k}{(4nF\dot{N}_f/iN_{\text{cell}}) - k}$$ (5.13)

which, similar to Eq.(5.11), contains only known constants and input parameters and can be used to exactly predict the steady-state fuel utilization of the system giving any set of input conditions.

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5.2 Efficiency

There are multiple ways of defining and measuring efficiency of fuel cell systems. A common definition using the electric power, $iV$, and the lower heating value, $L_{HV}$, is shown in Eq.(5.14). Parasitics such as compressors or fuel pumps are not considered part of the system for this analysis.

$$E = \frac{iV_{fc}}{L_{HV}N_fX_{1f}}$$  \hspace{1cm} (5.14)

The efficiency can be re-written in terms of the steady-state utilization. For the SR-tubular configuration, Eq.(5.13) is substituted into Eq.(5.14) and most of the constants are condensed into $c_A$, which results in

$$E = c_A \frac{U_{ss}V_{fc}}{1 + (U_{ss} - 1)k}$$  \hspace{1cm} (5.15)

where,

$$c_A = \frac{4nF}{N_{cell}L_{HV}}$$  \hspace{1cm} (5.16)

Similarly for the POX-planar configuration, Eq.(5.11) is substituted into Eq.(5.14) and the constants are condensed into $c_B$, resulting in

$$E = c_B U_{ss}V_{fc}$$  \hspace{1cm} (5.17)

where,

$$c_B = \frac{2nF[2 - O2C]}{N_{cell}L_{HV}}$$  \hspace{1cm} (5.18)

The above equations indicate that for general SOFC systems, the efficiency $E$ can be expressed in a compact form using steady-state utilization, $U_{ss}$, and voltage, $V_{fc}$. Steady-state utilization combines the effects of fuel cell current, $i$, and fuel flow rate, $N_f$, allowing efficiency as defined in Eq.(5.14) to be expressed with fewer independent variables.

Using the measured voltage of the fuel cell, it can be determined what utilization will produce the highest efficiency. Isothermal data from simulations shown in Figs. 5.1 and 5.2 indicates that the highest efficiency occurs when utilization is in the range of 90% to 95%. The efficiencies shown in the figures are calculated using Eqs.(5.15) and (5.17) with
the constant scaling factors $c_A$ and $c_B$ arbitrarily set equal to one. The actual efficiency values are not given in the figure since the actual factors would scale the efficiency up or down, but they will not affect location of the peak relative to the utilization.

![Figure 5.1: Isothermal Data showing Efficiency Peak at high Utilization for SR-tubular](image)

As mentioned in section 5.1, target utilizations are typically set at 80% to 90% which is slightly below the optimum range indicated by Figs. 5.1 and 5.2. The reason that this lower range is chosen is because during transients the utilization, $U$, tends to deviate from its steady-state value by varying margins depending on the severity of the transients. If these departures cause severe hydrogen starvation in the anode, meaning $U \approx 100\%$, physically detrimental effects result and can progressively decay the fuel cell decreasing its longevity. Therefore, by setting the target utilization values slightly below the optimal efficiency range, the risk of frequent hydrogen starvation is reduced.
Figure 5.2: Isothermal Data showing Efficiency Peak at high Utilization for POX-planar

5.3 A Generalized Analytical Approach

As mentioned earlier, fuel utilization is a critical variable that has a close bearing on cell voltage and fuel cell efficiency in SOFC systems. A typical range of 80% to 90% utilization is a favorable operating range for most SOFC systems. In Eqs.(5.11) and (5.13), closed-form algebraic expressions have been developed that relate $U_{ss}$ with the system inputs through a model-based analysis, for two different configurations of SOFC systems. A particularly interesting observation is that these relationships are independent of the rates of reforming reactions. This is advantageous as internal reaction rates are difficult to measure or predict. Furthermore, the relations are also independent of internal flow rates, species concentrations and temperatures. The above observation shows an invariance property of SOFC systems and can be incorporated into fuel utilization control schemes with reduced sensor requirements.

In this section, the generalization of the utilization for different SOFC system configurations is pursued. The approach will provide a common method for formulating fuel
utilization and deriving analytical expression with limited knowledge of the system. For a steam reformer based SOFC with methane as fuel and the reforming reactions given in Eqs.(3.41), from Eq.(5.3), $U$ can be expressed as

$$ U = 1 - \frac{\dot{N}_a P^T X_a}{\dot{N}_i n P^T X_r} \quad (5.19) $$

where,

$$ X_a ^T = [X_1 a, X_2 a, X_3 a, X_4 a, X_5 a] $$

$$ X_r ^T = [X_1 r, X_2 r, X_3 r, X_4 r, X_5 r] \quad (5.20) $$

$$ P^T = [4 \, 1 \, 0 \, 1 \, 0] $$

The invariance property of $U_{ss}$ can be deduced from the entries of the vector $P$. In this specific case, $P$ satisfies the following orthogonality property given below

$$ P^T M R = 0, \quad M = \begin{bmatrix} -1 & -1 & 0 \\ 1 & 0 & -1 \\ 0 & 1 & 1 \\ 3 & 4 & 1 \\ -1 & -2 & -1 \end{bmatrix}, \quad R = \begin{bmatrix} r_a \\ r_b \\ r_c \end{bmatrix} \quad (5.21) $$

where, $R$ is the vector of reaction rates and the columns of $M$ consist of the coefficients of species appearing in the reforming reactions in Eq.(3.41). Note that $P$ lies in the null-space of $M$, i.e. irrespective of the reaction rates in $R,$

$$ P^T M = 0 \quad (5.22) $$

The above orthogonality property of $P$ is necessary for invariance of $U_{ss}$ with respect to reaction rates. Generalization of the above property will involve developing a formal approach to constructing $P$ while maintaining the definition of $U$. One approach is as follows,

**Remark 1** The entries of vector $P$ that is used to define fuel utilization in SOFC systems, as given in Eq.(5.19),

- must be integer valued and positive,
must be representative of maximum potential hydrogen generation from fuel species using the internal reforming reaction scheme of the SOFC stack, and

must satisfy the orthogonality property of Eq.(5.22).

With the above approach, we first identify the combustible species (fuel) to be $CH_4$, $CO$ and $H_2$. Then, based on Eq.(3.41), one can infer that the maximum hydrogen produced from a molecule of $CH_4$, $CO$ and $H_2$ are four, one, and one molecules respectively. Hence, $P^T = [4 \ 1 \ 0 \ 1 \ 0]$. The entries are integer valued and positive and therefore suffices to be used a valid $P$ vector.

To verify the generality of this approach, we consider the following combination of species as fuels and derive their corresponding $P$ vectors:

\[
\begin{align*}
[CH_4 \ CO \ H_2] & \rightarrow P^T = [4 \ 1 \ 0 \ 1 \ 0] \\
[CH_4 \ CO_2 \ H_2] & \rightarrow P^T = [3 \ 0 \ -1 \ 1 \ 0] \\
[CO \ CO_2 \ H_2] & \rightarrow P^T = [0 \ -3 \ -4 \ 1 \ 0] \\
[CH_4 \ H_2 \ H_2O] & \rightarrow P^T = [2 \ 0 \ 0 \ 1 \ 1]
\end{align*}
\]

It can be verified that for all combinations shown in Eq.(5.23), the respective $P$ vectors satisfy Eq.(5.22). However, based on Remark 1, only $[CH_4 \ CO \ H_2]$ represents a valid combination. Others violate the fuel species condition and/or the positive integer value condition of Remark 1.

Let us verify this approach for the POX reformer based planar SOFC system described in chapter 3. Here, the reaction schemes for the fuel cell and the POX reformer are different from the steam reformer based SOFC system, discussed above. While the reaction scheme of the SOFC stack remains the same and is given by Eq.(3.41), i.e.

\[
\begin{align*}
(I) \quad CH_4 + H_2O & \leftrightarrow CO + 3H_2 \\
(II) \quad CO + H_2O & \leftrightarrow CO_2 + H_2 \\
(III) \quad CH_4 + 2H_2O & \leftrightarrow CO_2 + 4H_2
\end{align*}
\]

(5.24)
the POX reformer reaction scheme is given by

\[
\begin{align*}
(I) & \quad CH_4 + H_2O \leftrightarrow CO + 3H_2 \\
(IV) & \quad CH_4 + 1.0055O_2 \rightarrow 0.85CO + 0.15CO_2 + 1.139H_2 + 0.861H_2O
\end{align*}
\]

Note that for POX reforming, the steady-state rate of combustion reaction (IV) can be determined from the reformer’s mass-balance equations in Eq.(3.55). The rate expression is given in Eq.(5.7). Hence, the unknown reactions are (I), (II) and (III) in Eqs.(5.24) and (5.25). The combustible species (fuel) are \(CH_4\), \(CO\) and \(H_2\). From the stack internal reforming scheme in Eq.(5.24), it can be verified that \(P^T = [4 \ 1 \ 0 \ 0]\) satisfies all conditions of Remark 1. Furthermore, Eq.(5.22) is satisfied for both stack and POX reaction schemes in Eqs.(5.24) and (5.25) respectively. It is noted that for the stack,

\[
M = \begin{bmatrix}
-1 & -1 & 0 \\
1 & 0 & -1 \\
0 & 1 & 1 \\
3 & 4 & 1 \\
-1 & -2 & -1
\end{bmatrix}
\]

while for the POX reformer,

\[
M^T = [-1 \ 1 \ 0 \ 3 \ -1].
\]

Now the following remark is made:

**Remark 2** Given that a vector \(P\) exists that defines fuel utilization in an SOFC system using Eq.(5.19) and satisfies all conditions of Remark 1, then a closed-form expression of steady-state fuel utilization \(U_{ss}\) can be derived without the knowledge of the internal reforming reaction scheme of the stack, the corresponding reaction rates, the internal flow rates \(\dot{N}_{in}\) and \(\dot{N}_{o}\), intermediate species concentrations and temperatures. The resulting closed-form expression relates the steady-state fuel flow, current drawn and the fuel utilization.
Instead of providing a proof of the above remark, which is a subject of future research, the above observation is verified for the two SOFC configurations considered in this work.

**SR-tubular Configuration:** From the orthogonality property of \( P^T = [4 \ 1 \ 0 \ 1 \ 0] \), the definition of \( X_a \) and \( X_r \) in Eq.(5.20), and the definition of \( \dot{N}_{in} \) and \( \dot{N}_o \), we deduce that at steady-state, mass balance in the SOFC stack yields

\[
\dot{N}_{in} P^T X_r - \dot{N}_o P^T X_a = r_e = \frac{iN_{cell}}{nF} \quad (5.28)
\]

Similarly, steady-state mass balance in the reformer yields

\[
k \dot{N}_o P^T X_a - \dot{N}_{in} P^T X_r + 4 \dot{N}_f = 0 \quad (5.29)
\]

The above equations are written by considering that \( \dot{N}_{in} P^T X_r \) and \( \dot{N}_o P^T X_a \) represent an effective hydrogen content in the inlet and exit anode flows of the stack and by incorporating the effect of recirculation in the steam reformer based SOFC, Fig. 2.1(a). The equations are essentially steady-state hydrogen balance equations in the stack and the reformer. From Eqs.(5.19), (5.28) and (5.29), it can readily shown that

\[
U_{ss} = 1 - \frac{\dot{N}_o P^T X_a}{\dot{N}_{in} P^T X_r} = \frac{1 - k}{(4nF \dot{N}_f / iN_{cell}) - k} \quad (5.30)
\]

The validity of Eqs.(5.28) and (5.29) can be verified using Eqs.(5.20), (3.42) and (3.59). And the result in Eq.(5.30) matches that in Eq.(5.13).

**POX-planar Configuration:** As discussed earlier in this section, for this configuration \( P^T = [4 \ 1 \ 0 \ 1 \ 0] \) is valid. The steady-state hydrogen balance equation remains the same as in Eq.(5.28). Noting that there is no recirculation in the POX reformer based SOFC system, Fig.2.1(b), considering the oxidation reaction (IV) in Eq.(5.25), using Eq.(5.7), and the definition of \( O2C \) ratio in Eq.(5.9), the corresponding mass balance equation for
the POX reformer is

\[ \dot{N}_{in} P^T X_r = 4 \dot{N}_f \chi_{1f} - 2.011 r_d \]

\[ \Rightarrow \dot{N}_{in} P^T X_r = 4 \dot{N}_f \chi_{1f} - 2 \dot{N}_f \chi_{7f} = 2 \dot{N}_f \chi_{1f} (2 - O2C) \] (5.31)

From Eqs.(5.28) and (5.31), we get

\[ U_{ss} = 1 - \frac{\dot{N}_o P^T X_a}{\dot{N}_{in} P^T X_r} \bigg|_{ss} = \frac{i N_{cell}}{2 n F N_f \chi_{1f} (2 - O2C)} \] (5.32)

This result matches that found in Eq.(5.11).

Thus, the two different SOFC configurations considered in this work show a common invariance property of \( U \) under steady-state condition. Both systems, in spite of being nonlinear in nature, yield simple closed form relations between steady-state fuel utilization \( U_{ss} \) and the system inputs \( i \) and \( \dot{N}_f \). The approach outlined in this section provides a means for carrying out a generalized means for extracting these relationships. The resulting equations not only serve as predicting tools but can be incorporated into control designs for SOFC systems. The approach could potentially be extended to a wider variety of SOFC systems comprising of other reforming methods and more complex fuels such as diesel, JP8, etc.
Chapter 6

Simulation Results and Discussion

The POX-planar configuration, shown in Fig. 2.1(b), was modeled as described in Chapters 3 and 4. Simulations were performed to verify that the trends of the phenomena match with what is expected. Data gathered from those simulations is presented here. For more details on the system parameters used see the tables in the Appendix. Note that the parameter values used are reasonable estimations but are not calibrated to match a particular real system, so the results here are primarily qualitative.

Figure 6.1: Isothermal Polarization Curves for POX-planar
Polarization curves were generated from the model and are shown in Fig. 6.1, which demonstrate the major sources of loss in the fuel cell. The primarily linear trend corresponds to the ohmic loss, \( V_{\text{ohm}} \). For higher current demands the voltage drops off more sharply as the concentration loss, \( V_{\text{conc}} \), becomes more prominent. At higher temperatures the potential also decreases due to increases in both the concentration and activation losses, \( V_{\text{conc}} \) and \( V_{\text{act}} \). See Eqs.(3.66), (3.72), (3.73), and (3.74). Along with the voltage loss, power is also often presented as a function of current density as shown in Fig. 6.2. Figures like these are commonly given to characterize and compare various fuel cell systems. [4] gives sample curves that closely match the trends of Figs. 6.1 and 6.2.

Next, a set of open-loop simulation results are presented. For a constant incoming fuel flow (\( \dot{N}_f = 3.3 \times 10^{-3} \) mol/s, \( O2C = 0.5 \)) and air flow (\( \dot{N}_{\text{air}} = 50 \times 10^{-3} \) mol/s) the system was allowed to come to a steady state operating point with a current demand of 16.7 amps prior to the commencement of data collection at \( t = 0 \). The system is then subjected to step changes in the current demand as shown in Fig. 6.3. After every 200 seconds the
current is either increased or decreased instantaneously. At 200 seconds it is increased 0.5 amps to 17.2 amps, then at 400 seconds decreased by 1.2 amps to 16 amps. After this, it is increased at 600, 800, and 1000 seconds by 0.2, 0.3, and 0.4 amps respectively. Finally at 1200 seconds the current is reduced 0.2 amps to return to the original 16.7 amps.

The planar SOFC stack modeled contains 30 cells electrically connected in series. The voltage output of the entire stack is shown in Fig. 6.4. The voltage changes inversely to the current demand. The response initially occurs quickly, then dramatically slows down. For most of the steps, the voltage does not reach a steady state before the next jump in the current demand occurs. Because the incoming fuel rate remains constant, the total power from the stack should remain constant, but the lag in voltage response causes some fluctuation. Figure 6.5 shows the power output from the stack. Power is calculated by \( P = iV \). When the current changes instantaneously it causes a spike in the power, the voltage then responds fairly quickly to bring power back toward its steady state value, but the slow secondary response of the voltage prevents the power from leveling out completely.
Figure 6.4: Stack Voltage Response

Figure 6.5: Stack Power Output
The faster change in the voltage results from the reaction rate of the electrochemical reaction responding to the increased current demand. Figure 6.6 shows the molar flow rates of each species leaving the anode. When more current is demanded the amount of \( \text{H}_2 \) leaving the anode decreases because more is being consumed by the electrochemical reaction to produce current. Similarly the amount of \( \text{H}_2\text{O} \) increases as a product of that reaction. \( \text{N}_2 \) is non-reactive, so its flow rate does not change other than some small fluctuations due to pressure dynamics. There is no \( \text{O}_2 \) leaving the anode, because it was all consumed in the POX reformer before even entering the anode. \( \text{CH}_4 \) is also at negligible levels, having been reduced in the reformer and by steam reforming reactions in the anode. The additional heat and steam in the anode from the increased electrochemical reaction causes the rate of steam reforming to increase, particularly reaction (II) in Eq.(3.41) which consumes \( \text{CO} \) and produces \( \text{CO}_2 \). When the current demand decreases the opposite trends are observed; the flow rates of \( \text{H}_2 \) and \( \text{CO} \) increase while \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) flow rates decrease.

The slower response of the voltage can be correlated to how the temperature changes
in the stack, Fig. 6.7. The temperature of the stack inversely affects the voltage output by significantly increasing the loss factors, $\psi_{act}$ and $\psi_{conc}$ in Eq.(3.66). The anode temperature is the hottest because of the exothermic electrochemical reaction occurring there. When the reaction rates speed up to accommodate an increased current demand, then the heat generated also increases. The heat is conducted through the electrolyte to the cathode. The cathode air, despite being preheated by the combustor, is cooler than the rest of the stack, and actually serves to cool the stack. In a closed-loop simulation the air flow rate, $\dot{N}_{air}$, may be controlled to maintain a more constant temperature. The speed of the temperature transients, however, is extremely slow compared to the other dynamics in the system. As can be seen in Fig. 6.7, the temperatures are still transitioning from the previous step in current when the next one occurs 200 seconds later.

Unlike the slow temperature dynamics, the pressure dynamics are almost instantaneous. The pressure, being based on the ideal gas law, Eq.(3.23), is dependent on the temperature and the number of moles in the control volume. Looking at the pressure in the anode,
shown in Fig. 6.8, the visible transients follow those of the reaction rates and temperature. On this scale, the actual dynamics due to pressure are small quick spikes that occur too quickly to be accurately quantified by the data resolution collected in this simulation. Data was only recorded after every 0.25 seconds of simulation in order to reduce computation time. Figure 6.9 shows the pressures recorded at different points along the flow path of the fuel through the POX reformer, anode, and combustor.

The upstream components exhibit higher pressures than the downstream components. Within a component, the upstream elements of the discretized models also exhibit higher pressures than their downstream counterparts. The actual values for the pressure, however, may not be accurate. Without having data for a physical system to input into the parameter values, the volumes of various components may be disproportionate to each other causing larger pressure drops than would normally occur. Recall that pressure information propagates upstream through the model, so the outlet pressure of 1 atm serves as a reference point for the pressures.
The equipotential problem often encountered in discretized models was discussed in Section 3.3.2.5. The scheme developed there is applied to this model with $R_{cc} = 0.05 \ \Omega$. As can be seen in Fig. 6.10, the scheme successfully causes the voltages of each element to match. At the transients the greatest discrepancy between the two voltages occurs, but the relative error there is only 0.08%.

Another point of interest is the POX model which employs two elements. The first is 1mm in length, while the second is 9mm. As described in section 3.3.1.2, each element can have a different reaction scheme. In this case because oxygen is entering with the fuel, the first element is using the partial oxidation scheme. Since all the oxygen is consumed in the first element, the steam reforming scheme is applied in the second element. Figure 6.11 shows some of the species molar flow rates exiting each control volume in the reformer.

The fuel being supplied is $CH_4$ which is being consumed throughout the reformer, so its flow rate reduces from the first element to the second. Neither $CO$, $H_2$, nor $H_2O$ are being supplied to the reformer with the fuel, so the molar flow of each in the first element is the
Figure 6.10: Discretized Cell Voltage

Figure 6.11: Species Molar Flow Rate leaving POX Control Volumes
result of production in partial oxidation. In the second element steam reforming continues to produce more \( H_2 \) and \( CO \), but consumes \( H_2O \). Appropriately, the molar flows of \( H_2 \) and \( CO \) increase and that of \( H_2O \) decreases. The total amount of \( H_2 \) exiting the second element is almost double that of \( CO \). Further confirming the difference between the two regimes is the temperatures. The incoming fuel temperature is 500K. In the first element, POX reactions are exothermic and therefore greatly increase the temperature of the gas to over 1300K. The steam reforming reactions in the larger second element are endothermic, consuming heat and reducing the gas temperature to less than 1000K.

Finally, the performance parameter, fuel utilization, is calculated in the simulation using both the dynamic expression given in Eq.(5.3) and the steady-state predictive equation given in Eq.(5.11) These results are compared in Fig. 6.12. The dynamic utilization approaches the steady state value with a response time on the order of the chemical reaction rate response. The slow temperature dynamics do not appear to have a major affect the utilization transients. The results in Fig. 6.13 are from a simulation with the same current step as shown in Fig. 6.3, but the fuel flow rate, \( \dot{N}_f \), varies according to Eq.(5.11) with a prescribed steady state utilization, \( U_{ss} = 91\% \). In this case dynamic utilization stays fairly close to the steady state, not deviating with more than 0.5% relative error. This result can provide a starting point for future work in fuel cell control.
Figure 6.12: Dynamic Utilization Time Response

Figure 6.13: Dynamic Utilization with Modulated Fuel Flow Rate
Chapter 7

Conclusions and Future Work

This thesis set out to mathematically model a planar SOFC system with a POX reformer, building upon the tubular and steam reformer models previously developed in the HySES lab at RIT. The model as developed in chapter 3 was successfully implemented using the modeling management approaches outlined in Chapter 4. Results from simulations with this model are presented in Chapter 6. The results correlate with what is expected to occur in a fuel cell system. Due to the lack of published experimental data little more can be said of the correlations to the physical system. Two major improvements over the previous HySES models were developed and applied to both the new planar and POX models as well as the old tubular and SR models. The two features are the inclusion of pressure dynamics and solving the equipotential problem by redistributing the current demand. The hierarchical library system proved its worth by allowing simple retrofitting of models as the new schemes were being developed and tested.

Once the systems made physical and mathematical sense the simulation results could be analyzed. Three different dynamics are observed in the results: pressure, temperature, and chemical. The pressure dynamics are extremely fast, having only a slight transient effect on the order of tenths of seconds. Because of the speed of the pressure transients the length of the time steps used in the simulation had to be reduced in order to prevent errors in the numerical integration blocks. Shorter times steps increase the computational load, especially when attempting real-time simulation. Since the pressure effects occur on a much shorter time scale than other prominent transients, it may be possible to neglect them with minimal
error. Reverting to simpler constant pressure drop methods may prove advantageous for real-time simulations. The temperature dynamics, conversely, are extremely slow. To get an open-loop model anywhere close to being at steady-state in regards to temperature requires a simulation of more than thirty minutes of operation. Because of how long it takes the temperature to change significantly many analyses assume a constant temperature when dealing with only a few seconds of operation. The chemical dynamics take a few seconds to transition from one state to another. The transients in the molar flow rates evidence this as does the dynamic utilization. When the incoming fuel rate is modulated according to the steady state utilization equation, the deviation in the dynamic utilization is caused by two things, first is time for the new fuel flow to get through the reformer and into the anode, second is the time the reactions take to speed up once more fuel is available.

More detailed analysis of the transient behavior can be performed in future work from the HySES lab. At this point, quantifying all the results is futile due to the lack physical system data available. Many parameters in the model are simply best guesses, but without actual specifications or experimental data, they cannot be confirmed. When experimental data becomes available in the literature or an actual SOFC system can be purchased by the lab, the model should be thoroughly validated. Additional future work includes modifying bus structure the model to accommodate more species for dealing with larger hydrocarbons as fuel, and expanding the model library to include more components such as ATR reformers or compressors and turbines for combined SOFC-GT system modeling. The generalized approach to fuel utilization also needs further development to be proven and to become useful in a broader range of applications. Another exciting extension of this work that is already being put into practice in the HySES lab is the development of control strategies based on utilization. A model developed by this effort is being run on a real-time processor to operate as a virtual fuel cell and integrate with actual power electronics for studying hybrid control. Figures 7.1 and 7.2 show a schematic and photo of that system currently in place.
Figure 7.1: Hybrid Fuel Cell Control Schematic

Figure 7.2: Hybrid Fuel Cell Control Lab Setup
References


The following tables present the parameters used in the simulations which generated the results shown in Chapter 6. Additionally, gas species properties were calculated using formulas and coefficients given in [47] and [55].

Table 1: Planar Fuel Cell Geometry and Properties

<table>
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<th>Description</th>
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</thead>
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<td>[n/a]</td>
<td>$^a$</td>
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</tr>
<tr>
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<td>m$^2$</td>
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<tr>
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<td>m</td>
<td>[5]</td>
</tr>
<tr>
<td>Cathode Thickness</td>
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<td>m</td>
<td>[5]</td>
</tr>
<tr>
<td>Electrolyte Thickness</td>
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<td>m</td>
<td>[5]</td>
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<td>Interconnect Thickness</td>
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<td>[5]</td>
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<td>m$^3$</td>
<td>[20]</td>
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<tr>
<td>Cathode Volume</td>
<td>$2\times10^{-5}$</td>
<td>m$^3$</td>
<td>[20]</td>
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<tr>
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<td>$^b$</td>
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<td>[20]</td>
</tr>
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<td>[42]$^d$</td>
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$^a$ chosen arbitrarily
$^b$ tuned to match physical phenomena
$^c$ calculated from other geometry parameters
$^d$ value estimated from this reference
Table 2: POX Reformer Geometry and Properties

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<th>Description</th>
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<tr>
<td>Flow Constant</td>
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<td>c</td>
</tr>
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</tr>
<tr>
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a chosen arbitrarily  
b tuned to match physical phenomena  
c calculated from other geometry parameters  
d value estimated from this reference

Table 3: Combustor/Pre-heater Geometry and Properties

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<td>Pre-heated Air Volume</td>
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<td>m³</td>
<td>a, c</td>
</tr>
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<td>Combustion Flow Constant</td>
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<td>[n/a]</td>
<td>b</td>
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<tr>
<td>Pre-heated Air Flow Constant</td>
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<td>[n/a]</td>
<td>b</td>
</tr>
<tr>
<td>Combustion Convective Heat Transfer Coefficient</td>
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<td>W/(m²K)</td>
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<tr>
<td>Pre-heated Air Convective Heat Transfer Coefficient</td>
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<td>W/(m²K)</td>
<td>[47]d</td>
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a chosen arbitrarily  
b tuned to match physical phenomena  
c calculated from other geometry parameters  
d value estimated from this reference