Modeling of Solid Oxide Fuel Cell Performance with Coal Gasification

by

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Submitted to the Department of Mechanical Engineering
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Abstract

Growing concern over greenhouse gas emissions has driven research into clean coal power production alternatives. Novel coal power plant designs that lower CO₂ emissions are imperative in the coming decades to mitigate global temperature rise. High-efficiency stationary power systems that integrate coal gasification with solid oxide fuel cells (SOFCs) have been championed by the Department of Energy for the past couple of decades. However, many fundamental questions about this system still need to be addressed by modeling the complex coupling between SOFC’s and gasification. More specifically, work is needed to characterize SOFC performance with a range of syngas (H₂+CO) mixtures produced by coal gasification. This thesis used a multi-scale modeling approach to analyze SOFC performance with coal syngas at both the systems level and at the surface reaction scale.

The first investigation in this thesis couples an equilibrium gasifier model to a detailed 1D SOFC model to study the theoretical performance of the coupled system run on steam or carbon dioxide. The results of this study indicate that the system performs substantially better with steam gasification than with CO₂ gasification as a result of the faster electro-oxidation kinetics of H₂ relative to CO. The coupled system is then shown to reach higher current densities and efficiencies when the heat released by the fuel cell is sent to the gasifier instead of a bottoming cycle. 55-60% efficiency is then predicted for the system with heat transfer and steam gasification, making this technology competitive with other advanced system designs and almost twice as efficient as conventional coal-fired power plants.

The second study in this thesis investigates SOFC behavior with H₂ and CO (syngas) mixtures that come from coal gasification. SOFC models typically neglect CO electrochemistry in the presence of H₂ and H₂O, assuming that the water-gas-shift reaction proceeds faster than CO electro-oxidation. The results of this study show, however, that CO electro-oxidation cannot be neglected in syngas mixtures, particularly at high current densities for high CO-content syngas. First the simulations demonstrate that incoming CO is not all shifted to form H₂ by reforming reactions before reaching the electrochemical reaction sites. Furthermore, the results of this study confirm that direct electro-oxidation of CO contributes non-negligible current relative to H₂ at high anode overpotentials. Together these results show that CO electro-oxidation plays an important role in
SOFC performance not only via water-gas-shift reforming, but also via direct electro-oxidation when H$_2$ is also present. This work suggests that accurate models for both surface reforming and direct electro-oxidation of CO in SOFC anodes must be included in order to capture performance when using coal syngas mixtures.

Finally, a multi-step mechanism for the simultaneous electro-oxidation of H$_2$ and CO in SOFCs is implemented and studied. This mechanism combines a couple of reaction pathways: hydrogen (H) spillover to the electrolyte, and oxygen (O) spillover to hydrogen and CO on the anode. This mechanism is successfully verified in the model against a wide range of experimental data for mixtures of CO/CO$_2$, H$_2$/N$_2$, H$_2$/H$_2$O, H$_2$/CO, and H$_2$/CO$_2$. The simulations show that H spillover is the dominant source of current at low anode activation overpotentials, but also demonstrate that the currents produced by O spillover are non-negligible at high overpotentials. Furthermore, it is shown that the current produced by O spillover to CO is not limited by the rate of CO adsorption on nickel, which leads CO to contribute more to cell performance at high currents. Together these three modeling studies demonstrate how coal can be efficiently converted to electricity via gasification and the simultaneous electro-oxidation of H$_2$ and CO in a solid oxide fuel cell.

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To my three beautiful children: Nicholas, Benjamin and Evelyn. May you, your children and your grandchildren inherit a peaceful, sustainable world.

Love, Mom
Table of Contents

1 INTRODUCTION ................................................................. 15
  1.1 MOTIVATION ................................................................. 15
  1.2 THESIS OVERVIEW ..................................................... 19
  1.3 REFERENCES ............................................................... 21

2 LITERATURE REVIEW ....................................................... 23
  2.1 INTRODUCTION TO FB/SOFCs ........................................ 23
    2.1.1 Comparison of DCFC Types ..................................... 23
    2.1.2 SOFC Fundamentals .............................................. 28
    2.1.3 FB/SOFC Fundamentals ....................................... 31
  2.2 STATE-OF-THE-ART .................................................... 33
    2.2.1 FB/SOFC Models .................................................. 33
    2.2.2 FB/SOFC Experiments ......................................... 37
  2.3 OPERATIONAL CONSIDERATIONS ................................... 45
    2.3.1 Steam vs. Carbon Dioxide ....................................... 45
    2.3.2 Anode Recycle .................................................... 46
    2.3.3 Desulfurization .................................................. 47
  2.4 MODELING CONSIDERATIONS ....................................... 49
    2.4.1 Fluidized Bed Modeling .......................................... 49
    2.4.2 SOFC Modeling with H₂ and CO ................................ 51
  2.5 CONCLUSIONS ............................................................ 54
  2.6 REFERENCES ............................................................. 54

3 CARBON FUEL CELL SYSTEM OPTIMIZATION .......................... 63
  3.1 INTRODUCTION ........................................................... 63
  3.2 MODEL DESCRIPTION .................................................. 65
    3.2.1 CFC System Model ............................................... 66
    3.2.2 Gasifier Model .................................................... 73
    3.2.3 Fuel Cell Model ................................................... 74
  3.3 SIMULATION PROCEDURE ............................................. 81
List of Figures

Figure 1.1: Total U.S. carbon dioxide emissions by sector for 2008.......................... 16

Figure 1.2: Past and projected coal-fired electricity generation for 1990-2035 .................. 17

Figure 1.3: Efficiencies of several energy conversion systems for electrical power generation. 18

Figure 1.4: A schematic flow-chart illustrating the multi-scale structure of this thesis........ 20

Figure 2.1: Reversible efficiencies vs. temperature for the oxidation of H₂, CO, and solid graphitic carbon .................................................................................................................................................. 24

Figure 2.2: Molten carbonate direct carbon fuel cell schematic ........................................ 26

Figure 2.3: Schematic of a DCFC with an oxygen ion conducting ceramic electrolyte.......... 27

Figure 2.4: Solid oxide fuel cell (SOFC) schematic .............................................................. 29

Figure 2.5: Performance of a SOFC button cell for different H₂/H₂O mixtures (upper left), CO/CO₂ mixtures (upper right) and H₂/CO mixtures (bottom) .......................................................... 31

Figure 2.6: Schematic depiction of gas flows in a FB/SOFC system run on H₂O and CO₂..... 33

Figure 2.7: Schematic of a DCFC plant ................................................................................ 34

Figure 2.8: Flow-chart of packed carbon bed DCFC model ................................................. 36

Figure 2.9: Domain and dimensions for the 1D-DCFC model at Tsinghua University ........ 37

Figure 2.10: Indirect carbon fuel cell experimental set-up at Tsinghua University .............. 39

Figure 2.11: Experimental performance curves of Tsinghua’s SOFC button cell at 800°C .... 40

Figure 2.12: a) schematic of the two-compartment DCFC apparatus at Stanford; b) performance curves of the given fuel cell .............................................................................................................. 41
Figure 2.13: Cell voltage, efficiency and power density curves for a tubular SOFC run on gasified Alaskan coal char at 850°C ................................................................. 43

Figure 2.14: Performance curves at 850°C for a tubular SOFC directly coupled to a steam gasifier (with no catalyst) vs. the same cell run on H₂ ........................................................................ 44

Figure 2.15: Conceptual depiction of a FB/SOFC with CO₂ recycle and capture............................................. 47

Figure 2.16: Map of the different fluidized bed regimes based on increasing velocity......................... 50

Figure 3.1: Model drawings of the ICFC (A) and G+FC (B) systems ......................................................... 70

Figure 3.2: 1D MEA model discretization and species flows .............................................................. 76

Figure 3.3: Simulation procedure flow-chart to generate a polarization curve and performance data for the carbon fuel cell system model ................................................................. 82

Figure 3.4: Gasifier equilibrium output vs. temperature for H₂O recycle (B,D) and CO₂ recycle (A,C) from the anode to the gasifier ................................................................. 86

Figure 3.5: Fuel cell operating voltage and power density curves vs. temperature for the ICFC system with CO₂ recycle (A) and H₂O recycle (B). Maximum power densities for H₂O and CO₂ recycle are also compared vs. temperature (C)................................................................. 90

Figure 3.6: Fuel cell overpotentials as a function of current density for the ICFC system with CO₂ recycle (A,C) and H₂O recycle (B,D)........................................................................ 91

Figure 3.7: Operating voltage and efficiency curves of the gasifier, fuel cell and combined system for the G+FC (A,C) and ICFC (B,D) systems................................................................. 95

Figure 3.8: G+FC system (A,C) and ICFC system (B,D) efficiency curves for CO₂ recycle (A-B) and H₂O recycle (C-D) with T_{FC} = 800°C................................................................. 97

Figure 3.9: Exergy efficiency curves for the gasifier, fuel cell and combined system with a bottoming cycle ............................................................................................................. 99

Figure 4.1: Simulation procedure to generate a polarization curve for a given anode mixture. 120
Figure 4.2. Polarization curves for the fitted model compared to experimental data for H₂/H₂O mixtures in a SOFC at 800°C ................................................................. 126

Figure 4.3. Polarization curves for the fitted model compared to experimental data for CO/CO₂ mixtures in a SOFC at 800°C ........................................................................ 127

Figure 4.4: Polarization curves for the fitted model compared to experimental data for H₂/CO mixtures in a SOFC at 800°C. ....................................................................................... 128

Figure 4.5: Cell polarization curves for four syngas mixtures at 800°C. Model results with and without reforming and CO electro-oxidation are compared to experimental data...... 130

Figure 4.6: Gas-phase profiles of H₂ and CO throughout the anode for four syngas mixtures, with and without reforming ........................................................................................................ 132

Figure 4.7: Current densities from electro-oxidation of H₂ and CO versus anode activation overpotential for four syngas mixtures at 800°C .......................................................... 134

Figure 4.8: Percentage breakdown of the usage of incoming CO to the anode between direct oxidation (O), surface reforming (R) and anode exhaust (E) for four syngas mixtures at 800°C .................................................................................................................................................. 136

Figure 5.1: Depiction of the reaction steps at the TPB for the hydrogen spillover mechanism (A) and oxygen spillover mechanism (B) ........................................................................................................ 151

Figure 5.2: Simulation procedure to generate a polarization curve for a given fuel mixture.... 158

Figure 5.3: Comparison of polarization characteristics between model and data for mixtures of CO and CO₂ at 800°C and 1 atm ........................................................................................................ 164

Figure 5.4: Comparison of polarization characteristics between model and data for mixtures of H₂+N₂ (A) and H₂+H₂O (B) at 800°C and 1 atm .......................................................... 167

Figure 5.5: Comparison of polarization characteristics between model and data for mixtures of H₂+CO₂ (A) and H₂+CO (B) at 800°C and 1 atm ........................................................................... 169
Figure 5.6: Sensitivity analysis of model fitting parameters for the case of 43% H$_2$ + 57% N$_2$ at 800°C and 1 atm

Figure 5.7: Current densities of the H spillover and O spillover pathways as a function of activation anode overpotential for an anode fuel mixture of 20% H$_2$ and 80% N$_2$

Figure 5.8: Modeled polarization curves alongside experimental data for an anode fuel mixture of 20% H$_2$ and 80% N$_2$

Figure 5.9: Modeled TPB coverages for an anode fuel mixture of 20% H$_2$ and 80% N$_2$

Figure 5.10: Current densities of the H spillover and O spillover pathways as a function of activation anode overpotential for an anode fuel mixture of 20% H$_2$ and 80% CO

Figure 5.11: Modeled polarization curves alongside experimental data for an anode fuel mixture of 20% H$_2$ and 80% CO

Figure 5.12: Modeled TPB coverages for an anode fuel mixture of 20% H$_2$ and 80% CO

Figure 6.1: A schematic diagram summarizing the contributions of this thesis by chapter.
List of Tables

Table 1.1: Estimated cost and performance comparison for pulverized coal (PC), integrated gasification combined cycle (IGCC), and integrated gasifier fuel cell (IGFC) plants... 18

Table 2.1: Main types of direct carbon fuel cells (DCFCs)................................. 25

Table 2.2: Summary of studies published on FB/SOFCs. ........................................ 44

Table 2.3: Syngas compositions of typical entrained-flow coal gasifiers ...................... 48

Table 3.1: Classification of Carbon Fuel Cell systems with different levels of coupling. .... 66

Table 3.2: Constant operational and structural parameters for the SOFC. ..................... 84

Table 4.1: Coverages of hydrogen and carbon monoxide on nickel at the TPB at open-circuit conditions for several syngas mixtures.................................................. 119

Table 4.2: Constant operational and structural parameters for the SOFC model. ............. 123

Table 4.3: Parameters obtained by fitting the model to porous anode experimental data. .... 124

Table 5.1: Kinetic constants and parameters for the charge-transfer steps of both spillover pathways ........................................................................................................ 154

Table 5.2: Constant operational and structural parameters for the SOFC model............. 161
Chapter 1
Introduction

Novel coal power plant designs with lower CO₂ emissions are imperative in the coming decades to mitigate global temperature rise. High-efficiency stationary power systems that integrate coal gasification with solid oxide fuel cells (SOFCs) have been championed by the Department of Energy for the past couple of decades [1]–[3]. However, many fundamental questions about this system still need to be addressed by modeling the complex coupling between SOFC’s and gasification. A higher-level modeling analysis that scopes out the efficiency and power output for the combined gasifier and fuel cell system is needed. In addition, work is needed to characterize SOFC performance with a range of syngas (H₂+CO) mixtures produced by coal gasification [4]. Understanding the parallel electro-oxidation pathways of H₂ and CO in a SOFC is fundamental to predicting power system performance. This chapter first provides motivation for coupling coal gasification with SOFCs, and then outlines how this thesis addresses the modeling challenges of this system.

1.1 Motivation

As world population grows and nations develop, the demand for energy accelerates. The current infrastructure is heavily reliant on fossil-based fuels, which contribute to pollution and global warming. Coal-fired power plants, in particular, are responsible for a large share of the carbon dioxide emitted, as shown in Figure 1.1. In fact, coal power plants are responsible for almost one third of U.S. CO₂ emissions, which is greater than the CO₂ emitted by the entire ground
transportation sector [5]. New technologies and policies are therefore needed to mitigate CO₂ emissions from coal-fired power plants in order to protect the environment.

![Pie chart showing total U.S. carbon dioxide emissions by sector for 2008 [5].](image)

Figure 1.1: Total U.S. carbon dioxide emissions by sector for 2008 [5].

Although there are many proponents who advise abandoning fossil fuels and replacing them with renewable sources like wind and solar, the technology and infrastructure are not prepared to make this transition rapidly. Fossil fuels are projected to play a major role in the global energy mix for the coming decades, particularly in industrializing nations like China and India where energy demand is booming. Even with new energy policies in place, the IEA projects a global rise in coal-fired generation over the next few decades, as shown in Figure 1.2. Therefore, innovations that allow coal to produce power with fewer CO₂ emissions are imperative as the world transitions away from the current fossil fuel infrastructure over the next few decades.
Carbon dioxide emissions from coal power plants can be lowered by raising system efficiency in addition to sequestering excess CO₂. Figure 1.3 compares the efficiencies of the state-of-the-art fossil power generation technologies as a function of power output. This plot demonstrates that fuel cell hybrid systems have the greatest potential for high efficiency stationary power production. The combination of a high-temperature solid oxide fuel cell (SOFC) with a gas turbine bottoming cycle can reach 60-70% efficiency, a remarkable value that is only achievable because fuel cells are direct energy converters. Fuel cell systems can also facilitate sequestration because the CO₂ leaving the fuel cell is already separated from the oxidant stream, which is not the case for coal combustion.
Recent scoping studies on advanced coal power plants have also shown favorable efficiency and cost metrics for systems with fuel cells, as shown in Table 1.1. The results of four different studies are compared here for a traditional pulverized coal (PC) plant, an integrated gasification combined cycle (IGCC) plant, and an integrated gasifier + fuel cell (IGFC) plant run at both atmospheric and pressurized conditions. These studies consistently predict that IGFC plants will have substantially higher efficiencies and lower capital and operational costs than PC or IGCC plants. There is therefore a financial incentive to pursue fuel cell integration into coal-fired power generation in addition to the previously mentioned benefit of lowering CO₂ emissions.

Table 1.1: Estimated cost and performance comparison for pulverized coal (PC), integrated gasification combined cycle (IGCC), and integrated gasifier fuel cell (IGFC) plants [3].
1.2 Thesis Overview

Integrating gasifiers and SOFC stacks into coal-fired power plants has the potential to substantially lower global CO₂ emissions by raising plant efficiency. However, before this technology can be adopted, a better understanding of the fundamental characteristics of system coupling and performance is needed. This thesis addresses this requirement by building on an existing 1D SOFC model that can handle both H₂ and CO reforming and electro-oxidation [7]. Although this work is purely computational, results are repeatedly verified against a landmark experimental paper with extensive data for porous anode SOFCs [8].

The over-arching goal of this thesis is to model the performance of a SOFC with coal syngas. In order to accomplish this goal, this thesis takes a multi-scale modeling approach, as depicted in Figure 1.4. Chapters 2-3 analyze the system-level coupling of a gasifier and fuel cell, while Chapters 4-5 model the detailed transport and electro-chemistry within the fuel cell.
Chapter 2 gives a literature review of the modeling and experimental aspects of coupling a gasifier to a fuel cell. This chapter focuses on a closely coupled design, called the fluidized bed/SOFC, which integrates the gasifier directly into the fuel cell compartment. Chapter 3, in comparison, analyzes a less coupled variation of this system, called the indirect carbon fuel cell. In this chapter,
an equilibrium gasifier model is coupled to the 1D SOFC model to determine what efficiencies and power densities can be expected under different operating conditions. Chapter 4 then focuses on the SOFC model when different syngas mixtures are sent from the gasifier to the anode. This chapter uses detailed reforming and electro-oxidation models to determine how much power is coming from CO relative to hydrogen. Finally, Chapter 5 focuses on the interface of the SOFC anode and electrolyte, where most of the electrochemical reactions occur. Specifically, this chapter implements a detailed electrochemical mechanism and studies which reaction pathways produce current under different conditions. Together these four chapters characterize the performance of a SOFC coupled to a coal gasifier and provide insight into how coal is ultimately converted to power in this advanced system.

1.3 References


Chapter 2
Literature Review

Growing concern over greenhouse gas emissions has driven research into clean coal power production alternatives. Direct carbon fuel cell (DCFC) systems are a promising technology capable of highly efficient power production from coal, releasing a pure CO₂ stream ready for capture and sequestration [1]. However, conventional DCFC systems either use highly corrosive molten materials, or achieve low power densities because of the sluggish carbon and CO oxidation kinetics. One promising DCFC design that has been explored for the last couple of decades is the fluidized bed/solid oxide fuel cell (FB/SOFC) system. This particular design forgoes molten materials and sluggish carbon oxidation kinetics by coupling gasification to a ceramic fuel cell run on gaseous fuels. First, this chapter introduces DCFCs and provides some background on the components and coupling in the FB/SOFC system. Next, the state-of-the-art in modeling and experiments for the FB/SOFC design is presented. Finally, a survey of both the operational and the modeling challenges associated with the FB/SOFC system is given.

2.1 Introduction to FB/SOFCs

2.1.1 Comparison of DCFC Types

A direct carbon fuel cell (DCFC) is a device that generates electricity through the direct electrochemical oxidation of solid carbon. A direct carbon fuel cell (DCFC) has a single process chamber for solid fuel conversion contacting the anode. The advantage of this design over indirect CFC’s is that having a single chamber minimizes process steps and thermally couples the fuel cell to the gasifier, increasing the maximum power output of the system [2]. From a thermodynamic
standpoint, direct carbon conversion on the anode attains higher reversible efficiencies than is possible for fuel cells run on gaseous fuels, as shown in Figure 2.1. Therefore, there is a strong incentive to pursue DCFCs to raise the efficiency of fossil fuel power production systems.

Figure 2.1: Reversible efficiencies vs. temperature for the oxidation of H₂, CO, and solid graphitic carbon: \( \varepsilon_{rev} = \frac{\Delta G}{\Delta H} = -n_eFE_{rev}/\Delta H^0 \), reproduced from [3].

Table 2.1 depicts the different types of DCFCs under development, which can be classified into three categories based on electrolyte: molten hydroxide, molten carbonate and solid oxygen ion conducting ceramic. The solid ceramic category can be further sub-categorized based on fuel/anode design: fluidized bed, molten metal, and molten salt. The only DCFC design that does not use molten material in the electrolyte or anode is the solid oxygen ion ceramic electrolyte coupled to the fluidized bed anode.
Table 2.1: Main types of direct carbon fuel cells (DCFCs), reproduced from [4].

<table>
<thead>
<tr>
<th>Fuel/Anode</th>
<th>Electrolyte</th>
<th>Cathode</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid graphite rod as fuel &amp; anode</td>
<td>Molten hydroxides</td>
<td>Air as oxidant</td>
<td>500-600</td>
</tr>
<tr>
<td>Carbon particles as fuel in MC &amp; anode</td>
<td>Molten carbonates</td>
<td>Air as oxidant</td>
<td>800</td>
</tr>
<tr>
<td>Carbon particles in a fluidized bed</td>
<td>Oxygen ion conducting ceramic</td>
<td>Air as oxidant</td>
<td>700-900</td>
</tr>
<tr>
<td>Molten tin + carbon</td>
<td>Oxygen ion conducting ceramic</td>
<td>Air as oxidant</td>
<td>700-900</td>
</tr>
<tr>
<td>Molten salt + carbon particles</td>
<td>Oxygen ion conducting ceramic</td>
<td>Air as oxidant</td>
<td>700-900</td>
</tr>
</tbody>
</table>

Molten hydroxide DCFCs consist of solid carbon immersed in a molten hydroxide electrolyte, as shown in Figure 2.2. In this configuration, the solid carbon acts as a consumable anode, and CO₂ bubbles are released as a gas through the molten electrolyte. This type of cell was first implemented by William Jacques in 1896 [5], and later studied by Scientific Applications and Research Associates [6]. The fundamental challenge facing molten hydroxide electrolytes is corrosion via electrochemical formation of carbonates [7]. In addition, the power densities of current molten hydroxide DCFC prototypes are too low to be commercially viable. Molten carbonate DCFCs can either utilize a carbon rod [8] or dispersed carbon particles [9] as the anode in molten carbonate. Experiments have been done to enhance fuel surface groups to promote carbon conversion [6],[7], but a low power density of 100 mW cm⁻² has been obtained in repeated tests [12]. Corrosion of the metal bipolar plates also limits cell life-time, and as a result, there is little commercial interest in further developing molten carbonate technology at this stage.
Figure 2.2: Molten carbonate direct carbon fuel cell schematic [13]. The electrochemical reaction sites (ers) occur at the interface of the molten electrolyte, solid carbon, and CO₂ gas phases.

The third type of DCFC utilizes an oxygen ion conducting ceramic electrolyte, such as the YSZ conventionally used in a solid oxide fuel cell (SOFC). This DCFC design, shown in Figure 2.3, has an anode chamber filled with carbon particles dispersed in a gaseous medium, molten metal, or molten salt. The molten metal and salt designs are implemented to enhance the anode’s electrical conductivity and contact area with the carbon fuel to promote faster conversion. However, the molten material corrodes the fuel cell electrolyte with time, and as a result, low power densities and efficiencies have been reported [14],[15]. In the fluidized bed design, fuel can either oxidize directly at the anode or indirectly react with a gaseous fuel that is then oxidized.
at the anode. The direct oxidation approach requires solid-to-solid contact between the fuel and electrolyte at the triple phase boundary (TPB). Direct oxidation has been reported by pressing a consumable carbon anode against the electrolyte [16],[17], and also by pyrolytic decomposition of a hydrocarbon fuel such as methane [18]–[20]. However, the consumable anode design only obtained a power density of 20 mW cm\(^{-2}\), and the pyrolytic decomposition method has the disadvantage of requiring intermittent charging.

![Schematic of a DCFC with an oxygen ion conducting ceramic electrolyte](image)

**Figure 2.3:** Schematic of a DCFC with an oxygen ion conducting ceramic electrolyte [13].

Formation and oxidation of CO is likely the favored mechanism over direct oxidation of carbon in ceramic electrolyte DCFCs due to faster reaction kinetics and relative ease of travel for gas [21]. Therefore, the most commonly reported mode of oxidizing carbon in a ceramic electrolyte DCFC is to use a packed or fluidized bed a short distance from the anode [22], [23]. Thus, carbon is
oxidized indirectly in the SOFC by converting the carbon to a synthesis gas (CO + H₂) that is then electrochemically oxidized at the anode. Although the carbon fuel is oxidized indirectly, this design is still considered a direct CFC due to the close proximity of the gasifier and fuel cell, which leads to both thermal and gas phase coupling. This particular DCFC design that couples a fluidized bed (FB) gasifier to a high-temperature SOFC is called a FB/SOFC here for short. The FB/SOFC is selected here over the alternative DCFC designs due to reportedly higher power densities and less potential for corrosion.

2.1.2 SOFC Fundamentals

Solid oxide fuel cells (SOFCs) are typically selected over other fuel cell types to be used in conjunction with a fluidized bed in a DCFC configuration because they operate at high temperatures (700-1000°C). This allows the cell to run on CO in addition to H₂ as a fuel, as shown in Figure 2.4, which makes it more compatible with hydrocarbon gasification. The temperature range is also similar to that of a fluidized bed gasifier, which makes thermal coupling of the two components more feasible. SOFCs typically consist of a thin ceramic yttria-stabilized zirconia (YSZ) electrolyte, a nickel/YSZ anode, and a lanthanum-strontium manganate (LSM) cathode. Many numerical models have been developed to capture the reaction kinetics, heat transfer, flow fields and performance metrics of SOFCs [24]. However, the electrochemical oxidation mechanisms in a SOFC, particularly for fuels other than H₂, are still poorly understood.
The global reactions for CO and H₂ oxidation are:

\[
\text{CO} + O^{2-} \rightarrow CO_2 + 2e^- \quad (2.1)
\]

\[
H_2 + O^{2-} \rightarrow H_2O + 2e^- \quad (2.2)
\]

Some SOFC models implement global kinetic expressions, but it’s more accurate to break these reactions down into more detailed mechanisms. Detailed mechanisms have been proposed for H₂ oxidation [25],[26] and CO oxidation [27] in porous Ni-YSZ anodes. More experimental data is needed to determine the rate parameters for each step in the mechanisms, so certain steps must be assumed to be rate-limiting in order to fit models to experimental data [28], [29]. There is also considerable debate about whether the mechanisms are governed by fuel spilling over to the electrolyte or oxygen spilling over to the anode [30]. It is also still unclear if and how the H₂ and CO mechanisms are affected when both species are being oxidized simultaneously. Studies on
SOFCs with special composite anodes have found that the presence of CO/CO₂ inhibits H₂ oxidation [31], so it is plausible that a similar phenomenon could occur on a Ni-YSZ anode.

Jiang & Virkar provide the most comprehensive set of experimental data for porous Ni-YSZ anode-supported SOFCs with H₂, CO and H₂+CO oxidation [32]. They ran tests at 800°C for a wide range of compositions in order to characterize SOFC performance and compare H₂ to CO oxidation. Their performance curves for H₂/H₂O, CO/CO₂, and H₂/CO mixtures are shown in Figure 2.5. The SOFC performs significantly better with H₂/H₂O than it does with corresponding CO/CO₂ mixtures, due to the relatively sluggish diffusion and reaction rates of CO. The SOFC, however, performs comparably well with H₂-dominant H₂/CO and H₂/H₂O mixtures, which the authors attribute to the water gas shift reaction, which converts most of the CO to H₂ in the presence of H₂O. This set of experiments provides a baseline set of data for fitting parameters in H₂ and CO oxidation models. More experimental and modeling work is needed to determine the H₂, CO and H₂+CO oxidation mechanisms on Ni-YSZ in order for SOFCs to be coupled effectively to coal or biomass gasification.
2.1.3 FB/SOFC Fundamentals

Because both H₂ and CO can be oxidized at the anode of an SOFC, this allows some flexibility in the choice of gasification medium. CO₂ or H₂O are conventionally used to gasify carbon in the fluidized bed gasifier according to the Boudouard and steam-carbon reactions:

\[ \text{CO}_2 + C \leftrightarrow 2\text{CO} \]  \hspace{2cm} (2.3)

\[ \text{H}_2\text{O} + C \leftrightarrow \text{CO} + \text{H}_2 \]  \hspace{2cm} (2.4)

The CO and H₂ generated in the gasifier are subsequently oxidized at the anode. In the presence of steam, however, a large percentage of the CO sent to the fuel cell will shift to produce more H₂ before it is oxidized at the TPB:

\[ \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \]
Thus, steam gasification coupled with water-gas-shift can produce a high percentage yield of \( H_2 \).

Figure 2.6 depicts the gas flows associated with the FB/SOFC system when \( CO_2 \) and/or \( H_2O \) are sent to the gasifier. The gasifier is fueled with coal, biomass or carbon particles that can range in diameter from to order of microns to millimeters. If only \( CO_2 \) is sent through the gasifier, then \( CO \) is the primary fuel that exits the gasifier and is then oxidized on the porous Ni/YSZ anode. If, however, steam is sent to the gasifier, then syngas (\( H_2 + CO \)) will be produced, and both fuels will be oxidized at the anode.

The physical proximity of the gasifier to the anode will impact both the thermal coupling and the rate of product (\( H_2O + CO_2 \)) diffusion back to the gasifier. Placing the carbon particles closer to the anode also improves the cell’s theoretical performance because the open-circuit voltage increases when carbon is directly oxidized on the anode [2]. For these reasons, there is a strong incentive to incorporate the fluidized bed gasifier and SOFC into the same chamber (DCFC) instead of placing the gasifier in a separate chamber further upstream (indirect CFC).
2.2 State-of-the-Art

The concept of a fluidized bed with a SOFC (FB/SOFC) was first patented by a group at Stanford in the early 1990s [22]. That research group and another group at Tsinghua University have since developed FB/SOFC models and run several experiments. Their modeling and experimental work is summarized here, and more detail can be found in a recent review paper published by the Stanford group [13].

2.2.1 FB/SOFC Models

The most fundamental modeling analysis of the FB/SOFC system was published by the group at Stanford in 2009 [2]. This analysis drew a control volume around the FB/SOFC and an air-side heat exchanger, as shown in Figure 2.7. Several simplifying assumptions were made about the fuel cell performance and operating conditions, then system efficiency was computed according
to: \[ \eta' = \frac{\dot{W}_{\text{out,net}}}{m_{\text{fuel}}HHV_{\text{fuel}}} \]. The performance of the system was then analyzed for different fuels: pure carbon, a couple of grades of coal, and a few varieties of biomass. An efficiency of 58% was reported for pure carbon, while efficiency ranged from 40-55% for the alternative fuel candidates.

The Stanford group also compared their DCFC system to a couple of alternative systems where the gasifier was separated from the fuel cell. System efficiency changed little in the second system because the fuel cell and gasifier were still thermally coupled. In the third system, however, performance dropped substantially because the gasifier relied on autothermal reforming, so all

---

Figure 2.7: Schematic of a DCFC plant; gray partition represents SOFC stack [2].
excess heat from the fuel cell was wasted. This study laid the foundation for understanding the thermodynamic advantage of a DCFC system. However, the SOFC model was overly simplified and the gasifier was modeled at equilibrium. More detailed analysis was still needed to understand the kinetic behavior of a FB/SOFC system and understand the complex interplay between the gasifier and fuel cell.

The same group at Stanford came out with a more detailed DCFC model a few years later [33]. This model was of a 2-D axisymmetric SOFC and packed fuel bed, developed in both Matlab and Comsol [33]. This model accounts for cell electrochemistry, heat transfer, gasification kinetics, and convection/diffusion of species as shown in Figure 2.8. For a fixed geometry and current density, the steady-state temperature, velocity, pressure, and concentration profiles can be resolved. This model answered some important questions about DCFC operation, such as the minimum gasifier bed height to provide a given current for different fuels.
However, there are a couple of limitations to the recent model developed by Stanford. One is that the convection/diffusion module is based on the assumption of a packed bed, and would require significant modification to account for fluidization of particles. Gas flow would no longer be governed by diffusion or laminar plug flow once the bed reaches minimum fluidization, so the results of this model are only applicable at low flow-rates when fuel particles are stationary. Another drawback of this work is that it only focuses on a C/CO/CO$_2$ system, so it cannot model H$_2$O gasification or H$_2$ oxidation. As explained later, there is a strong incentive to go with H$_2$O over CO$_2$ in a FB/DCFC to speed up reaction kinetics, so a model that can handle H$_2$/H$_2$O chemistry is necessary to scope out system performance.
A group at Tsinghua has also published a model for a gasification DCFC within the last couple of years [34]. Their model domain is 1D and couples a packed fuel bed to a SOFC with a scandium-based electrolyte, as shown in Figure 2.9. Their model uses a multi-step carbon CO₂ gasification mechanism for a packed bed, similar to gasification module implemented by Stanford. The model at Tsinghua is similarly limited to C/CO/CO₂ systems and cannot account for H₂O gasification or H₂ oxidation. However, their model provides matches their experimental data well for both CO₂ and inert gas flows, and it provides insight into the gas species profiles throughout the carbon bed and anode. It also allowed the group to test the impact of adding a potassium-based catalyst to the gasifier bed [35].

![Figure 2.9: Domain and dimensions for the 1D-DCFC model at Tsinghua University [34].](image)

### 2.2.2 FB/SOFC Experiments

The group at Tsinghua University currently has an experimental set-up for indirect CFC testing, as shown in Figure 2.10. The gasifier packed bed was made up of amorphous carbon black
particles, and the SOFC button cells were composed of the material layers shown in Figure 2.9. The packed carbon bed is placed in a separate chamber approximately 50 cm upstream from the SOFC. Therefore, separate furnaces are needed to heat the carbon bed and SOFC because they are not thermally coupled. Some experiments were performed on the gasifier and SOFC separately, but some data was also collected on both components simultaneously. Inert argon and CO₂ were flowed separately to the carbon bed for temperatures ranging from 800-950°C. They used Gas Chromatography to determine the composition of the gasifier effluent in order to calculate the carbon conversion ratio in the packed bed. Platinum wires were also used to collect current and voltage data at the anode and cathode in order to plot the polarization curve for the SOFC.
The group at Tsinghua was able to calculate carbon conversion in the gasifier and power density in the SOFC for a range of temperatures and flow-rates. As expected, they found that increasing the temperature led to faster carbon conversion in the bed and higher performance in the cell. They also found that the cell performed best when CO₂ was sent to the system and worst with an inert gas flow, as shown in Figure 2.11. The maximum power density obtained with CO₂ flow was roughly 210 W cm⁻² whereas the maximum power density was only about 100 W cm⁻² for Ar flow.
This result confirms that CO₂ is producing CO in the gasifier via the Boudouard reaction, which is then oxidized at the fuel cell to produce power. The performance curve with 0 scem also confirms that some CO is produced in the gasifier by CO₂ that diffuses back from the fuel cell to the bed.

![Graph showing experimental performance curves of Tsinghua's SOFC button cell at 800°C when Ar, CO₂ and no flow are sent to the upstream gasifier.

Figure 2.11: Experimental performance curves of Tsinghua's SOFC button cell at 800°C when Ar, CO₂ and no flow are sent to the upstream gasifier [36].

The group at Stanford has also published experimental data for FB/SOFCs. Figure 2.12 portrays their initial experimental set-up, which is similar to the one used at Tsinghua. It contains a YSZ-based SOFC button cell downstream from a tray of carbon pellets, all enclosed in a quartz tube. The carbon and fuel cell are thermally decoupled, so the temperature of each compartment is be controlled independently by separate furnaces. The carbon gasifier section was operated between
524-955°C whereas the fuel cell section was always operated above 800°C. Gür and Huggins from Stanford were granted a patent for this design along with concepts that involve thermal coupling and fluidized gasification [37]. Their initial experiments led to low power densities, on the order of mW cm\(^{-2}\) because there was no gasification medium and a large distance for CO\(_2\) to traverse from the fuel cell to the carbon pellets. However, their work proved the concept for the FB/SOFC.

![Diagram](image)

**Figure 2.12:** a) schematic of the two-compartment DCFC apparatus at Stanford; b) performance curves of the given fuel cell at 932°C with the carbon bed held at 725°C and 955°C [22],[4].

41
Nakagawa and Ishida also performed button cell SOFC experiments with a charcoal bed adjacent to the anode [38]. They placed charcoal blocks in a crucible 5 mm away from the anode and flowed inert nitrogen gas over the charcoal at temperatures ranging from 802-1002°C. They analyzed the product gas in the anode chamber to confirm that CO was being produced by the Boudouard reaction. Their results confirmed that CO₂ was diffusing back from the anode to react with carbon in the charcoal blocks to produce CO. The University of Akron has also been performing FB/SOFC experiments on button cells in order to study the impact of several anode and cathode catalysts [39]. They were able to obtain power densities ranging from 50-150 mW cm⁻² for short-term experiments before ash built up on the anode [40]. They also reported that coal outperformed coal gas and methane in this configuration.

The group at Stanford later improved upon their initial experiment by fluidizing pulverized carbon particles directly on the anode, a better approximation of an actual FB/SOFC due to the fluidization and direct contact. In these experiments, they also explored different fuel types: carbon, almond shells and coal [41]. They used CO₂ to fluidize and gasify the carbon in the particles, and obtained power densities up to 140 mW cm⁻² for the synthesized carbon particles at 900°C. This corresponds to two orders of magnitude in improvement over Stanford’s initial experiments.

The Stanford group obtained an even higher power density, 220 mW cm⁻², in initial tests performed on tubular SOFCs instead of planar button cells [2]. A maximum power density of 450 mW/cm² was later achieved with Stanford’s anode-supported tubular SOFC run on devolatilized coal at 0.64 V and 850°C, as shown in Figure 2.13. This power output stands as the highest performance value reported for this system in literature. However, it corresponds to an experimental set-up where the Boudouard gasifier is external to the SOFC chamber, making it easier to couple the two components. In general, performance of indirect gasifier + fuel cell systems is superior to direct
designs, but the efficiency is lower. Thermal coupling and direct carbon oxidation have the potential to raise system efficiency when the gasifier is integrated directly with the fuel cell.

![Graph](image)

**Figure 2.13:** Cell voltage, efficiency and power density curves for a tubular SOFC run on gasified Alaskan coal char at 850°C [42].

Most FB/SOFC experiments have focused on CO₂ and purge gases, but a recent study conducted by the China University of Mining & Technology used H₂O in a direct CFC set up [43]. They tested a tubular SOFC with carbon black particles directly on the anode, with and without catalyst particles dispersed in the fuel bed. They obtained relatively poor performance in their uncatalyzed steam DCFC compared to a similar cell run on H₂, as shown in Figure 2.14. However, this discrepancy may be a result of the nitrogen used to deliver steam to the gasifier, which lowers the
theoretical potential of the cell. Their experiment was able to prove the viability of using H\textsubscript{2}O instead of CO\textsubscript{2} as the gasifying agent in a FB/SOFC.

![Performance curves at 850°C for a tubular SOFC directly coupled to a steam gasifier (with no catalyst) vs. the same cell run on H\textsubscript{2} [43].](image)

Figure 2.14: Performance curves at 850°C for a tubular SOFC directly coupled to a steam gasifier (with no catalyst) vs. the same cell run on H\textsubscript{2} [43].

A summary of the key modeling and experimental FB/SOFC published studies is given in Table 2.2. The bulk of the studies have focused on CO\textsubscript{2} or purge gas, and not all of them have directly coupled the gasifier to the fuel cell in the same chamber. Stanford University has published the most work on the FB/SOFC design, and they have laid the groundwork for the concept’s viability and feasibility through both experimental and modeling efforts.

Table 2.2: Summary of studies published on FB/SOFCs.
2.3 Operational Considerations

2.3.1 Steam vs. Carbon Dioxide

All FB-DCFC models and experiments to date have used CO₂ as the gasifying agent instead of H₂O because it’s easier to work with and model. From a thermodynamic standpoint, there’s little incentive to use steam over CO₂ because they lead to similar energy outputs per unit flow-rate of fuel [2]. However, from a power density standpoint, steam has an advantage over CO₂ by a factor of 2-6 in a direct carbon fuel cell system due to faster gasification and oxidation kinetics. This translates into smaller, cheaper gasifiers and SOFC stacks to obtain the same power output, so steam is worth investigating as an alternative to CO₂ in FB/SOFC systems.

Steam gasification is reported to proceed faster than CO₂ gasification [45], and it also generates H₂ along with CO, which the fuel cell favors electrochemically [46]. Steam is more commonly
used than CO₂ in gasifiers because steam gasification proceeds 2-6 times faster than CO₂ gasification [47]–[50]. Steam gasification reaction kinetics have been extensively studied for decades [57–61]. Several heterogeneous reaction mechanisms have been proposed for steam gasification using empirical data and Langmuir-Hinshelwood kinetics [56], [57]. Hydrogen oxidation is known to proceed more rapidly than CO oxidation in SOFC’s [27], [58]. The maximum power density obtained using pure CO is only 40-50% of that obtained using pure H₂ [32], [59]. Therefore there is a great incentive to utilize steam gasification instead of CO₂ gasification in order to produce H₂ that will optimize cell performance.

Steam gasifiers have been placed upstream of SOFC stacks in configurations like fuel cell turbine hybrids [60], and IGCC plants [61], [62]. A steam gasifier is also included in the FutureGen prototype plant, which is the world’s first coal-to-gas plant configured to optimize hydrogen production and carbon capture [63], [64]. However, steam gasification has yet to be integrated directly with a fuel cell in an experiment or model.

2.3.2 Anode Recycle

Figure 2.15 depicts a FB/SOFC system with CO₂ gasification and recycle. Coal particles are fed into a bed fluidized by CO₂ below a SOFC element. In this scenario, no external supply of CO₂ is necessary to run the system at steady-state because CO₂ is simply extracted from the anode exhaust and recycled back through the fluidized bed. Some of the CO₂ produced at the anode may also diffuse back into the gasifier by the “CO shuttle mechanism” if the gas flow-rate is sufficiently slow [23]. These mechanisms make the FB/SOFC self-sustaining in an ideal scenario because only solid fuel must be provided externally to keep the reactions going. However, when H₂O gasification is desired, recycling becomes more of a challenge because the steam must be condensed out of the flue before it can be sent back to the gasifier. This requires dropping the
temperature of the flue gas significantly before recycling, and it also means that some H₂O must still be provided externally to the gasifier to make up for the moisture that inevitably escapes the recycle loop in the flue after condensation.

Figure 2.15: Conceptual depiction of a FB/SOFC with CO₂ recycle and capture [23].

2.3.3 Desulfurization

Most experiments and models of FB/SOFCs use either char or pure carbon in order to simplify computation and clean-up. In reality, pure carbon particles are not a cheap, readily available fuel source for stationary power generation. Therefore, biomass and coal are more likely candidates for integration in a large-scale FB/SOFC. Coal and biomass are composed of volatile materials in addition to carbon, so the syngas composition leaving the gasifier in a FB/SOFC will likely contain sulfur-based elements, like those listed in Table 2.3.
Table 2.3: Syngas compositions of typical entrained-flow coal gasifiers [65].

<table>
<thead>
<tr>
<th>Gasifier</th>
<th>Coal</th>
<th>Syngas compositions (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td>Texaco</td>
<td>Illinois 6</td>
<td>30.28</td>
</tr>
<tr>
<td>Illinois 6</td>
<td>Illinios 6</td>
<td>26.74</td>
</tr>
<tr>
<td>Shell</td>
<td>Texas lignite</td>
<td>27.57</td>
</tr>
<tr>
<td>Destec</td>
<td>Texas lignite</td>
<td>24.6</td>
</tr>
</tbody>
</table>

Dealing with coal or biomass adds to the modeling complexity of the gasifier portion of a FB/SOFC because there are side reactions with volatiles that must be accounted for. This realistic syngas composition is also problematic in an experimental set-up because the sulfurous gases can quickly degrade the fuel cell. H₂S levels as low as 1-10ppm have been shown to be detrimental to nickel-YSZ anodes [66]. These trace levels cannot easily be obtained using limestone or calcium carbonate additives [67], [68]. Therefore, it is likely that the syngas will need to undergo an additional sulfur scrubbing step at a lower temperature before going to the anode. The alternative to this approach is to select a more sulfur-resistant anode material, such as GDC, which can handle a few hundred ppm of H₂S without degrading [69]. However, this material change comes with a tradeoff of lower cell performance, so it’s still an area for further investigation.

In addition to dealing with gas-phase contaminants, an actual FB/SOFC system would need to deal with ash clean-up. One simple configuration to mitigate the impact of ash on the fuel cell is to place the gasifier below the fuel cell, as shown conceptually in Figure 2.15. That way, solid particulates settle to the bottom of the gasifier rather than collecting on the anode, which can lead
to a performance drop within hours [40]. This configuration, however, cannot prevent fly ash from colliding with the anode and potentially clogging the porous anode. Some sort of a porous grate must be placed above the gasifier bed in order to filter out fly ash and allow only gases to pass through to the anode. This approach has been implemented before, and has the potential to minimize fouling of the anode [33]. Additional modeling and experimental efforts are needed to determine how to sustainably operate a FB/SOFC with coal and biomass by accounting for both gaseous and solid contaminants from the gasifier.

2.4 Modeling Considerations

2.4.1 Fluidized Bed Modeling

Although fluidized beds have been implemented for decades, the concept of coupling a gas fluidized bed directly with a fuel cell is a relatively new concept [22]. The more common configuration involves a fluidized bed gasifier upstream of a fuel cell stack in an Integrated Gasification Combined Cycle (IGCC) power plant [62]. Several researchers have investigated molten fluidized bed electrodes in which fuel particles are suspended in a bubbling bed of molten carbonate or metal [70], [71]. A few groups have begun modeling and experimenting with FB gasification directly coupled to the fuel cell. However, the state-of-the-art models for FB/SOFCs typically assume a packed carbon bed rather than developing a model for fluidization.

Fluidized bed technology was first commercialized for coal gasification in 1926, and has since been used in a diverse range of industrial applications. The advantages of using a fluidized bed are ease of continuous operation, enhanced heat and mass transfer, and protection against rapid temperature changes [72]. FB dynamics have been extensively studied and characterized based
on particle properties, bubble size and gas flow regimes [73]–[79]. The basic flow regimes are shown conceptually in Figure 2.16 in order of increasing gas velocity.

![Fluidized Bed Regimes Diagram](image)

Figure 2.16: Map of the different fluidized bed regimes based on increasing velocity [80].

In all likelihood, gasification in a DCFC configuration would fall under either the fixed bed or bubbling regime because flow within fuel cells is typically slow and laminar. For this reason, many researchers have assumed a packed bed in their FB/SOFC models and used packed carbon pellets in their experiments. However, a more comprehensive model that accounts for bubbling regime behavior should be developed in order to cover a wider range of potential operating conditions in a FB/SOFC and study the impact of flow rate on carbon conversion and gasifier characterization. The transition from fixed to bubbling regimes is dependent on minimum fluidization [81], which is a strong function of particle size [82], [83]. Therefore, it is conceivable that bubbling could occur in a FB/SOFC with finely ground fuel particles.

In order to create a fluidized bed model for a DCFC, established correlations for fluidization regimes based on particle classification would be needed to characterize the velocities of bubbles
and particles in the bed. The simple two phase (STP) model [53], which subdivides fluidized beds into bubble and solid emulsion phases, could be used to estimate fluidized bed behavior. Bed hydrodynamics and heat and mass transfer coefficients in the bed could then be determined based on STP empirical correlations [84],[72]. Although the STP model is less accurate than using CFD, it would provide a better estimate for gasifier behavior than the packed bed model does for FB/SOFC models with flow-rates exceeding minimum fluidization.

2.4.2 SOFC Modeling with H₂ and CO

A key advantage of solid oxide fuel cells (SOFCs) is their ability to electrochemically oxidize CO, which allows them to run on various abundant hydrocarbon fuels in addition to hydrogen [85]–[87]. SOFCs can potentially be coupled to a gasifier that converts coal, biomass or other solid carbonaceous fuels to syngas [44], [88], [89]. Because syngas is primarily composed of H₂ and CO, which can both be directly oxidized on SOFCs [32], it is an ideal fuel stream once contaminants have been removed [90]. However, it has also been shown that H₂ electro-oxidation proceeds 2-3 times faster than CO electro-oxidation on Ni/YSZ [46], [90]. Therefore, the importance of including a model for CO electro-oxidation in SOFC anodes is debatable when H₂ is also present. Previous researchers have often used a hydrogen-spillover oxidation model but neglected CO electro-oxidation even when both species are present [28], [91]. Neglecting CO electrochemistry is often justified by the following arguments: (1) the rate of CO conversion via surface reforming exceeds the rate of CO electrochemical oxidation [32], [90], and (2) H₂ dominates over CO in charge transfer chemistry [59]. However, these two assumptions may not hold for syngas mixtures with high CO content and low H₂O content, like the output of a coal gasifier [65]. The water-gas-shift reforming reaction, in particular, can only convert CO to H₂ when sufficient H₂O is present [27]. Therefore, it is plausible that non-negligible quantities of CO
could reach the triple-phase-boundary (TPB) to react electrochemically for certain syngas mixtures.

A couple of reaction mechanism types have been proposed to represent H₂ electrochemical oxidation at the triple-phase boundary (TPB) of Ni-YSZ: (1) hydrogen spillover and (2) oxygen spillover. Hydrogen (H) spillover mechanisms involve a charge-transfer step where hydrogen spills over from nickel to YSZ to react with oxygen on the electrolyte. Oxygen (O) spillover mechanisms, on the other hand, involve a charge-transfer step where oxygen spills over from YSZ to nickel to react with hydrogen on nickel. Hydrogen electro-oxidation models typically select only one spillover pathway rather than implementing the H and O spillover pathways simultaneously. Although a few researchers have used O spillover mechanisms to describe H₂ electro-oxidation [92], [93], the majority have proposed variations of the H spillover mechanism [25], [28], [94]–[99]. A few researchers have compared these spillover pathways and concluded that H spillover mechanisms are better than O spillover mechanisms at consistently predicting patterned-anode experimental data for H₂/H₂O mixtures [100]–[102]. One group has also developed an H spillover mechanism that accounts for rate-limiting H₂ adsorption at high currents [95], but a similar study is needed for the O spillover mechanism.

Although CO electro-oxidation has been typically neglected in SOFC models with syngas, several researchers have proven its importance in CO+CO₂ systems [103]. Experimental groups have tested nickel-pattern anodes and Ni-YSZ porous anodes with CO mixtures to study the power output from direct electrochemical oxidation [32], [59], [104], [105]. A few mechanisms for CO electro-oxidation on YSZ electrodes have also been proposed [106]–[108]. A comprehensive analysis of CO charge transfer and reaction kinetics on Ni-YSZ anodes appears in Yurkiv et al [109]. Although these researchers agree that the rate of CO electro-oxidation is smaller than that
of hydrogen, results indicate that their rates only differ by a factor of two or three [110]. Furthermore, some experimental studies of syngas electrochemical oxidation on Ni-YSZ conclude that CO electro-oxidation is non-negligible in comparison to H₂ [27], [46], [105]. These results motivate the investigation of CO electro-oxidation in Ni-YSZ anodes when both fuel species are present.

Although the mechanisms for both H₂ and CO electro-oxidation have been studied individually, few researchers have attempted to model the simultaneous electro-oxidation mechanism which is needed to characterize SOFC behavior with syngas mixtures [111]. It is a complicated task to simulate H₂ + CO co-oxidation in SOFCs because it involves modeling parallel charge transfer pathways, water-gas shifting and interactions between gaseous and adsorbed species. Moyer et al. [30] recently performed a modeling study on H₂ + CO co-oxidation that accounts for detailed heterogeneous thermochemistry as well as both spillover mechanisms. They fitted the kinetic parameters of each charge-transfer step in the hydrogen and oxygen spillover pathways to patterned-anode Tafel plots for mixtures containing H₂ + H₂O + CO + CO₂ [92]. Moyer’s model was best able to predict that data set when both the H and O spillover pathways were active instead of just one pathway. However, questions remain regarding the relative importance of these two spillover pathways and the roles of H₂ and CO in these pathways. Charge-transfer steps were also always assumed rate-limiting in this study, so the possibility of fuel adsorption on nickel as rate-limiting processes in these mechanisms requires further investigation.

A recent study by Fu et al [112] has provided needed insight on the spillover pathways of H₂ and CO electro-oxidation on Ni/YSZ from a micro-structural perspective using first principles simulations and the Monte Carlo method. This group found evidence to support previous claims that CO electro-oxidation can only proceed through the O spillover pathway. More importantly,
Fu et al found that the O spillover pathway plays a vital role in H₂ electro-oxidation in addition to H spillover. Their work therefore motivates the development of a MEA model that includes O spillover charge-transfer pathways to both CO and H₂ on nickel in addition to H spillover to YSZ. Such a model is needed to accurately capture the reaction pathways of both fuels at the anode triple-phase-boundary (TPB) of SOFC’s exposed to syngas fuels.

2.5 Conclusions

Direct carbon fuel cells (DCFCs) have been proposed as an efficient technology for coal power production with CO₂ capture. Although much research has been done on DCFCs with molten materials, more research is needed to examine the fluidized bed + solid oxide fuel cell (FB/SOFC) design, which is capable of higher efficiencies and a longer life-span. The few available FB/SOFC models are 1D or 2D-axisymmetric with CO₂ gasification in fixed beds. More modeling work is needed to study steam gasification, fluidization in the gasifier, and the 2D coupling of the gasifier and fuel cell. Preliminary bench scale experiments have also proven the FB/SOFC concept, but more experimental work is needed to test performance with steam gasification and in-situ desulfurization. Finally, understanding the complex coupling in the FB/SOFC system hinges on a proper understanding of SOFC behavior with synthesis gas fuels. Accurate models for parallel H₂ and CO electro-oxidation in the SOFC anode are a precursor to modeling SOFC interactions with a fluidized bed gasifier.

2.6 References


[31] D. M. Bierschenk and S. a. Barnett, “Electrochemical characteristics of La0.8Sr0.2Cr0.82Ru0.18O3–δ–Gd0.1Ce0.9O2 solid oxide fuel cell anodes in H2–H2O–CO–CO2 fuel mixtures,” *J. Power Sources*, vol. 201, pp. 95–102, 2012.


58


Chapter 3

Carbon Fuel Cell System Optimization

An indirect carbon fuel cell (ICFC) system that couples coal gasification to a solid oxide fuel cell (SOFC) is a promising candidate for high efficiency stationary power. Although the ICFC system does integrate the gasifier into the same chamber as the fuel cell (like the FB/SOFC from Chapter 2), it is still capable of high efficiency due to heat transfer between the two components. This study couples an equilibrium gasifier model to a detailed 1D MEA model to study the theoretical performance of an ICFC system run on steam or carbon dioxide. Results show that the fuel cell in the ICFC system is capable of power densities greater than 1.0 W cm\(^{-2}\) with H\(_2\)O recycle, and power densities ranging from 0.2-0.4 W cm\(^{-2}\) with CO\(_2\) recycle. This result indicates that the ICFC system performs better with steam than with CO\(_2\) gasification as a result of the faster electro-oxidation kinetics of H\(_2\) relative to CO. The ICFC system is then shown to reach higher current densities and efficiencies than a thermally decoupled gasifier + fuel cell (G+FC) system because it does not include combustion losses associated with autothermal gasification. 55-60% efficiency is predicted for the ICFC system coupled to a bottoming cycle, making this technology competitive with other state-of-the-art stationary power candidates.

3.1 Introduction

Growing concern over greenhouse gas emissions has driven research into cleaner power production alternatives. However, even with progressive energy policies in place, the IEA projects a global rise in coal-fired power generation over the next few decades due to the industrialization
of developing nations [1]. Clean coal technologies with higher system efficiency and CO₂ capture are therefore necessary in the coming decades to mitigate harmful emissions. The carbon fuel cell (CFC) system is a promising candidate for highly-efficient coal power production that releases a diluent-free CO₂ stream ready for capture and sequestration [2]. This paper focuses on a non-molten CFC system design that couples a ceramic solid oxide fuel cell (SOFC) to a gasifier [3].

Several bench-scale experiments and models have demonstrated the concept of this CFC system with CO₂ as the gasification agent [4]–[6]. On the other hand, steam gasification has been largely neglected in previous work because it requires more pre-heating and it produces H₂S, which quickly degrades SOFC performance [7]. However, steam has a couple of significant advantages over CO₂ in a CFC system: 1) H₂O gasification proceeds 2-6 times faster than CO₂ gasification [8], [9]; and 2) the H₂ produced by steam gasification can be oxidized 2-3 times faster than CO is oxidized on the SOFC anode [10]. Therefore, there is a strong incentive to consider H₂O as an alternative to CO₂ in a CFC system to improve performance.

Two fundamental questions still need to be answered for this CFC system: 1) how much will system power density increase if steam is used instead of carbon dioxide as the gasifying agent?; and 2) how much will system efficiency increase when a gasifier is coupled to a SOFC? A preliminary CFC modeling study on this topic coupled an equilibrium gasifier to a SOFC with fixed voltage and current [11]. That study compared a few CFC systems with varying degrees of coupling between components, and used thermodynamic analyses to compare the performance of these systems with both CO₂ and H₂O. Although the paper gave a good overview of the different systems, it did not find an advantage of using H₂O over CO₂ because the model fixed cell voltage and did not include finite-rate kinetics for SOFC surface reforming and electrochemistry.
Similarly, that thermodynamic analysis did not accurately assess the efficiency gained by thermal coupling because a finite-rate kinetic model is needed to accurately determine fuel cell efficiency. This paper addresses these fundamental questions about the CFC system using an equilibrium gasifier model coupled to a 1D-MEA model with finite-rate kinetics. The gasifier can be modeled in equilibrium because it is in a separate compartment upstream of the SOFC stack and can therefore be sized to ensure sufficient residence time. The SOFC model, on the other hand, includes finite-rate kinetics in order to accurately compare the H₂ and CO electrochemical oxidation rates and assess the various losses in the cell. First the CFC system model is presented along with an explanation of the different CFC system classifications. Next the governing equations are presented for the gasifier and fuel cell components of the model. Finally, the two fundamental questions posed earlier are addressed sequentially with two modeling studies. The first study compares the impacts of H₂O and CO₂ gasification on system performance over a range of temperatures. The second study explores the impact of thermal coupling between the gasifier and fuel cell on system efficiency.

3.2 Model Description

The objective of this model is to determine CFC system power and efficiency over a range of current densities and operating conditions. The combined CFC system is presented first, followed by descriptions of the equilibrium gasifier model and fuel cell model. The fuel cell model has been previously validated against experimental data for many syngas mixtures at 800°C, and the governing equations of the model are described in detail elsewhere [12], [13].
3.2.1 CFC System Model

3.2.1.1 System Classifications

There is considerable debate over the proper terminology to describe CFC systems [14]. Table 3.1 breaks down the CFC system classification adopted here by the extent of coupling between the gasifier and SOFC. Systems listed higher are more coupled and theoretically capable of obtaining higher efficiencies, but at the expense of more complex integrated designs. The model in this paper focuses on the indirect CFC (ICFC) and gasifier + fuel cell (G+FC) systems, as described and justified below.

Table 3.1: Classification of Carbon Fuel Cell systems with different levels of coupling.

<table>
<thead>
<tr>
<th>Forms of Coupling</th>
<th>Solid carbon oxidized directly on anode</th>
<th>Carbon conversion in anode chamber</th>
<th>Heat transfers from anode to gasifier</th>
<th>Gases produced by carbon sent to anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classification</td>
<td></td>
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<tr>
<td>Direct Oxidation Carbon Fuel Cell</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Direct Carbon Fuel Cell (DCFC)</td>
<td></td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Indirect Carbon Fuel Cell (ICFC)</td>
<td></td>
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<td>X</td>
<td></td>
</tr>
<tr>
<td>Gasifier + Fuel Cell (G+FC)</td>
<td></td>
<td></td>
<td>X</td>
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</tbody>
</table>

The most integrated design in Table 3.1, the direct oxidation CFC, is theoretically capable of high efficiencies across a wide range of operating temperatures based on the high Gibb’s free energy of the direct carbon oxidation reaction, \( C + O_2 \leftrightarrow CO_2 \) [15]. However, bench-scale experiments have demonstrated that direct oxidation of solid carbon in SOFCs produces negligible current relative to gaseous fuels, which can diffuse to the electrochemical sites throughout the porous anode [16], [17]. Furthermore, all direct oxidation CFC proof-of-concept experiments have
required a clamping mechanism to provide a high-pressure contact between a solid carbon pellet and the anode in order to produce current. Therefore, scaling up the direct oxidation CFC to an operational system with continuous solid fuel delivery poses a serious design challenge.

The direct-CFC (DCFC) design does not require physical contact between solid carbon particles and anode electrochemical sites, but still offers some efficiency gains by having carbon gasification occur in close proximity to the anode. This design promotes both chemical and thermal coupling between the gasification and electrochemical reactions, which happen in the same chamber. Several bench-scale experiments have successfully demonstrated that this DCFC concept is capable of competitive performance on a variety of solid fuels [18]–[20]. A couple of DCFC models have also been developed to complement these bench-scale experiments [6], [21]. The main drawback of the DCFC design is that solid fuels must be pre-processed into pure carbon because impurities like ash and H₂S quickly degrade SOFC performance if they are produced in the same chamber as the anode [5], [7], [22]. Therefore, DCFC experiments typically involve activated carbon or char particles that have been chemically and thermally pre-treated to remove volatiles and enhance surface reactivity [14].

In comparison with the DCFC, carbon gasification reactions occur in a physically separate compartment upstream of the anode in the ICFC. Therefore, the ICFC system does not allow the gases produced by fuel cell oxidation to diffuse back to the solid carbon fuel and react with it further. However, the ICFC system does still allow the heat produced by fuel cell electrochemistry to transfer back to the endothermic gasification reactions. Practical implementation of the ICFC system therefore depends on a sophisticated heat exchanger composed of high temperature-rated materials. The least coupled system presented in Table 3.1 is simply a gasifier upstream of a fuel cell (G+FC). This combination of components has already appeared in several pilot plant designs.
[23], [24], but lacks the potential efficiency gains offered by the more integrated CFC configurations.

The direct-CFC (DCFC) system is promising, and will be pursued in future studies with a more coupled model. The focus of this paper, however, is on the last two CFC systems listed in Table 3.1: the indirect-CFC (ICFC) and the gasifier + fuel cell (G+FC). The key distinction between the ICFC and G+FC systems, shown in Figure 3.1, is the source of heat to the endothermic gasification reactions. The gasifier and fuel cell are thermally coupled in the ICFC, so heat is supplied to the gasifier from the exothermic fuel cell reactions. In contrast, the gasifier and fuel cell are not thermally coupled in the G+FC system, so the gasifier must operate auto-thermally by burning extra fuel. In both systems, $\dot{W}$ is the electrical power generated by the fuel cell, $\dot{Q}_{FC}$ is the rate of heat release from the fuel cell, and $\dot{Q}_G$ is the heat rate input required by the gasifier, all measured per unit fuel cell area [W cm$^{-2}$].
A: Indirect Carbon Fuel Cell (ICFC) System Model.

Recycle

\[ \dot{Q}_G \]

Solid fuel feed

\[ \dot{n}_C \]

Air feed

\[ \dot{n}_{air,FC} \]

Fuel gas

\[ \dot{n}_{i,G} \]

\[ \dot{n}_{i,R} \]

Anode exhaust

\[ \dot{n}_{i,An} \]

Cathode exhaust

\[ \dot{n}_{i,Ca} \]

\[ \dot{W} \quad \dot{Q}_{FC} - \dot{Q}_G \]

B: Gasifier + Fuel Cell (G+FC) System Model.

Recycle

Solid fuel feed

\[ \dot{n}_C \]

Air feed

\[ \dot{n}_{air,G} \]

Fuel gas

\[ \dot{n}_{i,G} \]

\[ \dot{n}_{i,R} \]

Anode exhaust

\[ \dot{n}_{i,An} \]

Cathode exhaust

\[ \dot{n}_{i,Ca} \]

\[ \dot{W} \quad \dot{Q}_{FC} \]
Figure 3.1: Model drawings of the ICFC (A) and G+FC (B) systems, as defined in Table 3.1. Molar flow-rates of species are denoted by $\dot{n}_j$.

3.2.1.2 System Assumptions and Equations

The following assumptions apply to both the ICFC and G+FC systems from Figure 3.1 in order to simplify the analysis and isolate the impact of gasifier/fuel cell coupling on system performance:

1) Solid fuel is represented ideally here as pure carbon, which is supplied to the gasifier at the same rate that it's consumed by reactions. This carbon could be supplied in the form of coal char that has been heat pre-treated and ground into fine particles to enhance reactivity [14].

2) The residence time in the gasifier is long enough for gases to reach chemical equilibrium before entering the anode. This condition can be achieved by adjusting flow-rates and/or increasing gasifier size because the gasifier is a separate component from the fuel cell.

3) Steam or carbon dioxide can be supplied to the gasifier by extracting the needed species from the anode exhaust stream and recycling it back to the gasifier.

4) Any work or heat inputs required for separation before recycle are negligibly small and can be ignored in this analysis. Similarly, heat loads required to pre-heat incoming streams are neglected because the enthalpy of the streams exiting this system closely match those entering the system.

The following assumptions are only applicable to the ICFC system, as shown in subplot A of Figure 3.1:

5A) The fuel cell operates at or above the operating temperature of the gasifier to promote the flow of heat in the desired direction. A novel high-temperature heat exchanger transfers
heat rejected from the fuel cell stack to the gasifier (e.g. using high-temperature heat pipes [25], [26]).

6A) The heat rejected by the fuel cell stack is sufficient to supply the heat demand of the gasifier ($\dot{Q}_{FC} \geq \dot{Q}_G$). This assumption is checked and holds true for all results presented.

The energy and exergy efficiencies of the ICFC and G+FC systems are defined here as the ratio of fuel cell power output to the chemical potential of the fuel consumed:

$$\eta_{sys} = \frac{\dot{W}}{[\dot{n}_c HHV_c - \sum_i \dot{n}_{i,An} HHV_i]}$$  \hspace{1cm} (3.1)

$$\eta_{sys}^{ex} = \frac{\dot{W}}{[\dot{n}_c e_{c}^{ch} - \sum_i \dot{n}_{i,An} e_{i}^{ch}]}$$  \hspace{1cm} (3.2)

where $HHV_c$ is the higher heating value of carbon, and $\sum_i \dot{n}_{i,An} HHV_i$ is the total heating value of the anode exhaust after the recycle stream is extracted. Similarly, $e_{c}^{ch}$ is the chemical exergy of carbon, and $\sum_i \dot{n}_{i,An} e_{i}^{ch}$ is the total chemical exergy of the anode exhaust after recycle extraction.

Note that $\eta_{sys}$ and $\eta_{sys}^{ex}$ will differ for the two systems because the carbon flow-rate to the gasifier ($\dot{n}_c$) is larger in the G+FC system, which involves combustion to supply gasifier heat.

The previous definition of efficiency is based on the system boundaries shown in Figure 3.1, which can have a substantial net heat rejection. However, in a realistic system, high quality heat rejected by a system at 700-800°C would not go to waste. Therefore, a second set of system efficiencies are defined here in which the heat rejected by the ICFC or G+FC is sent to a bottoming cycle:

$$\eta_{sys, bottom} = (\dot{W} + \eta_{bottom, rej} \dot{Q}_{rej})/[\dot{n}_c HHV_c - \sum_i \dot{n}_{i,An} HHV_i]$$  \hspace{1cm} (3.3)

$$\eta_{sys, bottom}^{ex} = (\dot{W} + \eta_{bottom, rej} \dot{Q}_{rej})/[\dot{n}_c e_{c}^{ch} - \sum_i \dot{n}_{i,An} e_{i}^{ch}]$$  \hspace{1cm} (3.4)
where $\eta_{\text{bottom}}$ is the thermal efficiency of the bottoming cycle and $Q_{\text{ref}}$ is the net heat rejected by the CFC system. Note that the net heat rejected by the system is simply $Q_{\text{FC}}$ for the G+FC system, and $(Q_{\text{FC}} - Q_G)$ for the ICFC system, as shown in Figure 3.1.

Efficiencies can also be defined for the gasifier and fuel cell components individually. Cold gas efficiency is used here to quantify gasifier performance, and an analogous expression is used to express gasifier exergy efficiency:

\[
\eta_G = \sum_i \dot{n}_{i,G} HHV_i / [\dot{Q}_G + \dot{n}_c h_c + \dot{n}_{j,R} h_{j} + \dot{n}_{\text{air},G} h_{\text{air}}] \quad (3.5)
\]

\[
\eta_G^{\text{ex}} = \sum_i \dot{n}_{i,G} e_i^{ch} / [\dot{E}_G + \dot{n}_c e_c + \dot{n}_{j,R} e_{j} + \dot{n}_{\text{air},G} e_{\text{air}}] \quad (3.6)
\]

where $\dot{Q}_G = 0$ for the G+FC system and $\dot{n}_{\text{air},G} = 0$ for the ICFC system, as shown in Figure 3.1, and $\dot{E}_G$ is the rate of exergy transferred by heat to gasifier (W cm$^{-2}$). These definitions of efficiency only account for the chemical energy and exergy of the species exiting the gasifier, but account for both the chemical and thermal energy and exergy of the species entering the gasifier. Enthalpy values for each species are calculated with the Shomate equation using NIST-JANAF coefficients [27], and standard chemical exergy values all come from Szargut et al [28]. The total exergy of a given material stream, $e_i$, accounts for both chemical and physical exergy, as detailed in [29].

The energy and exergy efficiencies of the fuel cell are defined here as:

\[
\eta_{\text{FC}} = \dot{W} / [\sum_i (\dot{n}_{i,G} - \dot{n}_{i,An}) HHV_i] \quad (3.7)
\]

\[
\eta_{\text{FC}}^{\text{ex}} = \dot{W} / [\sum_i (\dot{n}_{i,G} - \dot{n}_{i,An}) e_i^{ch}] \quad (3.8)
\]

These definitions only account for the fuel that participates in cell electrochemistry because unspent fuel in the exhaust can still be used downstream.
3.2.2 Gasifier Model

For both CFC systems, solid carbon fuel is sent to the gasifier along with a recycled stream of either pure H₂O or pure CO₂. Air is also sent to the gasifier for combustion in the G+FC system.

The following gasification reactions are modeled together in equilibrium:

\[ \text{C(s)} + \text{CO}_2(g) \leftrightarrow 2\text{CO}(g) \]  (G.1)

\[ \text{C(s)} + \text{H}_2\text{O}(g) \leftrightarrow \text{CO}(g) + \text{H}_2(g) \]  (G.2)

\[ \text{C(s)} + 2\text{H}_2(g) \leftrightarrow \text{CH}_4(g) \]  (G.3)

\[ \text{C(s)} + \text{O}_2(g) \rightarrow \text{CO}_2(g) \]  (G.4)

where (s) denotes the solid phase and (g) denotes the gas phase. The steam-carbon and methanation reactions (G.2)-(G.3) are omitted from the model when CO₂ is the gasifying medium because no hydrogen compounds are present in that system. Similarly, the combustion reaction (G.4) is omitted in the ICFC system, which doesn’t require autothermal operation. The water-gas-shift reaction \([\text{H}_2\text{O}(g) + \text{CO}(g) \leftrightarrow \text{CO}_2(g) + \text{H}_2(g)]\) and partial oxidation reaction \([\text{C(s)} + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}(g)]\) are already accounted for in this model because they are linear combinations of the other gasification reactions listed. The equilibrium expressions for the four gasification reactions are:

\[ \frac{p_{\text{CO}}}{p_{\text{CO}_2}P} = K_{eq,1} = \exp(-\Delta G_1/RT_G) \]  (3.9)

\[ \frac{p_{\text{CO}}p_{\text{H}_2}}{p_{\text{H}_2\text{O}}P} = K_{eq,2} = \exp(-\Delta G_2/RT_G) \]  (3.10)

\[ \frac{p_{\text{CH}_4}P}{p_{\text{H}_2}^2} = K_{eq,3} = \exp(-\Delta G_3/RT_G) \]  (3.11)

\[ \frac{p_{\text{CO}_2}}{p_{\text{O}_2}} = K_{eq,4} = \exp(-\Delta G_4/RT_G) \]  (3.12)
Where \( P \) is the total pressure and \( \Delta G_i \) is determined by taking the difference in Gibbs free energies between the products and reactants of the given reaction. The resulting equilibrium gas phase mixture is then determined by solving equations (3.9)-(3.12) for a fixed total pressure. The final constraint equations are derived from mass balances on reactions (G.1)-(G.4).

The heat input required by the gasifier can be determined by a component energy balance:

\[
\dot{Q}_G = \sum_i [(\dot{n}_{i,G} - \dot{n}_{i,R})h_i] - \dot{n}_c h_c - \dot{n}_{air,G} h_{air}
\]

where the summation term occurs over all gaseous species present. \( \dot{n}_{i,G}, \dot{n}_{air,G} \) and \( \dot{n}_{i,R} \) are the molar flow-rates of each gas species entering and exiting the gasifier per unit fuel cell area [mol s\(^{-1}\) cm\(^{-2}\)]. Enthalpy and Gibbs data are calculated for each species using the Shomate equation with NIST-JANAF coefficients [27]. Note that this model considers air instead of pure oxygen as the input feed to the combustion reaction because it doesn’t require an air separation unit. In the G+FC system, which involves autothermal gasification, air flow-rate into the gasifier is adjusted until \( \dot{Q}_G = 0 \).

### 3.2.3 Fuel Cell Model

The fuel cell model calculates the current density-voltage curve of a button SOFC for a given fixed temperature, pressure and fuel composition. This model applies to a porous anode-supported SOFC composed of the traditional material composites: a Ni/YSZ anode, YSZ electrolyte and LSM/YSZ cathode. Air is fed into the cathode, and the equilibrium output from the gasifier model is fed into the anode. The model domain is isothermal and 1D with respect to distance from the triple-phase-boundary (TPB). The fuel cell model captures multiphysics processes of transport through porous electrodes, thermochemical surface reforming, and electrochemical oxidation mechanisms for both H\(_2\) and CO [12],[30]. The fuel cell model has already been validated against...
experimental data from a porous anode-supported SOFC button cell fueled by various mixtures of H₂/H₂O, CO/CO₂ and H₂/CO [13]. The H₂ and CO oxidation mechanisms and governing equations are presented briefly here and in detail elsewhere [12], [31].

3.2.3.1 Conservation Equations

Gas and surface mass conservation equations are applied over a series of m discrete nodes in both electrodes, as shown in Figure 3.2. Gas-phase mass conservation is modeled using the dusty-gas-model (DGM), which accurately represents bulk and Knudsen diffusion in porous media [32]. Gas-phase reactions in the anode are neglected due to the relatively fast catalytic surface reactions on nickel at 700-800°C [12]. Reforming reactions on nickel occur throughout the anode, and are modeled using a well-established 42-step heterogeneous mechanism [33], [34]. The electrochemical reactions occur only at the mth node, where the triple-phase boundary (TPB) is located [34], [35].
The molar fluxes of gas phase species at the anode TPB are:

\[
J_{H_2,m} = \frac{i_{H_2}}{2F}; \quad J_{H_2O,m} = -\frac{i_{H_2}}{2F}; \quad J_{CO,m} = \frac{i_{CO}}{2F}; \quad J_{CO_2,m} = -\frac{i_{CO}}{2F}
\]  \hspace{1cm} (3.14)

The flow-rates of species from the gasifier to the anode, \(\dot{n}_{i,G}\), are then calculated based on a mass balance of H\(_2\) or CO on the anode:

\[
\dot{n}_{i,G} = \frac{x_{i,G}}{x_{k,G}} \left\{ \frac{j_{k,m}}{u_f} - \sum_l A_s \dot{s}_{surf,k} \right\} \quad k = \begin{cases} H_2 & \text{(for H\(_2\)O recycle)} \\ CO & \text{(for CO\(_2\) recycle)} \end{cases}
\]  \hspace{1cm} (3.15)
where $u_f$ is the input fuel utilization and $\sum_i^{m} A_i s_{surf,k}$ is the total production rate of H$_2$ or CO from surface reforming reactions in the anode. Equation (3.15) is defined in terms of CO for systems with CO$_2$ recycle, and in terms of H$_2$ for systems with H$_2$O recycle. The flux of O$_2$ at the cathode TPB is given by: $J_{O_2,m} = (i_{H_2} + i_{CO})/4F$. The flow-rate of air into the cathode is then:

$$\dot{n}_{air} = J_{O_2,m}/.21u_{O_2}$$

for a given oxygen utilization, $u_{O_2}$. The heat released by the fuel cell, $\dot{Q}_{FC}$, is then given by energy conservation:

$$\dot{Q}_{FC} = \sum_{i=1}^{K_g} (\dot{n}_{i,G} - \dot{n}_{i,An}) h_i + (\dot{n}_{air} h_{air} - \dot{n}_{O_2,ca} h_{O_2} - \dot{n}_{N_2,ca} h_{N_2}) - \dot{W}$$

(3.17)

where $K_g$ is the total number of gaseous species in the anode.

### 3.2.3.2 Electro-oxidation Mechanisms

This model implements multi-step mechanisms for both H$_2$ and CO electro-oxidation, which are presented briefly here and described in detail elsewhere along with experimental validation [12], [30].

Hydrogen electro-oxidation is modeled by five elementary hydrogen spillover steps [36]:

$$H_2(g) + 2(Ni) \leftrightarrow 2H(Ni)$$

(H.1)

$$H(Ni) + O^{2-}(YSZ) \leftrightarrow (Ni) + OH^-(YSZ) + e^-(Ni)$$

(H.2)

$$H(Ni) + OH^-(YSZ) \leftrightarrow (Ni) + H_2O(YSZ) + e^-(Ni)$$

(H.3)

$$H_2O(YSZ) \leftrightarrow H_2O(g) + (YSZ)$$

(H.4)

$$O^x_0(YSZ) + (YSZ) \leftrightarrow O^{2-}(YSZ) + V_0^{**}(YSZ)$$

(H.5)
It has been shown that the second charge-transfer step (H.3) is rate-limiting for lower current densities, such that all other steps can be modeled in equilibrium [12], [37]. At higher current densities, a better fit to experimental data is obtained by assuming that the hydrogen adsorption step (H.1) becomes rate-limiting [12].

The mechanism for CO oxidation involves three elementary steps [30]:

\[
CO(g) + (Ni) \leftrightarrow CO(Ni) \quad \text{(CO.1)}
\]
\[
O_0^+(YSZ) + (YSZ) \leftrightarrow O^-(YSZ) + V_0^+(YSZ) + e^-(Ni) \quad \text{(CO.2)}
\]
\[
O^-(YSZ) + CO(Ni) \leftrightarrow CO_2 + (YSZ) + (Ni) + e^-(Ni) \quad \text{(CO.3)}
\]

The adsorption step (CO.1) is always modeled in equilibrium because CO has a strong affinity to Ni and CO charge-transfer kinetics are sluggish. Charge-transfer steps (CO.2) and (CO.3) are then modeled as equally rate-limiting, which is a necessary constraint to maintain a constant coverage of \( O^- (YSZ) \) at steady-state [30].

### 3.2.3.3 Cell Overpotentials

At finite current, the operating cell voltage can be expressed as the difference between the reversible cell potential and various overpotentials:

\[
E_{cell} = E_{rev} - \eta_{act,a} - \eta_{act,c} - \eta_{con,a} - \eta_{con,c} - \eta_{ohm} \quad (3.18)
\]

where \( \eta_{act,a} \) and \( \eta_{act,c} \) are the activation overpotentials at the anode and cathode, \( \eta_{con,a} \) and \( \eta_{con,c} \) are the concentration overpotentials at the anode and cathode, and \( \eta_{ohm} \) is the total ohmic overpotential. The reversible potential, or open circuit voltage (OCV), of the cell is given by:

\[
E_{rev} = RT/4F \ln(p_{O_2,c}/p_{O_2,a}) \quad (3.19)
\]
where $p_{O_{2,c}}$ and $p_{O_{2,a}}$ are the equilibrium oxygen partial pressures at the cathode and anode channels, respectively. Reversible potential must be defined in terms of oxygen, rather than the reactants and products of a single global reaction, because there are two parallel charge-transfer pathways for H$_2$ and CO [38].

The anode activation overpotential, $\eta_{act,a}$, is a function of the currents produced by both the H$_2$ and CO electro-oxidation mechanisms. Butler-Volmer expressions can be derived for each rate-limiting step in these mechanisms to relate current to anode activation overpotential. The following Butler-Volmer expressions are applied to the H$_2$ mechanism:

$$i_{H_2} = \begin{cases} 
    i_0 \left[ \exp \left( \frac{3F\eta_{act,a}}{RT} \right) - \exp \left( -\frac{F\eta_{act,a}}{RT} \right) \right]; & (H.3) \text{ rate-limiting} \\
    i_{H_2}^* P_{H_2} \left[ 1 - \exp \left( -\frac{2F\eta_{act,a}}{RT} \right) \right]; & (H.1) \text{ rate-limiting} 
\end{cases} \quad (3.20)$$

where $i_0 = 3.5 \frac{P_{H_2}^{3/4} (K(H.1) P_{H_2})^{1/4}}{1 + (K(H.1) P_{H_2})^{1/2}}$ [37], and $i_{H_2}^* = \frac{0.0013(2F)}{\sqrt{2\pi M_{H_2}} RT}$ [12, 39]. The first expression applies at lower currents when step (H.3) is rate-limiting, and the second expression applies at higher currents when step (H.1) is rate-limiting. The "switch-over" from (H.3) to (H.1) as the rate-limiting step occurs when the current predicted by the second Butler-Volmer expression becomes less than the current predicted by the first one.

The following Butler-Volmer expression applies to the CO mechanism [30]:

$$i_{CO} = 2FI_{TPB} \left[ k_f \theta_{YSZ} \exp \left( \frac{FE}{2RT} \right) - k_b \theta_{O^{-},YSZ} \exp \left( -\frac{FE}{2RT} \right) \right] \quad (3.21)$$

where $I_{TPB}$ is the TPB length, which was determined by fitting the model to experimental data. YSZ vacancy and O$^-$ coverages, $\theta_{YSZ}$ and $\theta_{O^{-},YSZ}$, are resolved by assuming that O$^-$ and O$^{2-}$ are the only active species on YSZ and that $\theta_{O^{2-},YSZ} = .9$ [40].
Values for the kinetic rate constants, \( k_f \) and \( k_b \), were obtained previously by a least-squares fitting of the model to EIS patterned anode data at 700-775°C [10].

The electric potential difference across the anode-electrolyte double layer is given by: 
\[
E = E_{eq} + \eta_{act,a},
\]
where the equilibrium potential \( (E_{eq}) \) is determined by solving equation (3.22) for \( E \) with \( \eta_{act,a} = 0 \) and \( i_{CO} = 0 \). A more detailed derivation and fitting of this CO mechanism with all of the governing equations is provided elsewhere [30].

Cathode activation overpotential is related to total current by the Butler-Volmer equation [37]:

\[
i = i_0 \left[ \exp \left( \frac{F\eta_{act,c}}{2RT} \right) - \exp \left( -\frac{F\eta_{act,c}}{2RT} \right) \right]
\]

(3.22)

where \( i = i_{H_2} + i_{CO} \) and \( i_0 = 2.8 \frac{(P_{O_2}/P_{O_2}^0)^{1/4}}{1+(P_{O_2}/P_{O_2}^0)^{1/2}} \) [37].

At finite current, the species concentrations at the TPB differ from those in the channels due to transport limitations through the porous electrodes. This difference in reversible potential is accounted for in the model by concentration overpotentials at the anode and cathode:

\[
\eta_{con,a} = E_{rev,a} - E_{rev,a,TPB} = \frac{RT}{4F} \ln \left( \frac{p_{O_2,a,TPB}}{p_{O_2,a}} \right) \]

(3.23)

\[
\eta_{con,c} = E_{rev,c} - E_{rev,c,TPB} = \frac{RT}{4F} \ln \left( \frac{p_{O_2,c,TPB}}{p_{O_2,c}} \right)
\]

(3.24)

where subscripts \( a, TPB \) and \( c, TPB \) correspond to the anode and cathode triple-phase boundaries. Both concentration overpotentials are expressed in terms of oxygen partial pressures because there are two parallel charge transfer pathways (H_2 and CO).

Finally, the ohmic overpotential is given by [41]:
\[ \eta_{ohm} = iR_{el} = iL_{el}T/\left[\sigma_0 \exp\left(-\frac{E_{el}}{RT}\right)\right] \] 

(3.25)

where \( L_{el} \) is the electrolyte thickness [cm] and \( \sigma_0 \) is the ionic conductivity pre-factor [S cm\(^{-1}\)].

### 3.3 Simulation Procedure

In order to determine the performance of the CFC system over a range of current densities, the following sequence of steps are followed using a MATLAB\(^\text{®} \) script. Steps 3)-5) are repeated for increasing anode activation overpotential until the fuel cell polarization curve is complete, as shown in Figure 3.3.
Figure 3.3: Simulation procedure flow-chart to generate a polarization curve and performance data for the carbon fuel cell system model.

1) **Calculate gasifier output.**

Equations (3.9)-(3.12) are solved along with constraint equations for fixed total pressure and mass using Matlab’s non-linear “fsolve” function. When simulating autothermal gasification in the G+FC system, the air feed to the gasifier is incrementally increased until the net heat input to the gasifier approaches zero. Cantera’s “equilibrate” function is then applied to the output mixture to determine the gas-phase equilibrium composition exiting the gasifier to the fuel cell anode.

2) **Calculate reversible cell potential.**

The equilibrium potential of the fuel cell is then determined by equation (3.19), where oxygen partial pressure in the anode channel comes from the equilibrium output of the previous step.

3) **Resolve current densities and anode species profiles.**

Initial guesses for concentrations and coverages are used to estimate the current densities from H\textsubscript{2} and CO along with the initial fluxes of gas phase species at the anode TPB. These fluxes are boundary conditions to the gas species conservation and transport equations. Together these form a set of ordinary differential equations that can be solved simultaneously along with the surface reforming model for gas and surface species profiles until steady-state is reached using “ode15s” in MATLAB®. The H\textsubscript{2} and CO current densities are then updated based on the new concentration profiles, and this process repeats until the non-linear “fsolve” function converges on steady-state anode concentration profiles and current densities, as detailed in [12].

4) **Resolve cathode species profiles and cell overpotentials.**
A similar method is used to determine the species profiles in the cathode, but with no surface reforming and with pre-determined current densities and fluxes at the TPB. The cathode activation overpotential is then computed by applying the non-linear “fsolve” function to equation (3.26). The concentration overpotentials and ohmic overpotential are then determined by equations (3.27)-(3.29).

5) **Calculate power, flow-rates, heat rates and efficiencies.**

Cell power density is simply the product of total current density and operating voltage: \( \dot{W} = iE_{cell} \), where operating cell voltage comes from equation (3.18). The molar flow-rates of species into the anode and cathode are then given as functions of current density in equations (3.15)-(3.16). The needed molar flow-rates of carbon and CO\(_2\) or H\(_2\)O into the gasifier can then be determined based on mass balances applied to reactions (G.1)-(G.4). The air flow-rate into the autothermal gasifier of the G+FC system can then be determined by setting \( \dot{Q}_g = 0 \) in equation (3.13). For the ICFC system, air flow-rate to the gasifier is zero and heat input from the fuel cell to the gasifier is given by equation (3.13). The heat output of the fuel cell is then given by equation (3.17) for both systems, and efficiencies are given by equations (3.1)-(3.8).

### 3.4 Results and Discussion

The operating conditions and SOFC structural parameters used in these simulations are listed in Table 3.2. Temperature is only varied from 700-800°C to coincide with the temperature range of the experimental data that the rate constants were fitted to in the H\(_2\) and CO mechanisms [10], [42]. The only recycle stream compositions considered in this study are pure H\(_2\)O and pure CO\(_2\) in order to compare the performance of CFC systems with these two gasification mediums. Unity fuel and oxygen utilizations are used here in order to determine the maximum theoretical
performance of the system. Although conventional SOFC stacks have oxygen utilizations substantially lower than one, a near-perfect value is theoretically possible in a CFC system because the distributed heat removal from the stack to the gasifier eliminates the need to send excess air to the cathode for cooling purposes [25]. The anode is divided into ten nodes, which is the optimal resolution for minimizing run-time without sacrificing accuracy in the surface and gas species profiles. The majority of the structural parameters for the SOFC come from another group’s work that fitted a similar detailed model to porous anode experimental data [37]. The TPB length was derived by fitting the model to experimental data for CO/CO₂ mixtures [31], [42].

Table 3.2: Constant operational and structural parameters for the SOFC.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Operating Conditions</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature ((T))</td>
<td>700-800</td>
<td>°C</td>
</tr>
<tr>
<td>Pressure ((P))</td>
<td>1</td>
<td>atm</td>
</tr>
<tr>
<td>Recycle stream composition ((X_{i,R}))</td>
<td>(X_{CO₂,R} = 1) OR (X_{H₂O,R} = 1)</td>
<td>--</td>
</tr>
<tr>
<td>Fuel utilization ((u_f))</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>Oxygen utilization ((u_{O₂}))</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>Bottoming cycle efficiency ((\eta_{bottom}))</td>
<td>.3</td>
<td>--</td>
</tr>
<tr>
<td><strong>Structural Parameters</strong> [37]</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Anode</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of nodes ((m))</td>
<td>10</td>
<td>--</td>
</tr>
<tr>
<td>Thickness ((L_a))</td>
<td>1220</td>
<td>µm</td>
</tr>
<tr>
<td>Porosity ((\varepsilon))</td>
<td>0.35</td>
<td>--</td>
</tr>
<tr>
<td>Tortuosity ((\tau_a))</td>
<td>3.50</td>
<td>--</td>
</tr>
<tr>
<td>Specific catalyst area ((A_x))</td>
<td>1080</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>Triple phase boundary length ((l_{TPB}))</td>
<td>15</td>
<td>m cm⁻²</td>
</tr>
<tr>
<td><strong>Cathode</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of nodes ((m))</td>
<td>10</td>
<td>--</td>
</tr>
<tr>
<td>Thickness ((L_c))</td>
<td>30</td>
<td>µm</td>
</tr>
<tr>
<td>Porosity ((\varepsilon))</td>
<td>0.35</td>
<td>--</td>
</tr>
<tr>
<td>Tortuosity ((\tau_c))</td>
<td>3.50</td>
<td>--</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
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<td></td>
</tr>
<tr>
<td>Thickness ((L_e))</td>
<td>25</td>
<td>µm</td>
</tr>
</tbody>
</table>

84
<table>
<thead>
<tr>
<th>Activation energy of O²⁻ ($E_{el}$)</th>
<th>8.0*10⁴ J mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity pre-factor of O²⁻ ($\sigma_0$)</td>
<td>3.6*10⁵ S cm⁻¹</td>
</tr>
</tbody>
</table>

Figure 3.4 displays gasifier output as a function of temperature for the ICFC system (subplots A-B) and the G+FC system (subplots C-D). Subplots A and C correspond to systems with CO₂ sent to the gasifier, while subplots B and D correspond to systems with H₂O sent to the gasifier. Figure 3.4 demonstrates that the equilibrium output is strongly temperature-dependent for both H₂O and CO₂ feeds. Higher temperatures facilitate the formation of H₂ and CO, leading to a more fuel-rich output, which is beneficial to the SOFC. Subplot A shows that CO is the dominant species in the gasifier output when CO₂ is the gasification agent, particularly at higher temperatures. Subplot B shows that H₂ is the dominant fuel species in the gasifier output when H₂O is the gasifying medium, but a large portion of the stream is also composed of CO, which can later shift to form more H₂ on the fuel cell anode or be directly oxidized at the TPB to produce power.

Subplots C-D of Figure 3.4 correspond to the G+FC system, which operates autothermally because no heat is supplied externally from the fuel cell stack. In both of these cases, the gasifier output is significantly diluted by N₂ as a result of the combustion reaction with air. This in turn dilutes the fuel content of the gasifier output, which then lowers the potential of the SOFC. These results imply that one disadvantage of the G+FC system is the reduced fuel content of the gasifier output as a result of autothermal gasification. This loss could potentially be combatted by sending pure oxygen rather than air to the gasifier, but that would require an air separation unit, which would add a parasitic loss to the system. The gasifier outputs from Figure 3.4 are the same mixtures sent to the anode of the fuel cell in the results presented later for these CFC systems.
The following sub-sections seek to address the two questions posed in the introduction of this paper: 1) how much will power density improve when H$_2$O is used as the gasification medium instead of CO$_2$?; and 2) how much will system efficiency improve when the gasifier and SOFC are thermally coupled? In order to address these questions, the first sub-section focuses on the ICFC system and compares fuel cell performance when H$_2$O and CO$_2$ are sent to the gasifier over a range of temperatures. The second sub-section compares the efficiencies of the ICFC and G+FC systems.
systems to measure the benefit of transferring rejected heat from the fuel cell to the gasifier before using it in a bottoming cycle.

3.4.1 Steam vs. Dry Gasification

Previous experimental work has demonstrated that H₂ electro-oxidation proceeds 2-3 times faster than CO electro-oxidation on Ni-YSZ [43], resulting in a lower anode activation overpotential. It is therefore expected that the fuel cell will attain higher power densities when coupled to H₂O gasification than CO₂ gasification. Therefore, the goal of this section is to quantify this advantage of H₂O over CO₂ gasification in a CFC system. In order to isolate the impact of the gasification medium, results here focus on the ICFC system from subplot A of Figure 3.1, which does not require any air input to the gasifier. These results focus specifically on fuel cell performance, with corresponding input streams from the gasifier as shown in subplots A-B of Figure 3.4. Several fuel cell metrics are compared over a range of operating temperatures to gain insight on the relative advantage of steam over dry gasification when coupled to a fuel cell.

Figure 3.5 displays the current-voltage-power curves for CO₂ and H₂O recycle in an ICFC system over a range of operating temperatures. As expected, voltage and power curves shift up as temperature increases for both H₂O and CO₂ recycle systems. This trend is partly due to the more fuel-rich mixtures exiting the gasifier at higher temperatures, and also due to faster reaction kinetics in the fuel cell. The results for CO₂ recycle are shown in subplot A, and the results for H₂O recycle are shown in subplot B. A quick visual comparison between these two subplots confirms that the fuel cell attains significantly higher current and power densities when coupled to H₂O rather than CO₂ gasification.
Subplot C of Figure 3.5 also compares the maximum power densities for the H$_2$O and CO$_2$ system curves in subplots A-B as a function of temperature. The maximum power densities for CO$_2$ recycle range from about 0.2 to 0.4 W cm$^{-2}$, which are consistent with reported values from CFC bench-scale experiments with CO$_2$ gasification [11], [44]. The maximum power densities for H$_2$O recycle, on the other hand, reach values upward of 1.0 W cm$^{-2}$, which makes this system competitive with SOFCs run on H$_2$-rich synthesis gas [42]. From subplot C, it is clear that the ICFC system with H$_2$O recycle outperforms the same system with CO$_2$ recycle in terms of maximum power output by a factor of 3-5. These findings are consistent with previous experimental work demonstrating that a porous anode-supported SOFC attained significantly higher power densities with H$_2$+CO mixtures compared to CO+CO$_2$ mixtures [42].
A: ICFC with CO₂ Recycle

B: ICFC with H₂O Recycle

C: Maximum Power Densities

Operating Voltage (V) or Power Density (W cm⁻²)

Current Density (A cm⁻²)

Operating Voltage (V) or Power Density (A cm⁻²)

Current Density (A cm⁻²)

Power Density (W cm⁻²)

Temperature (°C)

H₂O Recycle

CO₂ Recycle
Figure 3.5: Fuel cell operating voltage and power density curves vs. temperature for the ICFC system with CO$_2$ recycle (A) and H$_2$O recycle (B). Maximum power densities for H$_2$O and CO$_2$ recycle are also compared vs. temperature (C).

In order to gain a clearer understanding of why the ICFC performs substantially better with H$_2$O recycle, it’s helpful to compare the different loss modes in the fuel cell. A breakdown of the fuel cell overpotentials as a function of current density is presented in Figure 3.6 for H$_2$O and CO$_2$ recycle at both 700°C and 800°C. As expected, most of the overpotentials are lower at the higher temperature (subplots C-D). This trend with respect to temperature is especially noticeable when comparing subplots A and C, which correspond to the system with CO$_2$ recycle. Raising the temperature by 100°C causes anode activation overpotential to drop dramatically in the CO$_2$ system, resulting in a limiting current density that’s approximately twice as large at 800°C. This result indicates that the CO oxidation mechanism is strongly dependent on temperature and has especially sluggish kinetics at lower operating temperatures.

However, at both temperatures, anode activation overpotential dominates over the other loss modes for CO$_2$ recycle (subplots A,C), contributing to a voltage drop of more than 0.4V in the limiting current regime. In contrast, anode activation overpotential remains below 0.1V for H$_2$O recycle (subplots B,D) until H$_2$ adsorption becomes rate-limiting at the end of the curve. These results show that the sluggish kinetics of CO oxidation relative to H$_2$ oxidation are the main factor contributing to worse cell performance with CO$_2$ recycle. Anode concentration overpotentials are also relatively higher for the CO$_2$ recycle system because CO diffuses more slowly through the anode than H$_2$ [30]. However, the anode concentration overpotentials are substantially lower than the anode activation overpotentials in the fuel cell with CO$_2$ recycle, so the sluggish CO diffusion is only a secondary factor in the lower performance curves observed in systems with CO$_2$ recycle.
Figure 3.6: Fuel cell overpotentials as a function of current density for the ICFC system with CO₂ recycle (A,C) and H₂O recycle (B,D). Subplots A-B are at 700°C; subplots C-D are at 800°C.

The previous two figures demonstrated that a fuel cell is capable of substantially higher performance when H₂O is sent to the gasifier instead of CO₂ because the electrochemical kinetics are much faster for H₂ than for CO. One might argue that the H₂O recycle system could outperform the CO₂ recycle system by an even greater factor if a higher steam-to-carbon ratio was implemented in the gasifier, which typically produces a more H₂-rich yield that could benefit the fuel cell. However, it was found in this study that raising the steam-to-carbon ratio did not
significantly boost the hydrogen yield of the gasifier because lower temperatures are needed to promote the water-gas-shift reaction. Therefore, steam-to-carbon is fixed at one for the results presented here to optimize performance.

However, maximum power densities are still 3-5 times larger when H₂O is used instead of CO₂ in the ICFC system, even with a low steam-to-carbon ratio. This result provides a clear incentive to select H₂O over CO₂ as the gasifying medium for the ICFC system. However, implementing steam in this system presents a couple of practical design challenges: 1) poisonous H₂S will be produced by untreated solid fuels in the gasifier, and 2) steam must be condensed out of the anode exhaust for recycle. This would likely result in a more complex system with additional components like a desulfurizer and a condenser. This would also lead to parasitic losses because these components operate at lower temperatures than the rest of the system, and additional steam would need to be supplied to the gasifier to compensate for water vapor escaping in the anode exhaust after the condenser. However, the staggering advantage of steam over CO₂ from a power density perspective would likely outweigh these challenges.

### 3.4.2 Impact of Thermal Coupling

The previous results all focused on the ICFC system from subplot A of Figure 3.1, which assumes that the heat demand of the gasifier can be supplied by the fuel cell’s rejected heat. Such a system would require a sophisticated high-temperature heat exchanger between the two components and a finite temperature gap to promote the flow of heat. Therefore, the ICFC system poses more design challenges than the decoupled gasifier + fuel cell (G+FC) system in subplot B of Figure 3.1. However, the ICFC has a theoretically higher efficiency than the G+FC because fuel doesn’t need to be burned to supply the gasifier with heat. This section seeks to quantify the efficiency
advantage of the ICFC over the G+FC for both H₂O and CO₂ recycle at the optimal temperature of 800°C.

Figure 3.7 compares the component and system efficiencies of the G+FC (subplots A,C) to the ICFC (subplots B,D), as defined in equations (3.1), (3.3) and (3.4). Subplots A-B show results for these systems with CO₂ recycle, while subplots C-D show results for the system with H₂O recycle. The gasifier efficiency remains relatively constant with respect to current density in all four cases because flow-rates of gas species into and out of the equilibrium gasifier simply scale with current. The gasifier efficiency is also high due to the idealized pure carbon feed, which bypasses gasifier losses to devolatilization and other side reactions.

The other efficiencies shown in Figure 3.7 closely follow the cell operating voltage curves, which drop off with current density as overpotentials increase. This negative trend highlights the intrinsic trade-off between power and efficiency in the CFC system: theoretically high efficiencies can be obtained when very little current is drawn, but efficiencies diminish when cell power output is maximized. It is clear from Figure 3.7 that the CFC system efficiency is strongly dependent on the operating point of the fuel cell along the polarization curve. Because system efficiency closely tracks with the fuel cell polarization curve, the systems with H₂O recycle attain higher efficiencies and reach higher current densities than the systems with CO₂ recycle. This result is consistent with the key finding of the previous section that system performance is substantially higher with H₂O recycle due to the faster kinetics of H₂ oxidation in the fuel cell.

A comparison between the G+FC (subplots A,C) and ICFC (subplots B,D) systems of Figure 3.7 demonstrates that the coupled ICFC system is capable of attaining significantly higher system efficiencies and current densities. This difference is mostly due to the fact that about 30% of the
incoming carbon fuel is sacrificed to combustion in the G+FC system. This results in a lower system efficiency because more fuel is sent to the system for a given fuel cell power output.

A secondary cause for this system performance gap can be observed by comparing the fuel cell efficiencies, which extend to higher current densities in the ICFC system than in the G+FC system. This is due to the fact that the autothermal gasifier output in the G+FC system is diluted by N₂, as shown in subplots C-D. This in turn lowers the fuel content of the mixture sent to the anode of the G+FC, resulting in both a lower open-circuit potential and a higher anode activation overpotential. Therefore, performance of the G+FC system is hurt by both the combustion of fuel in the gasifier and also by the diluted gasifier output from the air feed.
Figure 3.7: Operating voltage and efficiency curves of the gasifier, fuel cell and combined system for the G+FC (A,C) and ICFC (B,D) systems. Results are shown for CO$_2$ recycle (A-B) and H$_2$O recycle (C-D) all at $T = 800^\circ$C.

Although the results in Figure 3.7 show a large performance gap between the ICFC and G+FC systems, it is important to address a couple of idealized assumptions that were made in order to reach those results. First of all, it was assumed that the gasifier and fuel cell could operate at the same temperature in the ICFC system despite the fact that heat must be transferred between them. In a real system, however, a temperature drop of roughly $\Delta T = 10-15^\circ$C would be needed between the components for a conventional heat exchanger to transfer heat. A more conservative estimate of $\Delta T = 50^\circ$C is used here to account for the fact that this system would require a novel high-temperature heat exchanger, such as liquid sodium heat pipes [29].

The other idealized assumption taken earlier comes from the definition of system efficiency in equation (1), which does not account for useful work that could be extracted from rejected heat. This particularly hurts the efficiency of the G+FC system, which rejects all fuel cell heat to the environment according to this assumption. A more realistic comparison of the two systems uses efficiency as defined in equation (2), which allows the heat rejected by the system to power a bottoming cycle. By accounting for a bottoming cycle and a temperature drop between ICFC components, a more fair comparison between the ICFC and G+FC systems is possible.

Figure 3.8 compares the efficiencies of the ICFC and G+FC systems before and after these two real-world adjustments have been made. Consistent with previous findings, all efficiency curves are higher and reach larger current densities for the systems with H$_2$O recycle than for the systems with CO$_2$ recycle. The G+FC system plots (subplots A,C) indicate that the inclusion of a bottoming cycle significantly boosts efficiency. This result is expected because all heat rejected
by the fuel cell stack goes to waste according to the original definition of system efficiency for the G+FC. Adding a bottoming cycle also boosts system efficiency in the ICFC results (subplots B,D) because there’s still a net heat output after heat is sent to the gasifier. However, the extent of the efficiency gain is noticeably smaller with the addition of a bottoming cycle in the ICFC system compared to the G+FC system because the net heat output is smaller. Despite the fact that the G+FC system efficiency increases more with the addition of a bottoming cycle, the ICFC system still attains superior performance even with the inclusion of a bottoming cycle.

A more fair comparison between the systems in Figure 3.8, however, is between the G+FC with the bottoming cycle and the ICFC with the bottoming cycle and the lower gasifier temperature. Operating the gasifier 50°C cooler causes the ICFC system efficiency to drop because a lower gasifier temperature translates to less fuel exiting the gasifier and entering the anode. This in turn lowers the efficiencies of both the gasifier and the fuel cell and therefore the overall system. However, even when a conservatively large temperature drop is assumed, the ICFC system still performs more efficiently than the G+FC system and reaches higher currents. Thus, the ICFC system has a performance advantage over the G+FC system even when a couple of practical operating considerations are factored into the comparison. The efficiency of the adjusted ICFC system is still highly dependent on the operating point along the polarization curve. However, even at the high-current point of maximum power output, the ICFC system with a bottoming cycle reaches 59% and 55% efficiencies with CO₂ and H₂O, respectively. These values are within a few percentage points of the predictions made in a previous analysis of a similar ICFC system operating at 0.7V with CO₂ and H₂O [11]. These predicted efficiencies upward of 55% also make this CFC system competitive with other state-of-the-art stationary power candidates, such as gas turbine combined cycles and SOFC/gas turbine hybrid systems [24], [45].
Figure 3.8: G+FC system (A,C) and ICFC system (B,D) efficiency curves for CO₂ recycle (A-B) and H₂O recycle (C-D) with T₆ = 800°C. Solid lines take the system efficiency as defined in equation (1); dashed lines take the system efficiency as defined in equation (2). Vertical lines denote the current densities that correspond to maximum power output.

Finally, the exergy efficiencies of the G+FC and ICFC systems with CO₂ and H₂O recycle are compared in Figure 3.9. Efficiencies versus current density are shown for the gasifier, fuel cell and combined system with a bottoming cycle, as defined in equations (3.6), (3.8) and (3.4). The heat exchanger temperature drop of ΔT =50°C is implemented again here for the ICFC system (subplots B,D), which requires a heat transfer from the fuel cell to the gasifier across a finite temperature drop. The exergy efficiency curves in Figure 3.9 closely resemble the energy efficiency curves of the gasifier, fuel cell and system from Figure 3.7. Gasifier exergy efficiencies
are constant with respect to current density because all terms in that expression scale with flow-rate and therefore current. Fuel cell exergy efficiencies, on the other hand, drop with respect to current as a result of increasing overpotentials in the cell. The system exergy efficiencies follow a similar trend with respect to current as a result of increasing fuel cell losses.

The gasifier efficiencies in Figure 3.9 are also consistently higher than 0.8 as a result of using pure carbon fuel, whereas the fuel cell efficiencies drop off to values below 0.3 as a result of increasing cell voltage losses in the limiting current regime. These results indicate that the fuel cell is the component where most of the system’s exergy destruction occurs, not the gasifier. Therefore, CFC system performance is likely limited by the fuel cell, particularly at higher current densities, which correspond to maximum power operation. The system efficiency curves in Figure 3.9 also confirm that the coupled ICFC system (subplots B,D) outperforms the de-coupled G+FC system (subplots A,C). Similarly, a comparison of the system efficiencies indicates that recycling H2O (subplots C-D) rather than CO2 (subplots A-B) boosts performance in terms of both efficiency and power density. These trends are all consistent with the results of the energy efficiency analysis from Figure 3.8, which also highlighted the benefits of a thermally-coupled ICFC system run on steam.
A detailed 1D MEA model is coupled to an equilibrium gasifier to model a carbon fuel cell (CFC) system. The purpose of this study is twofold: 1) to quantify the advantage of recycling H$_2$O rather than CO$_2$ from the anode to the gasifier, and 2) to quantify the advantage of direct thermal coupling between the gasifier and fuel cell in a CFC system. The results of the first study show that the fuel cell consistently performs better when H$_2$O is recycled from the anode to the gasifier instead of CO$_2$. A dominant anode activation overpotential loss in the fuel cell run on CO$_2$ recycle indicates that the sluggish kinetics of CO electrochemical oxidation are responsible for this discrepancy in
performance. Fuel cell performance curves from 700-800°C show that the fuel cell performs 3-5 times better with H₂O instead of CO₂ recycle, with maximum power density values exceeding 1.0 W cm⁻² in the H₂O recycle system.

The results of the second study show that the ICFC system reaches significantly larger current densities and efficiencies than the G+FC system. This advantage arises because the autothermal gasifier in the G+FC system sacrifices carbon fuel and dilutes the gasifier output with nitrogen. Finally, it is shown that the ICFC system still outperforms the G+FC system when a bottoming cycle is included and a finite temperature drop is applied between the ICFC components. Overall system efficiencies of 55-60% are predicted for the final ICFC system when operating at maximum power. An exergy analysis of the different components and systems indicates that the fuel cell is the largest source of lost work potential, especially at high currents. These preliminary findings indicate that the CFC system will perform best when steam is sent to the gasifier and when fuel cell heat is transferred to the gasifier. Such a system is capable of state-of-the-art efficiencies that could significantly reduce CO₂ emissions from coal conversion in the stationary power generation sector. However, further work must go into the design of a high-temperature heat exchanger between the gasifier and fuel cell stack in order to implement this concept. Furthermore, a 2D model for a direct CFC (DCFC) should be developed to study the added benefits of allowing gasification and electrochemical oxidation to occur simultaneously in the same chamber.

### 3.6 References


Chapter 4

Study of Syngas Behavior in SOFCs

One of the distinct advantages of solid oxide fuel cells (SOFCs) is their ability to directly oxidize CO in addition to H₂, which allows them to be run on syngas mixtures. However, membrane-electrode-assembly (MEA) models typically neglect CO electrochemistry in the presence of H₂ and H₂O, assuming that the water-gas-shift reaction proceeds faster than sluggish CO electrooxidation. In this paper, however, we demonstrate with a comprehensive 1D-MEA model that CO electro-oxidation cannot be neglected in syngas mixtures, particularly at high current densities for high CO-content syngas. We first demonstrate that incoming CO is not all shifted to form H₂ before reaching the triple-phase boundary, as previously assumed, due to the equilibrium limitation of the water-gas-shift reaction at 800°C. Furthermore, we confirm that direct oxidation of CO contributes non-negligible current relative to H₂ at high anode overpotentials in syngas mixtures. Together these results show that CO electro-oxidation plays an important role in SOFC performance not only via water-gas-shift reforming, but also via direct oxidation even when H₂ is present. This work suggests that accurate models for both surface reforming and direct electro-oxidation of CO in SOFC anodes must be included in order to capture performance when using syngas mixtures.

4.1 Introduction

A key advantage of solid oxide fuel cells (SOFCs) is their ability to electrochemically oxidize CO, which allows them to run on various abundant hydrocarbon fuels in addition to hydrogen [1]–[3]. SOFCs can potentially be coupled to a gasifier that converts coal, biomass or other solid carbonaceous fuels to syngas [4]–[6]. Because syngas is primarily composed of H₂ and CO, which
can both be directly oxidized on SOFCs [7], it is an ideal fuel stream once contaminants have been removed [8]. However, it has also been shown that H₂ electro-oxidation proceeds 2-3 times faster than CO electro-oxidation on Ni/YSZ [8], [9]. Therefore, the importance of including a model for CO electro-oxidation in SOFC anodes is debatable when H₂ is also present.

Previous researchers have often used a hydrogen-spillover oxidation model but neglected CO electro-oxidation even when both species are present [10], [11]. Neglecting CO electrochemistry is often justified by the following arguments: (1) the rate of CO conversion via surface reforming exceeds the rate of CO electrochemical oxidation [7], [8], and (2) H₂ dominates over CO in charge transfer chemistry [12]. However, these two assumptions may not hold for syngas mixtures with high CO content and low H₂O content, like the output of a coal gasifier [13]. The water-gas-shift reforming reaction, in particular, can only convert CO to H₂ when sufficient H₂O is present [14]. Therefore, it is plausible that non-negligible quantities of CO could reach the triple-phase-boundary (TPB) to react electrochemically for certain syngas mixtures.

Although CO electro-oxidation has been typically neglected in SOFC models with syngas, several researchers have proven its importance in CO+CO₂ systems [15]. Experimental groups have tested nickel-pattern anodes and Ni-YSZ porous anodes with CO mixtures to study the power output from direct electrochemical oxidation [7], [12], [16], [17]. A few mechanisms for CO electro-oxidation on YSZ electrodes have also been proposed [18]–[20]. A comprehensive analysis of CO charge transfer and reaction kinetics on Ni-YSZ anodes appears in Yurkiv et al [21]. Although these researchers agree that the rate of CO electro-oxidation is smaller than that of hydrogen, results indicate that their rates only differ by a factor of two or three [22]. Furthermore, some experimental studies of syngas electrochemical oxidation on Ni-YSZ conclude that CO electro-
oxidation is non-negligible in comparison to H₂ [9], [14], [17]. These results motivate the investigation of CO electro-oxidation in Ni-YSZ anodes when both fuel species are present.

The goal of this work is to quantify the extent to which CO impacts SOFC performance via surface reforming and direct electro-oxidation for a range of syngas mixtures. More specifically, this study breaks down the impact of CO into two parallel pathways: 1) reforming throughout the anode to produce H₂, and 2) direct electro-oxidation at the TPB. This paper implements a 1D MEA model with detailed surface reforming and electrochemical mechanisms for both CO and H₂ electro-oxidation. Anode structural parameters in the model are first fitted to H₂/H₂O and CO/CO₂ experimental data sets. Model polarization curves are then compared to H₂/CO experimental data in order to determine carbon monoxide’s impact on cell performance via reforming and direct oxidation in syngas mixtures.

4.2 Model Description

The objective of the MEA model is to calculate the polarization voltage-current density curve for a given temperature, pressure and syngas fuel composition. The model is isothermal and the domain is 1D with respect to distance from the TPB. The model captures multiphysics processes of transport through porous electrodes, thermochemical reactions, and electrochemical mechanisms for both H₂ and CO [23]–[25]. The governing equations for conservation, transport and thermochemistry are introduced first, followed by a breakdown of how each cell overpotential is modeled. The focus of this study is to isolate the role of CO in the anode by comparing the model to experimental polarization data by Jiang and Virkar [7]. Therefore, anode concentration and activation overpotentials are modeled in detail to capture the complex coupling of H₂ and CO via reforming and oxidation. However, open-circuit potential, ohmic losses and cathode
overpotentials are taken directly from the experiment in order to minimize uncertainty and isolate
the role of CO in the anode.

4.2.1 Conservation Equations

The gas phase mass conservation equation in the porous electrodes is:

\[ \varepsilon \frac{\partial c_k}{\partial t} = A_s \dot{s}_{surf,k} + \dot{s}_{gas,k} - \nabla \cdot J_k \quad (k = 1, \ldots, K_g) \] (4.1)

where \( \varepsilon \) is the porosity, \( c_k \) is the concentration of gas species \( k \) [mol m\(^{-3}\)], \( J_k \) is the molar flux of \( k \) [mol m\(^{-2}\) s\(^{-1}\)], \( \dot{s}_{surf,k} \) is the production rate of \( k \) by heterogeneous reactions [mol m\(^{-2}\) s\(^{-1}\)], \( A_s \) is the specific catalyst area per unit volume of electrode [m\(^{-1}\)], and \( K_g \) is the total number of gas species. The surface production rates of the gas species on nickel, \( \dot{s}_{surf,k} \), are obtained from the heterogeneous reforming model, described in more detail in the thermochemistry section. The production rate of gas species \( k \) by gas-phase reactions is assumed to be negligible in comparison with the catalytic surface reaction rates on nickel (\( \dot{s}_{gas,k} = 0 \)). This assumption is an accurate representation of the relative rates of reforming reactions at the high operating temperatures of SOFCs when a nickel catalyst surface is involved. The molar fluxes, \( J_k \), in equation (1) are determined by the dusty gas model (DGM), which is described further in the section on transport in porous media. The molar fluxes of gas phase species at the TPB are determined by H\(_2\) and CO currents:

\[ J_{H_2,a} = i_{H_2}/2F; J_{H_2,a} = -i_{H_2}/2F; J_{CO,a} = i_{CO}/2F; J_{CO_2,a} = -i_{CO}/2F; J_{O_2,c} = (i_{H_2} + i_{CO})/4F \] (4.2)

where the subscript \( a \) denotes the anode TPB, and the subscript \( c \) denotes the cathode TPB. Fluxes are defined here as positive into the electrolyte and negative away from the electrolyte.
The surface species mass conservation equation in the porous anode is:

\[ \frac{\partial c_{\text{surf},k}}{\partial t} = \dot{s}_{\text{surf},k} \quad (k = 1, \ldots, K_s) \quad (4.3) \]

where \( c_{\text{surf},k} \) is the concentration of surface species \( k \) [mol m\(^{-2}\)], \( \dot{s}_{\text{surf},k} \) is the production rate of \( k \) by heterogeneous reactions [mol m\(^{-2}\) s\(^{-1}\)], and \( K_s \) is the total number of surface species.

These gas and surface mass conservation equations are applied over a series of \( m \) discrete nodes in both electrodes. Surface reforming occurs along all nodes of the anode because nickel is dispersed throughout the anode. The electrochemical reactions, however, occur only at the \( m \)th node of each electrode, where the TPB is located. Although YSZ is dispersed throughout the anode thickness, the diffusion of \( O^{2-} \) ions through YSZ in the anode is slow relative to the rate of electrochemical oxidation. Therefore, although the TPB is theoretically distributed throughout the entire anode, it’s reasonable to assume that electrochemical reactions occur at the last node of the anode model, since the TPB is localized to a small region (~10 \( \mu \)m thick) adjacent to the electrolyte [11], [26]. Moreover, we note that this localized electrochemistry assumption applies to the experiment considered here because the cell is anode-supported (~1 mm thick). Because the model is 1D with respect to distance from the TPB, it physically represents a button cell configuration, like the set-up of the experiment of interest.

### 4.2.2 Transport in Porous Media

The gas phase fluxes \( J_k \) from equation (4.1) are computed using the dusty gas model (DGM), an extension of the Stefan-Maxwell diffusion equations [27]. The DGM is a convenient approach to modeling combined bulk and Knudsen diffusion, and can explain physical phenomena in porous
media that cannot be captured by Fick’s model [28]. The DGM can be written as an implicit relationship among molar concentrations, molar fluxes and concentration gradients:

\[-\nabla c_i = \sum_{j \neq i} \frac{1}{c_i D_{ij}} (c_j J_i - c_i J_j) + \frac{J_i}{D_{iM}} + \frac{B_0}{\mu_{mix}} \frac{c_i}{D_{iM}} \nabla p \]  

(4.4)

where \( c_t = \frac{p}{RT} \) is the total molar concentration [mol m\(^{-3}\)], \( D_{ij} \) is the effective binary diffusion coefficient in the porous medium [m\(^2\) s\(^{-1}\)], \( \mu_{mix} \) is the mixture viscosity [kg m s\(^{-1}\)], \( B_0 \) is the permeability [m\(^2\)], and \( D_{iM} \) is the effective Knudsen diffusion coefficient [m\(^2\) s\(^{-1}\)].

The effective Knudsen diffusion coefficient for component \( i \) is governed by [27]:

\[ D_{iM} = d_0 \varepsilon \sqrt{\frac{8RT}{\pi M_i}} \]  

(4.5)

where \( d_0 \) is the average pore diameter [m], \( M_i \) is the molar mass of species \( i \) [kg mol\(^{-1}\)], and \( \frac{\varepsilon}{\tau} \) is the ratio of porosity to tortuosity in the electrode. The transport of gaseous species through porous electrodes is affected by electrode microstructure parameters such as porosity (\( \varepsilon \)), permeability (\( B_0 \)), pore size (\( d_0 \)), and tortuosity (\( \tau \)). A more detailed description of the mass transport model with definitions and equations for each term in the DGM relationship is given elsewhere [23].

### 4.2.3 Thermochemistry

Because of the high temperatures (700-800°C) and catalytic surfaces in the anode, various thermochemical reactions occur throughout the anode. This model implements a detailed surface mechanism on nickel that was first developed by Hecht et al [3], and then extended to a wider temperature range by Janardhanan and Deutschmann [11]. This mechanism consists of 42
reactions involving six gaseous species and twelve surface species. The net production rate of gas or surface species $k$ due to heterogeneous reactions is given by:

$$
\dot{s}_{surf,k} = \sum_i R_{surf,i} V_{i,k}
$$

(4.6)

where $R_{surf,i}$ is the rate of heterogeneous reaction $i$ [mol m$^{-2}$s$^{-1}$] and $V_{i,k}$ is the stoichiometric coefficient of species $k$ in reaction $i$. This surface species production term appears in equations (4.1) and (4.3), the species conservation equations for the gas and surface phases. A list and detailed description of the full surface reforming mechanism on nickel is presented elsewhere [11].

### 4.2.4 Cell Overpotentials

In order to determine the polarization curve, an accurate model for cell operating voltage as a function of current density is needed. First, the equilibrium potential of the cell at open-circuit conditions is given by [15]:

$$
E_{rev} = \frac{RT}{4F} \ln \left( \frac{p_{O_2,c}}{p_{O_2,a}} \right)
$$

(4.7)

where $p_{O_2,c}$ and $p_{O_2,a}$ are the equilibrium oxygen partial pressures at the cathode and anode channels, respectively. This equation was previously derived from the standard Nernst equation for OCV under conditions when chemical equilibrium can be assumed in the anode channel [15]. The cathode oxygen partial pressure is simply $p_{O_2,c} = .21P$ for air sent to the cathode. Here, reversible potential must be defined in terms of oxygen concentration because there are two parallel charge-transfer pathways.

At non-zero current, the operating cell voltage is lower than the OCV due to several loss modes quantified as overpotentials. Operating voltage can thus be expressed as the difference between the reversible cell potential and these various voltage losses:
where $\eta_{\text{act,a}}$ and $\eta_{\text{act,c}}$ are the activation overpotentials at the anode and cathode, $\eta_{\text{con,a}}$ and $\eta_{\text{con,c}}$ are the concentration overpotentials at the anode and cathode, and $\eta_{\text{ohm}}$ is the total ohmic overpotential.

Detailed physical models for the anode activation and concentration overpotentials are implemented here to accurately capture all the major reforming and charge-transfer reactions involving CO and H2. The values for ohmic and cathodic overpotentials, however, are taken directly from experimental measurements previously published by Virkar’s group [29]. Similarly, OCV values are matched to the same experimental data set by adjusting the anode mixture for air leakage. This approach is taken to isolate the impact of CO on anode overpotentials while comparing the model predictions to experimental data for operating voltage.

### 4.2.4.1 Experimental Overpotentials

In order to focus on how CO impacts cell performance, physical models are replaced with experimental data for portions of the model outside the anode. First, the model and experimental OCVs are matched by introducing air leakage into the anode channel until the reversible potential from equation (7) matches the experimental OCV for that anode mixture. This is necessary to account for the offset between theoretical and experimental OCV’s, which is a common problem encountered in SOFC modeling, and is often attributed to electronic or gas leakages [7], [10], [30]. Some previous groups have accounted for this offset by introducing an electronic leakage overpotential term that gets subtracted off from the reversible potential [10], [23]. It is assumed here, however, that the OCV difference is caused by air leakage into the anode chamber rather than electronic leakage, consistent with claims made by the experimental group of interest here.
This model accounts for air leakage by adjusting the reported fuel stream mixture at the anode channel until theoretical and experimental OCV’s match, as described in the simulation procedure. This novel approach of physically accounting for air leakage into the anode channel is explored and compared against the electronic leakage model in more detail elsewhere [31].

The total cathode and ohmic overpotentials are fitted to experimental values versus current provided by the same research group that the polarization curves in this study come from [29]. A simple polynomial curve fit to their total cathode overpotential data yields:

\[
\eta_{\text{tot},c} = \eta_{\text{con},c} + \eta_{\text{act},c} = 0.0018i^5 - 0.019i^4 + 0.076i^3 - 0.15i^2 + 0.18i + 0.010
\]  

(4.9)

where \( i \) [A cm\(^{-2}\)] is the total cell current density \( (i = i_{H_2} + i_{CO}) \). This curve-fit provides an excellent fit \( (R^2 = .9995) \) to Jiang & Virkar’s 40 wt% LSC+60 wt% SDC cathode at 800°C for current densities ranging up to 4 A cm\(^{-2}\) based on a pure H\(_2\) data set [29]. Because cathode losses are purely a function of current, and independent of the anode fuel composition, this curve-fit is widely applicable to all fuel mixtures tested later using the same cell and temperature [7].

The total ohmic overpotential of this same button cell is:

\[ \eta_{\text{ohm}} = iR_{\text{tot}} = .0588i \]  

(4.10)

where \( R_{\text{tot}} \) [\( \Omega \) cm\(^{-2}\)] is the total resistance of the cell to ion and electronic flow, obtained by a linear regression on the same group’s experimental data [29]. Their button cell contains a bi-layer SDC+YSZ electrolyte, and the majority of the ohmic losses are attributed to ionic resistance in the electrolyte [29].
4.2.4.2 Anode Overpotentials

Unlike the other loss modes that are taken directly from the experimental data, the anode overpotentials are represented by detailed physical models in order to study the impact of CO on cell performance. Anode concentration overpotential accounts for losses associated with the diffusion of gas species through the thick porous anode to reach the TPB at the last node. Anode concentration overpotential is modeled as the difference between reversible cell potential at the anode channel and at the anode TPB:

\[ \eta_{\text{con,a}} = E_{\text{rev}} - E_{\text{rev,a,TPB}} = \frac{RT}{4F} \ln \left( \frac{p_{O_2,a,\text{TPB}}}{p_{O_2,a}} \right) \]

where \( p_{O_2,a} \) and \( p_{O_2,a,\text{TPB}} \) are the equilibrium partial pressures of O\(_2\) at the anode channel and TPB, respectively. The equilibrium partial pressure of O\(_2\) at the anode channel (\( p_{O_2,a} \)) is determined by introducing an air leak into the reported anode channel mixture until the modeled and experimental OCV’s match. The equilibrium partial pressure of O\(_2\) at the TPB is determined at each current by solving the transport equations in the anode until steady-state species profiles are obtained, as described in the simulation procedure and in previous publications [23].

The anode activation overpotential is a function of currents from both H\(_2\) and CO. Detailed multi-step mechanisms for both species are implemented in this model, resulting in Butler-Volmer expressions that relate current to anode activation overpotential. Although alternative models have been suggested [32], Butler-Volmer expressions are still considered the standard model for capturing non-linear behavior at low current densities [33]. Certain steps must be assumed rate-limiting in each mechanism due to a lack of available kinetic data to implement the full mechanisms. These rate-limiting steps were selected based on previous researchers’ work, and both the H\(_2\) and CO mechanisms have been previously published [23], [24].
4.2.4.2.1 Hydrogen Electro-oxidation Mechanism

The mechanism for H₂ oxidation consists of five elementary reactions [10], [34]:

- Adsorption of hydrogen on nickel:

  \[
  H_2(g) + 2(Ni) \leftrightarrow 2H(Ni) \quad (H.1)
  \]

- Transfer of oxygen ion from bulk to surface YSZ sites:

  \[
  O_0^X(YSZ) + (YSZ) \leftrightarrow O^{2-}(YSZ) + V_0^{**}(YSZ) \quad (H.2)
  \]

- Charge-transfer reactions at the TPB:

  \[
  H(Ni) + O^{2-}(YSZ) \leftrightarrow (Ni) + OH^-(YSZ) + e^-(Ni) \quad (H.3)
  \]

  \[
  H(Ni) + OH^-(YSZ) \leftrightarrow (Ni) + H_2O(YSZ) + e^-(Ni) \quad (H.4)
  \]

- Desorption of steam from YSZ:

  \[
  H_2O(YSZ) \leftrightarrow H_2O(g) + (YSZ) \quad (H.5)
  \]

It has been shown that the second charge-transfer step (H.4) is rate-limiting for lower current densities such that all other steps can be modeled in equilibrium [23], [10]. When (H.4) is rate-limiting, the following Butler-Volmer expression can be derived:

\[
i_{H_2(H.A)} = i_0 \left[ \exp \left( \frac{3F\eta_{act,a}}{2RT} \right) - \exp \left( - \frac{F\eta_{act,a}}{2RT} \right) \right]
\]

where \( i_0 = i_{(H.A)}^* \left( \frac{p_{H_2}^{1/4}P_{H_2}^{1/4}}{1+(K_{H_2})^{1/2}} \right) \) [10]. At higher current densities, a better fit to experimental data can be obtained by assuming that the hydrogen adsorption step (H.1) becomes rate-limiting [23], resulting in the following Butler-Volmer expression:
\[ i_{H_2,(H.1)} = i^*_{(H.1)} P_{H_2} \left[ 1 - \exp \left( -2 \frac{F\eta_{act,a}}{RT} \right) \right] \] (4.13)

where \( i^*_{(H.1)} = \frac{a_{TPB}(2F)\gamma_{H_2}}{\sqrt{2\pi M_{H_2}RT}} \) [23], [25] and the sticking coefficient of hydrogen is \( \gamma_{H_2} = 0.01 \) [11].

The “switch-over” from (H.4) to (H.1) as the rate-limiting step occurs when the current predicted by equation (4.13) becomes less than the current predicted by equation (4.12):

\[ i_{H_2} = \min\{i_{H_2,(H.1)}, i_{H_2,(H.4)}\} \] (4.14)

This switch-over point can be easily observed in later plots, where voltage drops off abruptly near the limiting current density. The unknown parameters \( i^*_{(H.4)} \) and \( a_{TPB} \) in equations (4.12)-(4.13) are determined by fitting the model to experimental H2/H2O data later.

**4.2.4.2.2 Carbon Monoxide Electro-oxidation Mechanism**

The global electro-oxidation reaction for CO can be written in Kroger-Vink notation as:

\[ CO(g) + O^X_0(YSZ) \leftrightarrow CO_2(g) + V_0^{**}(YSZ) + 2e^-(Ni) \] (4.15)

where \( O^X_0(YSZ) \) is an oxygen ion on a YSZ oxygen surface site, and \( V_0^{**}(YSZ) \) is a vacant YSZ oxygen surface site. A mechanism that includes three elementary reactions on a Ni-YSZ patterned anode is used here [24]:

- Adsorption of CO on nickel:
  \[ CO(g) + (Ni) \leftrightarrow CO(Ni) \] (CO.1)

- Charge-transfer reactions at the TPB:
  \[ O^X_0(YSZ) + (YSZ) \leftrightarrow O^-(YSZ) + V_0^{**}(YSZ) + e^-(Ni) \] (CO.2)
  \[ O^-(YSZ) + CO(Ni) \leftrightarrow CO_2(g) + (YSZ) + (Ni) + e^-(Ni) \] (CO.3)
The adsorption step (CO.1) is always modeled in equilibrium because CO charge-transfer kinetics are relatively sluggish and CO has a strong affinity to nickel \( \gamma_{CO} = 0.5 \) [10]. Current from CO is simply given by the sum of the currents produced by the two charge-transfer steps, since oxygen only spills over to CO in this model:

\[
i_{CO} = i_{(CO,2)} + i_{(CO,3)}
\]  

(4.16)

where \( i_{(CO,2)} \) and \( i_{(CO,3)} \) are the currents produced by steps (CO.2) and (CO.3), respectively [A cm\(^{-2}\)]. Although the rates of the two charge-transfer reactions are not necessarily equal, the currents produced by each step must be the same because they are sequential steps in the only pathway for global oxidation of CO. Therefore, equation (4.16) simply reduces to \( i_{CO} = 2i_{(CO,2)} \) because \( i_{(CO,2)} = i_{(CO,3)} \) [24]. The individual currents for each charge-transfer step can be expressed as functions of the local electric potential [24]:

\[
i_{(CO,2)} = Fl_{TPB} \left\{ k_{2,f} \Gamma_{YSZ} \theta_{YSZ} \exp \left( \frac{FE}{2RT} \right) - k_{2,b} \Gamma_{YSZ} \theta_{O^-} \exp \left( \frac{-FE}{2RT} \right) \right\}
\]  

(4.17)

\[
i_{(CO,3)} = Fl_{TPB} \left\{ k_{3,f} \Gamma_{YSZ} \theta_{O^-} \Gamma_{Ni} \theta_{CO} \exp \left( \frac{FE}{2RT} \right) - k_{3,b} \Gamma_{YSZ} \theta_{YSZ} \Gamma_{Ni} \theta_{Ni} \frac{p_{CO_2}}{RT} \exp \left( \frac{-FE}{2RT} \right) \right\}
\]  

(4.18)

where \( l_{TPB} \) is the TPB length [m cm\(^{-2}\)], \( p_{CO_2} \) is the partial pressure of CO\(_2\) at the TPB [Pa], and \( k_{i,f} \) and \( k_{i,b} \) are the forward and backward reaction rate constants of (CO.i). \( \Gamma_{YSZ} \) and \( \Gamma_{Ni} \) are the total surface site densities of YSZ and nickel, respectively [mol m\(^{-2}\)], \( \theta_{O^-} \) and \( \theta_{CO} \) are the surface coverages of O\(^-\)(YSZ) and CO(Ni), and \( \theta_{YSZ} \) and \( \theta_{Ni} \) are the vacancy coverages of YSZ and nickel at the TPB.

The forward and backward rate constants come from previous work that fitted this mechanism to patterned-anode Tafel plot data [24]. Arrhenius expressions were derived for each rate constant to
fit the model to data at temperatures of 700-775°C. A minor extrapolation is made here to 800°C, the operating temperature for the experimental data presented later. Evaluating the rate constants at 800°C yields the following values: \( k_{2,f} = 6.5 \times 10^2 \) [m s\(^{-1}\)], \( k_{2,b} = 5.95 \times 10^6 \) [m s\(^{-1}\)], \( k_{3,f} = 3.78 \times 10^0 \) [m\(^3\) mol\(^{-1}\) s\(^{-1}\)] and \( k_{3,b} = 3.6 \times 10^4 \) [m\(^6\) mol\(^{-2}\) s\(^{-1}\)].

Vacancy coverages on YSZ and nickel in equations (4.17)-(4.18) are determined by taking the difference between total surface site densities and adsorbed species surface densities [mol m\(^{-2}\)]. A few species are present on the YSZ surface when both the H\(_2\) and CO mechanisms are active: O\(^2-\)(YSZ), O\(^-\)(YSZ), OH\(^-\)(YSZ) and H\(_2\)O(YSZ). However, coverages of OH\(^-\)(YSZ) and H\(_2\)O(YSZ) are negligibly small in comparison to the coverages of O\(^2-\)(YSZ) and O\(^-\)(YSZ), based on previous detailed YSZ modeling efforts [35]. It has also been shown that O\(^2-\)(YSZ) is the dominant species on YSZ oxygen surface sites with a surface coverage approximately equal to 0.9 [35]. This coverage is nearly constant across a wide range of conditions because it is mostly a function of the yttrium doping level in YSZ [36]. Therefore, assuming that O\(^2-\)(YSZ) is fixed at 0.9, the YSZ vacancy coverage can be approximated as:

\[
\theta_{YSZ} = 1 - \theta_{O^2-} - \theta_{O^-} - \theta_{OH^-} - \theta_{H_2O} \approx 1 - \theta_{O^2-} - \theta_{O^-} \approx 0.1 - \theta_{O^-} \quad (4.19)
\]

Similarly, the vacancy coverage of nickel at the TPB is given by:

\[
\theta_{Ni} = 1 - \sum_k k^S \theta_k \quad (4.20)
\]

where the summation occurs over all twelve surface species on nickel at the last node. These coverages are determined by solving the transport equations throughout the anode along with the 42-step heterogeneous thermochemical mechanism [11]. Because CO has a stronger affinity to nickel than H\(_2\), its relative coverage is larger than indicated by the ratio of CO:H\(_2\) in the gas-phase.
As an example, the coverages of \( CO(Ni) \) and \( H(Ni) \) at the TPB are listed in Table 4.1 for several syngas mixtures at open-circuit conditions. These cases show that CO occupies a disproportionately large fraction of the available nickel surface sites at the TPB, which further motivates this investigation of the importance of CO electro-oxidation.

Table 4.1: Coverages of hydrogen and carbon monoxide on nickel at the TPB at open-circuit conditions for several syngas mixtures.

<table>
<thead>
<tr>
<th>Gas-phase composition at anode channel</th>
<th>TPB coverage of ( H(Ni) )</th>
<th>TPB coverage of ( CO(Ni) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>54% ( H_2 ) + 46% ( CO )</td>
<td>.17</td>
<td>.40</td>
</tr>
<tr>
<td>45% ( H_2 ) + 55% ( CO )</td>
<td>.15</td>
<td>.42</td>
</tr>
<tr>
<td>32% ( H_2 ) + 68% ( CO )</td>
<td>.12</td>
<td>.44</td>
</tr>
<tr>
<td>20% ( H_2 ) + 80% ( CO )</td>
<td>.10</td>
<td>.47</td>
</tr>
</tbody>
</table>

\( E \) in equations (4.17)-(4.18) is defined as the electric potential difference across the anode-electrolyte double layer, which can be expressed as the sum of the equilibrium potential difference and the anode activation overpotential: \( E = E_{eq} + \eta_{act,a} \). Equilibrium potential is defined as the anode-electrolyte double layer potential difference at open-circuit conditions, and \( E_{eq} \) is determined by solving equations (4.17)-(4.18) with \( \eta_{act,a} = 0 \), \( i_{(CO,2)} = 0 \), and \( i_{(CO,3)} = 0 \). At steady-state, equations (4.17)-(4.18) can be solved for \( \theta_0 \) because \( i_{(CO,2)} = i_{(CO,3)} \) at steady-state in order to maintain a constant surface coverage of \( \theta_0 \)–[24]. Total current from CO can then be calculated from equation (4.16), which reduces to \( i_{CO} = 2i_{(CO,2)} \) at steady-state.
4.3 Simulation Procedure

Temperature, pressure and experimental OCV are inputs to the model, which generates a current density-voltage curve by iterating through anode activation overpotential. Steps 2)-3) are repeated for increasing anode activation overpotential until a full polarization curve is generated. The following steps are implemented in a MATLAB® script for each cell performance curve, as shown in Figure 4.1.

Figure 4.1: Simulation procedure to generate a polarization curve for a given anode mixture.

1) Calculate the equilibrium mixture at the anode channel.

2) Resolve current densities and anode species profiles.

Iterate through anode activation overpotential.

3) Calculate cell overpotentials and operating voltage.

1) Calculate the equilibrium mixture at the anode channel.
As mentioned earlier, the reversible cell potential from equation (4.7) is typically larger than the experimental OCV for a reported anode mixture as a result of air leakage into the anode. Therefore, the anode channel composition in the model is adjusted by incrementally adding air to the experimentally reported anode mixture until the theoretical and experimental OCV values match, as detailed in Appendix A. The final equilibrated gas mixture is also assumed to be the actual mixture present in the anode channel because oxygen leaking into the anode reacts very quickly with H₂ and CO. Gas-phase equilibrium is also a good assumption for this particular experimental set-up because the gases have a long residence time in the fuel delivery system before reaching the cell [7]. The anode channel mixture determined in this step is also used in the following steps for finite current to accurately represent the physical impact of air leakage on cell performance.

2) Resolve current densities and anode species profiles.

The final equilibrium anode channel mixture from step 1) is the mixture used in the anode channel for the model. Because anode activation overpotential is an input, current densities from H₂ and CO can be estimated along with an initial guess for TPB concentrations using equations (4.14) and (4.16). The initial fluxes of gas-phase species at the TPB are then given by equation (4.2), and these fluxes are boundary conditions to equation (4.4), which is cast in matrix form as:

\[-\nabla c_i - \frac{B_0}{\mu_{mix}} \frac{c_i}{D_i^e} \nabla P = \sum_{j \neq i} \frac{1}{c_t D_{ij}^e} (c_j J_i - c_i J_j) + \frac{I_i}{D_i^e} = [H][J]\]

(4.21)

where [J] is a flux column vector and [H] is a matrix defined by:

\[h_{kl} = \left[ \frac{1}{D_{kl}^e} + \sum_{j \neq k} \frac{x_j}{D_{kj}^e} \right] \delta_{kl} + (\delta_{kl} - 1) \frac{x_k}{D_{kl}^e}\]

(4.22)
The left-hand-side of equation (4.21) is calculated using present values for concentrations and boundary conditions, estimating $\nabla c_i$ using a forward difference approximation. The matrix $[H]$ is also calculated using present concentrations. The molar fluxes are then given by the system:

$$[J] = [H]^{-1}[LHS]$$

and fluxes $J_k$ can then be substituted into gas species conservation equations (4.1) and (4.3). These conservation equations become a set of ordinary differential equations when equation (4.23) is cast into a finite-volume form using the flux boundary conditions at the interface.

The surface generation rates in the conservation equations are calculated using the heterogeneous reforming model based on the present gas surface species concentrations. The gas and surface species are solved simultaneously using the "ode15s" function in MATLAB® until steady-state is reached [23]. The H$_2$ and CO current densities are then updated based on the new concentration profiles, and this process is repeated until the non-linear "fsolve" function converges on anode concentration profiles and current densities.

3) **Calculate cell overpotentials and operating voltage.**

Once the anode profiles and currents are resolved, all of the cell overpotentials can be computed. The anode concentration overpotential is given by equation (4.11), where the equilibrium partial pressure of oxygen at the anode TPB is given by running the Cantera "equilibrate" function on the actual gas mixture at the last node where the TPB is located. Total cathode ohmic overpotentials are determined as functions of total current densities using equations (4.9) and (4.10). Finally, the operating voltage is given by subtracting all overpotentials from the reversible cell potential, according to equation (4.8).
4.4 Simulation Results

Table 4.2 lists all the constant operating conditions and anode structural parameters, which are mostly taken directly from Virkar’s experimental group [7]. This approach is taken to minimize uncertainty and to match this model to their particular experiment, which provides the most comprehensive published data set for anode-supported Ni/YSZ SOFCs with CO/CO₂, H₂/H₂O and H₂/CO mixtures.

Table 4.2: Constant operational and structural parameters for the SOFC model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Operating Conditions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>800</td>
<td>°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>$P$</td>
<td>1</td>
<td>atm</td>
</tr>
<tr>
<td><strong>Anode Structural Parameters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of nodes</td>
<td>$m$</td>
<td>10</td>
<td>--</td>
</tr>
<tr>
<td>Thickness</td>
<td>$L_a$</td>
<td>1100</td>
<td>μm</td>
</tr>
<tr>
<td>Porosity</td>
<td>$\varepsilon$</td>
<td>0.54</td>
<td>--</td>
</tr>
<tr>
<td>Average pore radius</td>
<td>$r_p$</td>
<td>0.50</td>
<td>μm</td>
</tr>
<tr>
<td>Average particle diameter [10]</td>
<td>$d_p$</td>
<td>2.50</td>
<td>μm</td>
</tr>
<tr>
<td>Specific catalyst area [10]</td>
<td>$A_s$</td>
<td>1080</td>
<td>cm⁻¹</td>
</tr>
<tr>
<td>YSZ surface site density [21]</td>
<td>$\Gamma_{YSZ}$</td>
<td>1.3*10⁻⁵</td>
<td>mol m⁻²</td>
</tr>
<tr>
<td>Nickel surface site density [11]</td>
<td>$\Gamma_{Ni}$</td>
<td>2.66*10⁻⁵</td>
<td>mol m⁻²</td>
</tr>
</tbody>
</table>

Results are presented here in two sections: 1) parameter fitting and 2) syngas studies. The first section fits unknown physical parameters in the model to H₂/H₂O and CO/CO₂ experimental data.
sets [7]. The combined model is then validated against H₂/CO data from the same group to ensure that the fitted values accurately represent the cell used in all their experiments. The impact of CO is then investigated by comparing experimental H₂/CO data to the model with and without reforming and CO electro-oxidation enabled.

### 4.4.1 Fitting the Model

Unknown parameters in the anode are determined by fitting the model to H₂/H₂O and CO/CO₂ data sets [7]. These parameters are intentionally fit to data sets from the same experimental group providing the H₂/CO data used later in order to accurately represent the physical anode structure of the cells used throughout these experiments. The four fitting parameters are listed in Table 4.3 along with their corresponding equations.

Table 4.3: Parameters obtained by fitting the model to porous anode experimental data. $i^*_e(H₂, A)$ and $a_{TPB}$ come from fitting to H₂/H₂O mixtures; $l_{TPB}$ and $τ$ come from fitting to CO/CO₂ mixtures. The equations these parameters show up in are given in the last column.

<table>
<thead>
<tr>
<th>Name</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Equation(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exchange current density pre-factor</td>
<td>$i^*_e(H₂, A)$</td>
<td>10</td>
<td>A cm² atm⁻³/₄</td>
<td>(12)</td>
</tr>
<tr>
<td>Nominal TPB area</td>
<td>$a_{TPB}$</td>
<td>.013</td>
<td>--</td>
<td>(13)</td>
</tr>
<tr>
<td>TPB length</td>
<td>$l_{TPB}$</td>
<td>300</td>
<td>m cm²</td>
<td>(17)-(18)</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>$τ$</td>
<td>2.0</td>
<td>--</td>
<td>(5)</td>
</tr>
</tbody>
</table>

The two parameters fitted to H₂/H₂O data, $i^*_e(H₂, A)$ and $a_{TPB}$, are unknown constants that appear in equations (4.12) and (4.13), the Butler-Volmer expressions for the two rate-limiting steps in the H₂ mechanism. $i^*_e(H₂, A)$ is an exchange current density pre-factor that includes rate constants from
other steps in the mechanism [10], and $a_{TPB}$ is a dimensionless ratio of TPB area to cell footprint area. $i_{(H, A)}^*$ fits the model to operating voltage data at lower currents while $a_{TPB}$ fits the model to operating voltage data at higher current densities where hydrogen adsorption is rate-limiting. The values of these two fitting parameters are the same order of magnitude as previously reported values ($i_{(H, A)}^* = 8.5, a_{TPB} = .0086$) that correspond to a different set of structural parameters than those given in Table 4.2 [23].

The resulting performance curves for this fitted model are plotted against experimental data [7] for four H$_2$/H$_2$O mixtures in Figure 4.2. These results demonstrate that the H$_2$ electro-oxidation model is capable of accurately predicting cell performance away from the limiting current regime over a wide range of H$_2$/H$_2$O mixtures. The switch-over to rate-limiting H$_2$ adsorption can be readily observed in these plots as the points where operating voltage begins to rapidly drop off. This switch-over causes the model to under-predict experimental limiting current for lean H$_2$/H$_2$O mixtures. However, the model would significantly over-predict experimental limiting current densities if this switch-over to rate-limiting adsorption were not accounted for [10], [23]. Overall, the fit of this model to H$_2$/H$_2$O data is an improvement over previously published efforts to fit the same data set [10].
The two parameters that are fitted to the CO/CO₂ data, \( l_{TPB} \) and \( \tau \), are unknown anode structural constants that appear in equations (4.17)-(4.18) and (4.5), respectively. TPB length, \( l_{TPB} \), is a physical parameter that shows up in the two Butler-Volmer expressions for the CO mechanism. Note that this parameter does not appear explicitly in the H₂ mechanism equations because it is embedded along with other constants in the pre-factor terms, which were derived by assuming a rate-limiting step. Tortuosity is another unknown physical parameter that is needed to determine the effective diffusivities in the porous transport DGM equation (4.4), which models the transport of all gas species including H₂ and H₂O.
The performance curves for the fitted CO model are plotted against experimental data [7] for three different CO/CO₂ mixtures in Figure 4.3. The model predicts limiting current density well for the two moderate CO/CO₂ mixtures. In addition, the model provides a reasonable fit to experimental data for 100% CO. Although the model provides a rough estimate of the experimental CO/CO₂ data, it is the first published model to fit this data set. Because the fitted model reasonably predicts a wide range of H₂/H₂O and CO/CO₂ mixtures, it can also be applied to a wide range of syngas mixtures to predict cell performance.

![Figure 4.3. Polarization curves for the fitted model compared to experimental data for CO/CO₂ mixtures in a SOFC at 800°C \(I_{TPB}= 300 \text{ m cm}^{-2}, \tau = 2.0\).](image)

For the combined model with both H₂ and CO electrochemical oxidation, all fitting parameters are the same as those presented in Table 4.3. This full version of the model includes the effects of
both surface reforming and direct electro-oxidation of both species. Although the fundamental oxidation mechanisms for \( \text{H}_2 \) and \( \text{CO} \) are not altered when both species are oxidized simultaneously, the two species interact via surface reforming and also compete for active sites on nickel. Therefore, the current contributions of \( \text{H}_2 \) and \( \text{CO} \) are inter-dependent because partial pressures and surface coverages of both species at the TPB are accounted for in both mechanisms. The predictions of this combined model agree well with experimental data over a wide range of \( \text{H}_2/\text{CO} \) mixture, as shown in Figure 4.4. This indicates that the \( \text{H}_2 \) and \( \text{CO} \) mechanisms fitted individually to \( \text{H}_2/\text{H}_2 \text{O} \) and \( \text{CO}/\text{CO}_2 \) data can successfully be implemented together to model cell performance with syngas mixtures.

![Figure 4.4: Polarization curves for the fitted model compared to experimental data for \( \text{H}_2/\text{CO} \) mixtures in a SOFC at 800°C.](image)

128
4.4.2 Study of CO in SOFCs

In order to study the impact of CO on cell performance via reforming and direct electro-oxidation, three different versions of the model are compared here to experimental data: 1) no reforming or CO oxidation, 2) reforming but no CO oxidation, and 3) reforming and CO oxidation. This breakdown gives clear insight on how the addition of CO impacts cell performance via surface reforming reactions and direct electro-oxidation. Figure 4.5 compares the model to experimental data for four H₂/CO mixtures [7]. Each subplot in Figure 4.5 compares the experimental data set to these three versions of the model in order to isolate the impacts of CO on performance via reforming and direct oxidation. The model without reforming or CO oxidation reasonably predicts the data in subplot A, which has more H₂ than CO in the gas phase. This result implies that CO only makes a minor contribution to cell performance (via reforming and oxidation) when SOFCs are fed a hydrogen-rich syngas mixture.

However, the model without reforming or CO oxidation under-predicts the limiting current in the three cases where CO is the dominant species in the mixture (subplots B-D of Figure 4.5). The model with reforming but no CO oxidation shows a sizeable improvement over the model without reforming in those three cases, which indicates that CO contributes to cell performance via water-gas-shift reforming to produce H₂ in those cases. However, including reforming in the model without adding direct CO oxidation is still insufficient to predict high current data, particularly in CO-rich mixtures (subplots C-D). A sharp drop-off can still be observed in the second version of the model (as a result of the switch-over to rate-limiting H₂ adsorption, not concentration losses). This switch to rate-limiting hydrogen adsorption explains why the model under-predicts high current data when CO electro-oxidation is neglected. The third version of the model, however, is
able to accurately predict experimental data at high currents. This result indicates that CO electro-oxidation contributes to cell performance in the limiting current regime.

Figure 4.5: Cell polarization curves for four syngas mixtures at 800°C. Model results with and without reforming and CO electro-oxidation are compared to experimental data [7].

First, in order to determine how much carbon monoxide contributes to performance via reforming, we show the extent to which reforming impacts the gas species profiles in the anode. It is often assumed that the majority of CO entering the anode reacts with steam via the water-gas-shift reaction to form hydrogen before reaching the TPB. However, there may be insufficient steam
present in CO-rich mixtures to shift all of the incoming carbon monoxide. Furthermore, the extent to which CO shifts to form H₂ may be limited by the equilibrium constraint of the water-gas-shift reaction at high operating temperatures. Therefore, the importance of surface reforming in SOFCs fueled by syngas requires thorough investigation.

Figure 4.6 compares the H₂ and CO gas-phase profiles with and without surface reforming for the same four syngas mixtures presented in Figure 4.5. The left side of each subplot corresponds to the anode channel while the right side corresponds to the anode TPB where electrochemical oxidation of H₂ occurs (CO oxidation is disabled here to isolate CO’s impact via reforming). For each case, profiles were taken at the current density where switch-over occurred to rate-limiting hydrogen adsorption in the absence of reforming. This particular point along the curve was selected to ensure a sufficient rate of H₂ oxidation at the TPB without confounding the results by diffusion limitations that occur at higher currents. It is worth noting that the impact of surface reforming scales with current density because gas fluxes at the TPB scale with current.

In all four Figure 4.6 subplots, H₂ content is boosted and CO content is diminished at the TPB when reforming is enabled. These results confirm that the water-gas-shift reaction \( (H_2O + CO \leftrightarrow H_2 + CO_2) \) cannot be ignored in electrochemically active SOFC anodes run on syngas. However, these results also indicate that not all CO is shifted to form H₂ before reaching the TPB. This is the case for all four syngas mixtures, and is partly due to the fact that chemical equilibrium of the water-gas-shift reaction at 800°C predicts a roughly equal mixture of products and reactants. This trend is most pronounced in the CO-rich syngas cases (subplots C-D) because relatively less H₂O is produced at the TPB to shift incoming CO. These results indicate that CO in syngas mixtures will not all shift to form H₂ in SOFC anodes before reaching the TPB.
Figure 4.6: Gas-phase profiles of H$_2$ and CO throughout the anode for four syngas mixtures, with and without reforming. The anode-electrolyte interface (right boundary of all plots) is located 1100 micrometers from the anode-channel interface (left boundary of all plots). These profiles are taken at the current density where switch-over occurs in the absence of reforming (~3.0 A cm$^{-2}$ in A, 2.5 A cm$^{-2}$ in B, 1.5 A cm$^{-2}$ in C, 0.93 A cm$^{-2}$ in D). T = 800°C and direct CO oxidation is disabled in all cases shown.

It is clear from the previous figures that CO contributes indirectly to SOFC performance via water-gas-shift reforming for a range of syngas mixtures. However, the importance of direct CO electro-oxidation for different H$_2$:CO ratios still requires further investigation. In order to compare the relative contributions of CO and H$_2$ electro-oxidation, Figure 4.7 breaks down the current density contributions versus anode activation overpotential for the same four syngas mixtures presented
before. Increasing the anode activation overpotential is equivalent to increasing the cell current
density in Figure 4.5, and the switch-over point to rate-limiting H₂ adsorption can readily be
observed as the sharp bend in H₂ current in all four subplots. The slope of CO current vs. activation
overpotential also increases at these switch-over points to compensate for the declining rate of H₂
electro-oxidation when H₂ adsorption to nickel becomes rate-limiting.

The first key conclusion from Figure 4.7 is that current from H₂ dominates over current from CO,
particularly at lower currents before the switch-over point. This comparison holds true even for
the CO-rich syngas cases, and is consistent with the fact that H₂ oxidizes and diffuses faster than
CO in the anode. It appears that the contribution of CO via direct electro-oxidation is negligible
along the first part of the polarization curve for a range of syngas mixtures. However, the current
produced by direct electro-oxidation of CO picks up after the switch-over to rate-limiting H₂
adsorption occurs, so its contribution to cell performance cannot be ignored at higher currents.
This holds particularly true for the CO-rich mixtures, and the current produced by CO exceeds the
current from H₂ at the end of the curve for 80% CO + 20% H₂ in subplot D. These figures indicate
that CO plays a non-negligible role in electro-oxidation once H₂ current saturates due to rate-
limiting H₂ adsorption. This finding is consistent with the polarization curves from Figure 4.5,
which predict a sharp voltage drop-off in the absence of CO oxidation but a more gradual descent
when direct electro-oxidation of CO is accounted for.
The previous results indicate that CO contributes to cell performance via both reforming and direct electro-oxidation, particularly for higher CO-content mixtures towards the end of the polarization curve. However, in order to compare the relative contributions of CO via these two pathways, it’s helpful to know what fraction of incoming CO is consumed by each route. Figure 4.8 provides a break-down of how incoming CO is used for the same four syngas mixtures at the points of maximum power operation. These pie charts display the percentages of CO in the anode channel that get directly oxidized and consumed via reforming along with the percentage still present in
the anode exhaust after electrochemistry. Over 50% of the incoming CO is exhausted in all cases shown, which occurs because the model represents a button cell. In a realistic planar or tubular SOFC system, this CO in the exhaust would get consumed downstream in the anode flow channel via reforming and direct oxidation.

In order to compare the relative usage of CO via reforming and direct electro-oxidation, it's more instructive to focus on the relative sizes of the “R” and “O” portions of the pie charts in Figure 4.8. It's clear that both portions are non-negligible for the four cases shown. Direct oxidation of CO appears to be important relative to CO reforming even in the syngas mixtures that contain roughly equal parts of H₂ and CO (subplots A-B). As the CO content of the syngas mixture increases, the relative amount of CO consumed by direct oxidation increases, and outweighs reforming by a factor of more than 2.5 in the most CO-rich case (subplot D).
**A: 54% H₂ + 46% CO**

- Oxidized (O): 13%
- Reformed (R): 20%
- Exhausted (E): 67%

**B: 45% H₂ + 55% CO**

- Oxidized (O): 17%
- Reformed (R): 19%
- Exhausted (E): 63%

**C: 32% H₂ + 68% CO**

- Oxidized (O): 27%
- Reformed (R): 14%
- Exhausted (E): 59%

**D: 20% H₂ + 80% CO**

- Oxidized (O): 34%
- Reformed (R): 13%
- Exhausted (E): 53%

Figure 4.8: Percentage breakdown of the usage of incoming CO to the anode between direct oxidation (O), surface reforming (R) and anode exhaust (E) for four syngas mixtures at 800°C. These results are taken at the operating points of maximum power output for each polarization curve, which occur at the following current densities: 3.3 A cm⁻² in A, 3.0 A cm⁻² in B, 2.3 A cm⁻² in C, and 1.8 A cm⁻² in D.

### 4.5 Conclusions

Because SOFCs are capable of running on syngas, it is critical to determine the extent to which CO contributes to cell performance for syngas mixtures. In order to study carbon monoxide’s
impact on cell performance via reforming and direct oxidation when H\textsubscript{2} is also present, an MEA model with surface reforming and electrochemical mechanisms for both H\textsubscript{2} and CO oxidation is needed. The MEA model presented here possesses these features, and directly implements experimentally measured values for OCV and overpotentials outside the anode in order to isolate the role of CO in the anode. A comparison of three versions of the model to experimental syngas data indicates that CO contributions via both reforming and direct oxidation are non-negligible.

A close study of the anode gas species profiles shows that only a portion of incoming CO shifts to form H\textsubscript{2} before reaching the TPB as a result of the chemical equilibrium limit of the water-gas-shift reaction at 800°C. This result challenges the traditional assumption that water-gas-shift reforming is the dominant pathway for CO to contribute to cell current when syngas is sent to SOFCs. Furthermore, a comparison of the current contributions from direct electro-oxidation shows that current from CO is non-negligible relative to H\textsubscript{2} current towards the end of the polarization curve where H\textsubscript{2} current is limited by slow adsorption to nickel. Finally, it is shown that the relative importance of direct electro-oxidation versus reforming of CO increases as the CO-content of the syngas mixture is raised. These findings suggest that CO contributions via both reforming and direct electro-oxidation are critical in predicting SOFC performance with syngas mixtures, particularly at high currents.

4.6 References


Chapter 5

Mechanism for Syngas Electro-oxidation in a SOFC

An accurate, comprehensive model for the individual and simultaneous electro-oxidation of H₂ and CO on Ni-YSZ is necessary to predict SOFC performance for a range of gaseous fuels. A mechanism that combines hydrogen (H) spillover to YSZ with oxygen (O) spillover to hydrogen and CO on nickel is proposed. This combined spillover model is implemented in a previously-validated 1D-MEA model with detailed gas-phase transport and surface reforming kinetics in the anode. This model is then verified against a range of experimental porous anode polarization data for mixtures of CO/CO₂, H₂/N₂, H₂/H₂O, H₂/CO, and H₂/CO₂. The results of that fitting confirm that the proposed mechanism is capable of representing the individual and simultaneous electro-oxidation of H₂ and CO on Ni/YSZ. The current spillover pathways are then studied for two anode fuel mixtures: 20% H₂ + 80% N₂ and 20% H₂ + 80% CO. Although these studies confirm that H spillover is the dominant source of current at low anode activation overpotentials, they also show that the currents produced by O spillover are non-negligible at high overpotentials. Furthermore, it is shown that the current produced by O spillover to CO(Ni) is not limited by the rate of CO adsorption on nickel, whereas the currents produced by both H spillover and O spillover to H(Ni) are limited by the rate of H₂ adsorption at high anode overpotentials.
5.1 Introduction

The thermochemical and electrochemical reaction mechanisms within a SOFC anode are complex, particularly when hydrocarbon species are involved [1]–[3]. Elementary reaction steps are needed to accurately depict gas-phase chemistry, heterogeneous surface reforming, and heterogeneous charge-transfer reactions. Understanding the governing mechanisms for internal reforming and electrochemistry is paramount to optimize anode structure and operating conditions. More specifically, it is critical to identify the correct rate-limiting steps in these elementary mechanisms because those steps control the rate at which the cell can produce current. The elementary electrochemical oxidation reaction mechanisms for H2 and CO require special attention because these constitute the primary SOFC fuel candidates present in practical gaseous fuels such as hydrocarbons, natural gas, coal syngas and biogas [4].

A couple of reaction mechanism types have been proposed to represent H2 electrochemical oxidation at the triple-phase boundary (TPB) of Ni-YSZ: (1) hydrogen spillover and (2) oxygen spillover. Hydrogen (H) spillover mechanisms involve a charge-transfer step where hydrogen spills over from nickel to YSZ to react with oxygen on the electrolyte. Oxygen (O) spillover mechanisms, on the other hand, involve a charge-transfer step where oxygen spills over from YSZ to nickel to react with hydrogen on nickel. Hydrogen electro-oxidation models typically select only one spillover pathway rather than implementing the H and O spillover pathways simultaneously. Although a few researchers have used O spillover mechanisms to describe H2 electro-oxidation [5], [6], the majority have proposed variations of the H spillover mechanism [7]–[14]. A few researchers have compared these spillover pathways and concluded that H spillover mechanisms are better than O spillover mechanisms at consistently predicting patterned-anode experimental data for H2/H2O mixtures [15]–[17]. One group has also developed an H spillover
mechanism that accounts for rate-limiting H₂ adsorption at high currents [10], but a similar study is needed for the O spillover mechanism.

Although both CO and H₂ are both electrochemically active species on SOFCs, research on the subject of CO electro-oxidation is much less expansive, partly because the reaction rate of CO is lower than that of H₂ [18]–[21]. However, understanding the mechanism for CO electro-oxidation is still critical to accurately represent syngas mixtures because CO and H₂ electro-oxidation rates have the same order of magnitude [20], [22]. Researchers have typically found that CO electro-oxidation is governed by O spillover to nickel as opposed to CO spillover to YSZ, which is an unlikely pathway due to the strong affinity of CO to nickel [23]–[25]. However, most MEA models represent CO electro-oxidation as a global reaction rather than implementing the O spillover pathway due to a lack of reaction kinetic data. Charge-transfer is also typically assumed rate-limiting in CO electro-oxidation mechanisms, so a study on CO adsorption as a potentially rate-limiting step at high currents is needed.

Although the mechanisms for both H₂ and CO electro-oxidation have been studied individually, few researchers have attempted to model the simultaneous electro-oxidation mechanism which is needed to characterize SOFC behavior with syngas mixtures [26]. It is a complicated task to simulate H₂ + CO co-oxidation in SOFCs because it involves modeling parallel charge transfer pathways, water-gas shifting and interactions between gaseous and adsorbed species. Moyer et al. [27] recently performed a modeling study on H₂ + CO co-oxidation that accounts for detailed heterogeneous thermochemistry as well as both spillover mechanisms. They fitted the kinetic parameters of each charge-transfer step in the hydrogen and oxygen spillover pathways to patterned-anode Tafel plots for mixtures containing H₂ + H₂O + CO + CO₂ [5]. Moyer’s model was best able to predict that data set when both the H and O spillover pathways were active instead
of just one pathway. However, questions remain regarding the relative importance of these two spillover pathways and the roles of H₂ and CO in these pathways. Charge-transfer steps were also always assumed rate-limiting in this study, so the possibility of fuel adsorption on nickel as rate-limiting processes in these mechanisms requires further investigation.

A recent study by Fu et al [28] has provided needed insight on the spillover pathways of H₂ and CO electro-oxidation on Ni/YSZ from a micro-structural perspective using first principles simulations and the Monte Carlo method. This group found evidence to support previous claims that CO electro-oxidation can only proceed through the O spillover pathway. More importantly, Fu et al found that the O spillover pathway plays a vital role in H₂ electro-oxidation in addition to H spillover. An independent first principles study also found that adsorbed oxygen on nickel lowers the energy barrier for the oxidation of hydrogen via O spillover [29]. These recent findings motivates the development of a MEA model that includes O spillover charge-transfer pathways to both CO and H₂ on nickel in addition to H spillover to YSZ. Such a model is needed to accurately capture the reaction pathways of both fuels at the anode triple-phase-boundary (TPB) of SOFC’s exposed to syngas fuels.

The first part of this paper describes the integration of this newly-proposed combination of spillover pathways into a detailed 1D-MEA model [26]. Furthermore, the H and O spillover mechanisms described in this model account for rate-limiting H₂ and CO adsorption onto nickel at high currents. The validity of this detailed model is then tested by comparing model predictions to experimental polarization data for a wide range of anode fuel mixtures [21]. Finally, the study focuses on just two fuel mixtures in order to investigate the relative importance of the different spillover pathways and rate-limiting processes along the polarization curve.
5.2 Model Description

The objective of the MEA model is to calculate the voltage-current density curve for a given temperature, pressure and fuel composition. The model is isothermal and the domain is 1D with respect to distance from the triple-phase boundary (TPB). This representation is consistent with the geometry of a button cell, where the entire anode is exposed to the same anode fuel mixture. The previously-published [26] models for conservation, transport, thermochemistry and overpotentials will be briefly introduced, followed by a detailed description of the proposed hydrogen and oxygen spillover mechanism.

5.2.1 Conservation Equations

The gas phase mass conservation equation in the porous electrodes is:

\[
\varepsilon \frac{\partial c_k}{\partial t} = A_s \dot{s}_{surf,k} + \dot{s}_{gas,k} - (V \cdot J_k) = A_s \dot{s}_{surf,k} - (V \cdot J_k) \quad (k = 1, \ldots, K_g) \tag{5.1}
\]

where \(\varepsilon\) is the porosity, \(c_k\) is the concentration of gas species \(k\) [mol m\(^{-3}\)], \(\dot{s}_{surf,k}\) is the production rate of \(k\) by heterogeneous reactions [mol m\(^{-2}\) s\(^{-1}\)], \(A_s\) is the specific catalyst area per unit volume of electrode [m\(^{-1}\)], and \(K_g\) is the total number of gas species. The production rate by gas-phase reactions is assumed to be negligible in comparison with the catalytic surface reaction rates on nickel (\(\dot{s}_{gas,k} \ll A_s \dot{s}_{surf,k}\)).

The surface species mass conservation equation in the porous anode is:

\[
\frac{\partial c_{surf,k}}{\partial t} = \dot{s}_{surf,k} - (V \cdot J_{k,m}) \quad (k = 1, \ldots, K_s) \tag{5.2}
\]

where \(c_{surf,k}\) is the concentration of surface species \(k\) [mol m\(^{-2}\)], \(\dot{s}_{surf,k}\) is the production rate of \(k\) by heterogeneous reactions [mol m\(^{-2}\) s\(^{-1}\)], and \(K_s\) is the total number of surface species. These gas and surface mass conservation equations are applied over a series of \(m\) discrete nodes in both
electrodes with reforming occurring throughout the anode. The electrochemical reactions, however, occur only at the \( m \)th node of each electrode, where the TPB is located [30], [31]. Surface species fluxes (\( \nabla \cdot \mathbf{J}_{k,m} \)) therefore only occur at this last node:

\[
\begin{align*}
J_{H,a} &= \frac{i_{H-spill}}{F}; J_{H_2O,a} = -\frac{i_{H-spill}}{2F}; J_{O,a} = -\frac{i_{O-spill}}{2F}; J_{O_2,c} = \frac{i_{tot}}{4F}
\end{align*}
\]

where the subscript \( a \) denotes the anode TPB, and the subscript \( c \) denotes the cathode TPB. \( i_{H-spill} \) and \( i_{O-spill} \) are the currents associated with the hydrogen and oxygen spillover pathways, respectively, and the total combined current is: \( i_{tot} = i_{H-spill} + i_{O-spill} \). Fluxes are defined here as positive into the electrolyte and negative away from the electrolyte.

**5.2.2 Transport in Porous Media**

The gas phase fluxes (\( J_k \)) from equation (1) are computed using the dusty gas model (DGM), an extension of the Stefan-Maxwell diffusion equations that captures both Knudsen and binary diffusion [32]. The DGM can be written as an implicit relationship among the molar concentrations, molar fluxes, concentration gradients, and the pressure gradient:

\[
-\nabla c_i = \sum_{j \neq i} \frac{1}{c_i D_{ij}^e} (c_j J_i - c_i J_j) + \frac{J_i}{D_{ij}^M} + \frac{B_0}{\mu_{mix} D_{ij}^e} c_i \nabla p
\]

where \( c_t = \frac{p}{RT} \) is the total molar concentration [mol m\(^{-3}\)], \( D_{ij}^e \) is the effective binary diffusion coefficient in the porous medium [m\(^2\) s\(^{-1}\)], \( \mu_{mix} \) is the mixture viscosity [kg m s\(^{-1}\)], \( B_0 \) is the permeability [m\(^2\)], and \( D_{ij}^e \) is the effective Knudsen diffusion coefficient [m\(^2\) s\(^{-1}\)]. A more detailed description of the mass transport model with definitions of each term is provided elsewhere [10].
5.2.3 Thermochemistry

Surface reforming in the anode is usually modeled with simplifying assumptions, such as local equilibrium or global reaction kinetics [31], [33]. However, a detailed kinetic model is used here that was first developed by Hecht et al [3], and then extended to a wider temperature range by Janardhanan and Deutschmann [30]. This mechanism consists of 42 reactions, and involves six gaseous species and twelve surface species. The net production rate of gas or surface species $k$ due to heterogeneous reactions is given by:

$$
\dot{s}_{surf,k} = \Sigma_i R_{surf,i} v_{i,k}
$$

where $R_{surf,i}$ is the rate of heterogeneous reaction $i$ [mol m$^{-2}$s$^{-1}$] and $v_{i,k}$ is the stoichiometric coefficient of species $k$ in reaction $i$. This surface species production term appears in equations (5.1)-(5.2), the species conservation equations for the gas and surface phases. A list and detailed description of the full surface reforming mechanism on nickel is presented elsewhere [30].

5.2.4 Cell Overpotentials

Operating voltage can be expressed as the difference between the reversible cell potential and various overpotentials:

$$
E_{cell} = E_{rev} - \eta_{act,a} - \eta_{act,c} - \eta_{con,a} - \eta_{con,c} - \eta_{ohm}
$$

where $E_{rev}$ is the reversible (open-circuit) cell potential, $\eta_{act,a}$ and $\eta_{act,c}$ are the activation overpotentials at the anode and cathode, $\eta_{con,a}$ and $\eta_{con,c}$ are the concentration overpotentials at the anode and cathode, and $\eta_{ohm}$ is the total ohmic overpotential. Because the focus of this study is on the validity of the proposed electrochemical mechanisms on the anode, voltage terms outside the anode are taken directly from the experimental group to minimize uncertainty. The details of
this approach are given in a separate study that isolated the impact of CO electrochemistry on cell operating voltage [26].

First, the model and experimental OCVs are matched by introducing air leakage into the anode channel until the reversible potential matches the experimental OCV for that anode mixture:

\[ E_{\text{rev,calc}} = RT/4F \ln(p_{O_2,c}/p_{O_2,a}) = E_{\text{rev,exp}} \]  

where \( p_{O_2,c} = .21P \) is the equilibrium partial pressure of oxygen in the cathode channel, and \( p_{O_2,a} \) is the equilibrium oxygen partial pressure in the anode channel after adjusting for the air leak and gas-phase equilibrium. This approach of accounting for error in the open-circuit potential by physically adjusting the anode mixture with air is addressed in more detail elsewhere [26], [34].

Overpotentials in the electrolyte and cathode are also taken directly from the experimental group in order to minimize uncertainly in the model and focus on the impact of the anode mechanism. Ohmic and total cathodic overpotential are thus given by simple curve fits to their data sets:

\[ \eta_{\text{ohm}} = i_{\text{tot}}R_{\text{tot}} = .0588i_{\text{tot}} \]  

\[ \eta_{\text{tot,c}} = \eta_{\text{con,c}} + \eta_{\text{act,c}} = .0018i_{\text{tot}}^5 - .019i_{\text{tot}}^4 + .0755i_{\text{tot}}^3 - .1454i_{\text{tot}}^2 + .1833i_{\text{tot}} + .001 \]  

where \( i_{\text{tot}} \) [A cm\(^{-2}\)] is the total cell current density from both the hydrogen and oxygen spillover pathways, and \( R_{\text{tot}} = 0.0588 \ \Omega \ \text{cm}^2 \) is the total resistance of the cell to ion and electronic flow [35].

Unlike the other loss modes that are taken directly from Virkar et al’s experimental data, the anode overpotentials are represented physically in order to study the impact of the proposed electro-oxidation mechanisms on cell performance. Anode concentration overpotential is modeled as the difference in reversible cell potential at the anode channel and the anode TPB:
\[ \eta_{\text{con},a} = E_{\text{rev}} - E_{\text{rev},a,TPB} = \frac{RT}{4F} \ln\left(\frac{p_{O_2,a,TPB}}{p_{O_2,a}}\right) \]

where \( p_{O_2,a} \) is the equilibrium partial pressure of oxygen at the anode channel and \( p_{O_2,a,TPB} \) is the equilibrium partial pressure of oxygen at the anode TPB. The anode activation overpotential is treated as an input to the model because it is common to both electro-oxidation spillover pathways, which are described next in detail.

### 5.2.5 Electro-oxidation Mechanisms

The hydrogen spillover mechanism consists of five steps, and the oxygen spillover mechanism consists of ten steps, as depicted in Figure 5.1. Both mechanisms have two charge-transfer steps that come from previously proposed mechanisms [17]. All of the reactions that occur on nickel come from the 42-step surface reforming mechanism presented previously [30]. The novel aspects of this proposed mechanism are: 1) that it accounts for both spillover pathways for H\(_2\) electro-oxidation simultaneously, and 2) that it distinguishes oxygen spillover to H(Ni) from oxygen spillover to CO(Ni). This novel combination of three spillover pathways makes it possible to investigate how current is produced for a range of anode overpotentials and fuel mixtures later.
**A: Hydrogen Spillover Mechanism**

**B: Oxygen Spillover Mechanism**
Figure 5.1: Depiction of the reaction steps at the TPB for the hydrogen spillover mechanism (A) and oxygen spillover mechanism (B). Both mechanisms involve two charge-transfer steps across the Ni-YSZ TPB. The oxygen spillover mechanism (B) involves surface reactions with both H and CO on nickel.

The five-step mechanism for hydrogen (H) spillover is:

- Adsorption of hydrogen on nickel [30]:

\[ H_2(g) + 2(Ni) \leftrightarrow 2H(Ni) \]  \hspace{1cm} (H.1)

- Transfer of oxygen ion between bulk and surface defects of YSZ [17]:

\[ O^{2-}(YSZ,\text{bulk}) + (YSZ) \leftrightarrow O^{2-}(YSZ) + (YSZ,\text{bulk}) \] \hspace{1cm} (H.2)

- Charge-transfer reactions at the TPB [17]:

\[ H(Ni) + O^{2-}(YSZ) \leftrightarrow (Ni) + OH^-(YSZ) + e^-(Ni) \] \hspace{1cm} (H.3)

\[ H(Ni) + OH^-(YSZ) \leftrightarrow (YSZ) + H_2O(Ni) + e^-(Ni) \] \hspace{1cm} (H.4)

- Desorption of steam from nickel [30]:

\[ H_2O(Ni) \leftrightarrow H_2O(g) + (Ni) \] \hspace{1cm} (H.5)

The ten-step mechanism for oxygen (O) spillover for both H$_2$ and CO is:

- Adsorption/desorption of fuels on nickel [30]:

\[ H_2(g) + (Ni) \leftrightarrow 2H(Ni) \] \hspace{1cm} (O.1)

\[ CO(g) + (Ni) \leftrightarrow CO(Ni) \] \hspace{1cm} (O.2)

- Transfer of oxygen ion between bulk and surface defects of YSZ [17]:

\[ O^{2-}(YSZ,\text{bulk}) + (YSZ) \leftrightarrow O^{2-}(YSZ) + (YSZ,\text{bulk}) \] \hspace{1cm} (O.3)

- Charge-transfer reactions at the TPB [17]:

\[ O^{2-}(YSZ) \leftrightarrow O^-(YSZ) + e^-(Ni) \] \hspace{1cm} (O.4)
\( O^-(YSZ) + (Ni) \leftrightarrow O(Ni) + (YSZ) + e^- (Ni) \)  

- Reactions of fuels with oxygen on nickel [30]:

\( H(Ni) + O(Ni) \leftrightarrow OH(Ni) + (Ni) \)  
\( H(Ni) + OH(Ni) \leftrightarrow H_2O(Ni) + (Ni) \)  
\( CO(Ni) + O(Ni) \leftrightarrow CO_2(Ni) \)

- Desorption of products from nickel [30]:

\( H_2O(Ni) \leftrightarrow H_2O(g) + (Ni) \)  
\( CO_2(Ni) \leftrightarrow CO_2(g) + (Ni) \)

For both spillover mechanisms, \( (Ni) \) denotes species adsorbed on anode nickel sites, \( (YSZ) \) denotes species adsorbed on surface YSZ sites, \( (YSZ, bulk) \) denotes that oxygen occupies a bulk YSZ defect, and \( (g) \) denotes gas-phase species. The charge-transfer steps for the O spillover mechanism, (O.4)-(O.5), are fuel-independent, so the rates of O spillover to \( H_2 \) and \( CO \) are governed by their rates of reaction with \( O(Ni) \) in steps (O.6)-(O.8).

The step of oxygen transfer from bulk to surface YSZ sites is common to both mechanisms: (H.2) in H-spillover and (O.3) in O-spillover. This oxygen transfer step occurs rapidly at SOFC operating temperatures, and is thus modeled in equilibrium for both mechanisms according to the expression [17]:

\[
K_{H,2} = K_{O,3} = \exp \left( -\frac{\Delta G_{H_2}^0}{RT} \right) = \frac{x_{bulk}^{\theta_{O_2-YSZ}}}{x_{O_2-,bulk}^{\theta_{YSZ}}} = \frac{x_{bulk}^{\theta_{O_2-,YSZ}}}{(1-x_{bulk})^{\theta_{YSZ}}} 
\]

(5.11)

where \( x_{bulk} \) is the bulk vacancy fraction, \( x_{O_2-,bulk} \) is the fraction of occupied bulk sites, \( \theta_{YSZ} \) is the surface vacancy fraction, and \( \theta_{O_2-,YSZ} \) is the \( O^{2-} \) ion coverage on YSZ surface sites. The standard Gibbs energy of the reaction is \( \Delta G_{H_2}^0 = 8,600 \text{ J mol}^{-2} \), and the bulk defect fraction is set
by the yttrium doping level as $X_{bulk} = 0.0374$ for 8 mol % Y$_2$O$_3$ in ZrO$_2$ [17], [36]. The surface vacancy fraction is given by accounting for all potential species occupying surface YSZ sites:

$$\theta_{YSZ} = 1 - \theta_{O^{2-},YSZ} - \theta_{O^{-},YSZ} - \theta_{OH^{-},YSZ}$$  \hspace{1cm} (5.12)

Thus, equation (5.11) can be expressed as a function of three unknown YSZ surface coverages if equation (5.12) is substituted in for the surface YSZ vacancy fraction. The model this work is derived from included a more detailed reaction mechanism on the YSZ surface that has two types of surface sites [27]. However, this work omits these side-reactions with zirconia sites because their inclusion only added to the model complexity without tangibly altering charge-transfer rates.

5.2.5.1 Rate-limiting Charge-transfer

The charge-transfer processes, (H.3)-(H.4) and (O.4)-(O.5), are typically assumed to be the rate-limiting steps in both spillover pathways. When this is the case, the current densities associated with each charge-transfer step are given by the following expressions:

$$i_{(H.3)} = F l_{TPB} \left[ k_{H.3,f} \Gamma_{H,Ni} \Gamma_{O^{2-},YSZ} \exp(\beta_{H.3} fE) - k_{H.3,b} \Gamma_{Ni} \Gamma_{OH^{-},YSZ} \exp(-(1 - \beta_{H.3})fE) \right] (5.13)$$

$$i_{(H.4)} = F l_{TPB} \left[ k_{H.A,f} \Gamma_{H,Ni} \Gamma_{OH^{-},YSZ} \exp(\beta_{H.A} fE) - k_{H.A,b} \Gamma_{H_{2}O,NI} \Gamma_{YSZ} \exp(-(1 - \beta_{H.A})fE) \right] (5.14)$$

$$i_{(O.A)} = F l_{TPB} \left[ k_{O.A,f} \Gamma_{O^{2-},YSZ} \exp(\beta_{O.A} fE) - k_{O.A,b} \Gamma_{0^{-},YSZ} \exp(-(1 - \beta_{O.A})fE) \right] (5.15)$$

$$i_{(O.S)} = F l_{TPB} \left[ k_{O.S,f} \Gamma_{Ni} \Gamma_{0^{-},YSZ} \exp(\beta_{O.S} fE) - k_{O.S,b} \Gamma_{0,NI} \Gamma_{YSZ} \exp(-(1 - \beta_{O.S})fE) \right] (5.16)$$

where $F$ is the Faraday constant [C mol$^{-1}$], $l_{TPB}$ is the TPB length per unit cell [m cm$^{-2}$], $\beta_i$ are the Faradaic charge-transfer coefficients, $f = F/(RT)$ [C J$^{-1}$], and $E$ is the electric potential difference across the anode-electrolyte double layer [V]. The surface species site densities are simply given by the products of the surface species coverages and the total surface site densities of YSZ and Ni:

$$\Gamma_i,YSZ = \theta_i,YSZ \Gamma_{YSZ} \text{ and } \Gamma_i,NI = \theta_i,NI \Gamma_{NI} \text{ [mol m}^{-2}].$$
The forward rate constants are given by: \( k_{i,f} = A_i \exp\left(-\frac{E_{a,i}}{RT}\right) \), and the backward rate constants are simply given by dividing the forward rate constants by the equilibrium constants of each reaction: \( k_{i,b} = \frac{k_{i,f}}{K_i} \). The constants in these rate constant expressions are listed along with the symmetry constants in Table 5.1 for all of the charge-transfer reactions. These values come from a previous group that fitted both of the spillover mechanisms to Tafel plots from patterned-anode experiments conducted by Mizusaki et al at 0.83 atm and 750, 800 and 850°C [5].

Table 5.1: Kinetic constants and parameters for the charge-transfer steps of both spillover pathways, fitted to patterned anode experimental data for 750-850°C in a previous paper [27].

<table>
<thead>
<tr>
<th>Step</th>
<th>( A_i ) (mol, cm, s)</th>
<th>( E_{a,i} ) (kJ mol(^{-1}))</th>
<th>( \beta_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H.3)</td>
<td>( 1.00 \times 10^{15} )</td>
<td>50.0</td>
<td>0.500</td>
</tr>
<tr>
<td>(H.4)</td>
<td>( 1.00 \times 10^{13} )</td>
<td>50.0</td>
<td>0.300</td>
</tr>
<tr>
<td>(O.4)</td>
<td>( 1.00 \times 10^{98} )</td>
<td>50.0</td>
<td>0.500</td>
</tr>
<tr>
<td>(O.5)</td>
<td>( 6.00 \times 10^{11} )</td>
<td>50.0</td>
<td>0.600</td>
</tr>
</tbody>
</table>

The TPB species coverages on nickel (\( \theta_{i,Ni} \)) in equations (5.13)-(5.16) are resolved simultaneously with the anode concentration profiles and currents, according to the algorithm described in the simulation procedure section. These coverages are governed by the anode transport and mass conservation equations along with the detailed surface reforming mechanism, which accounts for twelve surface species [30]. The vacancy fraction of nickel at the TPB is then given by:

\[
\theta_{Ni} = 1 - \sum_{k=1}^{12} \theta_{k,Ni}^{K}
\]

(5.17)

where the summation occurs over all twelve possible surface species on nickel at the TPB: \( H, OH, H_2O, CH_4, CH_3, CH_2, CH, CO, CO_2, C, \) and \( HCO \).
The electric potential difference in equations (5.13)-(5.16) can be expressed as the sum of the equilibrium potential and the anode activation overpotential: \( E = E_{eq} + \eta_{act,a} \). The anode activation overpotential is a known input quantity in the simulation procedure, and the equilibrium potential is determined by solving for \( E_{eq} \) in equations (5.13)-(5.14) or (5.15)-(5.16) with \( \eta_{act,a} = 0 \) and \( i_{(k)} = 0 \), as detailed in Appendix B.1:

\[
E_{eq} = \frac{1}{f} \ln\left[\sqrt{H_{2,0,Ni} \theta_{Ni}/(aK_{H,3}K_{H,4}^{2}\theta_{H,Ni})}\right] (5.18)
\]

where \( a = \frac{K_{H,2}K_{O^{2-},bulk}}{X_{bulk}} \) and surface coverages are taken at the TPB under open-circuit conditions. The four unknown YSZ coverages \( (\theta_{YSZ}, \theta_{O^{2-},YSZ}, \theta_{O^{-},YSZ}, \theta_{OH^{-},YSZ}) \) can then be determined by setting the current densities of subsequent charge-transfer steps equal, as detailed in Appendix B.2.

Once the equilibrium potential \( (E_{eq}) \) and YSZ coverages are known, the current densities of each charge-transfer step can be determined by equations (5.13)-(5.16) for a given anode activation overpotential and steady-state TPB nickel coverages. The total current densities associated with the H and O spillover pathways are then given by:

\[
i_{H-spill} = i_{(H,3)} + i_{(H,4)} = 2i_{(H,3)} \quad (5.19)
\]

\[
i_{O-spill} = i_{(O,4)} + i_{(O,5)} = 2i_{(O,4)} \quad (5.20)
\]

The total steady-state current density is then the sum of these two spillover currents:

\[
i_{tot} = i_{H-spill} + i_{O-spill} = 2[i_{(H,3)} + i_{(O,4)}] \quad (5.21)
\]
Finally, the distribution of current between the two fuels, H₂ and CO, is determined directly from their rates of reaction at the TPB. Specifically, the current density produced by CO electro-oxidation is given by evaluating step (O.8) at steady-state:

\[ i_{CO} = 2F A_s (L_a/m) R R_{(0.8)} \]  \hspace{1cm} (5.22)

where \( A_s \) is the specific catalyst area [cm\(^{-1}\)], \( L_a \) is the total anode thickness [cm], \( m \) is the number of nodes in the anode model, and \( RR_{(0.8)} \) is the net rate of reaction (O.8) taken from the surface reforming mechanism with steady-state surface coverages [mol cm\(^{-2}\) s\(^{-1}\)] [30]. Current density associated with H₂ electro-oxidation is then the difference between total current density and CO current density:

\[ i_{H_2} = i_{tot} - i_{CO} \]  \hspace{1cm} (5.23)

Finally, the current associated with O spillover to H₂ is given by:

\[ i_{O-spill \ to \ H} = i_{H_2} - i_{H-spill} \]  \hspace{1cm} (5.24)

which is also equivalent to the difference in total O spillover current and current from CO.

5.2.5.2 Rate-limiting Fuel Adsorption

Although the charge-transfer processes are typically rate-limiting, it is possible that hydrogen adsorption or CO adsorption can become rate-limiting steps in the two pathways at higher current densities. This phenomenon is described in previous work as the "switch-over" mechanism, which provided a better fit to experimental H₂ + H₂O data in the limiting current regime for a H spillover model[10], [26]. If hydrogen adsorption onto nickel is rate-limiting, then the current for that pathway is given by the following Butler-Volmer relationship [10]:

\[ \text{156} \]
where $P_{H_2}$ is the partial pressure of $H_2$ in the gas-phase at the TPB, and the exchange current density pre-factor is given by: $i^*_0 = \frac{a_{TPB}(2F)Y_{H_2}}{\sqrt{2\pi M_{H_2}RT}}$ [10], [37]. This pre-factor is a function of a couple of dimensionless parameters: the area-specific TPB length ($a_{TPB}$) and the sticking coefficient of $H_2$ on nickel ($Y_{H_2}$).

Although $CO$ molecules adsorb more readily to nickel than $H_2$ [28], it is still conceivable that $CO$ adsorption could be a rate-limiting step under some conditions. Therefore, an analogous Butler-Volmer expression is developed to represent the current associated with $CO$ electro-oxidation when $CO$ adsorption to nickel is the rate-limiting step:

$$i_{CO-ads} = i^*_0 P_{CO} \left[ 1 - \exp \left( -2 \frac{F\eta_{act,a}}{RT} \right) \right]$$  \hspace{1cm} (5.26)

where $P_{CO}$ is the partial pressure of $CO$ in the gas-phase at the TPB, and the exchange current density pre-factor is given by: $i^*_0 = \frac{a_{TPB}(2F)Y_{CO}}{\sqrt{2\pi M_{CO}RT}}$. Because the area-specific TPB length ($a_{TPB}$) that appears in both of these adsorption expressions is unknown, it is treated as a fitting parameter to experimental data in the first results section.

The point at which fuel adsorption becomes the rate-limiting step in a given pathway is determined by comparing the currents predicted by the expressions for charge-transfer and adsorption. More specifically, $H_2$ adsorption becomes rate-limiting in the $H$ spillover mechanism when $i_{H-ads} < i_{H-spill}$ and in the $O$ spillover mechanism when $i_{H-ads} < i_{O-spill}$. Similarly, $CO$ adsorption becomes rate-limiting in the $O$ spillover mechanism when $i_{CO-ads} < i_{O-spill}$. Thus, there are theoretically three distinct points along the polarization curve where fuel adsorption becomes rate-limiting for the three fuel electro-oxidation pathways.
5.3 Simulation Procedure

Temperature, pressure and anode composition are inputs to the model, which generates a current density-voltage curve by iterating through anode activation overpotential, as shown in Figure 2. Steps 1)-2) are carried out once for a given anode mixture, then steps 3)-4) are repeated for increasing anode overpotential until an entire polarization curve is generated.

Figure 5.2: Simulation procedure to generate a polarization curve for a given fuel mixture.

The following steps are implemented in a MATLAB® script to generate each cell polarization curve:

4) **Calculate the equilibrium mixture at the anode channel.**
The reported anode mixture is adjusted in the model by incrementally adding air until the theoretical and experimental OCV values match, as detailed in Appendix A. Cantera’s “equilibrate” function is applied to each adjusted anode mixture at fixed temperature and pressure to determine the equilibrium partial pressure of oxygen, $p_{O_2,a}$. This value is then used in equation (5.7) to calculate the reversible cell potential, which is compared to the experimental OCV value for that mixture. This process is repeated for increasing air content until the calculated and experimental OCV values match. The final equilibrated fuel + air mixture is also assumed to be the actual mixture present at the anode channel to account for experimental air leakage and the quick reaction of oxygen with anode fuels.

5) **Calculate the equilibrium potential drop across the anode/electrolyte double-layer.**

The equilibrium potential difference across the anode/electrolyte double-layer ($E_{eq}$) is needed to determine the currents produced by the various charge-transfer steps, which are exponential functions of $E = E_{eq} + \eta_{act,a}$. $E = E_{eq}$ at open-circuit because $\eta_{act,a} = 0$, so the equilibrium potential difference can be determined by setting the individual currents in equations (5.13)-(5.14) or (5.15)-(5.16) to zero. For mixtures without H$_2$, O spillover is the only active pathway, so $i_{(O,4)}$ and $i_{(O,5)}$ are both set to zero, and equations (5.15)-(5.16) are solved along with equations (5.11)-(5.12) for $E_{eq}$ and the open-circuit coverages on YSZ. For mixtures containing H$_2$, the H spillover pathway is dominant at low currents, so $i_{(H,3)}$ and $i_{(H,4)}$ are set to zero, and equations (5.11)-(5.14) are solved for $E_{eq}$ and open-circuit YSZ coverages, as detailed in Appendix B.

6) **Resolve current densities and anode species profiles.**

The final equilibrium mixture adjusted for air leakage from step 1) is the mixture sent to the channel in the anode model. Because anode activation overpotential is an input to the model, current densities from both spillover pathways can be determined by solving equations (5.13)-
(5.16) simultaneously with the transport equations throughout the anode. The initial fluxes of surface species at the TPB, given by equation (5.3), are boundary conditions to the DGM transport equation (5.4), which is cast in matrix form. An ordinary differential equation solver, the “ode15s” function in MATLAB®, resolves the steady-state gas and surface species profiles throughout the anode. The steady-state current densities and YSZ surface coverages are updated with the new concentrations at the TPB, and then the fluxes of surface species at the TPB are updated based on the new current densities. These new fluxes are fed back into the DGM solver as boundary conditions, and this process repeats until the non-linear “fsolve” function converges on steady-state current densities, YSZ coverages, and anode species profiles. More details on the mechanics of this complex algorithm from an earlier version of this model are given elsewhere [10].

7) Calculate cell overpotentials and operating voltage.

Once the anode profiles and currents are resolved, all of the cell overpotentials can be readily computed. The anode activation overpotential is an input to step 3), so its value is known. The anode concentration overpotential is given by equation (5.10), where the partial pressure of oxygen at the anode TPB is determined by the Cantera “equilibrate” function applied to the anode gas mixture at the last node. Total cathode overpotential and ohmic overpotential are then given as functions of total current in equations (5.8) and (5.9). Finally, the operating voltage is determined by subtracting all overpotentials from the reversible cell potential, according to equation (5.6).

5.4 Simulation Results

The results are presented here in two sections: model verification and mechanism investigation. The first section presents the model against experimental porous anode polarization data for a wide range of mixtures with H₂ and/or CO. This comparison is conducted in order to confirm a reasonable fit for the combined hydrogen and oxygen spillover model against a wide range of
anode fuel stream conditions. The second section investigates how current is divided between the different spillover pathways for fuel mixtures with and without CO. This second study also investigates how the rate-limiting assumptions in the mechanism impact the current pathways and the accuracy of performance predictions.

The operating conditions and anode structural parameters that are held constant in all these simulations are listed in Table 5.2. All of the other parameters in the table are obtained directly from Jiang & Virkar’s experiment [21] unless otherwise indicated. This approach minimizes uncertainty and matches this model to their experimental button cell. Structural parameters are only listed for the anode in Table 5.2 because the electrolyte and cathode overpotentials are taken directly from Virkar’s experimental measurements [35], as described earlier. The triple-phase-boundary length selected here is the same one reported by Moyer et al [27] to fit the same hydrogen and oxygen spillover models to patterned-anode Tafel plots. This TPB length is also the same order of magnitude as the one calculated by Wilson et al [38] in their 3D reconstruction of a porous Ni-YSZ anode. The two highlighted rows, tortuosity and area-specific TPB, are the only two constants in the model that were treated as fitting parameters to match experimental data.

Table 5.2: Constant operational and structural parameters for the SOFC model [21].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Operating Conditions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>800</td>
<td>°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>$P$</td>
<td>1</td>
<td>atm</td>
</tr>
<tr>
<td><strong>Anode Structural Parameters</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of nodes</td>
<td>$m$</td>
<td>10</td>
<td>--</td>
</tr>
<tr>
<td>Thickness</td>
<td>$L_a$</td>
<td>1100</td>
<td>μm</td>
</tr>
<tr>
<td>Porosity</td>
<td>$\varepsilon$</td>
<td>0.54</td>
<td>--</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>$\tau$</td>
<td>2.0</td>
<td>--</td>
</tr>
<tr>
<td>Average pore radius</td>
<td>$r_p$</td>
<td>0.50</td>
<td>μm</td>
</tr>
<tr>
<td>Average particle diameter [9]</td>
<td>$d_p$</td>
<td>2.50</td>
<td>μm</td>
</tr>
</tbody>
</table>
Specific catalyst area [9] & $A_s$ & 1080 & cm$^{-1}$
YSZ surface site density [23] & $\Gamma_{YSZ}$ & $1.3 \times 10^{-5}$ & mol m$^{-2}$
Nickel surface site density [30] & $\Gamma_{Ni}$ & $2.66 \times 10^{-5}$ & mol m$^{-2}$
Triple-phase-boundary length [27] & $l_{TPB}$ & $1.83 \times 10^{5}$ & m cm$^{-2}$

| Area-specific triple-phase-boundary length | $a_{TPB}$ | .0065 | -- |

### 5.4.1 Model Verification

Before the different current pathways and rate-limiting processes of the proposed mechanism can be investigated, the model must be verified as a reasonable predictor of cell performance for mixtures with hydrogen, CO or both fuel species. Therefore, the model is presented here alongside a comprehensive set of porous anode SOFC experimental data for CO/CO$_2$, H$_2$/H$_2$O, H$_2$/N$_2$, H$_2$/CO, and H$_2$/CO$_2$ mixtures [21]. This particular experimental paper is cited by many modelers, but very few have presented a convincing fit to multiple data sets from this paper [39]. Therefore, fitting the model here to data for a wide range of mixtures will provide some evidence for the validity of the proposed mechanism.

Tortuosity and area-specific TPB length are the only parameters that were adjusted to match the model to this wide range of data, and their fitted values (listed in Table 5.2) are consistent with previously reported values in literature [9], [10], [21], [38]. The fact that this model implements believable values for all known and unknown fitted parameters provides supporting evidence for the proposed mechanism. Whereas previous modeling efforts have studied a similar mechanism with only syngas data [27], this work applies the mechanism to a variety of mixtures with and without H$_2$ and CO. This approach facilitates the independent verification of the mechanisms for O spillover and H spillover by comparing the model to mixtures with different charge-transfer pathways. Similar to the approach taken in the previous analysis [27], this study compares the
model to data in Tafel form (i.e. logarithm of current density as a function of anode activation overpotential). This comparison also purposely neglects the limiting current regime where concentration effects confound the impact of the electro-oxidation mechanism on operating voltage.

Figure 5.3 plots the model polarization curves along with experimental data for a couple of CO/CO₂ mixtures. This particular data set is unique in that no hydrogen compounds are present, which means that oxygen spillover to CO is the only electrochemically active pathway. Therefore, studying the fit of the model to this particular data set provides some insight on the oxygen spillover pathway. The model predicts the experimental data reasonably well at low currents, but some divergence occurs from the data set at higher currents. However, some level of error is anticipated for these CO/CO₂ mixtures because the kinetic parameters in the O spillover mechanism were fitted to mixtures of H₂/H₂O rather than mixtures of CO/CO₂ [17]. The reasonable fit of model to experimental CO/CO₂ data at low currents in Figure 5.3, however, does provide some verification that the O spillover pathway is a plausible model for CO electro-oxidation.
Figure 5.3: Comparison of polarization characteristics between model and data for mixtures of CO and CO$_2$ at 800°C and 1 atm. Oxygen spillover to CO(Ni) is the only charge-transfer pathway.

Figure 5.4 compares the simulated and experimental polarization curves for mixtures containing H$_2$ rather than CO, which provides insight on the application of the combined spillover mechanism to hydrogen electro-oxidation. The model is compared to data for mixtures of H$_2$ with N$_2$ (subplot A) and H$_2$ with H$_2$O (subplot B) in order to verify that the combined spillover mechanism is applicable to a wide range of H$_2$:H$_2$O ratios. The model is able to consistently reproduce experimental data in Figure 5.4 for a wide range of mixtures at moderate currents. Some deviation occurs from experimental values at very low currents, which is partly due to the fact that the open-circuit potential can only be fixed for one of the two spillover pathways, as described in Appendix B.1. The overall match between the simulated and experimental polarization curves in Figure 5.4
is a significant improvement over previous efforts to fit this full data set [9], [10]. This good fit over a wide range of $\text{H}_2:\text{H}_2\text{O}$ ratios indicates that the combined hydrogen and oxygen spillover model can be applied to mixtures where hydrogen is the only electro-active species.
A: $\text{H}_2 + \text{N}_2$ Mixtures

![Graph A: $\text{H}_2 + \text{N}_2$ Mixtures](image)

B: $\text{H}_2 + \text{H}_2\text{O}$ Mixtures

![Graph B: $\text{H}_2 + \text{H}_2\text{O}$ Mixtures](image)
Figure 5.4: Comparison of polarization characteristics between model and data for mixtures of 
H₂+N₂ (A) and H₂+H₂O (B) at 800°C and 1 atm. Both the hydrogen spillover and oxygen 
spillover charge-transfer pathways are active.

Figure 5.5 compares simulated and experimental polarization curves for mixtures where both H₂ 
and CO are present in gas-phase equilibrium. For these syngas mixtures, current is produced 
simultaneously by H spillover and by O spillover to both H₂ and CO. Therefore, these results 
provide verification that the combined spillover mechanism can accurately represent the 
simultaneous oxidation of H₂ and CO. The model is presented against experimental data for 
mixtures of H₂ and CO₂ (subplot A) and for mixtures of H₂ and CO (subplot B). Because the fuel 
stream is modeled in gas-phase equilibrium at the anode, these data sets cover a range of H₂:H₂O 
and CO:CO₂ ratios. The model fits the experimental data well at moderate currents but somewhat 
over-predicts voltage at lower currents. This discrepancy near open-circuit conditions can again 
be attributed to that fact that equilibrium potential across the anode-electrolyte double-layer can 
only be set for one spillover pathway. The combined spillover mechanism, however, provides 
reasonable prediction of cell operating voltage for a wide range of syngas mixtures and current 
densities in Figure 5.5. These fitting results in Figures 5.3-5 provide verification that the proposed 
mechanism can represent the electro-oxidation of H₂ and CO on Ni-YSZ when either or both 
species are present.
Figure 5.5: Comparison of polarization characteristics between model and data for mixtures of H₂+CO₂ (A) and H₂+CO (B) at 800°C and 1 atm. Both the hydrogen spillover and oxygen spillover charge-transfer pathways are active, and oxygen spills over to both hydrogen and CO on nickel.

Figures 5.3-5 demonstrate that the model is able to predict cell performance over a wide range of anode mixtures. Only two model parameters, tortuosity and area-specific TPB length, were varied to fit the model to data for all of these mixtures. Figure 5.6 shows how sensitive the model predictions are to changes in these two tuning parameters for the case of 43% H₂+57% N₂. All model parameters are held constant except for tortuosity in subplot A, and all parameters except for area-specific TPB length are held constant in subplot B. Both tuning parameters are adjusted from 50% to 150% of their fitted values (τ = 2, a_{TPB} = 0.0065) in these figures. The entire polarization curve is affected by changes in tortuosity, as demonstrated in subplot A, because this parameter always affects diffusion of gases to the TPB. Lowering the tortuosity raises current for a given voltage because the path for gases to reach the TPB is more direct.

In comparison, adjusting a_{TPB} in subplot B of Figure 5.6 only impacts model predictions at high currents because this term only appears in equations (5.25)-(5.26) where H₂ adsorption is rate-limiting. Lowering a_{TPB} causes the limiting current density to decrease because this parameter is proportional to the TPB length where electro-chemical reactions occur. Both subplots in Figure 5.6 demonstrate that the model is responsive to changes in the two tuning parameters. However, the flexibility of the model to fit a single data set by adjusting these two parameters does not compromise the verification in Figures 5.3-5 because varying these values affects the model’s fit to all data sets. Therefore, the model sensitivity to τ and a_{TPB} seems reasonable, given that the model is able to predict data for a wide range of fuel mixtures using fixed values for these two parameters.
A: Sensitivity to Tortuosity

B: Sensitivity to Area-specific TPB Length
5.4.2 Mechanism Investigation

The results from the previous section demonstrated the model's ability to reasonably predict cell performance for H₂, CO and simultaneous H₂+CO oxidation over a wide range of fuel mixtures. This section now focuses on the different spillover pathways in this electro-oxidation mechanism as a function of current density for mixtures with and without CO. This investigation will provide insight on the relative importance of the H and O spillover pathways under different conditions. This section will also explore the impact of rate-limiting assumptions in the spillover mechanisms at higher currents. More specifically, the model will be compared to experimental polarization curves for cases where charge-transfer is always assumed rate-limiting (Case 1) and cases where hydrogen adsorption becomes the rate-limiting step at higher currents (Case 2). Two hydrogen-lean mixtures, with and without CO, are selected for this study because experimental polarization data that extended into the limiting current regime was available for these mixtures. The spillover current pathways, polarization curves and TPB coverages are presented first for a mixture with only H₂ electro-oxidation (20% H₂ + 80% N₂), and then for a mixture with both H₂ and CO electro-oxidation (20% H₂ + 80% CO).

5.4.2.1 Only Hydrogen Present

The current produced by the H and O spillover pathways are compared in Figure 5.7 for an anode fuel mixture of 20% H₂ and 80% N₂. For this mixture, H₂ is the only electro-active species, but it can produce current by both the H spillover and O spillover pathways. If charge-transfer steps are always modeled as rate-limiting in both pathways (Case 1, Fig. 5.7A), then the majority of current is initially produced by the H spillover pathway, as predicted by previous literature. However, the
current produced by H spillover reaches a peak and declines at higher anode activation overpotentials while O spillover current escalates and surpasses H spillover current at high overpotentials. If hydrogen adsorption to nickel is modeled as rate-limiting for higher currents (Case 2, Fig. 5.7B), then the shapes of the curves change at higher anode activation overpotentials. H spillover is still the dominant source of current at low overpotentials in Case 2, but it reaches a lower peak value at a smaller overpotential when hydrogen adsorption becomes rate-limiting (denoted by “switch #1”). Once the H spillover pathway becomes limited by H₂ adsorption, the current produced by O spillover ramps up until that pathway also becomes limited by the rate of H₂ adsorption to nickel (denoted by “switch #2”). Beyond that point, the currents produced by both spillover pathways are equal because they are both governed by the rate of hydrogen adsorption to nickel. For both cases presented in Figure 5.7, it is evident that the H spillover pathway is the dominant source of current for H₂ electro-oxidation at low overpotentials. However, it is also clear that the O spillover pathway is a non-negligible source of current for H₂ electro-oxidation at moderate to high anode overpotentials.
**Figure 5.7:** Current densities of the H spillover and O spillover pathways as a function of activation anode overpotential for an anode fuel mixture of 20% H₂ and 80% N₂. The charge-transfer steps are always rate-limiting for both pathways in Case 1 (A); hydrogen adsorption is rate-limiting at high currents for both pathways in Case 2 (B). Arrows denote the points where the rate-limiting step switches from charge-transfer to hydrogen adsorption in each spillover pathway in Case 2.

The model polarization curves for Cases 1 and 2 are compared to experimental data in Figure 5.8 for an anode fuel mixture of 20% H₂ and 80% N₂. The modeled current densities in this plot account for the total current produced by both of the spillover pathways shown in Figure 5.7. More specifically, the dashed line in Figure 5.8 corresponds to Case 1 in Figure 5.7A, and the solid line and arrows in Figure 5.8 correspond to Case 2 in Figure 5.7B. The model for Case 1 in Figure 5.8 over-predicts current density towards the end of the polarization curve because it does not account for the limitation of hydrogen adsorption rates at high anode overpotentials. The Case 2 curve, on
the other hand, is able to predict the experimental voltage drop-off because it accounts for H₂ adsorption as the rate-limiting step at high overpotentials. These findings are consistent with the results of a previous modeling study based only on the H spillover mechanism [10].

The two cases of the model diverge at the second switch point in Figure 5.8, which is where H₂ adsorption becomes the rate-limiting step in the O spillover mechanism. Up to that point, the polarization curves for the two cases of the model match, despite the fact that H₂ adsorption is rate-limiting in the H spillover mechanism for Case 2 after the first switch point. This result indicates that the total current density for both cases is the same, which implies that more current is routed through the O spillover pathway in Case 2 once the H spillover pathway becomes limited by the rate of hydrogen adsorption. The fact that Case 2 of the model is able to better predict experimental polarization behavior provides reason to believe that the current pathway division in Figure 5.7B is more likely than the current breakdown in Figure 5.7A. Thus, it appears that the mechanism for H₂ electro-oxidation on Ni-YSZ is governed first by the rate of H spillover charge-transfer, then by the rate of O spillover charge-transfer, and finally by the rate of H₂ adsorption to nickel for both spillover pathways.
Figure 5.8: Modeled polarization curves alongside experimental data for an anode fuel mixture of 20% H₂ and 80% N₂. The charge-transfer steps are always rate-limiting for both pathways in model Case 1; hydrogen adsorption is rate-limiting at high currents for both pathways in model Case 2. Arrows denote the points along the polarization curve where the rate-limiting step switches from charge-transfer to hydrogen adsorption in each spillover pathway.

Figure 5.9 provides the surface coverages on nickel (Fig. 5.9A) and YSZ (Fig. 5.9B) at the TPB as a function of current for the same mixture of 20% H₂ + 80% N₂. These coverage profiles correspond to Case 2 in Figures 5.7 and 5.8, where rate-limiting hydrogen adsorption is enabled at high currents. This rate-limiting assumption can be observed in Figure 5.9B, where ionic species coverages spike at high currents. The increasing coverages of intermediate ionic species in Fig. 5.9B, $O^-(YSZ)$ and $OH^-(YSZ)$, are a reflection of the increasing currents of both the O spillover and H spillover pathways, respectively. Similarly, the increasing coverages of product species $O(Ni)$, $OH(Ni)$, and $H_2O(Ni)$ in Fig. 5.9A reflect the increasing current of both spillover...
pathways. In comparison, coverages of $H(Ni)$ and $O^{2-}(YSZ)$ in Figure 5.9 decline with current because they are both reactants in each of the two spillover pathways. Whereas the majority of YSZ sites are occupied by $O^{2-}$ ions, the majority of the nickel sites are vacant at the TPB. The orders of magnitude of the coverages presented in Figure 5.9 are consistent with predictions from previous models [17], [27], providing some verification for the implementation of the mechanism in this model.

Figure 5.9: Modeled TPB coverages for an anode fuel mixture of 20% $H_2$ and 80% $N_2$. Surface coverages on nickel are shown in (A); surface coverages on YSZ are shown in (B). Hydrogen adsorption becomes rate-limiting in both spillover pathways at high currents (Case 2).
5.4.2.2 Hydrogen and CO Present

Figures 5.6-9 focused on a mixture where hydrogen was the only electrochemically active species so that the relative importance of the hydrogen adsorption, H spillover charge-transfer and O spillover charge-transfer steps could be studied. Figures 5.10-12 build on the previous analysis by investigating an anode syngas mixture where both fuel species are present: 20% H₂ + 80% CO. For this syngas mixture, current can be produced by O spillover to CO(Ni) in addition to O spillover to H(Ni) and H spillover to YSZ. When CO is present, there is also the possibility that CO adsorption on nickel becomes a rate-limiting step in the O spillover mechanism at high anode activation overpotentials. Therefore, a detailed study of the current pathways and polarization curves for this syngas mixture should provide insight into the rate-limiting processes that govern cell performance when CO is present in the fuel stream.

Figure 5.10 shows the current densities associated with each spillover pathway as a function of anode activation overpotential for an anode syngas mixture of 20% H₂ and 80% CO. Current is produced here by three pathways: H spillover to YSZ, O spillover to H(Ni) and O spillover to CO(Ni). Figure 5.10A corresponds to Case 1, where charge-transfer steps are assumed rate-limiting for all spillover pathways across all anode overpotentials; Figure 5.10B corresponds to Case 2, where fuel adsorption steps can become rate-limiting at high currents. The relative magnitudes and shapes of the H spillover and O spillover to H curves in Figure 5.10 resemble those in Figure 5.7, indicating that the rate-limiting processes in the H₂ electro-oxidation mechanism are largely unaffected by the introduction of CO.

A more interesting comparison in Figure 5.10 is between the curves for oxygen spillover to H and oxygen spillover to CO. Although CO produces some current from oxygen spillover, substantially more current is produced via oxygen spillover to H₂. This finding is perhaps surprising given the
high concentration of CO in the gas phase, but it is consistent with the fact that $H(Ni)$ reacts faster than $CO(Ni)$ does with $O(Ni)$ [30]. This result challenges previous assertions that most oxygen spills over to CO in mixtures of H$_2$ + CO [27], and provides justification for modeling O spillover to $H(Ni)$ in addition to H spillover. Although the current produced by CO electro-oxidation is small, it appears to be non-negligible at high anode activation overpotentials for both cases in Figure 5.10. Therefore, accurate prediction of cell performance at high currents with CO-rich syngas may still require a model for CO electro-oxidation.

Figure 5.10B also provides some qualitative insight on the relative likelihoods of H$_2$ and CO adsorption to nickel becoming rate-limiting at high overpotentials. Similar to the results in Figure 5.7B, both H spillover and O spillover to H switch over to rate-limiting H$_2$ adsorption at high overpotentials (denoted by the “Switch #1” and “Switch #2” arrows, respectively). However, a similar switch to rate-limiting CO adsorption on nickel does not occur in Figure 5.10B. In fact, CO current density would have to exceed 10 A cm$^{-2}$ at these anode overpotentials in order for CO adsorption to become the rate-limiting step. This order-of-magnitude difference between H$_2$ and CO adsorption rates is consistent with the difference in these fuels’ sticking coefficients to nickel: $\gamma_{H_2} = .01$ and $\gamma_{CO} = 0.5$ [30]. Because CO molecules have such a strong affinity to nickel, the CO electro-oxidation mechanism is always limited by O spillover charge-transfer kinetics. The current produced by O spillover to $CO(Ni)$ can thus exceed the current produced by O spillover to at high anode activation overpotentials, where the hydrogen pathway is limited by the rate of H$_2$ adsorption to nickel.
Figure 5.10: Current densities of the H spillover and O spillover pathways as a function of activation anode overpotential for an anode fuel mixture of 20% H₂ and 80% CO. The charge-transfer steps are always rate-limiting for both pathways in Case 1 (A); hydrogen adsorption is rate-limiting at high currents for both pathways in Case 2 (B). Arrows denote the points where the rate-limiting step switches from charge-transfer to hydrogen adsorption in each of the hydrogen fuel electro-oxidation pathways.

The model polarization curves for Cases 1 and 2 are compared to experimental data for the anode mixture of 20% H₂ and 80% CO in Figure 5.11. The modeled current densities in this plot account for the total current produced by all three of the spillover pathways shown in Figure 5.10. As was the case in Figure 5.8, the model for Case 1 in Figure 5.11 over-predicts current density towards the end of the polarization curve because it does not account for the limitation of hydrogen adsorption rates at high anode overpotentials. The Case 2 curve, on the other hand, is able to better predict the experimental voltage curve at high currents because it accounts for H₂ adsorption as
the rate-limiting step. The two cases of the model again diverge at the second switch point in Figure 5.11, which is where H₂ adsorption becomes the rate-limiting step in the O spillover mechanism. The fact that Case 2 of the model is able to better predict experimental polarization behavior provides reason to believe that the current pathway division in Figure 5.10B is more likely than the current breakdown in Figure 5.10A. Thus, it appears that the mechanism for H₂ + CO electro-oxidation on Ni-YSZ is governed first by the rate of H spillover charge-transfer, then by the rate of O spillover to H(Ni), and finally by the rate of O spillover to CO(Ni) at high anode overpotentials.

Figure 5.11: Modeled polarization curves alongside experimental data for an anode fuel mixture of 20% H₂ and 80% CO. The charge-transfer steps are always rate-limiting for both pathways in model Case 1; hydrogen adsorption is rate-limiting at high currents for both pathways in model Case 2. Arrows denote the points along the polarization curve where the rate-limiting step switches from charge-transfer to hydrogen adsorption in each of the hydrogen fuel electro-oxidation pathways.
Figure 5.12 provides the TPB surface coverages on nickel and YSZ for Case 2 from Figures 5.10-11. The second switch point to rate-limiting hydrogen adsorption can be observed in Fig. 5.12B by the spike in intermediate ionic species coverages. The increase in both intermediate ionic species in Fig. 5.12B, $O^{-}(YSZ)$ and $OH^{-}(YSZ)$, is a reflection of the increasing currents produced by the O spillover and H spillover pathways, respectively. Similarly, the increasing coverages of product species $O(Ni)$, $CO_2(Ni)$, and $H_2O(Ni)$ in Fig. 5.12A reflects the increasing current of both spillover pathways. In comparison, coverages of $H(Ni)$, $CO(Ni)$, and $O^{2-}(YSZ)$ in Figure 5.12 decline with current because they are reactants in the spillover pathways. In comparison with Fig. 5.9A, there are fewer nickel vacancies in Fig. 5.12A because CO occupies a large number of nickel sites. This is a result of carbon monoxide’s strong affinity to nickel, which causes it to bind easily and prevents it from spilling over to YSZ. The orders of magnitude of the coverages presented in Figure 5.12 are also consistent with predictions from previous models [17], [27], providing further verification for this model. Overall, the results in Figures 5.10-5.12 provide some indication of the relative importance and rate-limiting steps of the H and O spillover pathways as a function of current for syngas mixtures.
Figure 5.12: Modeled TPB coverages for an anode fuel mixture of 20% H₂ and 80% CO. Surface coverages on nickel are shown in (A); surface coverages on YSZ are shown in (B). Hydrogen adsorption becomes rate-limiting in both spillover pathways at high currents (Case 2).

### 5.5 Conclusions

It is critical to understand the individual and simultaneous electro-oxidation mechanisms for H₂ and CO in SOFCs in order to optimize cell performance with practical gaseous fuel mixtures. Recent microstructural studies on Ni/YSZ anodes have demonstrated that H₂ electro-oxidation proceeds by means of both H and O spillover, while CO electro-oxidation can only proceed through the O spillover pathway [28]. This combined spillover pathway model is integrated into a 1D-MEA model here that also accounts for gas-phase transport and heterogeneous reforming on nickel in the anode. The steps of these H and O spillover pathways are outlined along with the governing equations and rate-limiting assumptions in the anode model.
This model is then compared to experimental porous anode polarization data for a wide range of anode fuel stream mixtures containing H$_2$ and/or CO. The model is able to predict these data sets well with only two unknown fitting parameters adjusted. These results imply that this combined spillover pathway model is capable of representing H$_2$ and CO electro-oxidation not only individually, but also in parallel. A break-down of current pathways versus anode activation overpotential is then given for two mixtures: 20% H$_2$ + 80% N$_2$ and 20% H$_2$ + 80% CO. These plots confirm that H spillover is the dominant source of current at low anode overpotentials, but also indicate that O spillover to H and CO contribute to cell performance at high anode overpotentials. These results challenge previous modeling assumptions that O spillover to H and CO are negligible sources of current compared to the H spillover pathway.

Finally, the model is compared to experimental polarization data for two cases: charge-transfer steps are always rate-limiting (Case 1) and fuel adsorption can become rate-limiting at high anode overpotentials (Case 2). It is found that CO adsorption to nickel is never a rate-limiting step, whereas H$_2$ adsorption to nickel becomes rate-limiting in both the H spillover and O spillover to $H(Ni)$ pathways. Thus, the O spillover pathway becomes an increasingly important source of current at high anode activation overpotentials, where H$_2$ adsorption to nickel is rate-limiting. Experimental measurements at the anode TPB could provide further evidence for the various current pathways and rate-limiting processes proposed in this study.

5.6 References


Chapter 6

Conclusions

Systems that integrate coal gasification with solid oxide fuel cells (SOFCs) are a promising candidate for high-efficiency stationary power production with lower CO₂ emissions. This thesis used a multi-scale modeling approach to analyze SOFC performance with coal syngas from the systems level down to the surface reaction scale. This work builds on a detailed 1D SOFC model [1], and repeatedly validates results against experimental data from another group [2] to scope out system and reaction interface behavior. This chapter first outlines the key contributions of this thesis, and then provides suggestions for future work on this topic.

6.1 Key Contributions

This thesis has contributed to understanding SOFC performance with coal syngas from both a systems and a surface reaction perspective. The key contributions of this thesis are summarized succinctly in Figure 1.4, and are enumerated in more detail by chapter below.

Chapter 2 provided a literature review of a highly-coupled fluidized bed gasifier + fuel cell system, known as the FB/SOFC. This chapter provided a summary of the state-of-the-art modeling and experimental work done on this system, and also described the key operational and modeling challenges associated with FB/SOFCs.

Chapter 3 used an equilibrium gasifier model coupled to a 1D SOFC model to determine that the coupled system is capable of 55-60% efficiency at maximum power operation. This chapter also compared system performance with steam and CO₂ as the recycled gas, and found
that 2-3 times the power density could be achieved when steam was selected due to faster H₂ electro-oxidation. Finally, this system modeling study determined that higher efficiencies and power outputs could be obtained when the heat output of the fuel cell stack was sent to the gasifier.

**Chapter 2**
- Literature review of coupled gasifier + fuel cell systems.

**Chapter 3**
- System efficiency: 55-60%
- Steam increases power output
- Internal heat transfer important

**Chapter 5**
- Two pathways for H₂ oxidation
- Oxygen spills over to H and CO
- Adsorption rate-limiting for H₂, not for CO

**Chapter 4**
- CO doesn’t all shift in anode
- CO produces non-negligible current in syngas mixtures

Figure 6.1: A schematic diagram summarizing the contributions of this thesis by chapter.
Chapter 4 used the 1D SOFC model to study how much current is produced by \( \text{H}_2 \) and CO for different coal syngas mixtures. This investigation found that a significant portion of CO does not react with steam in the anode before reaching the electro-chemical reaction sites. This study also found that a model for CO electro-oxidation is needed to accurately predict SOFC performance at high currents.

Chapter 5 implemented a detailed elementary mechanism for the simultaneous electro-oxidation of \( \text{H}_2 \) and CO. This study found that current is produced from \( \text{H}_2 \) by two different reaction pathways. This study also found that oxygen spills over to \( H(Ni) \) at lower currents and then to \( CO(Ni) \) at higher currents. Finally, this study confirmed that fuel adsorption onto nickel can be a rate-limiting step for \( \text{H}_2 \) electro-oxidation but not for CO electro-oxidation.

Together these chapters provided insight into the coupling of coal gasification with SOFCs to better predict and optimize system performance for efficient stationary power generation.

6.2 Future Work

The results from Chapter 3 indicate that state-of-the-art efficiencies near 60% are possible when the gasifier and SOFC stack are coupled by heat transfer. However, even higher efficiencies are theoretically possible with the FB/SOFC design from Chapter 2, which integrates the gasifier into the SOFC compartment. This highly-coupled system boosts efficiency by promoting heat and gas exchange between the gasifier and fuel cell. In order to accurately predict the performance of this FB/SOFC system, a 2D model should be developed to capture gas transport and heat transfer between the gasification and anode reactions occurring in parallel. Detailed kinetic models for both steam and CO\(_2\) coal gasification must be implemented and coupled with the detailed SOFC model from this work to capture the relative reaction rates and by-products.
Experimental work is also needed in this space to better understand the complex coupling of coal gasification with a SOFC stack under normal operating conditions. In particular, a bench scale experimental set-up with steam gasification of coal particles upstream from a SOFC button cell could be used to study the impact of sulfur contamination and clean-up strategies. This bench set-up could also be used to scope out SOFC performance for a range of coal types and temperatures. Finally, a pilot scale hardware-in-the-loop-simulation of a real coal gasifier coupled to a simulated SOFC stack is critical to investigate the complex coupling of these two components before implementing these technologies in a full-scale power plant. A similar pilot scale demonstration has been developed for a SOFC coupled to a gas turbine at the DOE National Energy Technology Laboratory [3], and has provided invaluable insight on transient system performance. This pilot scale system could also be used to test novel high-temperature heat exchangers between the fuel cell stack and gasifier. Future modeling and experimental studies on the coupling of coal gasification with SOFCs will pave the way for large-scale fossil fuel power production with substantially lower CO₂ emissions.

6.3 References


Appendices

Appendix A: Method for Obtaining Anode Mixture with OCV

The goal of this section is to provide further description of the method implemented in Chapters 4-5 to determine the actual anode fuel mixture based on the reported mixture and open-circuit voltage (OCV) given by the experimental paper [1]. The motivation for this approach is that multiple experimentalists cite air leakage as the culprit for their low open-circuit voltage measurements. In order to get the modeled OCV to match the experimentally reported OCV for a reported anode fuel mixture, the following procedure was used (also shown in Figure A.1):

1) The gas-phase chemical equilibrium mixture was calculated by running Cantera’s “equilibrate” function on the reported anode mixture at fixed temperature and pressure.

2) The OCV was then calculated using the following equation: 
   \[ OCV = \frac{RT}{4F} \ln\left(\frac{p_{O_2,c}}{p_{O_2,a}}\right) \]
   where \( p_{O_2,a} \) is the oxygen partial pressure in the equilibrated mixture from the previous step and \( p_{O_2,c} \) is simply the partial pressure of oxygen in the cathode air stream (\( p_{O_2,c} = 0.21P \)).

3) If the calculated OCV from the previous step is greater than the experimentally reported OCV (\( OCV > OCV_{exp} \)), then a small amount of air was added to the equilibrated anode mixture.

Steps 2)-3) were then repeated until \( OCV \leq OCV_{exp} \), at which point the adjusted anode mixture with air leakage and gas-phase chemical equilibrium was taken as the actual mixture seen by the anode in the model. Chemical equilibrium was assumed for the following reasons: 1) the gas delivered to the anode had a long upstream residence time, and 2) oxygen from the air leak would likely react quickly with fuels in the mixture.
IF OCV < OCV_{exp.} 

Start with equilibrated anode mixture.

Equilibrate anode mixture.

Calculate OCV for that mixture.

Converged on actual mixture at anode.

ELSEIF OCV > OCV_{exp.} 

Increase the air content of the anode mixture by a small increment.

Figure A.1: Flow-chart of the process for adjusting anode fuel mixture for air leakage to match experimental OCV values.

In order to illustrate how this method works, consider the mixture of 20% H_2 + 80% H_2O from Jiang and Virkar’s experimental paper. They provide an experimental polarization curve for that mixture that includes an open-circuit data point at 0.84 V. However, the calculated OCV for that equilibrated mixture is 0.04 V higher: $OCV = \frac{RT}{4F} \ln\left(\frac{0.21 \times 10^{13}}{7.23 \times 10^{-13}}\right) = 0.88 \text{ V}$. A small increment of air (0.1% of the overall mixture) is then added, resulting in the following anode mixture: 19.98% H_2 + 79.92% H_2O + .021% O_2 + .079% N_2. The calculated OCV for that equilibrated mixture is still almost 0.04 V higher than the experimental value, so another 0.1% of air is added. This process is repeated until $OCV \leq 0.84 \text{ V}$, which occurs for unequilibrated anode mixture of: 16.2% H_2 + 64.8% H_2O + 3.99% O_2 + 15.01% N_2. This mixture corresponds to 19% air by volume, as listed in the first row of Table A.1.

Table A.1: Calculated vs. experimental OCV values along with the percentage of air in the adjusted anode mixtures for each of the reported anode fuel mixtures from Jiang and Virkar [1].
<table>
<thead>
<tr>
<th>Reported Experimental Mixtures</th>
<th>Calculated OCV</th>
<th>Experimental OCV</th>
<th>Difference in OCV's</th>
<th>% Air in Adjusted Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 H₂-80 H₂O</td>
<td>0.88</td>
<td>0.84</td>
<td>0.04</td>
<td>19</td>
</tr>
<tr>
<td>34 H₂-66 H₂O</td>
<td>0.91</td>
<td>0.86</td>
<td>0.05</td>
<td>31</td>
</tr>
<tr>
<td>50 H₂-50 H₂O</td>
<td>0.94</td>
<td>0.89</td>
<td>0.05</td>
<td>38</td>
</tr>
<tr>
<td>55 H₂-45 H₂O</td>
<td>0.95</td>
<td>0.92</td>
<td>0.03</td>
<td>28</td>
</tr>
<tr>
<td>85 H₂-15 H₂O</td>
<td>1.02</td>
<td>0.98</td>
<td>0.04</td>
<td>27</td>
</tr>
<tr>
<td>100 H₂</td>
<td>1.26</td>
<td>1.02</td>
<td>0.24</td>
<td>27</td>
</tr>
<tr>
<td>85 H₂-15 N₂</td>
<td>1.25</td>
<td>1.01</td>
<td>0.24</td>
<td>27</td>
</tr>
<tr>
<td>68 H₂-32 N₂</td>
<td>1.24</td>
<td>1.00</td>
<td>0.24</td>
<td>26</td>
</tr>
<tr>
<td>50 H₂-50 N₂</td>
<td>1.23</td>
<td>0.99</td>
<td>0.24</td>
<td>24</td>
</tr>
<tr>
<td>43 H₂-57 N₂</td>
<td>1.22</td>
<td>0.97</td>
<td>0.25</td>
<td>27</td>
</tr>
<tr>
<td>33 H₂-67 N₂</td>
<td>1.21</td>
<td>0.96</td>
<td>0.25</td>
<td>24</td>
</tr>
<tr>
<td>20 H₂-80 N₂</td>
<td>1.19</td>
<td>0.93</td>
<td>0.26</td>
<td>21</td>
</tr>
<tr>
<td>85 H₂-15 CO₂</td>
<td>1.02</td>
<td>0.95</td>
<td>0.07</td>
<td>42</td>
</tr>
<tr>
<td>68 H₂-32 CO₂</td>
<td>0.98</td>
<td>0.94</td>
<td>0.04</td>
<td>31</td>
</tr>
<tr>
<td>50 H₂-50 CO₂</td>
<td>0.94</td>
<td>0.92</td>
<td>0.02</td>
<td>22</td>
</tr>
<tr>
<td>40 H₂-60 CO₂</td>
<td>0.92</td>
<td>0.90</td>
<td>0.02</td>
<td>22</td>
</tr>
<tr>
<td>32 H₂-68 CO₂</td>
<td>0.91</td>
<td>0.89</td>
<td>0.02</td>
<td>16</td>
</tr>
<tr>
<td>19 H₂-81 CO₂</td>
<td>0.88</td>
<td>0.87</td>
<td>0.01</td>
<td>5</td>
</tr>
<tr>
<td>20 H₂-80 CO</td>
<td>1.15</td>
<td>1.00</td>
<td>0.15</td>
<td>35</td>
</tr>
<tr>
<td>32 H₂-68 CO</td>
<td>1.13</td>
<td>1.00</td>
<td>0.13</td>
<td>35</td>
</tr>
<tr>
<td>45 H₂-55 CO</td>
<td>1.11</td>
<td>1.01</td>
<td>0.10</td>
<td>31</td>
</tr>
<tr>
<td>54 H₂-46 CO</td>
<td>1.11</td>
<td>1.01</td>
<td>0.10</td>
<td>31</td>
</tr>
<tr>
<td>68 H₂-32 CO</td>
<td>1.11</td>
<td>1.01</td>
<td>0.10</td>
<td>31</td>
</tr>
<tr>
<td>86 H₂-14 CO</td>
<td>1.12</td>
<td>1.02</td>
<td>0.10</td>
<td>27</td>
</tr>
<tr>
<td>18 CO-82 CO₂</td>
<td>0.87</td>
<td>0.75</td>
<td>0.12</td>
<td>28</td>
</tr>
<tr>
<td>32 CO-68 CO₂</td>
<td>0.91</td>
<td>0.86</td>
<td>0.05</td>
<td>31</td>
</tr>
<tr>
<td>44 CO-56 CO₂</td>
<td>0.93</td>
<td>0.88</td>
<td>0.05</td>
<td>37</td>
</tr>
<tr>
<td>100 CO</td>
<td>1.26</td>
<td>1.00</td>
<td>0.26</td>
<td>36</td>
</tr>
</tbody>
</table>
The percentages of air in all of the final anode mixtures used in this thesis are listed in the last column of Table A.1. The mean value of this column is 28%, which indicates that roughly one mole of air is leaking into the anode gas supply for every three moles of fuel mixture supplied. Although this seems like a high value, it’s not necessarily unreasonable given the following justifications:

1) Virkar’s experimental group cites air leakage as the most likely cause of open-circuit voltage dips in their paper [1].

2) This experimental group also reports higher air-side flow-rates than fuel-side flow-rates to their button cell (550 mL/min vs. 140 mL/min). Therefore, a small leak could still result in a relatively large air flow-rate across the membrane.

3) The air leakage percentages don’t vary much for different fuel mixtures, particularly those within the same data set (e.g. H₂ + N₂ mixtures only vary from 21-27% air leakage). This provides some indication of a constant air leak into the anode while experiments were performed.

Even in light of this evidence, it is still likely that air leakage is only one of the sources of loss in cell potential in this experiment. Other possible contributors are electronic leakage through the cell and morphological changes to the cell (i.e. carbon deposition) that degrade performance. However, the air leakage model described here was implemented because it consistently provided a better fit to the experimental data than the alternative electronic leakage model. Further research should be done to compare the competing theories for cell performance loss using detailed modeling and experimental data from multiple independent sources.
Appendix B: Detailed Solutions for Spillover Mechanism

The goal of this section is to provide some of the detailed steps in solving for equilibrium potential \( E_{eq} \) and YSZ coverages \( \theta_{YSZ}, \theta_{O^{2-},YSZ}, \theta_{O^{-},YSZ}, \theta_{OH^{-},YSZ} \) when the charge-transfer processes in the spillover mechanisms are rate-limiting. This explanation supplements the model description provided in Chapter 5, and is specific to the case when both the H spillover and O spillover pathways are active. A similar procedure can be applied to cases where only one spillover pathway is active to solve for equilibrium potential and the relevant YSZ coverages.

B.1 Equilibrium Potential

The equilibrium potential difference across the anode-electrolyte double-layer \( (E_{eq}) \) is needed to determine the currents for each charge-transfer step since \( E = E_{eq} + \eta_{act,a} \) in equations (5.13)-(5.16). The equilibrium potential \( E_{eq} \) is simply the potential difference at open-circuit conditions, where \( \eta_{act,a} = 0 \) and all currents are zero. Therefore, \( E_{eq} \) can theoretically be determined by setting \( E = E_{eq} \) and \( i_k = 0 \) in charge-transfer equations (5.13)-(5.16). In practice, however, this leads to an over-constrained system of equations with no solution. Thus, \( E_{eq} \) can only be determined by setting setting \( E = E_{eq} \) and \( i_k = 0 \) for either equations (5.13)-(5.14) or equations (5.15)-(5.16). The errors resulting from this simplification are minor when equations (5.13)-(5.14) are selected, since the H spillover mechanism is the dominant source of current near open-circuit.

Setting \( E = E_{eq} \) and \( i_k = 0 \) for equations (5.13)-(5.14) yields the following set of equations:

\[
0 = Fl_{TPB}\left\{k_{H.3,f}\theta_{O^{2-},YSZ}\theta_{H,Ni}u^{\beta_{H.3}} - k_{H.3,b}\theta_{OH^{-},YSZ}\theta_{Ni}u^{-(1-\beta_{H.3})}\right\} \quad (B.1)
\]

\[
0 = Fl_{TPB}\left\{k_{H.4,f}\theta_{OH^{-},YSZ}\theta_{H,Ni}u^{\beta_{H.4}} - k_{H.4,b}\theta_{YSZ}\theta_{H_{2}O,Ni}u^{-(1-\beta_{H.4})}\right\} \quad (B.2)
\]
where \( u = \exp(fE_{eq}) \). These expressions can both be re-arranged to solve for \( u \) as follows:

\[
  u = \frac{(\theta_{Ni}\theta_{OH,-YSZ})}{(KH_{3}\theta_{H,Ni}\theta_{O^{2-},YSZ})} \quad (B.3)
\]

\[
  u = \frac{(\theta_{H_{2}O,Ni}\theta_{YSZ})}{(KH_{4}\theta_{H,Ni}\theta_{OH,-YSZ})} \quad (B.4)
\]

where \( KH_{3} = k_{H,3,f}/k_{H,3,b} \) and \( KH_{4} = k_{H,4,f}/k_{H,4,b} \). An additional constraint needed to solve this system arises from equation (5.11), re-arranged to solve for \( \theta_{O^{2-},YSZ} \):

\[
  \theta_{O^{2-},YSZ} = a\theta_{YSZ} \quad (B.5)
\]

where \( a = k_{H,2}k_{O^{2-},bulk}/x_{bulk} \) is a known constant. Substituting (B.5) into (B.3), equating (B.3) to (B.4), and cancelling out \( \theta_{H,Ni} \) from each side results in the following equation:

\[
  \left(\frac{\theta_{Ni}\theta_{OH,-YSZ}}{aK_{H,3}\theta_{YSZ}}\right) = \left(\frac{\theta_{H_{2}O,Ni}\theta_{YSZ}}{K_{H,4}\theta_{OH,-YSZ}}\right) \quad (B.6)
\]

This equation can be re-arranged to obtain \( \theta_{OH-,YSZ} \) as a function of \( \theta_{YSZ} \):

\[
  \theta_{OH-,YSZ} = \sqrt{aK_{H,3}\theta_{H_{2}O,Ni}/(K_{H,4}\theta_{Ni})} \theta_{YSZ} \quad (B.7)
\]

Substituting (B.7) into (B.4) results in the following expression for \( u \):

\[
  u = \sqrt{aK_{H,3}K_{H,4}\theta_{Ni}^{2}/aK_{H,3}K_{H,4}\theta_{Ni}^{2}} \quad (B.8)
\]

And finally, solving for the equilibrium overpotential:

\[
  E_{eq} = \frac{1}{f}\ln[\sqrt{aK_{H,3}K_{H,4}\theta_{Ni}^{2}/aK_{H,3}K_{H,4}\theta_{Ni}^{2}}] \quad (B.9)
\]

where all the nickel coverages at the TPB can be determined by solving the governing equations in the anode at open-circuit conditions.
B.2 YSZ Coverages

Once $E_{eq}$ is calculated using equation (B.9), the double-layer potential difference at finite current ($E = E_{eq} + \eta_{act,a}$) is also a known quantity, since $\eta_{act,a}$ is a model input. The current densities associated with each charge-transfer step from equations (5.13)-(5.16) can then be written in terms of known nickel coverages and the four unknown YSZ coverages at the TPB:

\[
\begin{align*}
    i_{(H,3)} &= F_l_{TPB}\left\{\hat{k}_{H,3,f}\theta_{H,Ni}\theta_{O^{2-},YSZ} - \hat{k}_{H,3,b}\theta_{Ni}\theta_{OH^{-},YSZ}\right\} \quad (B.10) \\
    i_{(H,4)} &= F_l_{TPB}\left\{\hat{k}_{H,4,f}\theta_{H,Ni}\theta_{OH^{-},YSZ} - \hat{k}_{H,4,b}\theta_{H_2O,Ni}\theta_{YSZ}\right\} \quad (B.11) \\
    i_{(O,4)} &= F_l_{TPB}\left\{\hat{k}_{O,4,f}\theta_{O^{2-},YSZ} - \hat{k}_{O,4,b}\theta_{O^{-}YSZ}\right\} \quad (B.12) \\
    i_{(O,5)} &= F_l_{TPB}\left\{\hat{k}_{O,5,f}\theta_{Ni}\theta_{O^{-}YSZ} - \hat{k}_{O,5,b}\theta_{0,0Ni}\theta_{YSZ}\right\} \quad (B.13)
\end{align*}
\]

where known constants have been grouped together for the forward and backward terms of step $i$ as follows: $\hat{k}_{i,f} = k_{i,f}\Gamma_{Ni}\Gamma_{YSZ} \exp(\beta_{i}fE)$ and $\hat{k}_{i,b} = k_{i,b}\Gamma_{Ni}\Gamma_{YSZ} \exp(-(1 - \beta_{i})fE)$, where $\Gamma_{Ni}$ is omitted from $\hat{k}_{4,f}$ and $\hat{k}_{4,b}$.

At steady-state, two additional constraint equations arise: $i_{(H,3)} = i_{(H,4)}$ and $i_{(O,4)} = i_{(O,5)}$. These constraints are necessary at steady-state to ensure constant coverages of intermediate ionic surface species [2], [3]: $\theta_{OH^{-},YSZ}$ and $\theta_{O^{-}YSZ}$. These two constraints also point to the fact that the same amount of current must be produced by each charge-transfer step in a given pathway. Equating (B.10) to (B.11) and (B.12) to (B.13) results in the following two equations:

\[
\begin{align*}
    \hat{k}_{H,3,f}\theta_{H,Ni}\theta_{O^{2-},YSZ} + \hat{k}_{H,4,b}\theta_{H_2O,Ni}\theta_{YSZ} &= \hat{k}_{H,4,f}\theta_{H,Ni}\theta_{OH^{-},YSZ} + \hat{k}_{H,3,b}\theta_{Ni}\theta_{OH^{-},YSZ} \quad (B.14) \\
    \hat{k}_{O,4,f}\theta_{O^{2-},YSZ} + \hat{k}_{O,5,b}\theta_{0,Ni}\theta_{YSZ} &= \hat{k}_{O,5,f}\theta_{Ni}\theta_{O^{-}YSZ} + \hat{k}_{O,4,b}\theta_{O^{-}YSZ} \quad (B.15)
\end{align*}
\]

Two of the four unknown YSZ coverages in (B.14)-(B.15) can be eliminated by substituting (B.5) into equation (5.12), which results in the following two relationships:
\[ \theta_{O^2-,YSZ} = \frac{a}{1+a} (1 - \theta_{O-,YSZ} - \theta_{OH-,YSZ}) \quad (B.16) \]

\[ \theta_{YSZ} = \frac{1}{1+a} (1 - \theta_{O-,YSZ} - \theta_{OH-,YSZ}) \quad (B.17) \]

where \( a = \frac{K_{H,2}X_{O^2-,bulk}}{X_{bulk}} \) is a known constant. Substituting (B.16)-(B.17) into (B.14)-(B.15) and rearranging gives the following two expressions:

\[ (1 - \theta_{O-,YSZ} - \theta_{OH-,YSZ}) = b\theta_{OH-,YSZ} \quad (B.18) \]

\[ (1 - \theta_{O-,YSZ} - \theta_{OH-,YSZ}) = c\theta_{O-,YSZ} \quad (B.19) \]

where \( b \) and \( c \) are groups of known rate constants and nickel coverages at the TPB:

\[ b = (1 + a)(\tilde{k}_{H,3,b}\theta_{N_i} + \tilde{k}_{H,4,f}\theta_{H,N_i})/(a \tilde{k}_{H,3,f}\theta_{H,N_i} + \tilde{k}_{H,4,b}\theta_{H_{2}O,N_i}) \quad (B.20) \]

\[ c = (\tilde{k}_{O,4,b} + \tilde{k}_{O,5,f}\theta_{N_i})/(a\tilde{k}_{O,4,f} + \tilde{k}_{O,5,b}\theta_{O,N_i}) \quad (B.21) \]

Equating (B.18) to (B.19) then gives:

\[ \theta_{OH-,YSZ} = (c/b)\theta_{O-,YSZ} \quad (B.22) \]

(B.22) can then be substituted back into (B.19) to get the surface coverage of \( O^- (YSZ) \) as a function of known values:

\[ \theta_{O-,YSZ} = b/(b + bc + c) \quad (B.23) \]

Substituting (B.23) back into (B.22) gives a similar expression for the coverage of \( OH^- (YSZ) \):

\[ \theta_{OH-,YSZ} = c/(b + bc + c) \quad (B.24) \]
Finally, substituting (B.23)-(B.24) into (B.16)-(B.17) gives the following expressions for the coverages of $O^{2-}$ and vacancies on YSZ at the TPB:

$$\theta_{O^{2-},YSZ} = \frac{abc}{(1+a)(b+bc+c)}$$  \hfill (B.25) \\
$$\theta_{YSZ} = \frac{bc}{(1+a)(b+bc+c)}$$  \hfill (B.26)

The YSZ coverages in (B.23)-(B.26) can be used in equations (5.13)-(5.16) to determine the current densities associated with each charge-transfer step in the H spillover and O spillover mechanisms.

**References**


Publications Based on this Work

The contents of this thesis also appear in the following publications. The three journal papers correspond to the content presented in Chapters 3, 4 and 5 of this thesis, respectively. The conference paper is based on a preliminary version of the work presented in Chapter 4.

Peer-reviewed Journal Papers


doi: 10.1016/j.jpowsour.2016.02.050


doi:10.1016/j.ijhydene.2016.03.107


Peer-reviewed Conference Proceedings


doi: 10.1149/06801.3059ecst