ONE DIMENSIONAL MODELING OF PLANAR SOLID OXIDE FUEL CELL

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by
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Chapter 1  INTRODUCTION

For the past thirty years, there has been a lot of concern about using oil for power generation and automobile propulsion. Environmental pollution was another serious problem researchers had to deal with over this period. These two problems have been the main driving force behind the extensive research in fuel cells, a technology, which was invented about 150 years ago but is to be fully commercialized. Before the 1970s, the only fuel cell in practical use was that in space missions. Even though fuel cells were proven to be very efficient and environment friendly, their forbiddingly high cost, low lifetime and low power density limited their use to such extreme and exotic assignments. Thus, most of the current research in the field is aimed at finding remedies to these problems. Scientists are also working on problems specific to different types of fuel cells. Suitability of natural gas or synthetic gas from coal gasification for some types of fuel cells is also being investigated. Some prototypes have been successfully built and tested in the last several years.

Fuel cells are a potential source of prime power in near future. They offer many advantages over conventional power generators. However, before realizing the advantages of fuel cells, system design issues regarding their capability must be addressed. Many researchers strongly believe that fuel cells will soon be everywhere from automobiles to power plants. This chapter discusses about the fuel cell technology followed by the objective and significance of the research work.
1.1 OVERVIEW OF THE FUEL CELL TECHNOLOGY

1.1.1 TECHNOLOGY

Fuel cells are energy conversion devices that produce electricity directly from a gaseous fuel by electrochemical combination of the fuel with an oxidant. Fuel cells have many advantages compared to conventional electric power generation systems, such as high conversion efficiency, which is relatively independent of size, and is environmentally compatible. Fuel cells have recently attracted new attention due to their potential for use in stationary and distributed electric power stations as well as in transportation applications. Fuel cells are characterized by the electrolyte used, which in turn determines the operating temperature. The charge carrier can either be an oxygen ion conductor or a hydrogen ion (proton) conductor, the major difference between the two types is the side in which the water is produced inside the fuel cell viz the oxidant side in proton–conductor fuel cells and the fuel side in oxygen-ion-conductor ones. The basic operation of oxygen-ion-conductor fuel cell is shown in Figure 1.1.

![Figure 1.1 Schematic of Basic Fuel Cell](image-url)
1.1.2 TYPES OF FUEL CELLS

Based on the electrolyte employed, there are five types of fuel cells. They mainly differ in the composition of the electrolyte. Table 1.1 lists the main distinguishing features (such as operating temperatures, electrolytes, fuels, oxidant, catalyst used, reforming methods and cell efficiency) for the four main types of fuel cells summarized based on various recent publications [1,2].

<table>
<thead>
<tr>
<th>Features</th>
<th>Type 1</th>
<th>Type 2</th>
<th>Type 3</th>
<th>Type 4</th>
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<td>Name</td>
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<td>Phosphoric Acid</td>
<td>Molten Carbonate</td>
<td>Solid Oxide</td>
</tr>
<tr>
<td>Operating Temp (°C)</td>
<td>60-80</td>
<td>180-220</td>
<td>600-700</td>
<td>700-1000</td>
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<tr>
<td>Electrolyte</td>
<td>Ion exchange membrane</td>
<td>Phosphoric acid</td>
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<td>Yttria-stabilized zirconia</td>
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<tr>
<td>Fuels</td>
<td>H₂</td>
<td>H₂</td>
<td>Reformate/CO/CH₄</td>
<td>Reformate/CO/H₂/CH₄</td>
</tr>
<tr>
<td>Oxidant</td>
<td>O₂/air</td>
<td>O₂/air</td>
<td>CO₂/O₂/air</td>
<td>O₂/air</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Nickel</td>
<td>Nickel</td>
</tr>
<tr>
<td>Cell efficiency</td>
<td>40-50</td>
<td>40-50</td>
<td>50-60</td>
<td>50-60</td>
</tr>
<tr>
<td>Reforming</td>
<td>External</td>
<td>External</td>
<td>External/internal</td>
<td>External/individual</td>
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The different types of fuel cells are alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), proton-exchange membrane fuel cells (PEMFC), molten carbonate fuel cells (MCFC), and solid oxide fuel cells (SOFC). In all the types, there are different reactions at the anode and the cathode, where charged ions move through the electrolyte and electrons move round an external circuit. Another common feature is that the electrodes must be porous because the gasses must be in contact with the electrode and the electrolyte at the same time.

1.1.3 ADVANTAGES OF SOFC OVER OTHER TYPES

SOFC have exceptional potential for use as electric power generation systems, because of their high-energy conversion, efficiency that can reach up to 65%. In addition, SOFC have many advantages such as multi-fuel capability and simplicity of system design. Furthermore, the exhaust heat can be used as a heat source for a variety of processes. This together with the possibility of utilizing the remaining energy in a bottoming cycle for electric power generation leads to a further increase in the overall efficiency. The pressurized SOFC can be used to replace combustors in gas and steam turbines. Such integrated SOFC-combustion turbine power systems are expected to reach efficiencies approaching 70%. The high efficiency will contribute to reduced CO₂ emissions also.

The two primary fuel cells other then SOFC are Proton Exchange Membrane Fuel Cell (PEMFC) and Molten Carbonate Fuel Cell (MCFC). SOFC technology looks more promising compared to the other alternatives in fuel cells as a prime power source for the future.
Advantages of SOFC over MCFC are:

1. SOFC have a solid electrolyte, which eliminates the corrosiveness of the molten carbonate electrolyte.
2. SOFC have a solid electrolyte, which minimizes the liquid management problems of the MCFC i.e. no pumps are required to circulate the hot electrolyte.
3. Small planar SOFC of 1 kW could be constructed with very thin sheets, which results in a very compact package.

Advantages of SOFC over Proton Exchange Membrane Fuel Cell (PEMFC) are:

1. In the PEMFC an external reformer is required while SOFC can readily and safely use many common hydrocarbons fuels such as natural gas, diesel, gasoline, alcohol and coal gas.
2. In the PEMFC, the carbon monoxide is a poison, while in the SOFC it is a fuel.
3. Non-precious materials are used in the SOFC components unlike the platinum electrodes needed in PEMFC; hence SOFC material cost is cheaper.
4. SOFC has solid electrolyte, so the liquid electrolyte problems of PEMFC, are not encountered in SOFC.

1.2 SOLID OXIDE FUEL CELL

1.2.1 SOLID OXIDE FUEL CELL TECHNOLOGY

A Solid Oxide Fuel Cell (SOFC) consists of three main components: the anode, the cathode and the electrolyte. The fundamental reaction is based on transfer of oxygen ion (O²⁻) from the cathode through the electrolyte to the anode. It combines with hydrogen at the anode to produce water, and with carbon monoxide to form carbon dioxide. These dual reactions are critical when synthetic gas (the exhaust from the coal gasification) is considered as the main fuel to the fuel cell. A SOFC can be easily adapted to operate on synthetic gas or hydrocarbon fuels such as natural gas, propane and gasoline utilizing low cost reformers.
Direct Fuel Cells generate electricity with no combustion. SOFC is such a technology. In effect, they are like large continuously operating batteries that generate electricity as long as fuel such as synthetic gas or natural gas, is supplied. Since the fuel is not burned there is no pollution commonly associated with the combustion of fossil fuels. In addition, the high efficiency leads to more electrical power from lesser fuel and fewer emissions.

I COMPONENTS OF SOLID OXIDE FUEL CELL

A SOFC is mainly composed of two electrodes (the anode and the cathode) and a solid electrolyte. The fuel is important and is the principal parameter but independent of the other components as it is predominantly converted into hydrogen. The SOFC, relies on \( O^{2-} \) oxygen ion transport and also works with high purity hydrogen. However, it does not rely upon this as fuel which is expensive to produce and difficult to handle.

The main function of the electrode is to cause the reaction between the reactant (fuel or oxygen) and the electrolyte without being consumed or corroded. It must also bring into contact the three phases i.e. the gaseous fuel, the solid electrolyte and the electrode itself. The anode, which is used as the negative post of the fuel cell, disperses the hydrogen gas equally over its whole surface. It also conducts the electrons freed from hydrogen molecule to be used as a useful power in the external circuit. The cathode, the positive post of the fuel cell, distributes the oxygen fed to it onto its surface and conducts the electrons back from the external circuit where they can recombine with oxygen ions, passed across the electrolyte, and hydrogen to form water. The electrolyte determines the
operating temperature of the fuel cell and is used to prevent the two electrodes to come into electronic contact by blocking the flow of electrons.

It also allows the flow of charged ions from one electrode to the other to maintain the overall electrical charge balance.

**II MATERIALS OF SOLID OXIDE FUEL CELL**

**a) Electrolyte**

Current technology employs several ceramic materials for the active SOFC components. Although a variety of oxide combinations has been used for solid non-porous electrolytes, the most common electrolyte to date has been the stabilized zirconia. Its conductivity is based on oxygen ions \( \text{(O}_2^\text{-}) \). Especially yttria-stabilized zirconia (for example \( \text{Y}_2\text{O}_3 \)-stabilized \( \text{ZrO}_2 \) or YSZ, \( \text{(ZrO}_2\text{)}_{0.92}(\text{Y}_2\text{O}_3\text{)}_{0.08} \)) in which tiny amounts of the element yttrium\(^1\) is added to the zirconia during manufacture is under research \([2,3]\). This choice is mainly based on availability and cost.

**b) Anode**

Metals can be used as SOFC anode materials because of the reducing conditions of the fuel gas. Moreover, these metals must be non-oxidized since the composition of the fuel changes during the operation of the cell. SOFC anodes are fabricated from composite powder mixtures of electrolyte material (YSZ, GDC, or SDC) and nickel oxide \( \text{NiO} \) \([2,3]\). The nickel oxide is subsequently reduced to nickel metal prior to operation,

---

\(^1\) yttrium is a silvery-grey metal and is relatively stable in air. It occurs in nearly all of the rare-earth minerals.
which serves to inhibit sintering of the metal particles and also provides a thermal expansion coefficient comparable to those of the other cell materials.

c) Cathode

Because of the high operating temperature of the SOFC, only noble metals or electronic conducting oxide can be used as cathode materials. However, noble metals are unsuitable for practical applications because of their prohibitively high cost and insufficient long-term stability. Several hetero-metallic oxides have been proposed and tested. The choice of the electrode material depends on the target application, the specific ceramic electrolyte material, the desired operating temperature range, the electrochemical cell design, and the specific ceramic fabrication method. Some of the most common applications for these materials are as cathode materials for solid oxide fuel cells and as electrode materials for oxygen generation systems. Perovskite-type lanthanum strontium manganite, LaSrMnO₃ (LSM) and lanthanum calcium manganite, LaCaMnO₃ (LCM) offer excellent thermal expansion match with zirconia electrolytes and provide good performance at operating temperatures above 800°C [2, 3]. For applications requiring lower temperature operation (600–800°C) a range of alternative perovskite-structured ceramic electrode materials are available.

d) Fuel

SOFC require only a single partial oxidation reformer to pre-process their fuel which can be gasoline, diesel, natural gas, etc. The nature of the emissions from the fuel cell will vary correspondingly with the fuel mix. Hydrocarbons, for which a supply infrastructure is currently available, offers a variety of advantages over using hydrogen.
First, hydrocarbons are much easier to transport and store because they are in a stable state which requires no processing before use. They are also more efficient at producing energy. Methane, for example, yields eight electrons per molecule whereas hydrogen only yields two electrons. This advantage is magnified with the use of more complex hydrocarbons such as pentane. Synthetic gas obtained as exhaust from coal gasification acts as an alternative fuel for the hybrid power plants.

Gasification technology is the most efficient and the cleanest converter of coal and other solid fuels to low cost, clean, synthesis gas for the production of electric power, chemical products and transportation fuels. Gasification represent an important bridge to adoption of cleaner energy solutions as there are widely available low cost solid fuels which when converted to clean fuels can be used by advanced power technologies such as fuel cells. Currently, coal accounts for more than 50 percent of the electricity produced in the United States. National coal reserves are estimated to exceed a 250-year supply. Gasification Technology combined with Fuel Cells offer the most promising future for optimal efficiency, environmental benefits and low cost energy products. Gasification can be an effective way to produce hydrogen from hydrocarbon resources and water (steam). Using currently available technologies, hydrogen and carbon monoxide can be separated and purified from synthesis gas produced by gasification process. Contaminants are removed prior to using the synthetic gas as a fuel to the fuel cell application.

III  SOLID OXIDE FUEL CELL OPERATION

A Solid Oxide Fuel Cell operates on an oxidant (air or oxygen), which is introduced through a ceramic injector tube positioned inside the air channel of the cell.
Fuel is introduced in the fuel channel side and is electrochemically oxidized on the anode-electrolyte surface, while flowing from one end of the cell to the other, generating electron flow and hence electricity in the process. At the air channel side of the cell, the oxygen-depleted air exits the cell and is generally combusted with the partially depleted fuel in a furnace. Typically, 50 to 90% of the fuel is utilized in the electrochemical cell reaction. Part of the depleted fuel is re-circulated in the fuel stream and the rest combusted to preheat incoming air and/or fuel [2]. The exhaust gas from the fuel cell is at 600 to 900°C depending on the inlet operating conditions. A large number of cells have been electrically tested for about 25,000 hours. These cells perform satisfactorily for extended periods under a variety of operating conditions with less than 0.1% per 1000-hour performance degradation. The SOFCs have been found to tolerate small levels of air-side and fuel-side impurities without any significant long-term performance problems. The presence of moisture in air, results in a slight decrease in voltage, due to a small decrease in oxygen partial pressure.

1.2.2 ECONOMIC IMPACT

Woodward, in her cost model, found the mean cell costs as $7.00 per-cell for a 100 cm² cross-section area at 0.8W/cm², yielding an equivalent cost of $87.5/kW [4]. This cost is benchmarked against published estimates of ~ $80-$100/kW cost for cell components. The thinner electrolyte and anode layers at higher maximum power densities results in lower per-cell costs. The variation in the operation temperature requirement while holding the same maximum power density affects the cost per-cell. The operating temperature decrease, which increases the per-cell cost due to decrease in the process
capability at lower film thicknesses, results in significant yield loss. As the yield loss increases additional material and processing equipment are required to maintain production volume.

Woodward [4] found, for lower (<1W/cm²) power devices operating at 650°C, tape casting and screen-printing manufacturing processes are seen to be equivalent cost processes at equipment setup and process maturity. For higher (>1W/cm²), powered devices, screen-printing is consistently the lower cost process. The lower cost basis for screen-printing continues as the device operating temperature is increased from 650°C to ~800°C, after which tape casting and screen-printing shows an equivalent cost basis.

A study was done by Arthur D Little which provides a cost analysis for a planar SOFC operating at intermediate temperature. The study highlights the fact that fuel cell costs in the longer term will depend on production volumes, which will dictate the extent to which manufacturing, and assembly processes can be automated; and also impact on the costs of the SOFC materials such as ceramic powders. Arthur D Little [5], concludes that costs for an SOFC stack based on anode-supported cells can reach ~ 48-177 $/kW. This analysis is based on an anode-supported cells stack with a ferritic stainless steel interconnect and using economic volume production processes and assumes a production volume of 250 MW per year. The literature deduced that the area power density has a significant effect on the total cost estimate.

1.2.3 ENVIRONMENTAL IMPACT

Issues of efficiency and ecology converge at this time to renew interest in SOFC as systems for electricity generation [2]. In recent times, they have attracted serious
attention in the utility industries, particularly in co-generation of heat and power. The environmental impact of SOFC usage depends upon the source of the hydrogen-rich fuel used. If pure hydrogen is used, fuel cells have virtually no emissions except water and heat. As mentioned earlier, hydrogen is rarely used due to problems with storage and transportation but it is predicted that a solar-hydrogen economy will grow. In this scenario, photovoltaic cells would convert sunlight into electricity. This electricity would be used to split water (electrolysis) into hydrogen and oxygen in order to store the sun’s energy as hydrogen fuel. In this scenario, SOFC generating stations would have no real emissions of greenhouse or acid gases or any other pollutants. It is predominantly during the fuel processing stage that a fuel cell power plant releases atmospheric emissions. However, the high efficiency of SOFC results in less fuel being consumed to produce a given amount of electricity, which corresponds to a lower emission of carbon dioxide CO₂, the main ‘greenhouse gas’ responsible for global warming. When hydrogen from natural gas is used as a fuel, SOFC has no net emissions of CO₂ because any carbon released is taken from the atmosphere by photosynthetic plants. A reduction of carbon dioxide emissions by more than 2 million kg per year could be obtained. Moreover, emissions from SOFC systems will be very low with near-zero levels of NOₓ, SOₓ, and particulates, therefore eliminating 20,000 kg of acid rain and smog-causing pollutants from the environment. In any case, a SOFC generally provides the lowest emissions of any non-renewable power generation method such as traditional thermal power plants. This is very important with regard for energy related environment concerns.
SOFC, when combined with a heat engine that uses any waste heat, are the most clean and efficient devices available for this purpose. It can also provide high-quality waste heat that can be used to warm the home or provide refrigeration and air conditioning without harming the environment. If CO₂ can be removed at the source for disposal elsewhere, then SOFC would become the ultra-high efficiency, zero emissions power plant of the 21st century.

1.3 **MATHEMATICAL MODELING OF SOLID OXIDE FUEL CELL**

Mathematical modeling in fuel cell research has been successfully used for more than a decade now. Fuel cell modeling has become a design tool lately on a commercial basis. As a design tool, fuel cell modeling can be used to predict the performance of a particular design of fuel cell under various operating conditions. In addition, sometimes empirical models are used to model some processes for which underlying physics is either not fundamentally known or is very complex. The quality of data obtained from a numerical model depends upon the plausibility of the assumptions made. Numerical modeling is particularly valuable when intensive experimental investigation is very difficult due to instrumentation or other problems. It is for these reasons, that numerical modeling is recommended in solid oxide fuel cell research and development.

Mathematical modeling of a process involves formulating relationships between the important process variables and then solving them numerically to predict the behavior of the process for different sets of input conditions that control them. The mathematical relationships are derived from the physical laws that govern the process. The chemical
kinetics, conservation of mass, and conservation of energy equations are formulated for all the processes involved in fuel cell. Simplifying assumptions are made to reduce the number of variables and to obtain simple equations, due to very complex nature of chemical kinetics and thermal science involved in fuel cell. Hence, the model limits to the study of temperature and bulk concentration distribution within the fuel cell, while the mechanical breakdown due to thermal stresses in the cell and the rate of diffusion of gases normal to the flow direction is not discussed. The mathematical results obtained from the model reflect for the feasible outputs, which can be obtained from experiments operating under similar conditions. Hence, the mathematical model gives the cell performance, which forms a base to design a prototype of the fuel cell that suits the desired outputs.

1.4 SIGNIFICANCE OF WORK

As discussed earlier, SOFC is one of the cleanest source of power generation with high operational efficiency, hence the future energy provider. Hence, for utilizing the exhaust gases from coal gasification as a fuel for SOFC requires analyzing the behavior of carbon monoxide along with hydrogen on the fuel cell both in steady and dynamic state, which this model does. The model uses carbon monoxide as the second fuel along with hydrogen, as these are the primary product gases (called synthetic gas) from coal gasification, but the exact composition of the synthetic gas is not used in the model. Carbon monoxide, which is an exhaust from coal gasification, is supposed to be an environmental hazard, unless converted to other environmental friendly gases. Utilization
of carbon monoxide as a fuel for fuel cells helps to eliminate the pollution hazards associated with it and encourages alternative sources of fuels and compliments the development of hybrid power plants.

Behavior of SOFC can be characterized primarily to be in steady state. Initial start-up time is an important aspect that has deterred the commercialization of SOFC to a certain extent, due to its high start up time. It is an area researchers are looking into and this aspect will be analyzed in the dynamic model. Any experimentation sometimes includes fluctuations in operating conditions resulting in variation in the cell performance, hence, its analysis is important and the dynamic model will analyze the affects due to such fluctuations, its impact on cell performance and its recovery time. Finally, the degradation of cell behavior with time is another aspect, which is a major issue for cell material study, and this model, to an extent, will analyze that aspect for a specific case and will form the basis for further research. Numerical modeling of the dynamic effect of area specific resistance on cell performance of PSOFC; has been untouched in literature and makes the model only one of its kind. As such, dynamic parametric model analyses of PSOFC as a function of fuel gas (predominantly the research is on the primary components of synthetic gas which is CO + H₂ as fuel for SOFC); has not been investigated previously, makes this research unique. This research will form a basis for further research of the exact composition of synthetic gas as a fuel for PSOFC.

The model will do a performance study on the effects of fuel gas composition; i.e. fuel gas containing hydrogen and carbon monoxide on a single planar solid oxide fuel
The analysis is important as it gives an insight into the feasible operational outputs for a set of inputs, which includes varying the composition of fuel gas and the reactions occurring. Hence, the model can serve the purpose of analyzing carbon monoxide as a fuel gas by estimating the cell performance, before designing a prototype in future.

Development of a prototype for every feasible fuel gas composition and operational parameter is time consuming and expensive. The model will allow selection of the operating conditions from feasible process parameters, hence reducing the necessity of developing a prototype for each process. The dynamic model will give an idea about the possible variation in the temperature distribution, net voltage, fuel utilization, and power density as a function of fuel gas compositions, and hence will try to do a sensitivity analysis for certain variations in the input parameter. The model will try to analyze the dynamic effect of Area Specific Resistance (ASR) (obtained from experiment) on the cell performance. The simulation model results will give an idea about the potential outputs for a given set of ASR values, and can form a base for further analysis of ASR degradation from experimental data. The model to an extent, achieved to understand the cell performance as a function of fuel composition and operating parameters in both steady and dynamic level. The model can form a basis for further analysis of cell behavior with different fuel composition, ASR degradation and various operating conditions; hence establishing whether the development of a prototype is suitable and essential for a given set of physical and operational parameters and geometry.
1.5 **OBJECTIVE OF WORK**

The objective of this research is to do a parametric study of one-dimensional steady and dynamic state solid oxide fuel cell model subjected to specific operating conditions using the Aspen Custom Modeler\(^2\) as the simulation tool. The parametric study will serve two purposes, one it will give a better idea about carbon monoxide as a fuel gas and secondly will give an estimate of the fuel cell performance, including its degradation with time. To understand the performance degradation, the model includes experimentally derived ASR at various time intervals. Fuel Cell performances are mainly characterized by the net voltage developed, power density, fuel utilization and cell temperature during the operation. The cell performance and the effect of carbon monoxide as a fuel gas are dependent on each other, which primarily depends on the processes occurring within the fuel cell itself. The processes taking place are the heat and mass transfer of gases, which in turn depends on the electro-chemical reactions occurring. Hence, the parametric simulations on steady and dynamic state will form a base to identify the feasibility and the pros and cons of carbon monoxide as a fuel gas.

Fuel cell modeling will help, in understanding the processes that occur inside the fuel cells, to identify the critical processes and those processes which limit the performance. The mathematical model identifies the thermodynamic and chemical kinetic aspects of the reactions and formulates the mathematical equations associated with them. Hence, simulating the set of equations will give an extensive idea about the behavior of the cell, which in turn shows the significance of carbon monoxide as a fuel gas. The

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\(^2\) Aspen Custom Modeler is user defined thermo-chemical software licensed by Aspen Plus.
effects on various output parameters are in the form of fuel utilization, thermal heat
dissipation and net voltage due to the different reactions inside the fuel cell, which when
studied will give an idea about the relevance of the processes considered. Such
knowledge will add to the engineering database and should be useful in devising better
fuel cells.

The steady-state modeling gives an explicit idea about the polarization effects on
the fuel cell with and without considering the carbon monoxide as a fuel gas. Changing
the operating conditions and fuel composition can modify the amount of polarization
loss. Hence, the parametric study will provide avenues to improve the performance of the
fuel cell. This helps us to analyze whether inclusion of carbon monoxide as a fuel is a
feasible alternative.

The dynamic model will do sensitivity analyses of the operating parameters by
studying the fluctuations and recovery time i.e. the time taken to reach steady state after a
sudden change is included in one of the operating parameters (such as small variation in
inlet temperature or volumetric flow rate). The model will also give the start up time. In
addition, the dynamic model will try to analyze the cell performance degradation with
time and the variation in cell performance as a function of fuel gas composition. The
dynamic modeling will conclude on how, the fuel gas composition, the initial air/fuel
flow-rates and the inlet temperatures affect the performance of the cell; and how the fuel
cell performance will degrade over a period for a specific case. The model analysis of the
affect of ASR degradation on cell performance is characterized for a specific set of data,
but can be extended for further analysis for better quality data.
1.6  **SCOPE OF STUDY**

"Solid Oxide Fuel Cell Modeling" is a very general term, which may mean many different things depending on the researcher(s) from different groups. A ‘Fuel cell model’ can be categorized according to the level of application, i.e. cell, stack, and system models. A cell will refer to a unit consisting of air stream (as oxygen source), cathode, electrolyte, anode and the fuel gas stream. A stack is a unit, which consists of at least two or more fuel cells (may contain up to several hundred cells) arranged in a matrix to produce a desired power output. This study is neither concerned with stack nor with system models at this stage. The model can be classified according to the details as micro- or macro- models. The former indicating that details at smallest scales are being considered, e.g. at the level of pore sizes and/or surface irregularities, and the latter indicating that only the global parameters are being considered to account for a certain process in an integral sense. Another important distinction is the dimensionality of the models, namely, zero-, one-, two- and three-dimensional models. Zero-dimensional models consist of some algebraic relations. A ‘Mathematical model’ can further be distinguished based on steady state and dynamic state process. Dynamic state process takes into consideration a process which is subject to change with time, while steady state process is a condition of a system which is stable and does not vary with time. The cell geometry is another way of distinguishing the type of modeling. The model can be analyzed for tubular and planar fuel cell geometry. Tubular cell geometry has cell, fuel, and air channel as tubes, while planar geometry is flat and has plates assembled linearly.
The model used a macro (nodal) one-dimensional steady and dynamic state analysis of a single planar solid oxide fuel cell. This mathematical simulation will try to determine the effect of fuel composition and the operating parameters on the output parameters such as power density generated, fuel utilization, temperature distribution, and the net voltage developed.

The first chapter introduces the concept of SOFC technology and modeling; followed by the significance, objective and scope of this study. Chapter 2 gives a vivid idea about the history of fuel cells followed by a brief review on relevant work done in SOFC. The mathematical modeling details are dealt with in chapter 3 with an insight on the modeling tool, the modeling procedure applied, and the limitations and assumptions of the model. The detailed simulation results for both steady and dynamic state are discussed in Chapters 4. Chapter 5 discusses the conclusion derived from the simulations and future recommendations.
Chapter 2  LITERATURE REVIEW

2.1  HISTORY OF FUEL CELLS

Grove an English scientist in 1839 built a device that used water forming from reaction of hydrogen and oxygen, to produce electricity [6]. He used platinum electrodes and dilute sulfuric acid electrolyte. To make up for the low current generated by his cell Grove, in 1842, came up with a stack of 50 such cells that gave a notable current and called it the ‘gaseous voltaic battery’.

After 50 years, in 1889 Mond and Langer devised a new design of the fuel cell. This design used perforated electrodes that increased the oxidant interface. This resulted in a significant increase in current density and the term ‘fuel cell’ was coined [6]. Further research primarily concentrated in finding alternative fuels that were less expensive and readily available such as coal or carbon. However, much success was not encountered.

In 1959, Bacon of Cambridge University demonstrated the first use of the fuel cell. He used alkaline electrolyte and porous nickel electrodes which were cheaper than platinum electrodes and had good catalytic effect at elevated temperatures [6]. He also pressurized his cell to keep the electrolyte from boiling at the elevated operating temperature. His cell gave an output of 5 KW which could simultaneously power a welding machine, a circular saw and a 2-ton capacity forklift truck. Shortly after that, NASA saw the potential of fuel cells as power plants for space flights and funded an extensive research aimed at solving some of their basic problems. Eventually fuel cells
were used in the Gemini and Apollo series\(^3\) of space missions. In this process fuel cell (mainly alkaline electrolyte) saw a drastic development and companies like General Electric (GE) and United Technologies Corporation (UTC)\(^4\), under contracts from NASA, mastered the fuel cell technology. However, it was only after the 1973 energy crisis that administration began to consider the application of fuel cells in power generation and automobiles [7]. Until now many fuel cell powered transit buses and cars have been successfully developed and demonstrated by companies such as Ford and General Motors.

### 2.2 DEVELOPMENT ON SOLID OXIDE FUEL CELL

A ‘Solid oxide fuel cell’ (SOFC) is an advanced electrochemical reactor operating at a high temperature that produce electricity directly from a gaseous fuel by electrochemical combination of the fuel mainly hydrogen with an oxidant, pure air or supplied oxygen. SOFC is presently under development for a variety of electric power generation applications with high-energy conversion efficiency.

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\(^3\) Gemini and Apollo series developed by NASA in 1960’s was a three-part spacecrafts. These three parts are: the command module (CM), the crew’s quarters and light control section; the service module (SM) for the propulsion and spacecraft support systems; and the lunar module (LM), to take two of the crew to the lunar surface, support them on the Moon, and return them to the CSM in lunar orbit.

\(^4\) Fuel cell power plants designed, developed, and built by UTC Fuel Cells provides electrical power for NASA’s Space Shuttle Orbiter.
A ‘Solid oxide fuel cell’ (SOFC) has many advantages due to its high operation temperature such as high-energy conversion efficiency, flexibility of usable fuel type and high temperature exhaust gas. The high temperature of SOFC leads to high kinetic activity and this makes nickel act as a good catalyst, eliminating costly precious metal as catalyst. Fuel flexibility is achieved by using carbon monoxide as an additional fuel. However, the rapid start-up of SOFC is difficult due to its high operational temperature. The high operating temperature can lead to complex material problems including electrode sintering; interfacial diffusion between electrodes and electrolyte materials. The higher output power density and energy requirement, the less startup time, in conjunction with the high tolerance to thermal stress, make it possible for SOFC systems to act as a the power supply to various applications such as stationary power system and vehicles.

A three dimensional transient model for SOFC stack was described by Achenbach et al in 1994 [8]. The model included internal reforming of methane and computed spatial distributions of species, temperature and current density. Parametric study using the model concluded that counter flow cells were most efficient and recycling of anode gas would increase efficiency.

An analysis of the impact of electrode/electrolyte material (Ni/YSZ) properties with time and temperature was studied and discussed by Schafer et al in 1996 [9]. The study is oriented towards the optimization of the material properties for the interface between electrolyte and electrode and studied the cell performance for a long-term basis. They showed that by the use of interfaces made out of mixed conducting materials with small grain size, the best electrochemical performance could be achieved.
Studies conducted by Badwal et al in 1997 found that the degradation of cell performance of SOFC is due to forming of alloys of chromia at the interface of interconnect-airside [10]. The research concluded that there is subsequent deposition of Cr$_2$O$_3$ layer on the electrode/electrolyte surface and also formation of (CrMn)$_3$O$_4$ results in a detrimental effect on the cell performance.

Badwal et al, in 1998, analyzed the stability of electrolyte composition (Sc$_2$O$_3$ - Y$_2$O$_3$) – ZrO$_2$ (Al$_2$O$_3$) and emphasized the fact that the composition of electrolyte has an adverse effect on the time taken to reach chemical stability which in turn affects the conductivity of the material [11].

A detailed study on the durability of Ni/YSZ cermet anodes for solid oxide fuel cells was done by Primdahl et al in 1999 [12]. Experimental evaluation was conducted on three types of anodes at two different temperatures. The polarization resistance effect for a period is discussed. The degradation rate for the three types of anodes was analyzed and the results showed that the initial stabilization period for degradation is 300 hours and it varies linearly till 1000 hours. The degradation rate is around -100 mΩcm$^2$ at 800$^\circ$C and -10 – 50 mΩcm$^2$ at 1000$^\circ$C for Ni/YSZ cermet anodes.

S. Elangovan et al presented a study on the status of solid oxide fuel cell in 2000 [13]. The effect of area specific resistance on cell performance is discussed. The performance degradation observed had an initial stabilization time of 100 hours when the degradation rate varied rapidly, after which it is stable.

A detailed modeling of performance for flow inside an anode supported SOFC was done by Yakabe et al in 2000 [14]. The model calculated the species concentrations,
Nernst potential and over potential distributions. They concluded that the concentration polarization increases along the flow path in case of reformed fuel and the shift reaction helps reduce the concentration polarization for high fuel utilization.

Lukas et al designed an explicit dynamic model in 2001 [15] for direct reforming a carbonate fuel cell stack. The model incorporated control volume method for the calculations of flow temperature and species concentrations inside the cell. The model validates steady state results at several load points and sudden variation in load for a transient change.

In 2001, Chan et al studied the complete polarization model of solid oxide fuel cell in steady state [16]. The model accounts for the polarization effects on the cell performance. Later in 2002, they studied the effects of activation, ohmic and concentration polarization in electrolyte/electrode-supported SOFC [17]. They considered only a steady-state model, found significant polarization effects on the cell performance and showed that anode-supported cells have better performance compared to electrolyte-supported ones.

Gulzow et al did an investigation on the degradation of different nickel anode for alkaline fuel cells in 2002 [18]. The study comprised of testing three different types of electrodes, analysis of the degradation rate for each of them and in turn, the affects on the cell behavior. They concluded that along with the material structural property of the electrodes, the current density i.e. the loading, to an extent, also affects the stabilization time of the electrolyte conductivity.
Petruzzi et al, 2003 [19] developed a thermo-electrochemical three-dimensional model for SOFC and coded it in MATLAB. The model gives a vivid opinion about the designing criteria and operating strategy during development of SOFC systems as an auxiliary power unit (APU).

Li and Chyu in 2003 [20] developed a steady state two-dimensional model for a tubular SOFC. The model calculated temperature and species concentration distributions. The terminal voltage response of the SOFC to the operating parameter was also studied.

Larrain et al, 2004 [21] developed a generalized model for planar SOFC that computes distributions of specie concentration, reaction rates, temperature and overall performance of the cell. The model takes inputs from specific experiments by parameter estimating. The model is particularly true for different flow considerations and is validated with certain experimental results tested on a particular stack.

Khaleel et al (2004) developed a much-detailed SOFC model that could simulate dimensional geometry of SOFC. [22]. The model calculated the distribution of temperature, species concentrations, heat generation and current density inside the electrodes taking the temperature profile provided by MARC. The model uses MARC and EC as the software tool and is coupled together in an iterative process of getting the temperature profile and heat generation for a steady state solution.

Coal will likely be a major fuel for electrical power production in the future but more efficient and environment compatible production method must be devised. Coal gasification technology coupled with SOFC is an area researchers are investigating. Natural gas has been one of the sources of hydrogen production utilized in fuel cells.
Coal has big advantages over natural gas as a power source due to the abundance of coal on earth; coal will last another 250 years compare to 30 years of natural gas. Coal gasifiers operate with air or oxygen to achieve partial oxidation of coal and result in product gases. Air-blown coal gasifiers produce a low energy content gas composed of 10-15% CO₂, 15-30% CO, 10-30% H₂, and 0-5% CH₄ in a balance of N₂ [23]. Oxygen-blown coal gasifiers produce a slightly higher energy content product gas with 5-35% CO₂, 10-55% CO, 30-40% H₂, and 1-15% CH₄, with only 1-2% N₂ [23]. Hence, CO and H₂ are the main product gases of coal gasification.

The most challenging fuel for SOFC is coal gasification product gas. The concept behind this is using dirty gases such as synthetic gas as fuel gas for SOFC and utilizing pure H₂ produced from other methods for other types of fuel cells. Future integrated coal gasification fuel cell systems are likely to include SOFCs because of their relatively high tolerance to impurities, internal steam reforming potential and favorable thermal integration. To date, SOFCs running on coal gasification product gases have not been investigated much. Several techno-economic analyses of integrated coal gasification on fuel cell systems have been published but the technology still remains to be cultivated.

Cogeneration is an area where the SOFC will be a supplementary power source with combustion of coal. SOFCs are capable of low emission, high efficiency electrical power generation and produce heat as waste, typically at 900-1000°C which can be used for the production of hot water supply or hot gas supply steam for residences. SOFC systems have higher operating temperatures than other fuel cell systems resulting in better thermal integration between the fuel cell system and a reforming reactor required
to reform the hydrocarbon exhaust to hydrogen and carbon monoxide. In these high temperature systems internal reforming eliminates the need for an external fuel reformer.

Area specific resistance degradation with time is another area where a lot of investigation is being done. The following are some of the aspects that were acquired from literature:

1. The conductivity of the electrode/electrolyte interface surface has a significant effect on the polarization losses and the electrochemical behavior of the cell. The main phenomena described [9] are introduction of high polarization losses by coarsening of Ni particles in the anode and blocking of electrodes during long-term operation.

2. The generation of insulating interlayer by solid-state reactions between electrolyte and electrode creates grains or agglomerates which alter the properties of the material. For example, reaction of ZrO$_2$ electrolytes and LaMnO$_3$ cathodes led to formation of La$_2$Zr$_2$O$_7$ [9]. Another example is formation of MnAl$_2$O$_4$ due to reaction of Al$_2$O$_3$ particles in the electrolyte and Ca-doped LaMnO$_3$. Presumably, the unidentified solid-state reactions have a significant effect on the electrode/electrolyte material after duration of time.

3. Under anodic load, the presence of substantial amount of water in the central electrode area affects the effective surface area hence led to limited gas exchange [12]. Another aspect discussed is the purity of NiO powder used in the anode material which affects the structural stability of the electrode/electrolyte [12].
contaminants and additives in Ni/YSZ and its effect on the performance and durability are under research.

4. YSZ electrolyte conductivity assumes a general degradation with time due to formation of oxide vacancies. The degradation rate is about 20% @ 800°C and does not reach stability until 2000 hours in air [12].

5. The conductivity degradation behavior of the material is dependent on the ageing of temperature and its relationship to the equilibrium phase diagram and the electrolyte composition [11].

6. Ohm resistance primarily dominates polarization effect. Hence, ageing of the polarization is nearly similar to ageing of the electrical resistance value and thus depends on the electrical conductivity of the electrolyte/electrode material. Damage of the electrolyte/electrode interface results in coarsening of the material hence grains form. This in turn affects the electrical conductivity, active surface area of contact, porosity, resulting in changing the cell resistance for a period.

7. Electrochemical reactions occurring at the electrolyte/electrode surface affect the material property as deposition of layers may form provided the fuel gas have an element which is reactive with the electrolyte/electrode surface. For example, carbon monoxide may decompose to carbon and oxygen at high temperatures and result in formation of carbon layer which alters the material behavior. Hydrogen sulfide reacting with Ni or Pt; which is present in the electrodes, forms Ni$_2$S or Pt$_2$S [24].
8. Current density to an extent has an affect on the initial stabilization time required by the electrode/electrolyte [17].

The conclusion inferred from literature is that the initial increase in the degradation rate is mainly due the chemical stability time required by the solid-state electrode/electrolyte. The stabilization time can vary and depends on the composition of the electrolyte and electrode [11, 12, 13, 17, 25]. After the material properties reach stabilization and the conductivity of the material degrades linearly, the rate is determined by the composition of the material used for electrolyte/electrode. The factor which makes the huge final degradation are the coarsening of the grains of the electrode/electrolyte surface, formation of chemical layers hence changing the conductivity of the material, that in turn changes the area specific resistance [10, 12, 13, 26, 27]. The life of the material also varies, as does the resistivity; on the temperature of operation, load (current density) applied and the electrolyte/electrode composition and all these factors are correlated to each other with regards to the cell performance. The structural stability of the material is an aspect which determines the thermal expansion coefficient, chemical stability with respect to other cell components. Ionic and electrical conductivity is primarily the main aspect, which determines the initial stabilization time and the degradation rate of the cell with time.

During the operation of an SOFC system, the suppression of mechanical stress and the quick system response to a demand change are important. Mechanical stress, which leads to the mechanical breakdown of the cell components, can be classified into two types, i.e. residual thermal stress through fabrication and thermal stress caused by the
temperature distribution along the cell. In order to design the cell and stack, which can prevent the mechanical breakdown, the analysis of the temperature distribution is first necessary. Planar SOFC design potentially offers higher power density than tubular type SOFC. The study includes electrolyte-supported SOFC with thin anode and cathode hence reducing anode resistance.

Further, to apply SOFC systems to various applications, it is important to investigate the transient characteristics of the SOFC. Even after intensive research and significant progress, current SOFC represents an immature technology. SOFC requires development in the following features to achieve its mark as the prime power

1) Lower manufacturing cost
2) Increased efficiency and
3) Increased durability, which is comparable to other electrical generation methods

These developments require analyzing parameters such as the potential operating temperature, materials, geometries, dimensions, fuels, and others. Analysis by experimental approach to optimize the system design is necessary. However, it is time consuming to investigate the characteristics for all the cells at various operating conditions only by experimental approach to optimize the system design. Experimental advances are further hindered due to cost of physical prototyping, time consumed in setting up experiments and exploring a range of operating conditions. To establish SOFC on a wider market, development and understanding of SOFC is essential. Hence, it is highly desired to establish a mathematical model that incorporates the chemical kinetics; mass and heat transfer aspect of SOFC and predict its performance at different operating conditions.
Mathematical modeling is an effective tool for designing the optimal SOFC system and for predicting their characteristics at steady and transient operating states. The transient electrical response of a planar cell is studied using the conventional cell component materials. The results are unique as no previous literature reporting the dynamic characteristics of SOFC for different cell configurations and cell component materials are found. While there is a strong need to compare SOFC with different cell configuration and different cell components, an analysis and designing of the SOFC system requires interdisciplinary theoretical knowledge.
Chapter 3  PROJECT DETAILS

The fuel cell mathematical model discusses here the thermodynamic aspect and the associated electrochemical processes of the cell operation. A PSOFC consists of two electrodes sandwiched around a hard ceramic electrolyte such as Zirconia. Hydrogen and carbon monoxide is the fuel gas fed into the anode of the fuel cell and oxygen, from the air, enters the cell through the cathode. The electrode surface will allow oxygen ions to leave the electrolyte and react with the fuel, which when oxidized releases electrons \( (e^-) \). The reaction of the oxygen ion with the fuel creates an oxygen concentration gradient across the electrolyte, which attracts oxygen ions from the airside, or cathode, to the fuel side, or anode. The electrical connection between the cathode and the anode, allows the electrons to flow from the anode to the cathode, where a continuous supply of oxygen ions \( (O^{2-}) \) is maintained. Moreover, the oxygen ions move from the cathode to anode through the electrolyte, maintaining the overall electrical charge balance, thereby generating useful electrical power from the chemical reactions of the fuel.

3.1  GEOMETRY, PHYSICAL AND THERMAL PROPERTY OF CELL

The SOFC geometry and properties used in the model are based on the PSOFC tested at SOFCO, Alliance. The electro-active area of the SOFC is 4 X 4 inch\(^2\). The model considers an electrolyte-supported SOFC. The schematic of single channel PSOFC control volume is shown in Figure 3.1.

Thermal conductivity of the interconnect (Zirconia/ceramic) is given by:

\[
K_{\text{solid}} = 5.50072 + 1.65535e^{-3} \text{(Temperature)}
\]
The unit of $K_{\text{solid}}$ is in kJ/mh°C, and temperature is in Celsius.

![Schematic of One Channel of Single Planar Solid Oxide Fuel Cell](image)

**Figure 3.1: Schematic of One Channel of Single Planar Solid Oxide Fuel Cell**

The density for the solid is $\sim 6600$ kg/m$^3$ given by SOFCO, Alliance. The anode porosity of the electrodes is 40% and the tortuosity is 4.5. The specific heat capacity of the solid is 0.392 kJ/kgK. The anode exchange current density is 5300 A/m$^2$ and cathode exchange current density is 2000 A/m$^2$ [16, 17]. The fuel and air are in-flow; and a control volume$^5$ is used to analyze the electro-chemical and thermodynamic aspects of PSOFC. The cell geometry of the electrolyte supported PSOFC used in the model is shown in Table 3.1.

$^5$ Control volume: $(\Delta l+\Delta w)$ is the width of the cell, $(\Delta H_f+\Delta H_a)$ is the thickness of the cell, and $\Delta x$ is the length of the cell.
Table 3.1: Dimensions of Unit Cell Geometry of an Electrolyte Supported PSOFC

<table>
<thead>
<tr>
<th></th>
<th>Thickness (mm)</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>0.05</td>
<td>101.6</td>
<td>-</td>
</tr>
<tr>
<td>Cathode</td>
<td>0.05</td>
<td>101.6</td>
<td>-</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>0.15</td>
<td>101.6</td>
<td>-</td>
</tr>
<tr>
<td>Bipolar Plate</td>
<td>2.5</td>
<td>101.6</td>
<td>-</td>
</tr>
<tr>
<td>Air Channel</td>
<td>0.762 (ΔHₐ)</td>
<td>101.6</td>
<td>3.14 (ΔW)</td>
</tr>
<tr>
<td>Fuel Channel</td>
<td>1.143 (ΔHᵢ)</td>
<td>101.6</td>
<td>3.14 (ΔW)</td>
</tr>
<tr>
<td>Interconnect</td>
<td>-</td>
<td>101.6</td>
<td>2.572 (Δl)</td>
</tr>
</tbody>
</table>

3.2 MATHEMATICAL MODELING OF STEADY AND DYNAMIC STATE OF PLANAR SOFC

The planar SOFC operates on fuel such as hydrogen and carbon monoxide in various proportions. The water-shift reaction then occurs along with the electrochemical reaction at the anode and electrolyte interface. The model assumes that both the reactions occur simultaneously while the electrochemical carbon monoxide oxidation occurs at a much slower rate. The ratio of the current developed by the two electrochemical reactions is discussed in details later. The three reactions occurring are as follows:

\[ H₂ + \frac{1}{2} O₂ \rightarrow H₂O \]  \hspace{1cm} (1)
\[ CO + H_2O \rightarrow H_2 + CO_2 \]  \hspace{1cm} (2)

\[ CO + \frac{1}{2} O_2 \rightarrow CO_2 \]  \hspace{1cm} (3)

The operation of SOFC is based on the variation of CO, CO\(_2\), H\(_2\), and H\(_2\)O concentrations along the flow process and need to be determined the rate of chemical reactions occurring at equilibrium. In the analysis, the number of moles of H\(_2\), CO and CO reacting respectively in the reactions given by Equations (1) to (3) in a node of fuel channel, are represented by \( \Delta \text{mole}_{H_2,\text{oxidation}} \), \( \Delta \text{mole}_{\text{water-shift}} \) and \( \Delta \text{mole}_{CO,\text{oxidation}} \) respectively. Then the variation of mole number of all the species at a nodal section of the fuel channel can be calculated as:

\[ CO_{out}^{in} = CO_{in} - \Delta \text{mole}_{\text{water-shift}} - \Delta \text{mole}_{CO,\text{oxidation}} \]  \hspace{1cm} (4)

\[ CO_{2out}^{in} = CO_{2in} + \Delta \text{mole}_{\text{water-shift}} + \Delta \text{mole}_{CO,\text{oxidation}} \]  \hspace{1cm} (5)

\[ H_2_{out}^{in} = H_2_{in} + \Delta \text{mole}_{\text{water-shift}} - \Delta \text{mole}_{H_2,\text{oxidation}} \]  \hspace{1cm} (6)

\[ H_2O_{out}^{in} = H_2O_{in} - \Delta \text{mole}_{\text{water-shift}} + \Delta \text{mole}_{H_2,\text{oxidation}} \]  \hspace{1cm} (7)

The variation of the total mole numbers of the fuel flow from inlet to outlet of the given section becomes:

\[ M_f^{out} = M_f^{in} \]  \hspace{1cm} (8)

Similarly, the variation in the total number of moles of airflow from inlet to outlet of a given node can be calculated and is given by:

\[ O_2^{out} = O_2^{in} - 0.5\Delta \text{mole}_{H_2,\text{oxidation}} - 0.5\Delta \text{mole}_{CO,\text{oxidation}} \]  \hspace{1cm} (9)
3.2.1 **ELECTROCHEMICAL STEADY STATE MODEL**

Considering for a particular node, the reacted species are related to the current transfer rate across the electrolyte layer of the node, and the rate of consumption or destruction of species are given by:

\[ S = - \frac{(aI)}{nF} \]

where,

- \( a \rightarrow \) stoichiometric coefficient
- \( I \rightarrow \) current (A)
- \( n \rightarrow \) number of electrons per mole of fuel
- \( S \rightarrow \) Source or sink of species in g-mol/sec
- \( F \rightarrow \) Faraday’s constant

**Cathode Flow Model:**

\[ S_{O_2} = -(0.5(i_{H_2} + i_{CO})) / 2F \ (Oxygen \ consumed) \]  \hspace{1cm} (11)

**Anode Flow Model:**

\[ S_{H_2} = -i_{H_2} / 2F \ (Hydrogen \ consumed) \]  \hspace{1cm} (12)

\[ S_{H_2O} = i_{H_2} / 2F \ (Steam \ produced) \]  \hspace{1cm} (13)

\[ S_{CO_2} = i_{CO} / 2F \ (Carbon \ dioxide \ produced) \]  \hspace{1cm} (14)

\[ S_{CO} = -i_{CO} / 2F \ (Carbon \ monoxide \ consumed) \]  \hspace{1cm} (15)

where,
S_{O_2}, S_{H_2}, S_{H_2O}, S_{CO_2}, S_{CO} are the amount of specie consumed / produced

I_{H_2} is the current developed in the cell for hydrogen oxidation

I_{CO} is the current developed in the cell for carbon monoxide oxidation

F is the Faraday’s constant

The amount of hydrogen consumed by the oxidation process, results in water-shift reaction to happen; which tends to be in equilibrium [14, 19, 28]. The water produced in the electrochemical reaction is consumed by the water-shift reaction to re-produce some amount of hydrogen. That is, the reaction does not proceed completely to the left or to the right. Instead, the reaction proceeds to an equilibrium point, where both “products” and “reactants” remain [19, 28]. The equilibrium composition is dependent upon both the initial composition and the final temperature. The equilibrium concentrations; can be determined by the temperature dependent equilibrium constant, $K_{PS}$; and the equilibrium constant of the reaction is of the form [28]:

$$K_{PS} = \frac{P_{H_2}P_{CO_2}}{P_{CO}P_{H_2O}} = \exp\left(-\frac{\Delta G_{shift}}{RT}\right)$$

where, $P_{H_2O}, P_{H_2}, P_{CO}, P_{CO_2}$ are the ratios of the partial pressure over the standard pressure of 1.013×105 Pa for the corresponding species in fuel stream at the given section. The partial pressure of the gases can be expressed in terms of mole fraction of the species in the particular node. The extent of the water-shift reaction is given [28]:

$$r_{\text{shift}} = -\frac{b \pm (b^2 - 4ac)^{0.5}}{2a}$$

where, $a = (1 - K_{PS})$

$$b = \{(CO_2)[H_2] + K_{PS}(\{CO\} + \{H_2O\})\}$$

and, $c = \{CO_2[H_2] - \{CO\}[H_2O]K_{PS}\}$

$$r_{\text{shift}} = \left(1 - \frac{P_{H_2O}}{P_{CO}}\right)$$
\( P_{H_2}, P_{CO_2}, P_{CO}, \) and \( P_{H_2O} \) are the ratios of partial pressures over standard temperature and pressure

\( \Delta G^\circ_{\text{shift}} \) is the Gibb's free energy released from shift reaction (J/mol)

\( R \) is the Universal Gas constant (J/mol - K) and \( T \) is the temperature of cell (in degree Kelvin)

\( X_{\text{-shift}} \) is the rate of water-shift reaction (moles/sec)

\([CO_2],[H_2],[CO],\) and \([H_2O]\) are the concentrations of each specie

**Reversible Voltage:**

The ideal (reversible) open circuit voltage for a fuel cell is the electrical work done in moving charge through the fuel cell circuit and equals to the electrical work done per unit charge on one mole of electrons [28, 29].

\[
E_{rev} = \frac{\text{Electrical work}}{2F}
\]  

(18)

where, \( F \) is the Faraday constant, 96,485. The “2” in the denominator represents the number of electrons that flow for one mole of hydrogen oxidized. For an ideal system, the electrical work during the reaction is equal to the Molar Gibbs free energy released, \(-\Delta G\) [28, 29]. Hence,

\[
E_{rev} = \frac{-\Delta G}{2F}
\]  

(19)

Most of the performance indices are dependent on the ideal open circuit voltage \( E_{rev} \). \( E_{rev} \) is dependent on a variety of fuel-specific parameters and on the temperature of the reactions involved. The open circuit voltage of a basic fuel cell varies with the concentration of hydrogen supplied. The addition of carbon monoxide in conjunction with hydrogen affects the concentration and partial pressure of hydrogen.
The Nernst equation expresses the dependence of the Molar Gibbs free energy on reactant pressure and concentration, in addition to the dependence on reaction temperature. This dependence can be expressed as [30]:

\[ E_{\text{rev}} = E_{\text{STRP}} + \frac{RT_s}{nF} \ln \left( \prod \frac{(\text{reactant activity})}{(\text{product activity})} \right) \]  

(20)

where, \( E_{\text{STRP}} \) is the maximum open circuit voltage generated under standard conditions (1 atmospheric pressure);

\( R \) is the universal gas constant = 8.314 J/mol; and

\( T_s \) is the temperature of the electrode surface in Kelvin.

Reactant and product activities are dependent on the molar concentration of reactants/products. The Nernst equation for a hydrogen-oxygen based fuel cell (i.e. hydrogen as the only fuel) can be written as [30]:

\[ E_{\text{rev}} = E_{\text{STRP}} + \frac{RT_s}{2F} \ln \left( \frac{\prod (a - H_2)(b - O_2)^{1/2}}{\prod (c - H_2O)} \right) \]  

(21)

where, \( a \) is the activity of the specific reactant or product and is expressed in molarity (strength) of a solution. Activity can be expressed as:

\[ P = \text{Partial pressure/Standard pressure} = P / P_{\text{STRP}} \]

\[ E_{H_2} = E_{\text{STRP}} + \frac{RT_s}{2F} \ln \left( \frac{P_{H_2}P^{0.5}_{O_2}}{P_{H_2O}} \right) \]  

(22)

where,

\( E_{H_2} \) is the reversible Nernst voltage (Volt)

\( T_s \) is the temperature of cell (Kelvin)

\( R \) is the Universal gas constant (J/mol - K)

and, \( F \) is the Faraday's constant
and, \( E_{\text{STP}} = - \frac{\Delta G^0}{2F} \) is the reversible voltage developed for the electrochemical oxidation reaction of hydrogen, and \( \Delta G^0 \) is the variation of standard state \((1.013 \times 10^5 \text{ Pa})\) Gibbs free energy of the reaction for equation (1), and \( P_{H_2}, P_{O_2}, \text{and} P_{H_2O} \) are the activity mentioned above.

Similarly, there is a parallel Nernst equation for the electrochemical oxidation of carbon monoxide to carbon dioxide and can be given by:

\[
E_{\text{CO, oxidation}} = E_{\text{STP,C0}} + \frac{RT_s}{2F} \ln\left(\frac{P_{CO}^{0.5}}{P_{CO_2}}\right)
\]

\( E_{\text{CO, oxidation}} \) is the reversible Nernst voltage
\( P_{H_2}, P_{H_2O}, P_{CO}, P_{CO_2}, \text{and} P_{O_2} \) are the ratios of partial pressures over standard pressure
\( T_s \) is the temperature of cell (Kelvin)
\( R \) is the Universal gas constant \((\text{J/mol} \cdot \text{K})\)
\( F \) is the Faraday's constant

and, \( E_{\text{STP, CO}} = - \frac{\Delta G^0}{2F} \) is the reversible Nernst voltage developed for the electrochemical oxidation reaction of carbon monoxide, and \( \Delta G^0 \) is the variation of standard state \((1.013 \times 10^5 \text{ Pa})\) Gibbs free energy of the reaction of equation (3), and \( P_{O_2}, P_{CO_2}, P_{CO} \) are the activity mentioned above.

Considering for both the electrochemical oxidation of \( CO, H_2 \) and the water shift reaction, the current from the electrochemical reaction of \( CO, I_{CO} \), adds up to the total current. Figure 3.2 gives an electrical analogy of how the current is distributed within the fuel cell \([19, 31]\), and solving the network circuit gives the voltage profile.
Figure 3.2: Schematic of the Electrical Analogy

The three unknowns $I, I_{H_2}, I_{CO}$ are calculated from the following equations, according to the equivalent electrical circuit given in the above figure [19, 31].

\[
\begin{align*}
V &= V_{rev,H_2} - (R_c + R)I - R_A I_{H_2} = V_{rev,CO} - (R_c + R)I - R_A I_{CO} \\
V &= V_{rev,H_2} - \eta_c - RI - R_A I_{H_2} = V_{rev,CO} - \eta_c - RI - R_A I_{CO}
\end{align*}
\]  

where, $I = I_{CO} + I_{H_2}$,

$R_c$ = resistance due to concentration loss

$R = \frac{\text{Area Specific resistance}}{\text{Surface cell area}}$
where, \( i_{o,a} = 5300 \, \text{A/m}^2 \) (anode exchange current density)
\( i_{o,c} = 2000 \, \text{A/m}^2 \) (cathode exchange current density)
\( T_s \) is the cell temperature, \( n_e \) is the no. of electrons displaced.
\( F \) is the Faraday's constant, \( R \) is the Universal gas constant.
\( V_{\text{rev},H_2} \) is the reversible voltage developed by H\(_2\) oxidation process.
\( V_{\text{rev},CO} \) is the reversible voltage developed by CO oxidation process.

\[ \eta_c = IR_c \]  

In the electrochemical reaction proceeding at temperature \( (T_s) \), the changes of chemical enthalpy, \( \Delta H \) (J/mol), entropy, \( \Delta S \) (J/mol-K) and Gibbs free energy, \( \Delta G \) (J/mol), have the thermodynamic relationship, given by:

\[ \Delta G = \Delta H - T \Delta S \]  

Theoretically, the Gibbs free energy (-\( \Delta G \)) is converted into electrical power while the entropy term (-\( T \Delta S \)) is released in the form of thermal energy during the electrochemical reaction. Along with the consumption and production of the gas species in the fuel and airflows, the mass fractions of the reactants and the products from the reactions also vary in the flow streams of fuel and air.

3.2.2 ELECTROCHEMICAL DYNAMIC STATE MODEL:

Gas component balance:

The Continuity equation for 1D is given by:

\[ \frac{\partial u}{\partial x} = 0 \]  

(27)
**Governing Equation for mass conservation:**

The governing equations for dynamic flow of a gas mixture composed of different species are described by three equations, the mass conservation, along with momentum and energy equations for the mixture. The model approximates Darcy’s momentum equation for flow in porous media, and the energy equation determines the heat transfer within the cell.

The conservation of mass equation for the mixture can be written as:

\[
\frac{\partial \rho_i}{\partial t} + \bar{u} \frac{\partial \rho_i}{\partial x} = \frac{1}{Vol} \sum r_{ai}
\]  

(28)

where, \(\rho_i\) (mol/m\(^3\)), \(\bar{u}\) (m/s), vol (m\(^3\)) and \(r_{ai}\) (mol/s) are the molar mixture density, average velocity, volume of flow channel and rate of the reaction of specie ‘i’ respectively.

and, \(\sum r_{ai} = \text{summation of the rate of reactions of specie 'i'}\)

The conservation equation for the species in terms of molar concentration is given by:

\[
\frac{\partial c_i}{\partial t} + \bar{u} \frac{\partial c_i}{\partial x} = \sum r_{ai}
\]  

(29)

where, \(c_i\) indicate molar concentration of specie ‘i’ in mol/s.

The model takes into account the bulk convective molar fluxes. It is important to note that the molar diffusive fluxes are not considered in the mass conservation equation. This consideration is beyond the scope of this research and is recommended in future work. The momentum equation is simplified with Darcy’s Law for porous media by giving the value of \(\bar{u}\) and can be assumed to hold in the porous electrode. Separate
analysis of momentum equation is out of scope for this model. The model considers the average mass velocity as given by:

\[
\bar{u} = \frac{\sum_{i=0}^{n} m_i u_i}{\sum_{i=0}^{n} m_i}
\]  

(30)

where, \( m_i \) are the specie mole fractions and \( n \) is the number of species present in the mixture.

**Cathode Flow Model:**

\[
\frac{\partial m_{O_2}}{\partial t} + \bar{u}_c \frac{\partial m_{O_2}}{\partial x} = \left( \frac{RT_c}{P_c V_c} \right) r_{O_2, reacted}
\]

\[
m_{N_2} = 1 - m_{O_2}
\]

(31)

where,

- \( r_{O_2, reacted} \) is the amount of \( O_2 \) reacted (mol/s)
- \( m_{N_2}, m_{O_2} \) is the molar fraction of \( N_2, O_2 \)
- \( \bar{u}_c \) is the mixture velocity at the cathode surface (m/s)
- \( P_c \) is the pressure at the cathode (Pa)
- \( V_c \) is the volume of the air channel (m³)
- \( T_c \) is the temperature of the cell (Kelvin)
- \( R \) is the Universal gas constant (J/mol·K)

Using the molar fractions of oxygen, nitrogen and the cell temperature \( T_c \), the model uses the ideal gas law and thermodynamic properties to calculate the molar concentration of oxygen, and nitrogen in the cathode. From equation (10), Faraday’s law gives the rate of the electrochemical cell reaction:
This model captures the cathode airflow behavior, and is developed using the mass conservation principle and the thermodynamic and psychometric properties of air. Several assumptions are made such as:

1. All gases obey the ideal gas law,
2. The temperature of the air inside the cathode is equal to the cell temperature,
3. The properties of the flow exiting the cathode such as temperature, and pressure are assumed the same as those inside the cathode, and
4. The flow channel and cathode-backing layer are lumped into one volume, i.e. the spatial variations are ignored. The mass continuity equation is used to balance the mass of the two elements – oxygen, nitrogen inside the cathode volume.

**Anode Flow Model:**

This model is quite similar to the cathode flow model. The fuel gas partial pressure are determined by balancing the mass of hydrogen, carbon monoxide, carbon dioxide and steam in the anode/fuel channel and are given by:

\[
\begin{align*}
\frac{\partial m_{H_2}}{\partial t} + \bar{u}_a \frac{\partial m_{H_2}}{\partial x} &= \left(\frac{RT_s}{P_a V_a}\right) r_{H_2, reacted} \\
\frac{\partial m_{H_2O}}{\partial t} + \bar{u}_a \frac{\partial m_{H_2O}}{\partial x} &= \left(\frac{RT_s}{P_a V_a}\right) r_{H_2O, reacted} \\
\frac{\partial m_{CO}}{\partial t} + \bar{u}_a \frac{\partial m_{CO}}{\partial x} &= \left(\frac{RT_s}{P_a V_a}\right) r_{CO, reacted} \\
\frac{\partial m_{CO_2}}{\partial t} + \bar{u}_a \frac{\partial m_{CO_2}}{\partial x} &= \left(\frac{RT_s}{P_a V_a}\right) r_{CO_2, reacted}
\end{align*}
\]
where,

$\tilde{u}_a$ is the mixture velocity at the anode surface (m/s)

$r_{H_2, reacted}, r_{H_2O, reacted}, r_{CO, reacted}$ and $r_{CO_2, reacted}$ are the amount of each species reacted (mol/s)

$m_{CO}, m_{CO_2}, m_{H_2O}$, and $m_{H_2}$ are the molar fractions of each species

$P_a$ is the pressure at the anode (Pa),

$T_s$ is the temperature of cell (Kelvin)

$R$ is the Universal gas constant (J/mol·K)

and $V_a$ is the volume of the fuel channel (m$^3$)

The rates of the reactions are given by:

$$r_{H_2, reacted} = S_{cell, reaction} + S_{water, shift} = -\frac{I_{H_2}}{2F} + r_{shift}$$

$$r_{H_2O, produced} = S_{cell} + S_{water, shift} = \frac{I_{H_2}}{2F} + r_{shift}$$

$$r_{CO, reacted} = S_{water, shift} = r_{shift}$$

(34)

$$r_{CO_2, produced} = S_{water, shift} = r_{shift}$$

In this model, hydrogen and carbon monoxide gas are the fuels; and are supplied in equal proportions to the anode. The rate of hydrogen consumed in the reaction, $r_{H_2, reacted}$, is a function of the cell current produced by the hydrogen oxidation reaction and the amount of water shift reaction occurring to supplement for the hydrogen consumed in the electrochemical cell reaction, is given by equation (17).

**Polarization Effect on PSOFC Model:**

**OHM LOSS:**

This polarization occurs mainly due to the electrical resistance within the electrodes, and the obstruction encountered by the electrons to flow through the electrode
and electrolyte material. Generally, the ohm loss occurs in fuel cells as potential loss, due to resistance in electron transport through the electrodes, the bipolar plates, and the collector plates. The magnitude of the potential loss depends on the fabrication materials used in the construction of the fuel cells and the operating conditions of the cell. The value of this loss is proportional to the current flow and is given by:

$$\eta_{ohm} = iR_{el}$$

(35)

where,

$$R_{el} = \frac{l_e}{\sigma_e}$$, is termed as the electrolyte area specific resistance (Ω/cm²)

$$\sigma_e$$ is the electrical conductivity of the cell material (S/cm)

$$l_e$$ is the electrolyte thickness (cm)

This model accounts for an experimentally determined ASR expression, which includes the variation of the resistance of the electrodes with temperature, i.e. the value obtained accounts for ohm polarization loss; hence separate analysis is redundant.

**ACTIVATION/OVER-POTENTIAL POLARIZATION LOSS:**

The activation polarization loss is the voltage lost in driving the chemical reaction that transfers the electrons through the electrodes in a fuel cell. Therefore, there is a voltage loss when current flows through the electrode, and is proportional to the net reaction rate. This occurs due to the initial slowness of the gas molecules to react at the electrode/electrolyte surface. In SOFC, the activation over-potential at the anode is less as compared to that of the cathode. Activation polarization depends on factors such as the
material property of the electrode, ion-ion interactions, ion-solvent interactions, and characteristics of the electric double layer at the electrode-electrolyte interface.

The lower rate of activation polarization in SOFC can be accounted, as linearly proportional to current, and inversely proportional to the exchange current densities and is given by equation 37a. For higher value of activation polarization, Tafel equation is used and is given by [4]:

\[ \eta_{act} = \frac{RT_s}{n_e F i_o} i \] (37a)

\[ \eta_{act} = \frac{RT_s}{n_e \beta F} \ln\left(\frac{i}{i_o}\right) \] (37b)

where,

- \( i_0 \) = total exchange current density (anode and cathode limiting current density)
- \( i \) is the total current density (A/cm²)
- \( n_e \) is the no. of electrons flow for 1 mole of hydrogen oxidation
- \( F \) is the Faraday's constant, \( \beta = 0.5 \)
- \( T_s \) is the temperature of the cell (Kelvin)
- \( R \) is the universal gas constant (J/mol - K)

The SOFC model analysis generally considers low activation polarization effect on the output voltage and hence uses the linear equation until the value \( \eta_{act} < 0.1 \) V. For polarization voltage loss \( \eta_{act} > 0.1 \) V, the Tafel equation is used.

**MASS TRANSPORT/CONCENTRATION POLARIZATION:**

The concentration gradient is created by the reactants at the surface of the electrodes when some amount of fuel and oxygen diffuse through the porous electrodes. Mass transport loss becomes more significant when the fuel cell is operated at high
current density. In SOFC, the mass transport loss at the cathode can be negligible compared to the anode.

Using Yakabe et al. parallel pore model [14], the effective gas diffusion coefficient for component ‘i’ in the porous media can be expressed as follows:

\[
D_{ie} = \frac{\varepsilon}{\tau} \left( \frac{1 - \alpha_{im} y_i}{D_{i,m}} + \frac{1}{D_{K,i}} \right)^{-1}
\]

(38)

where,

\( \varepsilon \) is the volume fraction of pores,

\( \tau \) is the tortuosity factor,

\( D_{i,m} \) is the molecular diffusion coefficient of the multi-component ‘i’ (cm²/s),

\( y_i \) is the molar fraction, and

\( D_{K,i} \) is the Knudsen diffusion coefficient (cm²/s).

\( \alpha_{i,m} \) is defined as: \( \alpha_{i,m} = 1 - \left( \frac{M_i}{M_m} \right)^{1/2} \)

(39)

\( M_i \) is the molecular weight of the component ‘i’,

and, \( M_m \) is the average molecular weight.

The Knudsen diffusion coefficient for the component ‘i’ in the multi-component mixture gas is written by:

\[
D_{K,i} = \frac{2}{3} \left( \frac{8RT}{\pi M_i} \right)^{1/2} \bar{r}
\]

(40)

where, \( R \) is the gas constant (J/mol-K), \( T \) is the gas temperature (K), and \( \bar{r} \) is the average radius of the pore (cm). In a multi-component gas system, the molecular diffusion coefficient of the component ‘i’ is
where, \( D_{ik} \) (cm\(^2\)/s) is the binary diffusion coefficient in the system having components ‘i’ and ‘k’. Using the first order equation in Chapman–Enskog theory \([32]\), the binary diffusion coefficient \( D_{ik} \) is derived as:

\[
D_{ik} = 0.001858 \frac{T^3 (M_i + M_k) / M_i M_k} {p \sigma_{ik}^2 \Omega_D}
\]

(42)

where, \( \sigma_{ik} \) is the characteristic length, and \( \Omega_D \) is the collision integral.

Using the Lennard–Jones potential model \([14]\), \( \Omega_D \) is given by

\[
\Omega_D = \frac{A}{T_N^B} + \frac{C}{\exp(DT_N)} + \frac{E}{\exp(FT_N)} + \frac{G}{\exp(HT_N)}
\]

(43)

where, the constants \( A \) to \( H \) are \( A = 1.06036, B = 0.15610, C = 0.19300, D = 0.47635, E = 1.03587, F = 1.52996, G = 1.76474, H = 3.89411 \), and \( T_N \) is defined by

\[
T_N = \frac{kT}{\varepsilon_{ik}}
\]

(44)

where, \( k \) is the Boltzmann constant and \( \varepsilon_{ik} \) is the characteristic Lennard–Jones energy. Moreover, \( \sigma_{ik} \) and \( \varepsilon_{ik} \) are given by:

\[
\sigma_{ik} = \frac{\sigma_i + \sigma_k}{2}
\]

\[
\varepsilon_{ik} = \left( \varepsilon_i \varepsilon_k \right)^{1/2}
\]

(45)

where, \( \sigma_i \) is the diameter of the gas molecules colliding. The list of Lennard–Jones potentials used in the simulation is shown in Table 3.2 \([14]\).
Table 3.2: Lennard-Jones Potentials used in the Simulation

<table>
<thead>
<tr>
<th>Gas Species</th>
<th>$N_2$</th>
<th>$O_2$</th>
<th>CO</th>
<th>$CO_2$</th>
<th>$H_2$</th>
<th>$H_2O$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_i$</td>
<td>3.798</td>
<td>3.467</td>
<td>3.69</td>
<td>3.941</td>
<td>2.827</td>
<td>2.641</td>
</tr>
<tr>
<td>$\varepsilon_i$</td>
<td>71.4</td>
<td>106.7</td>
<td>91.7</td>
<td>195.2</td>
<td>59.7</td>
<td>809.1</td>
</tr>
</tbody>
</table>

The model takes into account the anode and cathode limiting current densities, which occur when the partial pressure of fuel at the anode/electrolyte interface is nearly zero. The model accounts for tertiary diffusion as the primary source of concentration variation at the electrode.

$$
\eta_{\text{conc,cathode}} = \frac{RT_s}{4F} \ln(1 - \frac{i}{i_{cs}})
$$

$$
\eta_{\text{conc,anode}} = \frac{RT_s}{2F} \ln(1 - \frac{i}{i_{as}}) - \frac{RT_s}{2F} \ln(1 + \frac{p_{H_2}i}{p_{H_2O}i_{as}})
$$

where,

- $i_{as}$ and $i_{cs}$ denote the limiting current densities for anode and cathode (A/cm$^2$)
- $i$ is the total current density developed (A/cm$^2$)
- $p_{H_2}, p_{H_2O}, p_{CO}, p_{CO_2}$ are the partial pressures of each specie over standard pressure
- $T_s$ is the cell temperature (Kelvin)
- $F$ is the Faraday's constant and $R$ is the Universal Gas constant (J/mol - K)

The effective diffusion rate considered for the anode are between $H_2$ and $H_2O$, $H_2$ and CO, $H_2O$ and $CO_2$, and between CO and $CO_2$ while at the cathode it is between $O_2$ and $N_2$, and hence depends on the electrode thickness.
\[ i_{ce} = \frac{4FP_{O_2}D_{eff,e}P}{(p - p_{O_2})RT_i l_e} \]

where, \( D_{eff,e} = \frac{V_{v,e}D_{O_2-N_2}}{\tau_e} \)

\[ i_{as} = \frac{2FP_{H_2}D_{eff,a}}{RT_i l_a} \]

where, \( D_{eff,a} = \frac{V_{v,a} \sum D_{i,m}}{\tau_a (1 - \alpha_{i,m} y_i)} \)

where, \( l_a, l_e \) are the electrode thicknesses

\( D_{eff,a} \) is the effective gas diffusion coefficient at the anode (cm^2 / s)

\( V_{v,a} \) is the porosity of the material

\( \tau_a \) is the tortuosity of the material

\( p_i \) is the partial pressure of the specie 'i' and \( p_{H_2} \) is the partial pressure of H_2

\( D_{i,m} \) is the molecular diffusion coefficient for the multi-components w.r.t. to specie 'i' (cm^2 / s)

\( l_a \) is the thickness of anode (cm)

\( \alpha_{i,m} = 1 - (\frac{M_i}{M_m})^{1/2} \)

\( M_i, M_m \) are the molecular wt. of specie 'i' and average molecular wt. of the mixture (g)

\( D_{eff,c} \) is the effective diffusion coefficient at the cathode (cm^2 / s)

\( D_{O_2-N_2} \) is the binary diffusion coefficient for O_2 and N_2 (cm^2 / s)

\( l_e \) is the thickness of the cathode (cm)

\( V_{v,c} \) is the porosity of cathode

\( \tau_e \) is the tortuosity of cathode

\( p_{O_2} \) is the partial pressure of O_2

The model assumes no Knudsen diffusion effect. Substituting the values into the reversible voltage equation gives the net voltage output for each cell. The actual operating voltage is as follows:
\[ V = V_o - \eta_{act} - \eta_{conc} - \eta_{ohm} \]  

(48)

Compared to the hydrogen reaction, the oxidation of CO in SOFC is accompanied by higher polarization over potentials. The presence of CO₂ lowers such over potentials. The role of CO₂ in the CO oxidation is similar to that of H₂O in the H₂ oxidation. However, in the presence of H₂O, the favorable path for the oxidation of CO is generating hydrogen by the water-shift reaction. Thus, for gas mixture that contains H₂, H₂O and CO, the anode is expected to have over potential comparable to that for H₂/H₂O mixtures.

\textit{Area Specific Resistance Calculation for Dynamic Model}

The ASR values used from experimental data to compute the degradation rate per hour are shown in Appendix B1. The ASR data used to simulate the second graph for H₂-N₂ dynamic model are shown in Appendix B2.

A better prediction of the ASR degradation requires good set of ASR data at various intervals of time. However, the data obtained are limited and scattered in nature. Hence, using these set of data, the model predicts for a specific case.

\textit{The ASR expression for H₂/N₂ model:}

\[
\text{ASR} (t) = \text{ASR} (t = 0) + [0.135\, t \, (-1) - 6.326e05 \, \exp(-t) - 1.33e-02 \, t \, (-0.5) + 3.38e-04] \times \text{time interval}
\]

This expression is obtained from the given set of available data, and is used to calculate the ASR degradation as a function of time. Figure 3.3 shows the curve of best fit for the given set of data.
The ASR expression used for $H_2$-CO dynamic model:

$$ASR(t) = ASR(t = 0) + [0.09085t^{-1} - 1.621e-07t - 2.109e07exp(-t)]*\{\text{time interval ('t')}\}, \quad \text{for } t > 10$$

This expression for ASR degradation is obtained by using the set of data for degradation rate per hour. The best-fit curve i.e. the function that follows that trend line is obtained, and is shown in Figure 3.4. The expression is used to calculate the ASR degradation as a function of time.

The ASR value are obtained from experiment, where the operating temperature of the cell is 1123K. The inlet fuel/air temperature for the dynamic model is assumed to be at 1123k. The model uses the calculated ASR from the graph as the first node value, and
includes the empirical ASR equation (49) to estimate the ASR variation as a function of temperature along the flow within the cell.

![Figure 3.4: Plot of degradation rate per hour, with time for CO-H₂](image)

The ASR value evaluated from the graph for dynamic model is computed in the following equation (49) to get the Ea value for initial temperature $T_s$ at 850°C. The Ea values obtained for a given ASR are shown in Appendix C. The temperature variation affect on ASR is analyzed by the following expression.

\[
\text{ASR expression} = 1.253e^{-5} \exp\left(\frac{\text{Ea}}{T_s + 273}\right) + 0.02396 + 9.364 \times 10^{-5} T_s - 1.384e^{-8} T_s^2.
\]

(49)

The calculated values of ASR for H₂-N₂ as fuel gas are shown in Table 3.3 and for H₂-CO as fuel gas are shown in Table 3.4.
Table 3.3: Calculated degradation rate and ASR for H₂-N₂

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Degradation rate per hour from data</th>
<th>Degradation rate per hour from graph</th>
<th>Degradation rate at time intervals</th>
<th>ASR value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000654955</td>
<td>0.000655086</td>
<td>0.04662031</td>
<td>0.959</td>
</tr>
<tr>
<td>71.1667</td>
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<td>0.000249968</td>
<td>0.012035933</td>
<td>1.0056203</td>
</tr>
<tr>
<td>119.3167</td>
<td>0.00185391</td>
<td>0.00185485</td>
<td>0.003280001</td>
<td>1.01765624</td>
</tr>
<tr>
<td>137</td>
<td>0.00181754</td>
<td>0.00129257</td>
<td>0.002951375</td>
<td>1.02388762</td>
</tr>
<tr>
<td>159.8333</td>
<td>0.0001192</td>
<td>6.09687E-05</td>
<td>0.003135824</td>
<td>1.0270234</td>
</tr>
<tr>
<td>211.2667</td>
<td>0</td>
<td>2.23594E-05</td>
<td>0.001713478</td>
<td>1.0287369</td>
</tr>
<tr>
<td>287.9</td>
<td>8.90313E-05</td>
<td>1.4184E-05</td>
<td>0.000615112</td>
<td>1.0293520</td>
</tr>
<tr>
<td>331.2667</td>
<td>0</td>
<td>1.07474E-05</td>
<td>0.001322282</td>
<td>1.0306743</td>
</tr>
<tr>
<td>454.3</td>
<td>0</td>
<td>1.42091E-05</td>
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<td>1.03165214</td>
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<tr>
<td>523.117</td>
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<td>0.00165235</td>
<td>1.0336838</td>
</tr>
<tr>
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<td>3.56001E-05</td>
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<td>1.039661</td>
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<tr>
<td>791.51667</td>
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<td>4.91107E-05</td>
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<tr>
<td>958.9167</td>
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<td>5.4383E-05</td>
<td>0.00378415</td>
<td>1.051666</td>
</tr>
</tbody>
</table>
Table 3.4: Calculated degradation rate and ASR for H₂-CO

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Degradation rate per hour from data</th>
<th>Degradation rate per hour from graph</th>
<th>Degradation rate at time intervals</th>
<th>ASR value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td>0.959</td>
</tr>
<tr>
<td>23</td>
<td>0.00178178</td>
<td>0.00178178</td>
<td>0.040980941</td>
<td>0.999980941</td>
</tr>
<tr>
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<td>0.000770181</td>
<td>0.070984971</td>
<td>1.070965912</td>
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<tr>
<td>138.5</td>
<td>0.000359195</td>
<td>0.0006335</td>
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<td>1.085747585</td>
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<tr>
<td>161</td>
<td>0.000753296</td>
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<td>0.012109132</td>
<td>1.097856717</td>
</tr>
<tr>
<td>164.3333</td>
<td>6.39946E-05</td>
<td>0.000526198</td>
<td>0.001753992</td>
<td>1.099610709</td>
</tr>
<tr>
<td>190.1667</td>
<td>0.000722394</td>
<td>0.00044691</td>
<td>0.011545188</td>
<td>1.111155897</td>
</tr>
<tr>
<td>258.6667</td>
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</tr>
<tr>
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<td>0.006244701</td>
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</tr>
<tr>
<td>286.25</td>
<td>0.000251453</td>
<td>0.00027098</td>
<td>0.001377484</td>
<td>1.139964788</td>
</tr>
<tr>
<td>300</td>
<td>-</td>
<td>0.000254205</td>
<td>0.003495324</td>
<td>1.143460112</td>
</tr>
<tr>
<td>350</td>
<td>-</td>
<td>0.00020284</td>
<td>0.010141999</td>
<td>1.153602111</td>
</tr>
<tr>
<td>400</td>
<td>-</td>
<td>0.00016229</td>
<td>0.008114497</td>
<td>1.16176608</td>
</tr>
<tr>
<td>450</td>
<td>-</td>
<td>0.00012895</td>
<td>0.006447506</td>
<td>1.168164114</td>
</tr>
<tr>
<td>500</td>
<td>-</td>
<td>0.000100657</td>
<td>0.005032873</td>
<td>1.173196987</td>
</tr>
</tbody>
</table>
Figure 3.5, 3.6 and 3.7 shows the degradation of ASR as a function of time with and without CO as the fuel gas. Two different simulations are conducted for H$_2$-N$_2$ as fuel gas, with two different sets of data. The first simulation uses all the available data, from which the degradation rate per hour is calculated and the function of best fit for degradation rate per hour is determined varying with time. This function is used to calculate the area specific resistance for case 1 and case 2.

Figure 3.5: Plot of ASR degradation with time obtained from graph with H$_2$-N$_2$

The second method of simulation is using a given set of data for a single test, and calculating the trend line from the data. Then the area specific resistance is calculated and the cell performance is analyzed. The second method cannot be applied to the model CO + H$_2$ as fuel gas, due to lack of data at regular and longer interval of time.
Fig 3.6: Plot of ASR degradation with time with $\text{H}_2$-$\text{N}_2$ (for single data set)

Fig 3.7: Plot of ASR degradation with time with $\text{CO}$-$\text{H}_2$
**FUEL UTILIZATION COEFFICIENT (μF)**

In practical situations, not all the hydrogen that enters the fuel cell is consumed in the electrochemical reaction. The fuel utilization coefficient, μF, is defined as [29]

\[
μF = \frac{\text{Mass of fuel reacted in cell}}{\text{Mass of fuel input to cell}}
\]

The mass of fuel reacted in the fuel cell is improved with fuel containing a high percentage of hydrogen.

**FUEL CELL EFFICIENCY (H):**

The fuel cell efficiency depends on the actual voltage generated in the fuel cell [28]. The cell efficiency η, is then given by:

\[
η = \frac{μFV}{V_0}
\]  

(50)

where,

μF is the fuel utilization

V is the net voltage developed

V₀ is the ideal voltage developed

### 3.2.3 HEAT TRANSFER EQUATIONS FOR STEADY AND DYNAMIC STATE:

**Conduction and forced convection**

The electrodes, electrolyte and interconnect are considered the solid material; therefore, the conduction theory is used to formulate and solve the heat energy equation for the solid. The convective heat transfer occurring at the fuel and air-channel is also
considered. The heat evolved during the electrochemical reactions i.e. hydrogen and carbon monoxide oxidation and the water-shift reaction is the heat source for sustaining the fuel cell reactions. Conduction heat transfer occurs axially from node to node through the solid. Transverse heat conduction (i.e. from electrode surface to interconnect surface) is assumed to be negligible or zero.

The convective heat transfer coefficient is based on laminar flow of the fluids and is given by the Nusselt number 3.66 [33, 34].

\[ Nu = \frac{hd_h}{k} \]  

\[ and, d_h = \frac{4 \text{Area} - \text{cross-section}}{\text{Wetted} - \text{perimeter}} \]  

where,

- \( d_k \) is the effective diameter of the flow channel (m)
- \( k \) is the thermal conductivity of gas mixture (W/mK)
- \( h \) is the convective heat transfer coefficient (W/m\(^2\)K)
- \( Nu \) is the Nusselt number = 3.66 for laminar flow

Moreover, the convective heat transfer is given by

\[ Q_c = h(T_s - T_{air/fuel}) \]  

where,

- \( Q_c \) is the convective heat transfer (J/s),
- \( h \) is the convective heat transfer coefficient (W/m\(^2\)K),
- \( T_s \), \( T_{air} \), and \( T_{fuel} \) are the temperature of cell, air channel and fuel channel respectively (Kelvin).

Although the total energy developed is \( \Delta H \), \( \Delta G \) amount of energy goes as electrical work done by the cell. The remaining amount is released as internal heat
source, which sustains the high temperature of operation of SOFC. The heat source is obtained from the net entropy generation given by the following expression:

\[ Q_{\text{source}} = -T_s \Delta S_{\text{cell}} \Delta Z - T_s \Delta S_{\text{shift}_\text{reaction}} \Delta Y - T_s \Delta S_{\text{co,oxidation}} \Delta W \]  

(52)

\[ \Delta H_{\text{cell}} = [\text{enthalpy} H_2 O(T_{\text{fuel}}) - \text{enthalpy} H_2 (T_{\text{fuel}}) - 0.5 \text{enthalpy} O_2 (T_{\text{air}})] \Delta Z \]

\[ \Delta H_{\text{shift}} = [\text{enthalpy} H_2 (T_{\text{fuel}}) + \text{enthalpy} CO_2 (T_{\text{fuel}}) - \text{enthalpy} H_2 O(T_{\text{fuel}}) - \text{enthalpy} CO(T_{\text{fuel}})] \Delta Y \]

\[ \Delta H_{\text{co,oxidation}} = [\text{enthalpy} CO_2 (T_{\text{fuel}}) - \text{enthalpy} CO(T_{\text{fuel}}) - 0.5 \text{enthalpy} O_2 (T_{\text{air}})] \Delta W \]

\[ \Delta S_{\text{cell}} = [\text{entropy} H_2 O(T_{\text{fuel}}) - \text{entropy} H_2 (T_{\text{fuel}}) - 0.5 \text{entropy} O_2 (T_{\text{air}})] \Delta Z \]

\[ \Delta S_{\text{shift}} = [\text{entropy} H_2 (T_{\text{fuel}}) + \text{entropy} CO_2 (T_{\text{fuel}}) - \text{entropy} H_2 O(T_{\text{fuel}}) - \text{entropy} CO(T_{\text{fuel}})] \Delta Y \]

\[ \Delta S_{\text{co,oxidation}} = [\text{entropy} CO_2 (T_{\text{fuel}}) - \text{entropy} CO(T_{\text{fuel}}) - 0.5 \text{entropy} O_2 (T_{\text{air}})] \Delta W \]

where,

\[ \Delta Z, \Delta Y \text{ and } \Delta W \text{ are the number of moles of } H_2, CO \text{ and } CO \text{ reacting in the equation (1) - (3) in moles} \]

\[ \Delta S \text{ is the entropy change(J/mol-K)} \]

\[ \Delta H \text{ is the enthalpy change(J/mol)} \]

**Radiation**

The model does not take into consideration the effect of radiation heat transfer, but a brief discussion on this form of heat transfer is given below.

The geometry of the planar solid oxide fuel cell allows some amount of heat transfer in the form of radiation to take place. The radiation occurs between two parallel surfaces i.e. from the cell surface (electrode/electrolyte) to the interconnect surface. In general, the radiation heat transfer between the two surfaces, 1 and 2 can be calculated as given below [33]:

\[ Q_{\text{rad}} = A_i F_{12} (\varepsilon_i \sigma T_i^4 - \varepsilon_2 \sigma T_2^4) \]  

(53)
While considering for the radiation heat transfer several simplifying assumptions are made such as the width of the gas channels is small (of the order of 1 mm) this would result in the product of partial pressure and path length to be small. When considering water vapor, in the fuel gas channel, a total emissivity is much less than 0.007. Therefore, the gas medium between the surfaces is considered non-participating. The interconnect surface and the separator plate are considered as black surfaces (having an emissivity, $\varepsilon=1$). Thus, the view factor, $F$, is assumed to be 1. Therefore, all emitted radiation from the cell surface is considered to be absorbed by the surface of the opposite interconnect plate. With these simplifications, the radiation heat transfer rate can be expressed as:

$$Q_{rad} = A_1 \sigma (T_1^4 - T_2^4)$$

(54)

where,

$T_1, T_2$ are the temperatures of the fuel cell surface, and interconnect surface respectively (in Kelvin)

$\sigma$ is the Stefan-Boltzman constant ($W^2/m^2K^4$)

$A_1$ is the area of cell exposed ($m^2$)

However, as discussed earlier, the model does not consider the effects of the radiation heat transfer, as it is assumed to be negligible compared to conduction and convection heat transfer. The detailed heat transfer processes occurring in the PSOFC is shown in Figure 3.8.
Figure 3.8: Heat Transfer within PSOFC

- Q – Conduction through solids in x-direction (axially from one node to the next one)
- Q - Radiation from anode surface to interconnect in fuel channel surface and cathode surface to interconnect in air channel surface
- Q – Convection from anode surface to fuel flow and cathode surface to oxygen flow in the channel
- Q – Conduction to interconnect in y-direction is neglected and is assumed zero
- From first law of thermodynamics, the enthalpy associated with the open circuit in the air channel
- From first law of thermodynamics, the enthalpy associated with the open circuit in the fuel channel

Q-source is the total heat energy dissipated by the reactions in the anode / electrolyte interface (i.e. the basic cell reaction, the water shift reaction and CO oxidation)
AT THE AIR CHANNEL

No heat generation occurs in the airside.

The governing energy equation for the air channel is:

\[ \rho_a C_{p_a} Vol \frac{\partial T_a}{\partial t} = \rho_a Vol C_{p_a} u_a \frac{\partial T_a}{\partial x} - h_a C_{\text{area}_a} a(T_a - T_a) \]

where,
\[ \rho_a \] is the density of gas mixture in air channel (mol/m³)
\[ C_{p_a} \] is the specific heat capacity of gas mixture in air channel (J/mol - K)
\[ u_a \] is the velocity flow rate of gas mixture in air channel (m/s)
\[ h_a \] is the convective heat transfer coefficient in air channel (W/m² K)
\[ T_a \] and \[ T_s \] are the temperature of air and solid (K)
\[ Vol \] is the volume of solid (m³)

AT FUEL CELL (ANODE/ELECTROLYTE INTERFACE)

The governing energy equation on the fuel cell surface:

\[ \rho_s C_{p_s} Vol \frac{\partial T_s}{\partial t} = k_s Vol \frac{\partial^2 T_s}{\partial x^2} + h_a C_{\text{area}_a} a(T_s - T_a) + h_f C_{\text{area}_f} f(T_s - T_f) + Q_{\text{source}} \]

where,
\[ \rho_s \] is the density of solid (mol/m³)
\[ C_{p_s} \] is the specific heat capacity of the solid (J/mol - K)
\[ T_s, T_a, \text{ and } T_f \] are the temperature of solid, air and fuel respectively (K)
\[ k_s \] is the thermal conductivity of solid (W/m - K)
\[ h_a, h_f \] are the convective heat transfer coefficient of air and fuel channel (W/m² - K)
\[ C_{\text{area}_a} \text{ and } C_{\text{area}_f} \] are the area of convection on air side and fuel side (m²)
\[ Q_{\text{source}} \] is the internal heat energy of the cell (J/s)
\[ Vol \] is the volume of solid in m³
AT FUEL CHANNEL

No heat generation occurs in the fuel side.

The governing energy equation for the fuel channel is:

\[ \rho_f C_{pf} Vol \frac{\partial T_f}{\partial t} = \rho_f C_{pf} u_f Vol \frac{\partial T_f}{\partial x} - h_f C_{area} a (T_s - T_f) \]

where

- \( \rho_f \) is the density of gas mixture in fuel channel (mol/m³)
- \( C_{pf} \) is the specific heat capacity of gas mixture in fuel channel (J/mol·K)
- \( u_f \) is the velocity of gas mixture in fuel channel (m/s)
- \( h_f \) is the convective heat transfer coefficient in fuel channel (W/m²·K)
- \( T_s \) and \( T_f \) are the temperatures of fuel and solid respectively (K)
- \( Vol \) is the volume of solid (m³)

INITIAL CONDITION FOR THE HEAT TRANSFER EQUATION, at \( t = 0 \)

is given by:

\[ T_a = \sim 700 - 875 °C \]
\[ T_f = \sim 700 - 875 °C \]

BOUNDARY CONDITIONS FOR HEAT TRANSFER EQUATION:

\[ \frac{\partial T_s}{\partial x} \bigg|_{x=0,t=t} = 0 \]
\[ \frac{\partial T_s}{\partial x} \bigg|_{x=l,t=t} = 0 \]

3.3 MODELING TOOL

Two sets of mathematical equations one representing the steady state model and the other, representing the dynamic state model equations of SOFC, are implemented in
Aspen Custom Modeler. Aspen custom modeler uses software based on thermal and chemical engineering equation solver. The mathematical model is coded in Aspen custom modeler with ‘user-defined-functions’.

The software has embedded procedures to call upon thermal and chemical parameters, and use numerical methods to solve the set of equations. It has its own syntax for coding the mathematical model, which is similar to Visual Basic Script.

A computer program is coded, for performing the calculations for the PSOFC model. The aspen software uses finite-difference method\(^6\) for solving the partial differential equations subjected to initial and boundary conditions.

### 3.4 MODELING PROCEDURE

The scheme used to solve the distributed domain is finite difference; and the x-direction is discretizationed into a number of nodal points, where each node is assumed a control volume; and the mass and heat transfer equations are analyzed and solved. The schematic of the nodal distribution of the x-axis used in the model is shown in Figure 3.9. The number of nodal points is decided from the simulation results. The number of nodes used for the analysis is 24 and the convergence criteria followed to do the nodal analysis, is discussed later in the chapter.

\(^6\) Finite difference is a method for solving partial differential equations (ODEs).
Figure 3.9: Nodal Distribution of Cell along X-axis

The model has fuel and air as in-flow and passes over the solid electrodes. The model presumes flow in one direction; hence, the momentum equation is not solved. Reynolds numbers for the fuel and air flow are calculated, and are found to be very low, so a turbulent flow model is not considered. In addition, the length of the fuel cell is very small compared to the boundary layer entrance length; hence, a fully developed channel flow is not considered. The model presumes that a constant current density is drawn from the cell and an analysis on that aspect is shown in Appendix D. The operating cell voltage varies depending on the input parameters.

The dynamic model uses the partial differential equation for the mass conservation to solve for the net molar concentration of the chemical species present at each node in the bulk flow. The initial conditions for the cases analyzed are varied, as is the input fuel composition. The rate of the two reactions considered, i.e. the water-shift
reaction and the hydrogen oxidation reaction are different depending on the fuel composition, and occurs simultaneously. Hence, the molar flow rates are iterated, and solved; which are related to the rate of electrochemical reaction. The molar fractions of the species are then calculated, and computed by the Nernst equation, to get the reversible cell voltage. The convective heat transfer coefficient is calculated from the Nusselt number for laminar flow, and for a given thermal conductivity of the solid/electrodes. The heat developed is the amount of heat evolved from the electrochemical reactions, which is computed as internal heat source into the energy conservation equation. The rate of internal heat energy developed varies as the fuel composition varies, and is a parameter, which determines the net temperature developed within the cell. The partial differential energy equations are solved to calculate the resulting temperatures of the fuel, gas and solid surface occurring within the control volume. The software tool is based on equation solver; hence, the operating parameters could easily be varied to get feasible results.

The steady state model differs from the dynamic model, as the molar concentrations at each node are solved algebraically and not by the mass conservation equation. The programs code for both steady and dynamic state models are given in Appendix E, F, G, H, I, J. The results are mostly dependent on the initial and the boundary conditions applied to partial differential equations, and some of the input variables. Non-linear solvers available in aspen custom modeler are Newton method, Newton method is the most robust but the slowest method. It calculates a new Jacobian matrix, at every iteration.
Fast Newton method\textsuperscript{8}, Hybrid method\textsuperscript{9} and Mixed Newton method\textsuperscript{10}. Mixed Newton method is used as the non-linear solver, due its speed and robustness in solving. The convergence criteria used by Aspen is the residual method\textsuperscript{11}.

\textit{Nodal Analysis}

The convergence criteria used to deduce the number of nodes is having the percentage variance among output parameters for consecutive nodes as within 0.5\%. Convergence value within 1.0 \% is a good approximation, but 0.5 \% was choosen as 1.0\% might be too high a value as the convergence of the simulation results may not be fully attend, and convergence criteria less than 0.5 \% may led to, too many data without much difference in the final analysis of the results. Some of the cell performance parameters obtained from the simulation may contain an error of 0.5\%, as full convergence is not attend on the number of nodes. The cell parameter's i.e. voltage, current density, power density, fuel utilization, average cell temperature is within 0.5\% change between 28 to 24 nodes; hence, all the simulations are conducted with 24 nodes. Appendix A shows the calculated cell performance values used for the nodal analysis.

\textsuperscript{8} Fast Newton is the fastest, but not the best method more some cases It updates the Jacobian matrix only when convergence progress is poor.

\textsuperscript{9} Hybrid is fast, but may not converge as well as other methods. It uses approximation update method, to estimate values of the numerical derivatives in the Jacobian matrix.

\textsuperscript{10} Mixed Newton method uses Newton method for initialization and steady state steps; and Fast Newton for dynamic steps. This is the best combination of speed and robustness for dynamic simulations.

\textsuperscript{11} Residual method converges by determining the difference between the left and right hand side of an equation.
3.5 MODEL LIMITATIONS

Following are some of the limitations in the model, which requires future research:

1. Cell area specific resistance varies only with temperature and time in dynamic mode and accounts for the total resistance in the cell. The ASR values obtained from experiments account for the total polarization loss in the cell. Hence, activation polarization, ohmic polarization and concentration polarization is not accounted separately in the dynamic model. Separate polarization analysis not done in dynamic mode, and is an area, which can be looked into in future.

2. There is no carbon deposition at the anode due to cracking of carbon monoxide. The two processes considered with carbon monoxide as fuel gas are the carbon monoxide oxidation and the water shift reaction for the steady state analysis and only water-shift reaction in the dynamic mode. The cracking of carbon monoxide into carbon is not considered, which is a limitation; as at elevated temperature the above reaction is a possibility.

3. One-Dimensional heat and mass transfer analysis in the x-direction/flow-direction is considered. Hence, the effects of the concentration gradient and temperature gradient along the normal direction of the flow remain uncultivated.

4. Diffusion losses accounted are based as concentration polarization loss of the fuel by tertiary diffusion through the electrode surface. The dynamic
model does not use the diffusion rate formula in mass conservation equation, hence it is not used to determine the rate of species consumed or destroyed; thus introducing some errors to the solution, as only bulk flow analysis is considered.

3.6 MODEL ASSUMPTIONS

Following are the assumptions used in the model:

1. Pressure at the anode and cathode are considered equal, and no pressure drop along the flow occurs [35]. The model uses 16 channels, hence divides the manifolds to a minimum, reducing any possibility of pressure drop.

2. Hydrogen is only electrochemically oxidized to steam [35]. The other probable reversible reaction is H₂ reacting with hydroxide ions (OH⁻) to form steam. Considering, both the reactions in equilibrium and calculating for the equilibrium partial pressures; it can be seen that the at 1073K and 1 bar, the molar fraction of H₂O is nearly ~1, which shows that the assumption is valid.

3. The water-shift reaction occurs at equilibrium and this assumption is supported by literatures. Due to continuous oxidation of hydrogen, the water-shift reaction occurs on a continuous basis to regain the equilibrium [14, 19, 28].
4. Reynolds number is assumed laminar. The Reynolds number calculation shows a value in the range of 15-20, which is very small and lies in the laminar region.

5. The dynamic response i.e. the sensitivity analysis of input parameters is done, assuming that the area specific resistance of the cell is remaining constant during that period. This analysis is primarily used to understand the cell performance, at the phase when the ASR is suppose to degrade linearly i.e. the semi-steady state. The time period under consideration being in the range of 45-60 seconds, it is assumed that the ASR variation will be zero.

6. A constant current is drawn as load, and is assumed taking into consideration practical applications.

3.7 MODELING UNCERTAINTY

Numerical predictions usually contain various errors, which arise from the assumptions and are called modeling errors. In addition to these, there can be an error of 0.5% introduced, as full convergence for the number of nodes is not attained. In order to make sure that the errors are within tolerable limits, the model is validated to results from other numerical models and the comparison has been discussed in the results. The validity of a numerical model is not established with any experimental results and hence, the model can be used to predict experimental results but cannot be compared to.
Chapter 4  RESULTS

4.1 GOAL

The goal of this project is to study the effects of carbon monoxide as an alternative fuel to a single Planar Solid Oxide Fuel Cell. The parametric study involves variation in the fuel composition, i.e. with and without carbon monoxide and analyzing the effects on the cell performance. The study also analyzes the effect of area specific resistance degradation on the cell performance with time.

The simulations conducted for steady state and dynamic state analysis are by considering the fuel gas, with and without carbon monoxide. While Case 1 considers only hydrogen as the fuel gas, Case 2 and Case 3 consider hydrogen and carbon monoxide as fuel gas. Carbon monoxide oxidation reaction is not considered in Case 2, where as Case 3 considers all the three reactions.

4.2 INPUT PARAMETERS AND OPERATING CONDITIONS

The initial and boundary conditions applied to the mathematical model are as follows:

1. The volumetric flow-rate of the fuel (hydrogen and carbon monoxide) and air
2. The inlet temperature of the fuel and air
3. The pressure in the system
4. The current density drawn from the cell

The other input parameters are as follows:

1. The geometry of the cell such as, the thickness of electrodes, cross section of the gas channels, in accordance to Table 3.1
2. The surface area of cell, porosity, tortuosity of electrode, the specific heat capacity, density and thermal conductivity of the solid
Table 4.1 gives the operating conditions used in the steady state model with and without carbon monoxide as a co-fuel.

Table 4.1: The Operating Conditions for Steady State PSOFC Model

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial System Pressure</strong></td>
<td>1 bar</td>
<td>1 bar</td>
<td>1 bar</td>
</tr>
<tr>
<td><strong>Excess oxygen ratio</strong></td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td><strong>Inlet Fuel Composition:</strong></td>
<td>$\text{H}_2 - 99.9 %, \text{H}_2\text{O} - 0.1 %$</td>
<td>$\text{H}_2 \sim 79.9 - 19.9 %, \text{CO} \sim 19.9 - 79.9 %, \text{H}_2\text{O} - 0.1 %, \text{CO}_2 - 0.1 %$</td>
<td>$\text{H}_2 \sim 49.9 %, \text{CO} \sim 49.9 %, \text{H}_2\text{O} - 0.1 %, \text{CO}_2 - 0.1 %$</td>
</tr>
<tr>
<td><strong>Inlet air composition</strong></td>
<td>$\text{O}_2 - 21 %, \text{N}_2 - 79 %$</td>
<td>$\text{O}_2 - 21 %, \text{N}_2 - 79 %$</td>
<td>$\text{O}_2 - 21 %, \text{N}_2 - 79 %$</td>
</tr>
<tr>
<td><strong>Fuel Flow rate</strong></td>
<td>$\sim 0.2 \text{ m}^3/\text{hr}$</td>
<td>$\sim 0.2 \text{ m}^3/\text{hr}$</td>
<td>$\sim 0.2 \text{ m}^3/\text{hr}$</td>
</tr>
<tr>
<td><strong>Air Flow rate</strong></td>
<td>$\sim 3.0 \text{ m}^3/\text{hr}$</td>
<td>$\sim 3.0 \text{ m}^3/\text{hr}$</td>
<td>$\sim 3.0 \text{ m}^3/\text{hr}$</td>
</tr>
<tr>
<td>**Current density (A/cm}^2)</td>
<td>$\sim 0.1 - 0.5$</td>
<td>$\sim 0.1 - 0.5$</td>
<td>$\sim 0.1 - 0.5$</td>
</tr>
<tr>
<td><strong>Inlet Temperature (Air and fuel)</strong></td>
<td>$\sim 700 - 800 \degree \text{C}$</td>
<td>$\sim 700 - 800 \degree \text{C}$</td>
<td>$\sim 700 - 800 \degree \text{C}$</td>
</tr>
<tr>
<td><strong>Number of channels</strong></td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td><strong>Reactions Considered</strong></td>
<td>$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$</td>
<td>$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}, \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$</td>
<td>$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}, \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2, \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$</td>
</tr>
</tbody>
</table>
As discussed earlier, the steady state expression for ohmic resistance of cell is a material property and is dependent primarily on electrical conductivity of electrode/electrolyte material, which in turn is a function of temperature. The ohmic resistance in the model is denoted as ASR, and is obtained from SOFCO, Alliance and is based on experiments performed by them and is specific to the material they use as electrode/electrolyte. The ohmic resistance (ASR) for the steady state is given by:

\[
\text{ASR} = 1.253e^5 \exp \left( \frac{11156}{T_s + 273} \right) + 0.02396 + 9.364e^{-5} T_s - 1.384e^{-8} T_s^2
\]

where, \(T_s\) is the cell temperature.

**4.3 STEADY STATE SIMULATIONS AND ANALYSIS**

*Model Validation for Steady State*

The Figure 4.1 shows the cell performance for an inlet cell temperature of 800°C with \(H_2\) as the fuel gas. The maximum power density of 0.261 W/cm\(^2\) is obtained at 500 mA/cm\(^2\) current density, with the operating cell voltage at 0.523 V. Khandkar et al [25], obtained the maximum power density 0.26 W/cm\(^2\) at 500 mA/cm\(^2\) for similar conditions, which is same as simulated by this model. Chan et al [17] simulated an SOFC model for similar conditions, which had the peak power density at 550 mA/cm\(^2\), the voltage is 0.519 V and the power density is 0.283 W/cm\(^2\), and is comparable with the present model.
Figure 4.1: Plot of current density, cell voltage and power density with inlet cell temperature @ 800°C (Case 1)

Figure 4.2, 4.3 and 4.4 shows the comparison of the hydrogen molar fraction, cell voltage and cell temperature along the flow of the fuel gas with current density 300 mA/cm², the air flow rate of 0.675 m³/hr, the fuel flow rate of 0.125 m³/hr, and the inlet temperature of 1073 K, with a reference model. The performance parameters of the cell
such as voltage, power density, and cell temperature; are represented graphically with respect to the x-domain\textsuperscript{12}.

Figure 4.2: Plot of hydrogen molar fraction along the distance from inlet (Case 1)

\textsuperscript{12}X-domain is the distance along the flow of fluid from the inlet
Figure 4.3: Plot of reversible voltage along the distance from inlet (Case 1)

Figure 4.4: Plot of cell temperature along the distance from inlet (Case 1)
Comparison of the power density developed, cell voltage and fuel utilization for the steady state model compared to the reference model is shown in Table 4.2 for case 1 and Table 4.3, for case 2.

**Table 4.2: Comparison of power density, cell voltage and fuel utilization (Case 1)**

<table>
<thead>
<tr>
<th></th>
<th>Steady State model</th>
<th>Reference model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power density developed per channel (W/cm²)</td>
<td>0.224</td>
<td>0.265</td>
</tr>
<tr>
<td>Cell voltage (V)</td>
<td>0.746</td>
<td>-</td>
</tr>
<tr>
<td>Cell voltage (V) with ohmic loss only</td>
<td>0.8806</td>
<td>0.883</td>
</tr>
<tr>
<td>Fuel utilization</td>
<td>0.398</td>
<td>0.407</td>
</tr>
</tbody>
</table>

**Table 4.3: Comparison of power density and cell voltage (Case 2)**

<table>
<thead>
<tr>
<th></th>
<th>Steady State model</th>
<th>Reference model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power density developed per channel (W/cm²)</td>
<td>0.227</td>
<td>0.256</td>
</tr>
<tr>
<td>Cell voltage (V)</td>
<td>0.755</td>
<td>-</td>
</tr>
<tr>
<td>Cell voltage (V) with ohmic loss only</td>
<td>0.891</td>
<td>0.855</td>
</tr>
</tbody>
</table>

Similar comparison of the present model with the reference model is shown in Figure 4.5, 4.6 and 4.7 with CO + H₂ as fuel gas i.e. for case 2. The graph shows
hydrogen, carbon monoxide, carbon dioxide, steam, oxygen molar fraction, cell temperature and cell voltage along the flow of the fuel gas. The current density is taken as 300 mA/cm$^2$, the airflow rate is 0.675 m$^3$/hr, the fuel flow rate is 0.125 m$^3$/hr, and the inlet temperature is 1073K. The simulated results are compared to the reference model developed by SOFCO, Alliance for case 1 and case 2. The comparison shows that the values calculated for power density, cell temperature, reversible voltage, molar fraction, and cell voltage are comparable for both the models. The % difference with the reference model for the average reversible voltage is ~5% for case 1 and ~9% for case 2.

Figure 4.5: Plot of H$_2$, H$_2$O, CO, CO$_2$, and O$_2$ molar fraction along the distance from inlet (Case 2)
Figure 4.6: Plot of cell temperature along the distance from inlet (Case 2)

Figure 4.7: Plot of reversible voltage along the distance from inlet (Case 2)
The reference model assumes, that the reversible voltage developed at the first node is the open circuit voltage at standard pressure and operating temperature. The correction factor in the Nernst equation is assumed zero; which the present model does not assume, hence resulting in some difference in the reversible voltage at the first node. These approximations in the reference model is included to correlate some experimental analysis, while the present model is a generalized model and does not include any approximations from experiments. The steady state cases 1 and 2 model with and without water-shift reaction considers diffusion polarization and activation polarization loss, and are simulated with constant current density; which the model developed by SOFCO, Alliance does not, hence the small variation in the calculated values of power density.

Figure 4.8 shows the distribution of polarization losses with varying current density for case 1. The figure shows that the polarization losses increase as the current density is increased. In this case for a 150 μm electrolyte supported PSOFC, the major polarization loss is the ohmic polarization. The cathode activation polarization is more then the anode activation polarization, while the concentration polarization due to the mass diffusion loss is minimal at low current density. The results obtained from the simulation agree well with that of Chan et al [16, 17]. Chan et al in his model has a constant ohmic loss of 0.5 Ωcm², operating temperature of 1073K and has a 500μm electrolyte thickness. The results obtained from this model showed that the ohmic resistance is the main resistance in a SOFC followed by cathode activation polarization, and anode activation polarization, while the concentration polarization is the least.
Figure 4.8 Plot of polarization losses, cell voltage and current density (Case 1)

Figure 4.9 and 4.10 shows the performance curves with CO + H₂ as fuel gas with the inlet temperature @ 1073K, and flow rate according to Table 4.1. The fuel composition is varied between ~100% H₂, and ~0% CO to ~20% H₂, and 80% CO. The power density and cell operating voltage developed is comparable up to ~80% CO concentration, and at current density around ~700 mA/cm². The simulated results for low current density is agreeable with experimental results obtained by Jiang et al [36], where the emphasis has been on varying the carbon monoxide concentration; and concluded that the performance curves with CO + H₂ as a fuel gas, are comparable to the cell performance with hydrogen fuel gas till ~80% CO at low current densities.
Figure 4.9: Plot of cell voltage vs current density (Case 1 & Case 2)

Figure 4.10: Plot of power density vs current density (Case 1 & Case 2)
The current produced when carbon monoxide and hydrogen oxidation reactions are considered develops two set of parallel reversible voltages, and the distribution of current are in the ratio as shown in Figure 4.11.

The distribution of current leads to less amount of hydrogen consumption, though the cell performance is comparable. The ratio of current produced is agreeable with the model simulated by Zhang et al [37]. The current ratio for the reference model for similar operating conditions was in the range of \( \sim 1.1 - 1.5 \) for current density between \( 0.1 - 0.7 \) A/cm\(^2\).

The water-shift reaction rate decreases, as the amount of water produced from the hydrogen oxidation process is lesser for same amount of current, as another reversible voltage developed from the Gibb’s free energy of the CO oxidation process, adds up.

![Figure 4.11: Plot of ratio of H\(_2\) to CO current density developed (Case 3)](image)
STEADY STATE ANALYSIS

The first goal was to analyze the cell parameters namely the Nernst voltage, operating cell voltage, power density, fuel utilization, cell temperature developed as a function of current density for case 1, case 2 and case 3. The numerical model is simulated for case 1, case 2 and case 3 with accordance to the operating parameters mentioned in Table 4.1 and the results are compared to analyze the effect of cell performance as a function of fuel gas composition.

The Figure 4.12 shows the variation of molar fraction along the distance from the inlet. When water-shift reaction is considered, the H₂ molar fraction is higher at the higher nodes compared to w/o water-shift reaction. The reason for higher H₂ concentration in the flow stream is due to the water-shift reaction producing some amount of H₂ back, which is oxidized to steam.

![Figure 4.12: Molar fraction of H₂ along the distance from inlet with and w/o water-shift reaction](image)
The Figure 4.13 shows the affect of change in molar fraction of H₂, on the Nernst voltage and cell voltage. The Figure shows due to higher molar fraction of H₂ with water-shift reaction, the Nernst voltage and the cell voltage developed is higher for this case 2.

Figure 4.13: Nernst and cell voltage along the distance from inlet with and w/o water-shift reaction

Figure 4.14 shows the effect of temperature with and without carbon monoxide as a fuel gas. The figure clearly shows the positive effect of increasing the temperature of operation, as the ASR of the electrode/electrolyte decreases with increase in temperature. As the current density is increased, carbon monoxide as a fuel gas enhances the power density produced by the cell.
The Figure 4.15 shows the effect of temperature and fuel gas composition on activation polarization. The activation polarization is linearly proportional to the temperature. Hence, the increase in temperature results in increase in the activation loss. The effect is reduced when carbon monoxide is a co-fuel, due to the distribution of current.
Figure 4.15: Activation polarization as a function of temperature and fuel composition (Case 1 & Case 3)

The Figure 4.16 shows the effect of temperature and fuel gas composition on ohmic polarization. The conductivity of the solid-state electrode/electrolyte increases with temperature, hence reduction in the electrical resistivity of the material. With carbon monoxide as a fuel gas, the cell temperature is more, as the internal source of heat energy (the total heat of reaction of the three processes) is higher. Therefore, the addition of carbon monoxide as a fuel gas decreases the ohmic polarization further within the single PSOFC.
The Figure 4.17 shows the effect of temperature and fuel gas composition on concentration polarization. With hydrogen as the only fuel, the concentration polarization remains nearly constant for a $50^\circ$ C change in temperature. Adding carbon monoxide to the fuel gas increases the concentration polarization. The reason being carbon monoxide and carbon dioxide molecules are larger and hence will have lower diffusion rate of the molecules, resulting in increase in concentration polarization. The empirical formula used to calculate the limiting current density, does take into account the molecular diameter of
the fuel gas constituents, hence the effect in variation in concentration loss seems to be realistic. This effect does not have a huge impact on the net cell voltage developed as the current density is within 0.5 A/cm² and the cell is electrolyte supported.

Figure 4.17: Concentration polarization as a function of temperature and fuel composition (Case 1 & Case 3)

Figure 4.18 and 4.19 compares the cell performance for all the three cases. The graph shows that carbon monoxide as a fuel gas increases the cell operating voltage and power density developed within the cell. The increase is mainly because the water-shift reaction produces some amount hydrogen back, which in turn enhances the reversible
voltage. The CO oxidation process increases the cell voltage, as two parallel reversible voltages produce the same current. The carbon monoxide oxidation process further increases the performance by increasing the cell operating voltage for same current density, as the activation polarization is reduced in case 3. However, the concentration polarization increases with addition of carbon monoxide, the effect being so small, so it does not have an impact on the net cell voltage.

\[
\text{Current density} \quad i_{H_2} = 1.0 \quad (1023K)
\]
\[
\text{Current density} \quad i_{H_2:CO} = 1:1 \quad (973K \text{ with water-shift})
\]

\[
\text{Current density} \quad i_{H_2:CO} = 1:1 \quad (1023K \text{ - with water-shift})
\]

\[
\text{Current density} \quad i_{H_2:CO} = 1:1 \quad (973 K \text{ - with CO oxidation & water-shift})
\]

\[
\text{Current density} \quad i_{H_2:CO} = 1:1 \quad (1023K \text{ - with CO oxidation & water-shift})
\]

---

**Figure 4.18: Cell voltage as a function of temperature and fuel composition (Case 1, Case 2 & Case 3)**
The Figure 4.20 shows that as the airflow stoic is decreased the cell temperature rise within the cell is increased, resulting in change in cell performance parameters. This highlights the fact that the volumetric flow rate of air will have an affect on the temperature of operation; which in turn affects the cell performance parameters.
Figure 4.20: Plot of cell temperature as a function of airflow rate (Case 1)
4.4 DYNAMIC STATE SIMULATIONS AND ANALYSIS

The goal is to analyze the cell parameters as a function of input parameters and ASR degradation for case 1, and case 2. The key input parameters given in Table 4.4.

Table 4.4: The operating conditions for Dynamic State PSOFC model

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Case 1</th>
<th>Case 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial System Pressure</td>
<td>1 bar</td>
<td>1 bar</td>
</tr>
<tr>
<td>Excess oxygen ratio</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Inlet Fuel Composition:</td>
<td>$\text{H}_2 - 49.9 %$, $\text{H}_2\text{O} - 0.1$ $%$, $\text{N}_2 - 50$ $%$</td>
<td>$\text{H}_2 \sim 34.9 - 64.9 %$, $\text{CO} \sim 34.9 - 64.9 %$, $\text{H}_2\text{O} - 0.1$ $%$, $\text{CO}_2 - 0.1$ $%$</td>
</tr>
<tr>
<td>Inlet air composition</td>
<td>$\text{O}_2 - 21 %$, $\text{N}_2 - 79$ $%$</td>
<td>$\text{O}_2 - 21 %$, $\text{N}_2 - 79$ $%$</td>
</tr>
<tr>
<td>Volumetric Flow rate (fuel)</td>
<td>$\sim 0.175$ m$^3$/hr</td>
<td>$\sim 0.175$ m$^3$/hr</td>
</tr>
<tr>
<td>Volumetric Flow rate (air)</td>
<td>$\sim 2.625$ m$^3$/hr</td>
<td>$\sim 2.625$ m$^3$/hr</td>
</tr>
<tr>
<td>Current density per channel</td>
<td>$\sim 0.1 - 0.75$ V</td>
<td>$\sim 0.1 - 0.75$ V</td>
</tr>
<tr>
<td>Initial Temperature (air and fuel inlet)</td>
<td>$\sim 850 \degree$C</td>
<td>$\sim 850 \degree$C</td>
</tr>
<tr>
<td>Number of channels</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Reactions Considered</td>
<td>$\text{H}_2 + \frac{1}{2}$ $\text{O}_2 \rightarrow \text{H}_2\text{O}$</td>
<td>$\text{H}_2 + \frac{1}{2}$ $\text{O}_2 \rightarrow \text{H}_2\text{O}$, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$</td>
</tr>
</tbody>
</table>

The detailed start up time and stabilization time for each cell parameter is given in Table 4.5a and 4.5b. The simulation results show that with and without carbon monoxide as a fuel gas; the start up time and the recovery time are comparable and are in the order of seconds.
Table 4.5a: Comparison of recovery time of the cell performance parameters with and without CO

<table>
<thead>
<tr>
<th></th>
<th>Start Up</th>
<th></th>
<th>Time taken to reach steady state w/o Water shift (~ sec)</th>
<th>Time taken to reach steady state with Water shift (~ seconds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td></td>
<td>Cell Parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Power density</td>
<td>18.0</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Operating Voltage</td>
<td>18.0</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cell Temperature</td>
<td>14.0</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fuel Utilization</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrogen consumption rate</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nernst Voltage</td>
<td>15.0</td>
<td>16.0</td>
</tr>
<tr>
<td>II</td>
<td></td>
<td>Start up time</td>
<td>18.0</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td>Inlet temperature change</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(25 degree C increase)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Power density</td>
<td>12.0</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Operating Voltage</td>
<td>19.0</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cell Temperature</td>
<td>19.0</td>
<td>16.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fuel Utilization</td>
<td>8.0</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrogen consumption rate</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nernst Voltage</td>
<td>12.0</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stability time</td>
<td>19.0</td>
<td>16.0</td>
</tr>
<tr>
<td>III</td>
<td></td>
<td>Volumetric Fuel flow rate (10% increase)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Power density</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Operating Voltage</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cell Temperature</td>
<td>-</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fuel Utilization</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrogen consumption rate</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nernst Voltage</td>
<td>5.0</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stability time</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>Cell Parameters</td>
<td>Time taken to reach steady state w/o Water shift (~ seconds)</td>
<td>Time taken to reach steady state with Water shift (~ seconds)</td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>--------------------------------------</td>
<td>------------------------------------------------------------</td>
<td>------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td><strong>Volumetric Air flow rate (10% increase)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Power density</td>
<td>12.0</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Operating Voltage</td>
<td>12.0</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cell Temperature</td>
<td>8.0</td>
<td>9.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fuel Utilization</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogen consumption rate</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nernst Voltage</td>
<td>5.0</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Stability time</strong></td>
<td>12.0</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>Current density (50 % decrease)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Power density</td>
<td>15.0</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Operating Voltage</td>
<td>15.0</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cell Temperature</td>
<td>15.0</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fuel Utilization</td>
<td>8.0</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogen consumption rate</td>
<td>8.0</td>
<td>8.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nernst Voltage</td>
<td>8.0</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Stability time</strong></td>
<td>15.0</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td>ASR degradation (Change in values)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Power density</td>
<td>~ 0.35 - 0.319</td>
<td>~ 0.367 - 0.308</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Operating Voltage</td>
<td>~ 0.484 - 0.439</td>
<td>~ 0.489 - 0.411</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cell Temperature</td>
<td>No change</td>
<td>No change</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fuel Utilization</td>
<td>No change</td>
<td>No Change</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogen consumption rate</td>
<td>No change</td>
<td>No change</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nernst Voltage</td>
<td>No change</td>
<td>No change</td>
<td></td>
</tr>
</tbody>
</table>
The values in Table 4.5a and 4.5b show that when the initial condition of the conservation of energy equation is changed, the recovery time is higher without water-shift reaction than compared to with water-shift reaction. For variation in the initial condition of the conservation of mass, the recovery time is same with and w/o water-shift reaction. This refers to change in volumetric fuel flow-rate, air flow-rate, and current density. The fuel consumption rate changes only when the current density is changed, hence the other input parameters do not vary the rate of the reactions.

When the inlet temperature is changed by ~ 3%, there is some variation in the time taken for the cell temperature and operating voltage to recover with and w/o water-shift reaction. The time taken for the cell temperature and operating voltage to recover for both cases is ~16 seconds and ~19 seconds respectively and is the determining output parameter for the stabilization period. The fuel consumption rate does not change as the inlet temperature is varied.

The recovery time for the output parameters for 50% decrease in current density only varies for the Nernst voltage and is ~8 seconds w/o water-shift reaction as compared to ~11 seconds with water-shift reaction. However, the stabilization time depending parameter for the change in the current density is the cell temperature and is ~15 seconds, and is same for both the cases. The response time for the other output parameter is also same with and w/o water-shift reaction.

For a particular input parameter change, Table 4.5a and 4.5b shows that the time taken for Nernst voltage to regain steady state values is generally lower or same as compared to the time taken for the cell temperature to converge. However, the exception
is when the volumetric fuel flow-rate is changed; as fuel flow-rate has minimum affect on cell temperature. The time taken by the cell temperature to reach steady state for change in fuel flow-rate is lower w/o water-shift reaction compared to with water-shift reaction. The reason being the 10% change in fuel flow rate, does not vary the internal source of energy as such, hence the time taken by the energy equation to recover the steady state value is negligible.

Figure 4.21 shows the variation of power density with time when H₂-N₂ is the fuel gas, for the first set of ASR values calculated from graph. The power density varies from ~ 0.35 to 0.319 W/cm² and the cell operating voltage varies from ~ 484 – 0.439 V. The current density is constant at 725 mA/cm², and the inlet air/fuel temperature is ~ 850 °C. Gulzow et al [18], analyzed the degradation of ASR for three different type of Ni electrode for AFC. The result obtained for type 1 (pure Raney-nickel and PTFE powder) has similar degradation rate as depicted by this model in Figure 4.19.
Figure 4.21: Power density vs time for ASR degradation with $H_2-N_2$ (for first data set)

Figure 4.22 shows the variation of ideal and actual power density with time when $H_2-N_2$ is the fuel gas, for the second set of ASR values. The set of ASR data used to simulate the dynamic model is shown in Appendix B2. The ideal power density takes into consideration the open circuit voltage for calculating the operating cell voltage, whereas the affect of concentration variation on Nernst potential along the flow is neglected. The comparison of ideal and actual power density shows that the affect of concentration gradient along the flow is substantial and cannot be neglected for estimating the actual values. The actual power density varies from $\sim 0.346$ to $0.218 \text{ W/cm}^2$ and the cell
operating voltage varies from $\sim 477 - 0.301$ V. The current density is constant at 725 mA/cm$^2$, and the inlet air/fuel temperature is $\sim 850$ °C.

Figure 4.22: Plot of ideal and actual power density with time for ASR degradation with H$_2$-N$_2$ (for single data set)

Figure 4.23 shows the variation of power density with time when H$_2$-CO is the fuel gas, for the ASR values calculated from graph. For similar operating conditions, the power density varies from $\sim 0.367$ to 0.308 W/cm$^2$ and the cell operating voltage varies from $\sim 489 - 0.411$ V.

The degradation rate calculated for the CO-H$_2$ as fuel gas has a very high value. The reason is that the time phase where the data is available is the stabilization phase. Hence, to approximate the linear phase after the stabilization phase is difficult and
unreasonable due to lack of data. To make a better approximation, the ASR degradation rate at higher period of time is required, which is unavailable. Therefore, the dynamic result that can be simulated; is the effect of initial degradation (due to initial stabilization of the electrode/electrolyte) on the cell performance, but a complete analysis with carbon monoxide, as fuel gas cannot be made, due to shortage of authentic data.

Figure 4.23: Plot of power density with time due to degradation of ASR with CO+H₂

Figure 4.24 shows the variation of power density with time when the percentage of H₂-CO ratio in the fuel gas is varied. The figure shows that for similar input parameters, the cell performance is best when the ratio is 1:1. At lower CO ratio (i.e. H₂:CO = 6.5:3.5), there is not enough CO to have a high water-shift reaction rate, while when CO concentration is high (i.e. H₂:CO = 3.5:6.5) there is not enough H₂ to develop a high reversible voltage.
Table 4.6: Comparison of dynamic model output parameters to experimental result

<table>
<thead>
<tr>
<th>Output Parameters</th>
<th>Molar Ratio (H₂:CO = 3.5:6.5)</th>
<th>Molar Ratio (H₂:CO = 1:1)</th>
<th>Molar Ratio (H₂:CO = 6.5:3.5)</th>
<th>Reference (exp. result)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Voltage (V)</td>
<td>0.807</td>
<td>0.818</td>
<td>0.822</td>
<td>0.76</td>
</tr>
<tr>
<td>ASR (ohm-cm²)</td>
<td>0.908</td>
<td>0.935</td>
<td>0.977</td>
<td>1.03</td>
</tr>
<tr>
<td>Reversible Voltage</td>
<td>0.993</td>
<td>1.014</td>
<td>1.019</td>
<td>0.973</td>
</tr>
<tr>
<td>Power density (W/cm²)</td>
<td>0.166</td>
<td>0.168</td>
<td>0.169</td>
<td>0.156</td>
</tr>
</tbody>
</table>

The experimental value of cell voltage, and ASR had an error of 0.5% and 0.08% respectively. The comparison shows that the experimental cell voltage, power density and reversible voltage are lower than that obtained from the model. The possible reasons for the variation in the result are probably,

1. The ASR value are different, hence will result in variation cell resistance
2. The fuel composition used in the model is different from that used in the experiment. Hence, the Nernst voltage developed will be different as the molar ratios are not the same.

The comparison of the start up time with and without carbon monoxide as a fuel gas is shown in Figure 4.25 and 4.26. The simulation results show that with and without carbon monoxide as a fuel gas; the start up time are comparable and are in the order of seconds.
For practical applications of PSOFC, the start up time should be as minimum as possible, to compensate for loss in time for power delivery. Petruzzi et al used an external heating system to enhance the start up of the PSOFC stack and incorporated an empirical heating rate to calculate the start up time [19]. The start up time obtained for heating up the stack was 900 seconds, which when compared to a single cell start up should be considerably less. Hence, the start up time result obtained from the simulation seems reasonable for practical purposes.
Figure 4.26: Plot of Start up time of temperature with and w/o CO

Figure 4.27 shows the response time of the dynamic model for case 1 and 2 after the current density is reduced by 50%. The simulation shows that when the current density is low, the rate of hydrogen consumption due to oxidation process is also low, hence the water-shift reaction rate is low, and results in less amount of hydrogen being regained.
The recovery time of each cell parameter is shown in Table 4.5b. The recovery time depicted by Tomoyuki et al [38] for tubular geometry SOFC and Brouwer [35] for single cell MCFC model, are also in the order of seconds. Hence the result obtained from the dynamic model seems reasonable. Another aspect, which can be deduced from Table 4.5a and 4.5b, is that the recovery time does not differ much as a function of fuel gas for a variation in the cell operating condition.

The Figure 4.28 shows the temperature response with ASR degradation. It is seen that the average cell temperature remains constant for a particular CO + H₂ composition,
but varies when the composition is changed. As the CO composition varies, the rate of water-shift reaction increases to reach the equilibrium, which in turn affects the internal heat developed from the reactions and hence, the cell temperature increases.

**Figure 4.28: Plot of temperature response for ASR degradation with varying CO**

Figure 4.29 shows the effect of temperature on power density developed in the cell with varying CO concentration. The temperature is changed from 1123 K to 1158 K and its effect on the other cell parameter is analyzed. Higher temperature lowers the water-shift reaction rate, as the equilibrium constant is lowered. As both the reactions are exothermic, water-shift reaction enhances the cell operating temperature. Lowering the equilibrium constant further slows the rate of reaction. Hence, less amount of \( \text{H}_2 \) is
regained from the water-shift reaction, resulting in lower molar fraction of H$_2$. However, higher temperature enhances the Nernst/Reversible voltage, which results in net increase in the cell voltage and consequently increases the power density. This increase is more when the CO concentration is less in the fuel gas, as the positive affect of the water-shift reaction is to an extent nullified by lower rate of water-shift reaction as temperature increases.

Figure 4.29: Plot of temperature sensitivity on power density with and w/o CO

The effect of temperature change on fuel utilization is studied in Figure 4.30. The figure shows that the maximum change in H$_2$ utilization is when the model has least
percentage of H₂ i.e. H₂ and CO ratio is 3.5:6:5. The CO utilization change is high, where the CO concentration is less i.e. H₂ and CO ratio is 6.5:3:5. The reason being, in a system, from ideal gas law, we know that the number of moles present is inversely proportional to the temperature.

Therefore, as the temperature increases the number of moles of fuel at the inlet is lower for same volumetric flow, resulting in higher fuel utilization. The rate of fuel consumption remains unaltered, as the current density is constant.

![Figure 4.30: Plot of temperature sensitivity on fuel utilization with and w/o CO](image)

- **H₂ only**
- **H₂:CO = 6.5:3.5 (H₂)**
- **H₂:CO = 5:5 (H₂)**
- **H₂:CO = 3.5:6.5 (H₂)**
- **H₂:CO = 6.5:3.5 (CO)**
- **H₂:CO = 5:5 (CO)**
- **H₂:CO = 3.5:6.5 (CO)**
The effect of fuel flow-rate on power density is shown in figure 4.31. The maximum effect is with the fuel gas having less amount of H₂. The increase of fuel input increases the molar fraction of H₂. Hence a higher Nernst Voltage is obtained resulting in higher power density.

![Figure 4.31: Plot of fuel flow-rate sensitivity on power density with and w/o CO](image)

As discussed in Section 3.4, the mass conservation equation and the energy equation is solved to get the molar specie concentration and temperature distribution...
one case with three different molar ratios. The molar ratios are $\text{H}_2: \text{N}_2 = 1:1$, $\text{H}_2: \text{CO} = 6.5:3.5$ and $\text{H}_2: \text{CO} = 1:1$.

The initial conditions and the rate of the reaction used in the mass conservation equation for $\text{H}_2: \text{N}_2 = 1:1$ model are:

\begin{align*}
\text{Mole} \_ \text{fraction} \_ \text{H}_2 &= 0.481 \\
\text{Mole} \_ \text{fraction} \_ \text{H}_2 \text{O} &= 0.018 \\
\text{Rate} \_ \text{H}_2 \_ \text{oxidation} &= 2.26 \times 10^{-6} \text{Kmol/hr}
\end{align*}

Similarly, the initial conditions and the rate of the reaction for the mass conservation equation for $\text{H}_2: \text{CO} = 6.5:3.5$ model are:

\begin{align*}
\text{Mole} \_ \text{fraction} \_ \text{H}_2 &= 0.634 \\
\text{Mole} \_ \text{fraction} \_ \text{H}_2 \text{O} &= 0.016 \\
\text{Mole} \_ \text{fraction} \_ \text{CO}_2 &= 0.001 \\
\text{Mole} \_ \text{fraction} \_ \text{CO} &= 0.349 \\
\text{Rate} \_ \text{H}_2 \_ \text{oxidation} &= 2.26 \times 10^{-6} \text{Kmol/hr} \\
\text{Average} \_ \text{Rate} \_ \text{watershift} \_ \text{reaction} &= 1.8 \times 10^{-6} \text{Kmol/hr}
\end{align*}

and, the initial conditions and the rate of the reaction for the mass conservation equation for $\text{H}_2: \text{CO} = 1:1$ model are,

\begin{align*}
\text{Mole} \_ \text{fraction} \_ \text{H}_2 &= 0.486 \\
\text{Mole} \_ \text{fraction} \_ \text{H}_2 \text{O} &= 0.014 \\
\text{Mole} \_ \text{fraction} \_ \text{CO}_2 &= 0.001 \\
\text{Mole} \_ \text{fraction} \_ \text{CO} &= 0.499 \\
\text{Rate} \_ \text{H}_2 \_ \text{oxidation} &= 2.26 \times 10^{-6} \text{Kmol/hr} \\
\text{Average} \_ \text{Rate} \_ \text{watershift} \_ \text{reaction} &= 3.64 \times 10^{-6} \text{Kmol/hr}
\end{align*}

The above values show that the initial condition and the rate of the water-shift reaction vary for the three different molar ratios. The recovery time taken due to 10% change in the fuel flow rate seems to be nearly the same. The rate of hydrogen oxidation
remains the same for all the cases, since it is assumed that a constant current density is drawn. The final values of the initial conditions and rate of reactions after the fuel flow-rate change are as follows:

For, $\text{H}_2: \text{N}_2 = 1:1$

- $\text{Mole fraction } \text{H}_2 = 0.4824$
- $\text{Mole fraction } \text{H}_2\text{O} = 0.0175$
- $\text{Rate } \text{H}_2\text{-oxidation} = 2.26e-06 \text{ Kmol/hr}$

For, $\text{H}_2: \text{CO} = 6.5:3.5$

- $\text{Mole fraction } \text{H}_2 = 0.635$
- $\text{Mole fraction } \text{H}_2\text{O} = 0.0144$
- $\text{Mole fraction } \text{CO}_2 = 0.001$
- $\text{Mole fraction } \text{CO} = 0.349$
- $\text{Rate } \text{H}_2\text{-oxidation} = 2.26e-06 \text{ Kmol/hr}$
- $\text{Average Rate watershift reaction} = 1.67e-06 \text{ Kmol/hr}$

For, $\text{H}_2: \text{CO} = 1:1$

- $\text{Mole fraction } \text{H}_2 = 0.487$
- $\text{Mole fraction } \text{H}_2\text{O} = 0.013$
- $\text{Mole fraction } \text{CO}_2 = 0.001$
- $\text{Mole fraction } \text{CO} = 0.499$
- $\text{Rate } \text{H}_2\text{-oxidation} = 2.26e-06 \text{ Kmol/hr}$
- $\text{Average Rate watershift reaction} = 3.58e-06 \text{ Kmol/hr}$

From the final values, it can be understood that the percentage variation from the final and initial is small, thus the time taken to achieve the steady state for the mass conservation equation variables is also small and is in the order of seconds.
As discussed, in section 3.4 the conservation of energy equation has an internal energy source that varies as the molar ratio varies. Considering the same three different molar ratios, the initial and the final internal heat source values are,

For, $H_2:N_2=1:1$

$Q_{\text{source\_initial}} = 2.3321\, KJ/hr$

$Q_{\text{source\_final}} = 2.3322\, KJ/hr$

For, $H_2:CO=6.5:3.5$

$Q_{\text{source\_initial}} = 3.369\, KJ/hr$

$Q_{\text{source\_final}} = 3.337\, KJ/hr$

For, $H_2:CO=1:1$

$Q_{\text{source\_initial}} = 4.45\, KJ/hr$

$Q_{\text{source\_final}} = 4.414\, KJ/hr$

Therefore, it can be seen that the rate of internal heat energy produced is different for all the three cases, and the response time is nearly same.

The Figure 4.32 shows that the power density values calculated with two different time intervals, gives us the same value of power density at a particular time. Hence, Figure 4.32 indicates that the response time calculated in the dynamic model; is the time required by each parameter to reach its steady state value and is independent of the computational time interval for the program.
Figure 4.32: Plot of fuel flow-rate sensitivity on power density with H₂ using two different time intervals

The Figure 4.33 compares the ideal and the actual power density, and the affect of change in fuel flow rate on the cell power performance. The equation used to calculate the ideal power density is given by:

\[
Power \_density = i(E^- - i \* ASR(t, T_s))
\]

where,

\( i = \) current density = 0.5 A/cm²

\( ASR(t, T_s) = \) area specific resistance of cell at \( t = 0, T_s = 1123K \)
\[ E'' = E_{\text{STP}} + \frac{RT_i}{2F} \ln \left( \frac{P_{H_2} P_{O_2}^{0.5}}{P_{H_2}(t)} \right) \]

where,

\( E'' \) is the reversible Nernst voltage at \( n \) node (Volt)

\( T_i \) is the inlet temperature of cell (Kelvin)

\( R \) is the Universal gas constant (J/mol·K)

and, \( F \) is the Faraday’s constant

\( P_{H_2}, P_{O_2}, \) and \( P_{H_2}(t) \) are the \( n \) node partial pressure for the respective gas species

\( n \) = number of electrons displaced for 1 mole of \( H_2 \) oxidizing

\( F \) = Faraday’s Law of constant

Figure 4.33: Plot of fuel flow-rate sensitivity on ideal and actual power density with and w/o CO

The actual power density calculated takes into account the change in molar ratio of gases inside the cell along the flow of the fluid and uses a conservation of mass equation to solve the molar ratio at each node, for a given rate of reaction. The Nernst
voltage involves a correction factor term, which takes into account the variation in cell voltage, due to change in partial pressure of gases along the flow. Figure 4.33 indicates that the affect of change in volumetric fuel flow rate does not change the ideal cell voltage, but has an effect in the actual cell voltage, due to the change in Nernst potential.

Figure 4.34 shows the effect of fuel flow rate on fuel utilization as a function of fuel gas. The figure shows that the fuel utilization of H₂ and CO decreases proportionately, as the inlet fuel concentration is increased.

![Figure 4.34: Plot of fuel flow-rate sensitivity on fuel utilization with and w/o CO](image)
The effect of air flow-rate on power density is shown in Figure 4.35. According to Figure 4.20, the increase in air flow-rate decreases the temperature of cell, as it takes away some amount heat. Therefore, the Nernst voltage that is proportional to the temperature also decreases. Hence, the cell operating and the power density decrease.

![Figure 4.35: Plot of air flow-rate sensitivity on power density with and w/o CO](image-url)
Chapter 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The goal of the research is to analyze the cell performance as a function of fuel gas composition. As discussed in section 2.2, carbon monoxide and hydrogen are the primary products from coal gasification, and this parametric modeling estimates the suitability of these gases as fuel for PSOFC. Some of the conclusions that can be drawn from the present work are discussed below.

Figure 4.19, at two different temperatures (973K and 1023K); show that the power density is higher with CO + H₂ as compared to w/o CO. The increase in power density with CO oxidation and water-shift reaction at 973K is ~ 20%, and with water-shift reaction alone it is ~ 14% compared to case 1 i.e. only H₂ oxidation. The increase is up to ~15% at 1023K, with both the reactions. The activation and ohmic polarization losses are ~ 33% and ~ 3% lower with CO, while the concentration polarization loss is ~ 66% higher with CO at 450 mA/cm² current density. From Figure 4.8 it can be deduced that the primary polarization loss is the ohmic loss, followed by the activation polarization. Hence, though the percentage increase of concentration polarization is much higher its effect on the reversible voltage is low which is ~ 0.01 – 0.025%, and so this increase does not effect the net cell voltage. Therefore, when CO oxidation process is considered, a higher cell voltage is obtained for same current density. Hence, the simulation indicates that the cell performance is enhanced with CO:H₂ ratio as 1:1 in the fuel gas in comparison to only H₂.
Figure 4.10 compares the steady state parametric study of case 1 and case 2, and shows that at current density below ~ 700 mA/cm² at 1073K, with CO + H₂ (considering water-shift reaction), a better cell performance is obtained than with H₂. The results show that with ~ 80% CO and ~ 20% H₂, the power density is ~ 5% more, than with ~ 100% H₂ at inlet temperature of 1073K. The water-shift reaction produces back some amount of the hydrogen that is oxidized, resulting in the higher reversible voltage (~ 1 – 2%). The increase in cell temperature associated with inclusion of CO lowers the ohmic polarization by ~ 3 - 5% depending on the inlet temperature. The activation polarization increases by ~ 0.5%, but it seems that it is not sufficient to nullify the effect of increase in reversible voltage and decrease of ohmic polarization. Hence, it appears from the results that inclusion of the water-shift reaction has a positive impact on the cell performance.

The analysis with H₂ as the fuel shows the affect of polarization losses on the cell voltage. The results indicate that the affect of ohmic polarization on reversible voltage is ~ 20% at peak power density, while the cathode and anode activation polarization affect is ~ 17%, ~ 8% respectively. The concentration polarization affect is around ~ 0.02%.

The response time of cell parameters for 10% increase in volumetric fuel/air flow-rate and 50% decrease in current density shows that the recovery time to reach steady state is nearly same with and without CO as fuel and are of the order of seconds. The start up time with CO + H₂ as fuel is also comparable to H₂ as fuel. Hence, it can be deduced that when the ASR degradation is assumed constant, for the mentioned variations in input parameters, the fuel composition has little effect on the recovery/start up time. From Table 4.5a and 4.5b, the results show that for ~3% change in inlet temperature the
response time is 16 seconds for CO:H₂=1:1 model and 19 seconds for H₂:N₂=1:1 model. This is the cell parameter when changed took the maximum time to recover to steady state, compared to other input cell parameters.

The dynamic model simulations indicated that with increase in CO ratio in H₂ + CO fuel gas, the temperature of cell increases, hence changing the cell performance. The cell performance seems to be best with the ratio at 1:1, at 500 mA/cm² current density. The power density variation is ~ 0.2% initially and increases to 1.5% at higher ASR.

The three set of experimental ASR values obtained by SOFCO, Alliance with N₂-H₂ as fuel gas had some uncertainty, as some experimental values did not show a general trend line. The ASR degradation rate for the data as calculated by the reference was in the range of ~ 3.5% - 8.3 % per 500 hours, excluding the experimental uncertainty associated with it [Appendix K]. The ASR degradation rate calculated from the graph is ~ 4.7% per 500 hours and the ASR degradation rate calculated from a single set of data is 8.5%. Hence, the dynamic results simulated are reasonable and can be related to experimental results. The ASR degradation rate can be accounted to happen at three phases and its affect on power density has been highlighted in the Fig. 4.21. The results show that the Nernst voltage and the fuel utilization do not change with ASR degradation when the current density i.e. the load is assumed constant.

The dynamic simulation of the area specific resistance indicates that the cell voltage and the power density are degrading. With H₂-N₂ as fuel gas, the cell performance starts to degrade after ~ 800 hours. The results show that the stabilization period with H₂ as the fuel is lower as compared to CO + H₂ as fuel gas. Hence, it can be
deduced from these simulations that the cell performance during the stabilization period with CO + H₂ as fuel will degrade more than with only H₂ as fuel. This aspect is agreeable with the experimental investigation done by Jiang et al [36], that Ni + YSZ anode has lower ASR degradation rate with H₂ then with CO + H₂ as fuel. An aspect, which is of some concern, is the set of experimental data of ASR used in the simulation. The dynamic performance degradation is directly proportional to the ASR value used in the model. Hence, for a given operating condition the performance will vary as the ASR varies. To generalize the model, it is required that we obtain a large amount of data at regular intervals of time. Therefore, the analysis of the ASR degradation on cell performance cannot be concluded completely, due to the quality and quantity of data available and has been recommended for future work.

5.2 RECOMMENDATIONS

Four recommendations are suggested as a continuation to the present work to accomplish the objective of understanding the cell behavior with CO + H₂ as fuel gas.

The model requires empirical relation of dynamic ASR degradation to analyze the impact on the cell performance. A shortfall of the present research is the complete analysis of the cell performance degradation with H₂ + CO, as an appropriate empirical relation for ASR degradation cannot be obtained and is recommended for future work. To set up the proper empirical relation, good quality and larger quantity of experimental data is required. Future work on the experiment part will require collection of experimental data of ASR degradation rate at shorter duration and at larger duration of time i.e. until
1000 hours, with H$_2$ + CO as fuel gas. From literature it is suggested that the general degradation of ASR for SOFC, has a stabilization period initially followed by linear degradation; the final degradation is expected at higher interval of time. Therefore, the stabilization period and the time when final degradation of ASR happens will be an important criterion, which will estimate the resulting cell performance degradation. The better quality and higher quantity of experimental data obtained, will give a good empirical relation and hence, an improved estimation of the cell performance degradation when included in the model. The data will be used, to compute the ASR at various intervals of time. The ASR values obtained can then be used to calculate the Ea value from equation (49), to include the temperature effect, and be included in the dynamic model to see the variation of cell performance as a function of ASR degradation. ASR is one of the important parameter, which affect the cell performance along with current density, fuel/air flow rate and temperature of operation. The present dynamic model takes into account most of the aspects, but the complete ASR degradation affect on the cell performance, with CO+H$_2$, as fuel gas requires further analysis. Hence, the results obtained from the recommended work can later be compared to the cell performance with H$_2$ as fuel gas and a complete analysis can be made on cell performance as a function of CO as fuel gas.

The response time analysis is conducted by varying a certain percentage change of the input parameters and studying the time taken by output parameters to regain the steady state values. A parametric analysis of varying the input parameter with different percentages and checking the response time as a function of fuel composition will help to
analyze and estimate whether there is any change in the response time. The present work shows that the time taken for the energy equation to regain the steady state value i.e. cell temperature is higher as compared to other output parameters for change in inlet temperature, air flow-rate and current density. Hence, the future work can concentrate on the energy equation for analyzing the response time for the parametric study of the mentioned input parameters. The change in volumetric fuel flow-rate has minimum effect on the conservation of energy equation, but has some effect on the mass conservation equation. Hence, the parametric study with varying percentage change of fuel volumetric flow-rate can concentrate on the mass conservation equation and the time taken for the Nernst voltage to regain steady state value.

One of possibility that the ASR will degrade finally with CO as fuel, is possibly due to carbon deposition caused by cracking of CO. Literature suggests that not much analysis has been done considering this reaction, hence is under considerations for various research work [36]. Further analysis on CO as fuel gas, can be done including the CO decomposition reaction and analyzing the affects of carbon decomposition on the cell performance.

The dynamic model does not include the CO oxidation process, which is likely to happen at such high operating temperature. The steady state model simulations suggest the positive impact on the cell performance when CO oxidation process is considered. Hence, future work can be done on including the CO oxidation reaction process at the dynamic model and analyzing its impact on the cell performance.
Some additional recommendations that are suggested as an extension to the present research are discussed below.

The results indicate that temperature plays a key role in determining the power density output. The simulation shows that with addition of CO, the cell temperature increases. The change in activation polarization, ohmic polarization and Nernst potential, due to the change in cell temperature as a function of fuel composition results in change in operating voltage. Hence, the affect of cell temperature on power density, is obtained, if the system is adiabatic with respect to the environment. Therefore, future work on experiments can be performed considering adiabatic process.

Synthetic gas, the exhaust from coal gasification has CO and H₂ as the primary components. The present model can be utilized for further analysis of the exact synthetic gas composition and is recommended.

Literatures suggest that PSOFC are generally operated with current density below or around ~500 mA/cm² to obtain the best cell performance. But improvement in the material properties can result in higher operational current density. At higher current density (i.e. above ~ 800-1000 mA/cm²), the rate of reaction is higher. Hence, the rate at which CO diffuses through the anode may be a determining factor. The affect will magnify if the cell geometry is an anode-supported cell. CO molecules having a higher diameter is supposed to have a lower rate of diffusion, hence at higher current density, the concentration polarization may take an active role in determining the cell performance. Hence, future work can be done on including diffusion rate equations in the dynamic mode and analyzing the effect at higher current density. The inclusion of
diffusion rate equation will require a two-dimensional analysis, which will also help to analyze the effect of temperature normal to the flow and is recommended for future work. A two-dimensional analysis will also take into account the reaction site for the SOFC reactions i.e. the anode/electrolyte interface. Hence, future work can be done on analyzing the reaction chemical kinetics at the anode/electrolyte interface.

The model can be further used to optimize the cell input parameters, i.e. the optimum current density, inlet temperature and molar flow-rate for a given power density which can be done as future work.

Radiation, the third type of heat transfer is assumed negligible in the model. The inclusion of radiation can be used to do an extensive and complete energy conservation analysis.
BIBLIOGRAPHY


[27] *Journal of Power Sources*, “Microstructure and cathodic performance of La$_{0.9}$Sr$_{0.1}$MnO$_3$ electrodes according to particle size of starting powder”, Jin H. Choi, Jong H. Jang, Ji H. Ryu, Seung M. Oh (1999)


[37] “Solid Oxide Fuel Cell Research”, Rapeeporn Suwanwarangkul, Wei Zhang, published by University of Waterloo

APPENDIX A: Nodal Analysis

Comparison of cell parameters with varying number of nodes for the finite difference method

<table>
<thead>
<tr>
<th></th>
<th>8 nodes</th>
<th>12 nodes</th>
<th>16 nodes</th>
<th>20 nodes</th>
<th>24 nodes</th>
<th>28 nodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net current density (A/cm²)</td>
<td>0.465324</td>
<td>0.475332</td>
<td>0.480825</td>
<td>0.48427</td>
<td>0.486568</td>
<td>0.488673</td>
</tr>
<tr>
<td>Total current (A)</td>
<td>3.03908</td>
<td>2.98946</td>
<td>2.96586</td>
<td>2.95196</td>
<td>2.94243</td>
<td>2.93827</td>
</tr>
<tr>
<td>Net Voltage (w/o diffusion)</td>
<td>0.98407</td>
<td>0.988208</td>
<td>0.990214</td>
<td>0.991523</td>
<td>0.992623</td>
<td>0.992976</td>
</tr>
<tr>
<td>Net Voltage (with diffusion)</td>
<td>0.983903</td>
<td>0.988016</td>
<td>0.990005</td>
<td>0.9913</td>
<td>0.992388</td>
<td>0.992733</td>
</tr>
<tr>
<td>Power density (W/cm²)</td>
<td>0.325727</td>
<td>0.332732</td>
<td>0.336578</td>
<td>0.33899</td>
<td>0.34059</td>
<td>0.342071</td>
</tr>
<tr>
<td>Average Cell Temperature</td>
<td>777.749</td>
<td>778.668</td>
<td>779.275</td>
<td>779.627</td>
<td>779.757</td>
<td>780.161</td>
</tr>
<tr>
<td>Fuel utilization of H₂</td>
<td>0.608215</td>
<td>0.598605</td>
<td>0.595068</td>
<td>0.592627</td>
<td>0.589659</td>
<td>0.59051</td>
</tr>
<tr>
<td>Fuel utilization of CO</td>
<td>0.628909</td>
<td>0.617123</td>
<td>0.612249</td>
<td>0.609034</td>
<td>0.605739</td>
<td>0.6056</td>
</tr>
<tr>
<td>Cell area between two</td>
<td>7.26E-05</td>
<td>4.84E-05</td>
<td>3.63E-05</td>
<td>2.90E-05</td>
<td>2.42E-05</td>
<td>2.07E-05</td>
</tr>
<tr>
<td>consecutive nodes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Comparison of percentage change in cell parameters values between consecutive nodes

<table>
<thead>
<tr>
<th></th>
<th>% diff bet. 12-8</th>
<th>% diff bet. 16-12</th>
<th>% diff bet. 20-16</th>
<th>% diff bet. 24-20</th>
<th>% diff bet. 28-24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Net current density</td>
<td>2.15076</td>
<td>1.15561</td>
<td>0.71648</td>
<td>0.47453</td>
<td>0.43262</td>
</tr>
<tr>
<td>Total current</td>
<td>-1.63247</td>
<td>-0.78971</td>
<td>-0.46842</td>
<td>-0.32289</td>
<td>-0.14128</td>
</tr>
<tr>
<td>Net Voltage (w/o diffusion)</td>
<td>0.42050</td>
<td>0.20299</td>
<td>0.13219</td>
<td>0.11094</td>
<td>0.03556</td>
</tr>
<tr>
<td>Net Voltage (with diffusion)</td>
<td>0.41803</td>
<td>0.20131</td>
<td>0.13081</td>
<td>0.10975</td>
<td>0.03476</td>
</tr>
<tr>
<td>Power density</td>
<td>2.15057</td>
<td>1.15589</td>
<td>0.71633</td>
<td>0.47449</td>
<td>0.43263</td>
</tr>
<tr>
<td>Fuel utilization of H₂</td>
<td>-1.58003</td>
<td>-0.59087</td>
<td>-0.41021</td>
<td>-0.50082</td>
<td>0.14432</td>
</tr>
<tr>
<td>Fuel utilization of CO</td>
<td>-1.87404</td>
<td>-0.78979</td>
<td>-0.52511</td>
<td>-0.54102</td>
<td>-0.02608</td>
</tr>
<tr>
<td>Average Cell Temperature</td>
<td>0.11816</td>
<td>0.07795</td>
<td>0.04517</td>
<td>0.01667</td>
<td>0.05181</td>
</tr>
</tbody>
</table>
APPENDIX B1: ASR values from experiments used to compute the degradation rate per hour

ASR History Comparison of SOFCo PSOFCs Utilizing Various Anode Gases.

\[ y = -1E-13x^5 + 1E-10x^4 - 6E-08x^3 + 1E-05x^2 - 0.0005x + 1.194 \]

\[ R^2 = 0.7348 \]

- ◇ 50 mol% H2/50 mol% N2
- □ Baseline Coal Syn Gas
- ▲ Coal Syn Gas and 214±4 ppm H2S
- Pol. (50 mol% H2/50 mol% N2)
Trial 4 - ASR History
Cell (KS1S040318-1)

CO Mix started at ~160 hrs
Lost air flow at ~200 hrs for 11 hrs
Lost fuel flow at ~300 hrs for 6 hrs
APPENDIX B2: Single set of ASR data from SOFCO

ASR value from SOFCO data

\[ y = 7 \times 10^{-10}x^3 - 1 \times 10^{-6}x^2 + 0.0007x + 0.9708 \]

\[ R^2 = 0.9455 \]
## APPENDIX C: Calculated $E_a$ values

### Calculated $E_a$ values computed in the dynamic model

<table>
<thead>
<tr>
<th>Time</th>
<th>ASR(N$_2$/H$_2$)</th>
<th>$E_a$ (N$_2$/H$_2$)</th>
<th>Time</th>
<th>ASR(N$_2$/H$_2$)</th>
<th>$E_a$ (N$_2$/H$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.959</td>
<td>12513.44727</td>
<td>0</td>
<td>0.9708</td>
<td>12528.65548</td>
</tr>
<tr>
<td>71.1667</td>
<td>1.00562031</td>
<td>12572.36856</td>
<td>71.1667</td>
<td>1.015804297</td>
<td>12584.83832</td>
</tr>
<tr>
<td>119.3166667</td>
<td>1.017656243</td>
<td>12587.09112</td>
<td>119.3166667</td>
<td>1.041274253</td>
<td>12615.4319</td>
</tr>
<tr>
<td>137</td>
<td>1.020936244</td>
<td>12591.07004</td>
<td>137</td>
<td>1.049730947</td>
<td>12625.40821</td>
</tr>
<tr>
<td>159.8333333</td>
<td>1.023887619</td>
<td>12594.63829</td>
<td>159.8333333</td>
<td>1.059994888</td>
<td>12637.39866</td>
</tr>
<tr>
<td>211.2666667</td>
<td>1.027023443</td>
<td>12598.41716</td>
<td>211.2666667</td>
<td>1.080653777</td>
<td>12661.15123</td>
</tr>
<tr>
<td>287.9</td>
<td>1.028736921</td>
<td>12600.47665</td>
<td>287.9</td>
<td>1.106147688</td>
<td>12689.78685</td>
</tr>
<tr>
<td>331.2666667</td>
<td>1.029352033</td>
<td>12601.21506</td>
<td>331.2666667</td>
<td>1.11839575</td>
<td>12703.28887</td>
</tr>
<tr>
<td>454.3</td>
<td>1.030674315</td>
<td>12602.80074</td>
<td>454.3</td>
<td>1.148055114</td>
<td>12735.32759</td>
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<tr>
<td>523.1167</td>
<td>1.031652136</td>
<td>12603.9719</td>
<td>523.1167</td>
<td>1.163536624</td>
<td>12751.69491</td>
</tr>
<tr>
<td>547.1167</td>
<td>1.032031429</td>
<td>12604.42586</td>
<td>547.1167</td>
<td>1.169085475</td>
<td>12757.50366</td>
</tr>
<tr>
<td>623.6166667</td>
<td>1.033683779</td>
<td>12606.40136</td>
<td>623.6166667</td>
<td>1.188200101</td>
<td>12777.28665</td>
</tr>
<tr>
<td>791.5166667</td>
<td>1.039661032</td>
<td>12613.51868</td>
<td>791.5166667</td>
<td>1.24548191</td>
<td>12834.56626</td>
</tr>
<tr>
<td>958.9166667</td>
<td>1.047882155</td>
<td>12623.23476</td>
<td>958.9166667</td>
<td>1.339741418</td>
<td>12922.89233</td>
</tr>
<tr>
<td>1028.5</td>
<td>1.051666305</td>
<td>12627.67893</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Calculated Ea values computed in the dynamic model**

<table>
<thead>
<tr>
<th>Time</th>
<th>ASR(CO/H₂)</th>
<th>Ea(CO/H₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.959</td>
<td>12513.4</td>
</tr>
<tr>
<td>23</td>
<td>0.999980941</td>
<td>12565.4</td>
</tr>
<tr>
<td>115.1666667</td>
<td>1.070965912</td>
<td>12650.1</td>
</tr>
<tr>
<td>138.5</td>
<td>1.085747585</td>
<td>12666.9</td>
</tr>
<tr>
<td>161</td>
<td>1.097856717</td>
<td>12680.6</td>
</tr>
<tr>
<td>164.3333333</td>
<td>1.099610709</td>
<td>12682.5</td>
</tr>
<tr>
<td>190.1666667</td>
<td>1.111155897</td>
<td>12695.3</td>
</tr>
<tr>
<td>258.6666667</td>
<td>1.132342603</td>
<td>12718.5</td>
</tr>
<tr>
<td>281.1666667</td>
<td>1.138587304</td>
<td>12725.2</td>
</tr>
<tr>
<td>286.25</td>
<td>1.139964788</td>
<td>12726.7</td>
</tr>
<tr>
<td>300</td>
<td>1.143460112</td>
<td>12625.61321</td>
</tr>
<tr>
<td>350</td>
<td>1.153602111</td>
<td>12637.4598</td>
</tr>
<tr>
<td>400</td>
<td>1.161716608</td>
<td>12646.84894</td>
</tr>
<tr>
<td>450</td>
<td>1.168164114</td>
<td>12654.25367</td>
</tr>
<tr>
<td>500</td>
<td>1.173196987</td>
<td>12660.00001</td>
</tr>
</tbody>
</table>
APPENDIX D: Analysis of percentage error of current density and cell voltage for the 2 types of model

Operating voltage calculated from constant voltage and constant current model, for same current density:

<table>
<thead>
<tr>
<th>Current Density (A/cm²)</th>
<th>0.47088</th>
<th>0.37923</th>
<th>0.28465</th>
<th>0.19311</th>
<th>0.109035</th>
<th>0.07201</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Voltage</td>
<td>0.56114</td>
<td>0.65866</td>
<td>0.75848</td>
<td>0.85952</td>
<td>0.96234</td>
<td>1.0151</td>
</tr>
<tr>
<td>(constant current model)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Operating Voltage</td>
<td>0.55</td>
<td>0.65</td>
<td>0.75</td>
<td>0.85</td>
<td>0.95</td>
<td>1</td>
</tr>
<tr>
<td>(constant voltage model)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% error</td>
<td>0.020262</td>
<td>0.013329</td>
<td>0.011315</td>
<td>0.011205</td>
<td>0.012989</td>
<td>0.01511</td>
</tr>
</tbody>
</table>
Current density calculated from constant voltage and constant current model, for same operating voltage:

<table>
<thead>
<tr>
<th>Operating Voltage (V)</th>
<th>0.974548</th>
<th>0.851647</th>
<th>0.742094</th>
<th>0.636889</th>
<th>0.526964</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current Density (constant current model)</td>
<td>0.1</td>
<td>0.2</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Current density (constant voltage model)</td>
<td>0.090294</td>
<td>0.191649</td>
<td>0.292069</td>
<td>0.391612</td>
<td>0.489647</td>
</tr>
<tr>
<td>% error</td>
<td>0.107495</td>
<td>0.043574</td>
<td>0.027155</td>
<td>0.021419</td>
<td>0.021144</td>
</tr>
</tbody>
</table>

The analysis showed that the error percentage is less when constant current density model is used; hence, that model is used for the simulations both in steady and dynamic mode.
APPENDIX E: Listing of the components used in the model

hydrogenlist, oxygenlist, waterlist, nitrogenlist, carbonmonoxidelist, carbondioxidelist as componentlistname;

hydrogen as input tp(Componentlist: hydrogenlist);
hydrogen.y("oxygen"):0.0;
hydrogen.y("water"):0.0;
hydrogen.y("nitrogen"):0.0;
hydrogen.y("carbondioxide"):0.0;
hydrogen.y("carbonmonoxide"):0.0;
hydrogen.y("hydrogen"):1.0;

oxygen as input tp(Componentlist: oxygenlist);
oxygen.y("water"):0.0;
oxygen.y("hydrogen"):0.0;
oxygen.y("nitrogen"):0.0;
oxygen.y("carbondioxide"):0.0;
oxygen.y("carbonmonoxide"):0.0;
oxygen.y("oxygen"):1.0;

water as input tp(Componentlist: waterlist);
water.y("hydrogen"):0.0;
water.y("oxygen"):0.0;
water.y("nitrogen"):0.0;
water.y("carbondioxide"):0.0;
water.y("carbonmonoxide"):0.0;
water.y("water"):1.0;

nitrogen as input tp(Componentlist: nitrogenlist);
nitrogen.y("water"): 0.0;
nitrogen.y("hydrogen"): 0.0;
nitrogen.y("oxygen"): 0.0;
nitrogen.y("carbon dioxide"): 0.0;
nitrogen.y("carbon monoxide"): 0.0;
nitrogen.y("nitrogen"): 1.0;

carbon monoxide as input tp(Componentlist: carbon monoxide list);
carbon monoxide.y("hydrogen"): 0.0;
carbon monoxide.y("oxygen"): 0.0;
carbon monoxide.y("carbon dioxide"): 0.0;
carbon monoxide.y("water"): 0.0;
carbon monoxide.y("nitrogen"): 0.0;
carbon monoxide.y("carbon monoxide"): 1.0;

carbon dioxide as input tp(Componentlist: carbon dioxide list);
carbon dioxide.y("hydrogen"): 0.0;
carbon dioxide.y("oxygen"): 0.0;
carbon dioxide.y("carbon monoxide"): 0.0;
carbon dioxide.y("water"): 0.0;
carbon dioxide.y("nitrogen"): 0.0;
carbon dioxide.y("carbon dioxide"): 1.0;
APPENDIX F: Initial and boundary conditions assignment for temperature

// initial conditions for temperature;
Ta(0) = Tin;
Tf(0) = Tin;

Ts(x.interior): initial;
Ts(x.interior): T_stack_ini;
Ta(x.interior + x.endnode): initial;
Ta(x.interior + x.endnode): Tin;
Tf(x.interior + x.endnode): initial;
Tf(x.interior + x.endnode): Tin;

// boundary conditions for temperature;

Ts(0).ddx = 0;
Ts(x.endnode).ddx = 0;
Ts(x.endnode).value : Ts(x.endnode-1);
APPENDIX G: Variable Assignment and calculation for steady state models:

1 as realparameter (0.1016);
n as integerparameter (24);
k_s as realvariable (fixed, 7.3); // KJ/hr.m.k
k_solid([0:n]) as realvariable; // KJ/hr.m.k
area_air_cs_channel1 as realvariable (fixed, 0.000002393);
area_fuel_cs_channel1 as realvariable (fixed, 0.000003589);
area_air_cs_channel as realvariable;
area_fuel_cs_channel as realvariable;
x as lengthdomain (highestorderclerivative:2,length:l,
spacingpreference:l/n, discretizationmethod:"BFD2");
Tin as temperature (fixed, 750);
p as pressure (fixed, 1.0);
Pt as pressure (fixed, 1.0);
u2 as volumetric_flow (fixed, 0.2); // Volumetric flow: m3/hr,
Scale:18;
uo2 as volumetric_flow (fixed, 3.0); // Volumetric flow: m3/hr,
Scale:18;
mol_f2_in as realvariable; //Kmol/hr;
mol_o2_in as realvariable ;
mol_h2_in as realvariable ; //Kmol/hr;
mol_air_in as realvariable ;
z([0:n]) as realvariable (upper:50000, lower:0.00000000000001,
value: 500); // shift of the reaction ;
z_shift([0:n]) as realvariable (lower:0.0,value:0.0000000000001);
mol_co2([0:n]) as realvariable (lower:0.0000000000001,value:0.0000001);
mol_co_eq([0:n]) as realvariable (lower:0.000000000001,value:0.000001);
mol1_co2([0:n]) as realvariable (lower:0.000000000001,value:0.000001);
mol1_co_eq([0:n]) as realvariable (lower:0.000000000001,value:0.000001);
mol2_co2([0:n])
\text{as realvariable (lower:0.000000000001, value:0.00000001);}
mol2_co_eq([0:n])
\text{as realvariable (lower:0.000000000001, value:0.00000001);}
mol_co_in
\text{as realvariable (lower: 0.000000000001);}
\text{as realvariable ; // KJ/m2.hr.k;}
h_a([0:n]), h_f([0:n])
\text{as distribution1D(xdomain is x, highestorderxderivative:2)}
Ts
\text{of temperature;}
Tf
\text{of temperature;}
Ta
\text{of temperature;}
v_visc
\text{as visc_vap; // mPa-s;}
v_cp([0:n])
\text{as cp_mol; // KJ/Kmol/k;}
v_cp_mix([0:n])
\text{as cp_mol; // KJ/Kmol/k;}
\text{as realvariable (fixed, 0.7);}
y(componentlist)
\text{as molefraction (fixed, 1.0);}
current_conc_loss_a([0:n])
\text{as realvariable (value:300); // amperes;}
current_conc_loss_c([0:n])
\text{as realvariable (value:100); // amperes;}
molf_co_in
\text{as realvariable;}
molf_o2([0:n])
\text{as realvariable (upper:1.0, lower: 0.0, value:0.2);}
molf_n2([0:n])
\text{as realvariable (upper:1.0, lower: 0.0, value:0.8);}
molf_h2([0:n])
\text{as realvariable (upper:1.0, lower: 0.0, value:0.9);}
molf_h2o([0:n])
\text{as realvariable (upper:1.0, lower: 0.0, value:0.1);}
molf_co2([0:n])
\text{as realvariable (upper:1.0, lower: 0.0, value:0.1);}
molf_co([0:n])
\text{as realvariable (upper:1.0, lower: 0.0, value:0.4);}
molf1_h2([0:n])
\text{as realvariable (upper:1.0, lower: 0.0, value:0.45);}
molfl_h2o([0:n]) as realvariable(upper:1.0, lower: 0.0, value:0.05);
molfl_co2([0:n]) as realvariable(upper:1.0, lower: 0.0, value:0.1);
molfl_co([0:n]) as realvariable(upper:1.0, lower: 0.0, value:0.1);
molfl_co2([0:n]) as realvariable(upper:1.0, lower: 0.0, value:0.1);
molfl2_co([0:n]) as realvariable(upper:1.0, lower: 0.0, value:0.1);
molfl2_co2([0:n]) as realvariable(upper:1.0, lower: 0.0, value:0.1);
molfl2_h2([0:n]) as realvariable(upper:1.0, lower: 0.0, value:0.4);
molfl2_h2o([0:n]) as realvariable(upper:1.0, lower: 0.0, value:0.05);
gtotal([0:n]) as enth_mol; // MJ/mol;
gtotal_shift([0:n]) as enth_mol;
gtotal_co([0:n]) as enth_mol;
g([0:n]) as enth_mol(value: -0.012); // MJ/mol;
gt_shift([0:n]) as enth_mol; // MJ/mol
htotal([0:n]) as enth_mol;
htotal_shift([0:n]) as enth_mol;
g([0:n]) as enth_mol; // MJ/mol
h([0:n]) as enth_mol; // MJ/mol
gibb([0:n]) as gibbs_mol_vap; // MJ/mol;
s([0:n]) as entr_mol; // KJ/Kmol.K;
stotal([0:n]) as entr_mol; // KJ/Kmol.K;
stotal_shift([0:n]) as entr_mol;
stotal_co([0:n]) as entr_mol; // KJ/Kmol.K;
idlvolt([0:n]) as voltage (lower:0);
idlvolt1([0:n]) as voltage (lower:0);
volt_idl_act([0:n]) as voltage(lower:0);
net1_volt as voltage(lower:0);
volt_act([0:n]) as voltage (lower:0);
Qsource([0:n]) as realvariable(value:0.1); // KJ/Kmol;
Qsource_shift([0:n]) as realvariable(value:0.01); // KJ/Kmol;
Qsource_co([0:n]) as realvariable(value:0.1); // KJ/Kmol;
Vol_solid1 as realvariable (fixed,0.0000048996); // m3,
area_conv1_h2 as realvariable (fixed,0.008567); // m2;
area_conv1_o2 as realvariable (fixed,0.007804); // m2;
area1_cell as realvariable (fixed,0.00006448); // m2;
Vol_solid as realvariable; // m3,
area_conv_h2 as realvariable; // m2;
area_conv_o2 as realvariable; // m2;
area_cell as realvariable; // m2;
area_exposed as realvariable;
equivDia_o2 as realvariable; // m;
equivDia_h2 as realvariable; // m;
equi_const_shift([0:n]) as realvariable (lower: 0.3, upper: 2.5, value: 1.5);
equi_const([0:n]) as realvariable (lower: 0.3, upper: 2.5, value: 1.5);
R as realvariable // KJ/Kmol.K;
current([0:n]) as realvariable (lower:0,value:0.2); // amperes;
current_act as realvariable (lower:0,value:0.2); // amperes;
current_act1([0:n]) as realvariable (lower:0,value:0.2); // amperes;
current_act2([0:n]) as realvariable (lower:0,value:0.2); // amperes;
net_current as realvariable; // amperes;
resist([0:n]) as realvariable (lower:0); // ohm;
ASR([0:n]) as realvariable (lower:0); //ohm-cm2;
temp_asr as realvariable ;
resist_temp as realvariable ;
zh2([0:n]) as realvariable (lower:0,value:0.0000001); // Kmol/hr;
zo2([0:n]) as realvariable (lower:0);
zh2o([0:n]) as realvariable (lower:0,value:0.00000001);
z1h2o([0:n]) as realvariable (lower:0,value:0.00000001);
z2h2o([0:n]) as realvariable (lower:0,value:0.00000001);
yco([0:n]) as realvariable (lower:0,value:0.00000001);
yco2([0:n]) as realvariable (lower:0,value:0.00000001);
yo2([0:n]) as realvariable (lower:0,value:0.00000001);
net_h2_con as realvariable;
net_h2_out as realvariable;
h2_moles_left([0:n]) as realvariable (lower:0);
h2_moles_left1([0:n]) as realvariable (lower:0);
h2_moles_left2([0:n]) as realvariable (lower:0);
o2_moles_left([0:n]) as realvariable (lower:0);
net_fuel_util as realvariable (lower:0);
net1_volt1 as realvariable (lower:0);
net_cell_eff as realvariable (fixed,4.5);
torosity as realvariable (fixed,0.4);
porosity as realvariable (fixed,0.005);
l_anode as realvariable (fixed,0.005);
l_cathode as realvariable (fixed,0.005);
r_curr_as([0:n]) as realvariable;
r_curr_cs([0:n]) as realvariable;
mol_wt_avg_a([0:n]) as realvariable;
mol_wt_avg_c([0:n]) as realvariable;
alpha_h2([0:n]) as realvariable (value:0.5);
alpha_h2o([0:n]) as realvariable (value:0.5);
alpha_co2([0:n]) as realvariable (value:0.5);
alpha_co([0:n]) as realvariable (value:0.5);
alpha_o2([0:n]) as realvariable (value:0.5);
alpha_n2([0:n]) as realvariable (value:0.5);
boltz_const as realvariable (fixed,5.67); // W/m2.K4
dia_h2 as realvariable (fixed,2.915); //m
dia_o2 as realvariable (fixed,3.433); //m
dia_h2o as realvariable (fixed,2.641); //m
dia_n2 as realvariable (fixed,3.681); //m
dia_co2 as realvariable (fixed,3.996); //m
dia_co as realvariable (fixed,3.59); //m
<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>le_jones_pot_h2</td>
<td>as realvariable(fixed,38); // K; leonard jones potential</td>
</tr>
<tr>
<td>le_jones_pot_h2o</td>
<td>as realvariable(fixed,856.1);</td>
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<tr>
<td>le_jones_pot_o2</td>
<td>as realvariable(fixed,113.0);</td>
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<tr>
<td>le_jones_pot_n2</td>
<td>as realvariable(fixed,91.5);</td>
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<tr>
<td>le_jones_pot_co2</td>
<td>as realvariable(fixed,190.0);</td>
</tr>
<tr>
<td>le_jones_pot_co</td>
<td>as realvariable(fixed,110.0);</td>
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<td>a_sigma</td>
<td>as realvariable(fixed,1.06036);</td>
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<tr>
<td>b_sigma</td>
<td>as realvariable(fixed,0.1561);</td>
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<tr>
<td>c_sigma</td>
<td>as realvariable(fixed,0.193);</td>
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<tr>
<td>d_sigma</td>
<td>as realvariable(fixed,0.47635);</td>
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<tr>
<td>e_sigma</td>
<td>as realvariable(fixed,1.03587);</td>
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<tr>
<td>f_sigma</td>
<td>as realvariable(fixed,1.52996);</td>
</tr>
<tr>
<td>g_sigma</td>
<td>as realvariable(fixed,1.76464);</td>
</tr>
<tr>
<td>h_sigma</td>
<td>as realvariable(fixed,3.89411);</td>
</tr>
<tr>
<td>sigma_d_h2_h2o</td>
<td>as realvariable;</td>
</tr>
<tr>
<td>sigma_d_h2_co</td>
<td>as realvariable;</td>
</tr>
<tr>
<td>sigma_d_h2_co2</td>
<td>as realvariable;</td>
</tr>
<tr>
<td>sigma_d_co2</td>
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<tr>
<td>sigma_d_co2_h2o</td>
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<tr>
<td>sigma_d_co2_h2o</td>
<td>as realvariable;</td>
</tr>
<tr>
<td>sigma_d_o2_n2</td>
<td>as realvariable;</td>
</tr>
<tr>
<td>diff1_h2_h2o</td>
<td>as realvariable;</td>
</tr>
<tr>
<td>diff1_o2_n2</td>
<td>as realvariable;</td>
</tr>
<tr>
<td>diff1_eff_h2_h2o</td>
<td>as realvariable;</td>
</tr>
<tr>
<td>diff1_eff_o2_n2</td>
<td>as realvariable;</td>
</tr>
<tr>
<td>diff_eff_h2_m</td>
<td>as realvariable;</td>
</tr>
<tr>
<td>diff_eff_o2_m</td>
<td>as realvariable;</td>
</tr>
<tr>
<td>diff_co_co2</td>
<td>as realvariable;</td>
</tr>
<tr>
<td>diff_co2_h2o</td>
<td>as realvariable;</td>
</tr>
<tr>
<td>diff_h2_co</td>
<td>as realvariable;</td>
</tr>
</tbody>
</table>
resist_co_act1([0:n]) as realvariable(lower:0, value:0.05);
ex_curr as realvariable(fixed, 0.53);
ex_curr_c as realvariable(fixed, 0.2);
volt_co([0:n]) as realvariable(lower:0, value:1.08);
curr_h2([0:n]) as realvariable(lower:0, value:0.05);
curr_co([0:n]) as realvariable(lower:0, value:0.03);
rate_co([0:n]) as realvariable;
Curr_co_r([0:n]) as realvariable;
rate_h2 as realvariable;
curr_h2_r as realvariable;
mol_h2o_in as realvariable;
net_curr_h2 as realvariable;
net_curr_co as realvariable;
net1_pow_dens as realvariable;
pow_dens([0:n]) as realvariable;
net1_volt_act as realvariable;
net_co_con as realvariable;
net_co_out as realvariable;
net_fuel_util_co as realvariable;
ohm_loss([0:n]) as realvariable;
net_op_volt1 as realvariable;
net_ohm_loss as realvariable;
net_conc_loss as realvariable;
net_act_loss_a as realvariable;
net_act_loss_c as realvariable;
net_act_loss as realvariable;
act_loss([0:n]) as realvariable;

n1 = 16; // no. of channels
n2 = 16; // no. of channels
area\_cell = (0.005714*(0.1016/(n)));

//Kmol of fuel & oxygen entering in per hr;
mol\_o2\_in = (p*100*uo2*0.21)/(n1*R*(Tin+273.15));
mol\_air\_in = (p*100*uo2)/(n1*R*(Tin+273.15));
mol\_f2\_in = (p*100*uf2)/(n1*R*(Tin+273.15));

Calculations in steady mode:

//temperature calculation;
net\_t\_avg = (sigma(ts))/(n+1);
total\_temp\_inc = (ts(x.endnode)-ts(0));
// net\_voltage:
net1\_volt = (sigma(volt\_idl\_act))/(n+1);
net1\_volt1 = (sigma(volt\_act))/(n+1);
// net current;
net\_current\_dens = current\_dens*n1;
net\_current = ((sigma(current))*n1)/(n+1);
// net hydrogen and CO consumed;
net\_h2\_con = sigma(zh2) - sigma(z\_shift);
net\_h2\_out = mol\_h2\_in - net\_h2\_con;
net\_co\_con = sigma(z\_shift);
net\_co\_out = mol\_co\_in - net\_co\_con;
// fuel utilization;
net\_fuel\_util = net\_h2\_con/mol\_h2\_in ;
net\_fuel\_util\_co = net\_co\_con/mol\_co\_in ;
// power, current, operating voltage;
net1\_pow\_dens = net\_current\_dens*net\_op\_volt1;
net\_current\_dens\_chan = (current\_dens);
net1\_pow\_dens\_chan = (sigma(pow\_dens))/(n+1);
net_op_volt1 = sigma(net_op_volt)/(n+1);

//polarization losses;
net_ohm_loss = sigma(ohm_loss)/(n+1);
net_conc_loss = sigma(volt_conc_loss)/(n+1);
net_act_loss_a = sigma(act_loss_a)/(n+1);
net_act_loss_c = sigma(act_loss_c)/(n+1);
net_act_loss = sigma(act_loss)/(n+1);
APPENDIX H: Steady State Model program

Main Iteration loop for hydrogen oxidation steady state model:

\[
\begin{align*}
\text{mol}_{\text{h2\_in}} &= 0.999\text{mol}_{\text{f2\_in}}; \\
\text{mol}_{\text{h2o\_in}} &= 0.001\text{mol}_{\text{f2\_in}}; \\
\text{for } xi \text{ in } x.\text{interior} + x.\text{endnode} \text{ do} \\
&\quad \text{// Calling specific heat,density,} \\
&\quad \text{call (hydrogen.v\_cp(xi)) = pcp_mol_vap(Tf(xi),p,hydrogen.y) hydrogenlist;} \\
&\quad \text{call (hydrogen.rho(xi)) = pdens_mol_vap(Tf(xi),p,hydrogen.y)hydrogenlist;} \\
&\quad \text{call (oxygen.rho(xi)) = pdens_mol_vap(Ta(xi),p,oxygen.y)oxygenlist;} \\
&\quad \text{call (oxygen.v\_cp(xi)) = pcp_mol_vap(Ta(xi),p,oxygen.y) oxygenlist;} \\
&\quad \text{call (carbonmonoxide.v\_cp(xi)) = pcp_mol_vap(Tf(xi),p,carbonmonoxide.y) carbonmonoxidelist;} \\
&\quad \text{call (carbonmonoxide.rho(xi)) = pdens_mol_vap(Tf(xi),p,carbonmonoxide.y)carbonmonoxidelist;} \\
&\quad \text{call (carbonmonoxide.rho(xi)) = pdens_mol_vap(Tf(xi),p,carbonmonoxide.y)carbonmonoxidelist;} \\
&\quad \text{call (carbon dioxide.v\_cp(xi)) = pcp_mol_vap(Tf(xi),p,carbon dioxide.y) carbon dioxide list;} \\
&\quad \text{call (carbon dioxide.rho(xi)) = pdens_mol_vap(Tf(xi),p,carbon dioxide.y) carbon dioxide list;} \\
&\quad \text{call (water.v\_cp(xi)) = pcp_mol_vap(Tf(xi),p,water.y) waterlist;} \\
&\quad \text{call (water.rho(xi)) = pdens_mol_vap(Tf(xi),p,water.y)waterlist;} \\
\rho_{\text{mix}}(xi) &= \text{hydrogen.rho}(xi)\cdot \text{molf1\_h2}(xi) + \text{water.rho}(xi)\cdot \text{molf1\_h2o}(xi); \\
\nu_{\text{cp\_mix}}(xi) &= \text{hydrogen.v\_cp}(xi)\cdot \text{molf1\_h2}(xi) + \text{water.v\_cp}(xi)\cdot \text{molf1\_h2o}(xi); \\
\kappa_{\text{solid}}(xi) &= 5.50072 + 1.65535e-3 * Ts(xi); \\
\text{(area\_conv\_h2\_h\_f}(xi))\cdot (Ts(xi) - Tf(xi)) &= (\rho_{\text{mix}}(xi)\cdot \nu_{\text{cp\_mix}}(xi)\cdot \text{uf2})\cdot (Tf(xi).ddx));
\end{align*}
\]
(area_conv_o2*h_a(xi))*(Ts(xi)-Ta(xi)) = ((rho_mix(xi) *v_cp_mix(xi) *uo2)
*(Ta(xi).ddx));

mol_wt_avg_a(xi)=(2*molfl_h2(xi)+18*molfl_h2o(xi));
mol_wt_avg_c(xi)=(32*molf_o2(xi)+28*molf_n2(xi));
alpha_h2(xi)=1-sqrt(2/mol_wt_avg_a(xi));
alpha_h2o(xi)=1-sqrt(18/mol_wt_avg_a(xi));
alpha_o2(xi)=1-sqrt(32/mol_wt_avg_c(xi));
alpha_n2(xi)=1-sqrt(28/mol_wt_avg_c(xi));
Tn_h2_h2o(xi)=Ts(xi)/sqrt(lejones_pot_h2*lejones_pot_h2o);
Tn_o2_n2(xi)=Ts(xi)/sqrt(lejones_pot_o2*lejones_pot_n2);
sigma_d_h2_h2o(xi)=
(a_sigma/(Tn_h2_h2o(xi)^b_sigma))+(c_sigma/exp(d_sigma*Tn_h2_h2o(xi)))+
(e_sigma/exp(f_sigma*Tn_h2_h2o(xi)))+
(g_sigma/exp(h_sigma*Tn_h2_h2o(xi)));
sigma_d_o2_n2(xi)=
(a_sigma/(Tn_o2_n2(xi)^b_sigma))+(c_sigma/exp(d_sigma*Tn_o2_n2(xi)))+
(e_sigma/exp(f_sigma*Tn_o2_n2(xi)))+
(g_sigma/exp(h_sigma*Tn_o2_n2(xi)));
diff_h2_h2o(xi)=(0.001858*(Ts(xi)^1.5)*(20/(2*18))^0.5)/
(1*((dia_h2+dia_h2o)/2)^2)*
sigma_d_h2_h2o(xi);
diff_o2_n2(xi)=(0.001858*(Ts(xi)^1.5)*(60/(28*32))^0.5)/
(1*((dia_o2+dia_n2)/2)^2)*
sigma_d_o2_n2(xi);
diff_h2_m(xi)=(1-molfl_h2(xi))/((molfl_h2o(xi)/diffl_h2_h2o(xi)));
diff_eff_h2_m(xi)=(porosity*diff_h2_m(xi))/
((1-molfl_h2(xi)*alpha_h2(xi))*torosity);
diff_o2_m(xi)=(1-molfl_o2(xi))/
(molfl_n2(xi)/diffl_o2_n2(xi));
diff_eff_o2_m(xi)=(porosity*diff_o2_m(xi))/
((1-molfl_o2(xi)*alpha_o2(xi))*torosity);

h_a(xi) = 3.66*KSolid(xi)/equivDia_o2; // KJ/m2.K.hr;
h_f(xi) = 3.66*KSolid(xi)/equivDia_h2; // KJ/m2.K.hr;
endfor
for xi in x.interior do

// Calling dynamic viscosity, entropy, enthalpy, gibbs-free energy;

call (hydrogen.h(xi)) = penth_mol(tf(xi),p,hydrogen.y) hydrogenlist;
call (hydrogen.s(xi)) = pentr_mol_vap(tf(xi),p,hydrogen.y) hydrogenlist;
call (hydrogen.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,hydrogen.y) hydrogenlist;

call (water.h(xi)) = penth_mol_vap(tf(xi),p,water.y) waterlist;
call (water.s(xi)) = pentr_mol_vap(tf(xi),p,water.y) waterlist;
call (water.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,water.y) waterlist;

call (carbonmonoxide.h(xi)) = penth_mol_vap(tf(xi),p,carbonmonoxide.y) carbonmonoxidelist;
call (carbonmonoxide.s(xi)) = pentr_mol_vap(tf(xi),p,carbonmonoxide.y) carbonmonoxidelist;
call (carbonmonoxide.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,carbonmonoxide.y) carbonmonoxidelist;

call (carbondioxide.h(xi)) = penth_mol_vap(tf(xi),p,carbondioxide.y) carbondioxidelist;
call (carbondioxide.s(xi)) = pentr_mol_vap(tf(xi),p,carbondioxide.y) carbondioxidelist;
call (carbondioxide.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,carbondioxide.y) carbondioxidelist;

call (oxygen.h(xi)) = penth_mol(ta(xi),p,oxygen.y) oxygenlist;
call (oxygen.s(xi)) = pentr_mol_vap(ta(xi),p,oxygen.y) oxygenlist;
call (oxygen.gibb(xi)) = pgibbs_mol_vap(ta(xi),p,oxygen.y) oxygenlist;

//governing equations of heat transfer;
(vol\_solid*k\_solid(xi)*x(1))*(Ts(xi).d2dx2) = (((area\_conv\_o2*h\_a(xi)*x(1))*(Ts(xi)-Ta(xi))+(area\_conv\_h2*h\_f(xi)*x(1))*(Ts(xi)-Tf(xi)))) - (Qsource(xi));

//delta\_enthalpy\_total:
htotal(xi) = water.h(xi) - hydrogen.h(xi) - 0.5*oxygen.h(xi);

//gibbs\_free\_energy\_total:
gtotal(xi) = water.g(xi) - hydrogen.g(xi) - 0.5*oxygen.g(xi);

//delta\_gibbs\_table:
gt(xi) = water.gibb(xi) - hydrogen.gibb(xi) - 0.5*oxygen.gibb(xi);

//delta\_entrophy\_total:
stotal(xi) = water.s(xi) - hydrogen.s(xi) - 0.5*oxygen.s(xi);

//delta\_enthalpy\_total\_shift:
htotal\_shift(xi) = carbondioxide.h(xi) - water.h(xi) + hydrogen.h(xi) - carbonmonoxide.h(xi);

//gibbs\_free\_energy\_total\_shift:
gtotal\_shift(xi) = carbondioxide.gibb(xi) - water.gibb(xi) + hydrogen.gibb(xi) - carbonmonoxide.gibb(xi);

//delta\_gibbs\_shift:
gt\_shift(xi) = carbondioxide.g(xi) - water.g(xi) + hydrogen.g(xi) - carbonmonoxide.g(xi);

//delta\_entrophy\_total\_shift:
stotal\_shift(xi) = carbondioxide.s(xi) - water.s(xi) + hydrogen.s(xi) - carbonmonoxide.s(xi);
// gibbs_each_component:
hydrogen.g(xi) = hydrogen.h(xi) - (((Tf(xi)+273.15)*hydrogen.s(xi))/1E06);
oxygen.g(xi) = oxygen.h(xi) - (((Tf(xi)+273.15)*oxygen.s(xi))/1E06);
water.g(xi) = water.h(xi) - (((TF(xi)+273.15)*water.s(xi))/1E06);
carbonmonoxide.g(xi) = carbonmonoxide.h(xi) -
((((TF(xi)+273.15)*(carbonmonoxide.s(xi)))/1E06);
carbondioxide.g(xi) = carbondioxide.h(xi) -
((((TF(xi)+273.15)*(carbondioxide.s(xi)))/1E06);

// resistance:

ASR(xi) = (1.253e-5 * exp(11156 / (Ts(xi)+273))) + 0.02396 + (9.364e-5 * Ts(xi)) -
(1.384e-8 * (Ts(xi)^2));
resist(xi) = ASR(xi)/(area_cell*10000);

// consumption:
zh2(xi) = (3.6*current(xi))/(2*96485);
zo2(xi) = 0.5*zh2(xi);
zh2o(xi) = zh2(xi) + zh2o(xi-1);

// mole fraction:
h2_moles_left(xi) = h2_moles_left(xi-1) - zh2(xi);
o2_moles_left(xi) = o2_moles_left(xi-1) - zo2(xi);
molf_h2(xi) = h2_moles_left(xi)/(h2_moles_left(xi) + zh2o(xi));
molf_h2o(xi) = zh2o(xi)/(h2_moles_left(xi) + zh2o(xi));

// assuming air as the input to cathode;
molf_o2(xi) = (o2_moles_left(xi)/mol_air_in);
molf_n2(xi) = 1 - molf_o2(xi);
// ideal voltage:
idlvolt(xi) = ((-1)*gt(xi)*1000000)/(2*96485)+((8.314*(ts(xi)+273.15))/(2*96485))*loge(((mol_f1_h2(xi)*mol_f2o2(xi)*0.5)/mol_f1_h2o(xi))*P^0.5)+((8.314*(ts(xi)+273.15))/(4*96485))*loge(P_t);
idlvolt1(xi) = ((-1)*gt(xi)*1000000)/(2*96485);

mol_f1_h2(xi) = h2_moles_left(xi)/mol_f2_in;
mol_f1_h2o(xi) = zh2o(xi)/mol_f2_in;

// ideal voltage:
volt_idl_act(xi) = (((-1)*gt(xi)*1000000)/(2*96485)+((8.314*(ts(xi)+273.15))/(2*96485))*loge(((mol_f1_h2(xi)*mol_f2o2(xi)*0.5)/mol_f1_h2o(xi))*P^0.5)+((8.314*(ts(xi)+273.15))/(4*96485))*loge(P_t);
corr_factor_volt(xi)=((8.314*(ts(xi)+273.15))/(2*96485))*loge(((mol_f1_h2(xi)*mol_f2o2(xi)*0.5)/mol_f1_h2o(xi))*P^0.5);
volt_act(xi) = volt_idl_act(xi) + r_curr_cs(xi)+r_curr_as(xi) - act_loss(xi);

// current;
current_dens=current(xi)/(area_cell*10000);
current(xi) = (volt_act(xi)-op_volt(xi))/resist(xi);
pow_dens(xi)=current_dens*op_volt(xi);

// polarization losses:
current_conc_loss_c(xi) = (4*96485*(mol_f2o2(xi)*1)*diff_eff_o2_m(xi))/((1-mol_f2o2(xi))*r*(ts(xi)+273)*1_cathode);
current_conc_loss_a(xi) = ((2*96485*(mol_f1_h2(xi)*1)*diff_eff_h2_m(xi))/(r*(ts(xi)+273)*1_anode));
r_curr_cs(xi) =(r*ts(xi)*loge(1-(current_dens/current_conc_loss_c(xi))))/(4*96485);
\[
\text{r}_\text{curr}\_\text{as}(\xi) = \frac{(r\times ts(\xi) \times \log_e(1 - \frac{(\text{current}\_\text{dens}/\text{current}\_\text{conc}\_\text{loss}\_\text{a}(\xi))}{2\times 96485}) - \frac{(r\times ts(\xi) \times \log_e(1 + ((\text{molfl}\_\text{h2}(\xi)\times \text{current}\_\text{dens})/(\text{molfl}\_\text{h2o}(\xi)\times \text{current}\_\text{conc}\_\text{loss}\_\text{a}(\xi))}}{2\times 96485})}{2\times 96485};
\]

\[
\text{volt}\_\text{conc}\_\text{loss}(\xi) = \text{volt}\_\text{idl}\_\text{act}(\xi) - \text{volt}\_\text{act}(\xi) - \text{act}\_\text{loss}(\xi);
\]

\[
\text{ohm}\_\text{loss}(\xi) = \text{current}(\xi)\times \text{resist}(\xi);
\]

\[
\text{act}\_\text{loss}\_\text{c}(\xi) = \frac{(8.314\times 2\times (273 + Ts(\xi)) \times \log_e(\frac{\text{current}\_\text{dens}/\text{ex}\_\text{curr}\_\text{cathode}}{96485})}{(96485)};
\]

\[
\text{act}\_\text{loss}\_\text{a}(\xi) = \frac{(8.314\times 273 + Ts(\xi)) \times \text{current}\_\text{dens}}{(96485\times \text{ex}\_\text{curr}\_\text{anode})};
\]

\[
\text{act}\_\text{loss}(\xi) = \text{act}\_\text{loss}\_\text{c}(\xi) + \text{act}\_\text{loss}\_\text{a}(\xi);
\]

// heat of reaction;
\[
Q_{\text{source}}(\xi) = ((-1)\times (Ts(\xi) + 273)\times \text{stotal}(\xi)\times \text{zh2}(\xi)\times n2);
\]

endfor
Main iteration loop with water-shift reaction model:

\[
\text{mol}_{\text{h}2}\text{.in} = 0.499 * \text{mol}_{\text{f}2}\text{.in} ; \\
\text{mol}_{\text{co2}}(0) = 0.001 * \text{mol}_{\text{f}2}\text{.in}; \\
zh2o(0) = zh2(0)+ 0.001 * \text{mol}_{\text{f}2}\text{.in}; \\
z2h2o(0) = 0.001 * \text{mol}_{\text{f}2}\text{.in} + zh2(0); \\
\text{mol}_{\text{co.in}} = 0.499 * \text{mol}_{\text{f}2}\text{.in} ; \\
\]

for xi in x.interior + x.endnode do \\
// Calling specific heat, density, \\
call (hydrogen.v_cp(xi)) = pcp_mol_vap(Tf(xi),p,hydrogen.y) hydrogenlist; \\
call (hydrogen.rho(xi)) = pdens_mol_vap(Tf(xi),p,hydrogen.y)hydrogenlist; \\
call (oxygen.rho(xi)) = pdens_mol_vap(Ta(xi),p,oxygen.y)oxygenlist; \\
call (oxygen.v_cp(xi)) = pcp_mol_vap(Ta(xi),p,oxygen.y) oxygenlist; \\
call (carbonmonoxide.v_cp(xi)) = pcp_mol_vap(Tf(xi),p,carbonmonoxide.y) carbonmonoxidelist; \\
call (carbonmonoxide.rho(xi)) = \\
pdens_mol_vap(Tf(xi),p,carbonmonoxide.y)carbonmonoxidelist; \\
call (carbon dioxide.v_cp(xi)) = pcp_mol_vap(Tf(xi),p,carbon dioxide.y) carbon dioxide list; \\
call (carbondioxide.rho(xi)) = pdens_mol_vap(Tf(xi),p,carbon dioxide.y) carbon dioxide list; \\
call (water.v_cp(xi)) = pcp_mol_vap(Tf(xi),p,water.y) waterlist; \\
call (water.rho(xi)) = pdens_mol_vap(Tf(xi),p,water.y)waterlist;

\[
\text{rho\_mix(xi)} = \text{hydrogen.rho(xi)} * \text{molf2\_h2(xi)} + \text{water.rho(xi)} * \text{molf2\_h2o(xi)} + \\
\text{carbonmonoxide.rho(xi)} * \text{molf1\_co(xi)} + \text{carbondioxide.rho(xi)} * \text{molf1\_co2(xi)}; \\
\text{v\_cp\_mix(xi)} = \text{hydrogen.v\_cp(xi)} * \text{molf2\_h2(xi)} + \\
\text{water.v\_cp(xi)} * \text{molf2\_h2o(xi)} + \text{carbonmonoxide.v\_cp(xi)} * \text{molf1\_co(xi)} + \\
\text{carbondioxide.v\_cp(xi)} * \text{molf1\_co2(xi)};
\]
\[ k_{\text{solid}}(x_i) = 5.50072 + 1.65535\times 10^{-3} \times T_s(x_i); \]

\[ (\text{area conv } h_2^* h_f(x_i) \times (T_s(x_i) - T_f(x_i)) = ((\rho_{\text{mix}}(x_i) \times v_{cp \_ \text{mix}}(x_i) \times u_f^2) \times (T_f(x_i).d\!d\!x)); \]

\[ (\text{area conv } o_2^* h_a(x_i) \times (T_s(x_i) - T_a(x_i)) = ((\rho_{\text{mix}}(x_i) \times v_{cp \_ \text{mix}}(x_i) \times u_{o2}) \times (T_a(x_i).d\!d\!x)); \]

\[ \text{mol wt avg } a(x_i) = (2 \times \text{mol } f_2^2(x_i) + 18 \times \text{mol } f_2 h_2 o(x_i) + 44 \times \text{mol } f_1 co_2(x_i) + 28 \times \text{mol } f_1 c o(x_i)) / (\text{mol } f_1 co(x_i) + \text{mol } f_1 co_2(x_i) + \text{mol } f_2 h_2(x_i) + \text{mol } f_2 h_2 o(x_i)); \]

\[ \text{mol wt avg } c(x_i) = (32 \times \text{mol } o_2(x_i) + 28 \times \text{mol } n_2(x_i)); \]

\[ \alpha_{h_2}(x_i) = 1 - \sqrt{2 / \text{mol wt avg } a(x_i)}; \]

\[ \alpha_{h_2 o}(x_i) = 1 - \sqrt{18 / \text{mol wt avg } a(x_i)}; \]

\[ \alpha_{co_2}(x_i) = 1 - \sqrt{44 / \text{mol wt avg } a(x_i)}; \]

\[ \alpha_{co}(x_i) = 1 - \sqrt{28 / \text{mol wt avg } a(x_i)}; \]

\[ \alpha_{o_2}(x_i) = 1 - \sqrt{32 / \text{mol wt avg } c(x_i)}; \]

\[ \alpha_{n_2}(x_i) = 1 - \sqrt{28 / \text{mol wt avg } c(x_i)}; \]

\[ T_n_{h_2 h_2 o}(x_i) = T_s(x_i) / \sqrt{(l e j o n e s g o t h_2 \times l e j o n e s g o t h_2 o)}; \]

\[ T_n_{h_2 c o}(x_i) = T_s(x_i) / \sqrt{(l e j o n e s g o t h_2 \times l e j o n e s g o t c o)}; \]

\[ T_n_{h_2 co_2}(x_i) = T_s(x_i) / \sqrt{(l e j o n e s g o t h_2 \times l e j o n e s g o t c o_2)}; \]

\[ T_n_{c o co_2}(x_i) = T_s(x_i) / \sqrt{(l e j o n e s g o t c o \times l e j o n e s g o t c o_2)}; \]

\[ T_n_{c o h_2 o}(x_i) = T_s(x_i) / \sqrt{(l e j o n e s g o t c o \times l e j o n e s g o t h_2 o)}; \]

\[ T_n_{c o_2 h_2 o}(x_i) = T_s(x_i) / \sqrt{(l e j o n e s g o t c o_2 \times l e j o n e s g o t h_2 o)}; \]

\[ T_n_{o_2 n_2}(x_i) = T_s(x_i) / \sqrt{(l e j o n e s g o t o_2 \times l e j o n e s g o t n_2)}; \]

\[ \sigma_{d h_2 h_2 o}(x_i) = (a_{sigma} / (T_n_{h_2 h_2 o}(x_i) \times b_{sigma})) + (c_{sigma} / \exp(d_{sigma} \times T_n_{h_2 h_2 o}(x_i))) + (e_{sigma} / \exp(f_{sigma} \times T_n_{h_2 h_2 o}(x_i))) + (g_{sigma} / \exp(h_{sigma} \times T_n_{h_2 h_2 o}(x_i)))); \]

\[ \sigma_{d h_2 c o}(x_i) = (a_{sigma} / (T_n_{h_2 c o}(x_i) \times b_{sigma})) + (c_{sigma} / \exp(d_{sigma} \times T_n_{h_2 c o}(x_i))) + (e_{sigma} / \exp(f_{sigma} \times T_n_{h_2 c o}(x_i))) + (g_{sigma} / \exp(h_{sigma} \times T_n_{h_2 c o}(x_i)))); \]
\[
\text{sigma\_d\_h2\_co2(xi)} = \frac{a_{\sigma \text{ipd}}(T_{n\_h2\_co2(xi)})}{c_{\sigma \text{ipd}}} + \frac{e_{\sigma \text{ipd}}}{h_{\sigma \text{ipd}}} + \frac{g_{\sigma \text{ipd}}}{h_{\sigma \text{ipd}}};
\]

\[
\text{sigma\_d\_co\_h2o(xi)} = \frac{a_{\sigma \text{ipd}}(T_{n\_co\_h2o(xi)})}{c_{\sigma \text{ipd}}} + \frac{e_{\sigma \text{ipd}}}{h_{\sigma \text{ipd}}} + \frac{g_{\sigma \text{ipd}}}{h_{\sigma \text{ipd}}};
\]

\[
\text{sigma\_d\_co2\_h2o(xi)} = \frac{a_{\sigma \text{ipd}}(T_{n\_co2\_h2o(xi)})}{c_{\sigma \text{ipd}}} + \frac{e_{\sigma \text{ipd}}}{h_{\sigma \text{ipd}}} + \frac{g_{\sigma \text{ipd}}}{h_{\sigma \text{ipd}}};
\]

\[
\text{sigma\_d\_co\_co2(xi)} = \frac{a_{\sigma \text{ipd}}(T_{n\_co\_co2(xi)})}{c_{\sigma \text{ipd}}} + \frac{e_{\sigma \text{ipd}}}{h_{\sigma \text{ipd}}} + \frac{g_{\sigma \text{ipd}}}{h_{\sigma \text{ipd}}};
\]

\[
\text{sigma\_d\_o2\_n2(xi)} = \frac{a_{\sigma \text{ipd}}(T_{n\_o2\_n2(xi)})}{c_{\sigma \text{ipd}}} + \frac{e_{\sigma \text{ipd}}}{h_{\sigma \text{ipd}}} + \frac{g_{\sigma \text{ipd}}}{h_{\sigma \text{ipd}}};
\]

\[
\text{diff\_h2\_h2o(xi)} = \frac{0.001858(T_{s(xi)})^{1.5}*(20/(2*18))^{0.5}}{1*(((\text{dia\_h2}+\text{dia\_h2o})/2)^2)}
\]

\[
\text{diff\_o2\_n2(xi)} = \frac{0.001858(T_{s(xi)})^{1.5}*(60/(28*32))^{0.5}}{1*(((\text{dia\_o2}+\text{dia\_n2})/2)^2)}
\]

\[
\text{diff\_co\_h2o(xi)} = \frac{0.001858(T_{s(xi)})^{1.5}*(46/(28*18))^{0.5}}{1*(((\text{dia\_co}+\text{dia\_h2o})/2)^2)}
\]

\[
\text{diff\_co2\_h2o(xi)} = \frac{0.001858(T_{s(xi)})^{1.5}*(62/(44*18))^{0.5}}{1*(((\text{dia\_co2}+\text{dia\_h2o})/2)^2)}
\]

\[
\text{diff\_co\_co2(xi)} = \frac{0.001858(T_{s(xi)})^{1.5}*(72/(28*44))^{0.5}}{1*(((\text{dia\_co}+\text{dia\_co2})/2)^2)}
\]

\[
\text{diff\_h2\_co(xi)} = \frac{0.001858(T_{s(xi)})^{1.5}*(20/(2*28))^{0.5}}{1*(((\text{dia\_h2}+\text{dia\_co})/2)^2)}
\]

\[
\text{diff\_h2\_co2(xi)} = \frac{0.001858(T_{s(xi)})^{1.5}*(46/(2*46))^{0.5}}{1*(((\text{dia\_h2}+\text{dia\_co2})/2)^2)}
\]
for xi in x.interior do

// Calling dynamic viscosity, entropy, enthalpy, gibbs-free energy;

call (hydrogen.h(xi)) = penth_mol(tf(xi), p, hydrogen.y) hydrogenlist;
call (hydrogen.s(xi)) = pentr_mol_vap(tf(xi), p, hydrogen.y) hydrogenlist;
call (hydrogen.gibb(xi)) = pgibbs_mol_vap(tf(xi), p, hydrogen.y) hydrogenlist;

call (water.h(xi)) = penth_mol_vap(tf(xi), p, water.y) waterlist;
call (water.s(xi)) = pentr_mol_vap(tf(xi), p, water.y) waterlist;
call (water.gibb(xi)) = pgibbs_mol_vap(tf(xi), p, water.y) waterlist;

call (carbonmonoxide.h(xi)) = penth_mol_vap(tf(xi), p, carbonmonoxide.y) carbonmonoxidelist;
call (carbonmonoxide.s(xi)) = pentr_mol_vap(tf(xi), p, carbonmonoxide.y) carbonmonoxidelist;
call (carbonmonoxide.gibb(xi)) = pgibbs_mol_vap(tf(xi), p, carbonmonoxide.y) carbonmonoxidelist;

endfor

h_a(xi) = 3.66*K_solid(xi)/equiv_dia_o2; // KJ/m2.K.hr;
h_f(xi) = 3.66*K_solid(xi)/equiv_dia_h2; // KJ/m2.K.hr;

for xi in x.interior do

// Calling dynamic viscosity, entropy, enthalpy, gibbs-free energy;

call (hydrogen.h(xi)) = penth_mol(tf(xi), p, hydrogen.y) hydrogenlist;
call (hydrogen.s(xi)) = pentr_mol_vap(tf(xi), p, hydrogen.y) hydrogenlist;
call (hydrogen.gibb(xi)) = pgibbs_mol_vap(tf(xi), p, hydrogen.y) hydrogenlist;

call (water.h(xi)) = penth_mol_vap(tf(xi), p, water.y) waterlist;
call (water.s(xi)) = pentr_mol_vap(tf(xi), p, water.y) waterlist;
call (water.gibb(xi)) = pgibbs_mol_vap(tf(xi), p, water.y) waterlist;

call (carbonmonoxide.h(xi)) = penth_mol_vap(tf(xi), p, carbonmonoxide.y) carbonmonoxidelist;
call (carbonmonoxide.s(xi)) = pentr_mol_vap(tf(xi), p, carbonmonoxide.y) carbonmonoxidelist;
call (carbonmonoxide.gibb(xi)) = pgibbs_mol_vap(tf(xi), p, carbonmonoxide.y) carbonmonoxidelist;

endfor
call (carbondioxide.h(xi)) = penth_mol_vap(tf(xi),p,carbondioxide.y) carbondioxidelist;
call (carbondioxide.s(xi)) = pentr_mol_vap(tf(xi),p,carbondioxide.y) carbondioxidelist;
call (carbondioxide.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,carbondioxide.y)
carbondioxidelist;

call (oxygen.h(xi)) = penth_mol(ta(xi),p,oxygen.y) oxygenlist;
call (oxygen.s(xi)) = pentr_mol_vap(ta(xi),p,oxygen.y) oxygenlist;
call (oxygen.gibb(xi)) = pgibbs_mol_vap(ta(xi),p,oxygen.y) oxygenlist;

//governing equations of heat transfer;
(vol_solid*k_solid(xi))*(Ts(xi).d2dx2) = (((area_conv_o2*h_a(xi))*(Ts(xi)-Ta(xi)))+((area_conv_h2*h_f(xi))*(Ts(xi)-Tf(xi)))) - (Qsource(xi)/x(l));

//delta_enthalpy_total:
htotal(xi) = water.h(xi) - hydrogen.h(xi) - 0.5*oxygen.h(xi);

//gibbs_free_energy_total:
gtotal(xi) = water.g(xi) - hydrogen.g(xi) - 0.5*oxygen.g(xi);

//delta_gibbs_table:
gt(xi) = water.gibb(xi) - hydrogen.gibb(xi) - 0.5*oxygen.gibb(xi);

//delta_enthropy_total:
stotal(xi) = water.s(xi) - hydrogen.s(xi) - 0.5*oxygen.s(xi);

//delta_enthalpy_total_shift:
htotal_shift(xi) = carbondioxide.h(xi) - water.h(xi) + hydrogen.h(xi) -
carbonmonoxide.h(xi);
//gibbs_free_energy_total_shift:
gtotal_shift(xi) = carbdioxide.gibb(xi) - water.gibb(xi) + hydrogen.gibb(xi) -
carbonmonoxide.gibb(xi);

//delta_gibbs_shift:
gt_shift(xi) = carbdioxide.g(xi) - water.g(xi) + hydrogen.g(xi) - carbonmonoxide.g(xi);

//delta_enthropy_total_shift:
stotal_shift(xi) = carbdioxide.s(xi) - water.s(xi) + hydrogen.s(xi) -
carbonmonoxide.s(xi);

//gibbs_each_component:
hydrogen.g(xi) = hydrogen.h(xi) - (((Tf(xi)+273.15)*(hydrogen.s(xi)))/1E06);
oxygen.g(xi) = oxygen.h(xi) - (((Tf(xi)+273.15)*(oxygen.s(xi)))/1E06);
water.g(xi) = water.h(xi) - (((TF(xi)+273.15)*(water.s(xi)))/1E06);
carbonmonoxide.g(xi) = carbonmonoxide.h(xi) -
(((TF(xi)+273.15)*(carbonmonoxide.s(xi)))/1E06);
carbdioxide.g(xi) = carbdioxide.h(xi) -
(((TF(xi)+273.15)*(carbdioxide.s(xi)))/1E06);

// resistance :

ASR(xi) = (1.253e-5 * exp(11156 / (Ts(xi)+273)))+ 0.02396 + (9.364e-5 * Ts(xi)) -
(1.384e-8 * (Ts(xi)^2));
resist(xi) = ASR(xi)/(area_cell*10000);

zh2(xi) = (3.6*current(xi))/(2*96485);
zo2(xi) = 0.5*zh2(xi);
zh2o(xi) = zh2(xi) + z1h2o(xi-1);
\[ z_{2h2o}(x_i) = zh2(x_i) + z2h2o(x_i-1) ; \]

// mole fraction:
\[
\begin{align*}
\text{h2}_\text{moles}_\text{left}(x_i) &= \text{h2}_\text{moles}_\text{left}(x_i-1) - zh2(x_i) ; \\
\text{h2}_\text{moles}_\text{left2}(x_i) &= \text{h2}_\text{moles}_\text{left}(x_i-1) - zh2(x_i) ; \\
\text{o2}_\text{moles}_\text{left}(x_i) &= \text{o2}_\text{moles}_\text{left}(x_i-1) - zo2(x_i) ; \\
\text{molf}_\text{h2}(x_i) &= \text{h2}_\text{moles}_\text{left2}(x_i)/(\text{h2}_\text{moles}_\text{left2}(x_i) + z2h2o(x_i)) ; \\
\text{molf}_\text{h2o}(x_i) &= z2h2o(x_i)/(\text{h2}_\text{moles}_\text{left2}(x_i) + z2h2o(x_i)) ;
\end{align*}
\]

// assuming air as the input to cathode;
\[
\begin{align*}
\text{molf}_\text{o2}(x_i) &= (\text{o2}_\text{moles}_\text{left}(x_i)/\text{mol}_\text{air}_\text{in}) ; \\
\text{molf}_\text{n2}(x_i) &= 1 - \text{molf}_\text{o2}(x_i) ; \\
\text{mol}_\text{co2}(x_i) &= \text{mol1}_\text{co2}(x_i-1) ; \\
\text{mol1}_\text{co}_\text{eq}(x_i) &= \text{mol1}_\text{co}_\text{eq}(x_i-1) ; \\
\text{molf}_{1-h2}(x_i) &= \text{h2}_\text{moles}_\text{left}(x_i)/\text{mol}_f2_{-in} ; \\
\text{molf}_{1-h2o}(x_i) &= zh2o(x_i)/\text{mol}_f2_{-in} ; \\
\text{molf}_{co}(x_i) &= \text{mol}_\text{co}_\text{eq}(x_i)/\text{mol}_f2_{-in} ; \\
\text{molf}_{co2}(x_i) &= \text{mol}_\text{co2}(x_i)/\text{mol}_f2_{-in} ;
\end{align*}
\]

// equilibrium constant calculation;
\[
\text{equi}_\text{const}_\text{shift}(x_i) = \exp((-1)*\text{gt}_\text{shift}(x_i)*1000000)/(R*(T_s(x_i)+273.15)) ;
\]

// Initial equilibrium constant calculation for shift reaction;
\[
\text{equi}_\text{const}(x_i) = \exp((4276/(T_s(x_i) + 273.15))-3.961) ;
\]

\[
\text{equi}_\text{const}_\text{shift}(x_i)=
((\text{molf}_{1-h2}(x_i)*1000)+z(x_i))*((\text{molf}_{co2}(x_i)*1000)+z(x_i))/(((\text{molf}_{co}(x_i)*1000)-z(x_i))*((\text{molf}_{1-h2o}(x_i)*1000)-z(x_i)));
\]
if (z(xi) > 0 ) and (z(xi) < 1E03) then
  
  \[ z\text{-shift}(xi) = (z(xi) \times (h2\text{-moles\_left}(xi) + zh2o(xi) + mol\_co\_eq(xi) + mol\_co2(xi))) / 1E03; \]
  
  else
  
  \[ z\text{-shift}(xi) = zh2(xi); \]
  
endif

\[ z1h2o(xi) = zh2o(xi) - z\_shift(xi); \]

\[ h2\text{-moles\_left1}(xi) = h2\text{-moles\_left}(xi) + z\_shift(xi); \]

\[ mol1\_co2(xi) = mol\_co2(xi) + z\_shift(xi); \]

\[ mol1\_co\_eq(xi) = mol\_co\_eq(xi) - z\_shift(xi); \]

\[ molf2\_h2(xi) = h2\text{-moles\_left1}(xi) / mol\_f2\_in; \]

\[ molf2\_h2o(xi) = z1h2o(xi) / mol\_f2\_in; \]

\[ molf1\_co(xi) = mol1\_co\_eq(xi) / mol\_f2\_in; \]

\[ molf1\_co2(xi) = mol1\_co2(xi) / mol\_f2\_in; \]

//ideal voltage:

\[ \text{volt\_idl\_act}(xi) = (((-1) \times gt(xi) \times 1000000) / (2 \times 96485)) + (8.314 \times (ts(xi) + 273.15) / (2 \times 96485)) \times \text{loge}(((molf2\_h2(xi) \times mol\_o2(xi)^{0.5}) / molf2\_h2o(xi)) \times P^{0.5}) + ((8.314 \times (ts(xi) + 273.15)) / (4 \times 96485)) \times \text{loge}(P); \]

\[ \text{current\_dens} = \text{current}(xi) / (\text{area\_cell} \times 10000); \]

\[ \text{corr\_factor\_volt}(xi) = ((((8.314 \times (ts(xi) + 273.15)) / (2 \times 96485)) \times \text{loge}(((molf2\_h2(xi) \times mol\_o2(xi)^{0.5}) / molf2\_h2o(xi)) \times P^{0.5})); \]

\[ \text{volt\_act}(xi) = \text{volt\_idl\_act}(xi) + r \times curr\_cs(xi) + r \times curr\_as(xi) \times \text{act\_loss}(xi); \]

\[ \text{net\_op\_volt}(xi) = \text{volt\_act}(xi) \times \text{current}(xi) \times \text{resist}(xi); \]

\[ \text{volt\_conc\_loss}(xi) = \text{volt\_idl\_act}(xi) \times \text{volt\_act}(xi) \times \text{act\_loss}(xi); \]

\[ \text{pow\_dens}(xi) = \text{current\_dens} \times \text{net\_op\_volt}(xi); \]

//polarization losses:
\[ r_{\text{curr}}_{\text{cs}}(\xi) = \left( r \cdot ts(\xi) \cdot \log_e \left( 1 - \frac{\text{current dens}}{\text{current conc loss c}(\xi)} \right) \right) / (4 \cdot 96485); \]
\[ r_{\text{curr}}_{\text{as}}(\xi) = \left( r \cdot ts(\xi) \cdot \log_e \left( 1 - \frac{\text{current dens}}{\text{current conc loss a}(\xi)} \right) \right) / (2 \cdot 96485) - \]
\[ \left( r \cdot ts(\xi) \cdot \log_e \left( 1 + \frac{\text{molf}_2_{\text{h2}}(\xi) \cdot \text{current dens}}{\text{molf}_2_{\text{h2o}}(\xi) \cdot \text{current conc loss a}(\xi)} \right) \right) / (2 \cdot 96485); \]
\[ \text{ohm loss}(\xi) = \text{current}(\xi) \cdot \text{resist}(\xi); \]
\[ \text{act loss c}(\xi) = \left( 8.314 \cdot 2 \cdot (273 + Ts(\xi)) \cdot \log_e \left( \frac{\text{current dens}}{\text{ex curr cathode}} \right) / (96485) ; \]
\[ \text{act loss a}(\xi) = \left( 8.314 \cdot (273 + Ts(\xi)) \cdot \text{current dens} / (96485 \cdot \text{ex curr anode}) ; \]
\[ \text{act loss}(\xi) = \text{act loss c}(\xi) + \text{act loss a}(\xi); \]
\[ \text{current conc loss c}(\xi) = \left( 4 \cdot 96485 \cdot (\text{molf}_o2(\xi) \cdot 1) \cdot \text{diff eff o2 m}(\xi) / (1 - \text{molf}_o2(\xi)) \cdot r \cdot (ts(\xi) + 273) \cdot 1_{\text{cathode}}; \]
\[ \text{current conc loss a}(\xi) = \left( 2 \cdot 96485 \cdot (\text{molf}_2_{\text{h2}}(\xi) \cdot 1) \cdot \text{diff eff h2 m}(\xi) / (r \cdot (ts(\xi) + 273) \cdot 1_{\text{anode}}) ; \]

// heat of reaction;
\[ \text{Qsource shift}(\xi) = ((-1) \cdot (Ts(\xi) + 273.15) \cdot \text{stotal shift}(\xi) \cdot z_{\text{shift}}(\xi) \cdot n2; \]
\[ \text{Qsource}(\xi) = ((-1) \cdot (Ts(\xi) + 273.15) \cdot \text{stotal}(\xi) \cdot z_{\text{h2}}(\xi) \cdot n2) + \text{Qsource shift}(\xi); \]

endfor

End
Main iteration loop with water-shift and CO oxidation reaction model:

\[
\begin{align*}
mol_{h2\_in} &= 0.499*mol_{f2\_in} \\
mol_{co2(0)} &= 0.001*mol_{f2\_in} \\
zh2o(0) &= zh2(0) + 0.001*mol_{f2\_in} \\
z2h2o(0) &= 0.001*mol_{f2\_in} + zh2(0) \\
mol_{co\_in} &= molf_{co\_in}*mol_{f2\_in} \\
\end{align*}
\]

for xi in x.interior + x.endnode do

// Calling specific heat, density,
\[
\begin{align*}
call (hydrogen.v\_cp(xi)) &= pcp\_mol\_vap(Tf(xi),p,hydrogen.y) \text{hydrogenlist;} \\
call (hydrogen.rho(xi)) &= pdens\_mol\_vap(Tf(xi),p,hydrogen.y) \text{hydrogenlist;} \\
call (oxygen.rho(xi)) &= pdens\_mol\_vap(Ta(xi),p,oxygen.y) \text{oxygenlist;} \\
call (oxygen.v\_cp(xi)) &= pcp\_mol\_vap(Ta(xi),p,oxygen.y) \text{oxygenlist;} \\
call (carbonmonoxide.v\_cp(xi)) &= pcp\_mol\_vap(Tf(xi),p,carbonmonoxide.y) \text{carbonmonoxidelist;} \\
call (carbonmonoxide.rho(xi)) &= pdens\_mol\_vap(Tf(xi),p,carbonmonoxide.y) \text{carbonmonoxidelist;} \\
call (carbondioxide.v\_cp(xi)) &= pcp\_mol\_vap(Tf(xi),p,carbondioxide.y) \text{carbondioxidelist;} \\
call (carbondioxide.rho(xi)) &= pdens\_mol\_vap(Tf(xi),p,carbondioxide.y) \text{carbondioxidelist;} \\
call (water.v\_cp(xi)) &= pcp\_mol\_vap(Tf(xi),p,water.y) \text{waterlist;} \\
call (water.rho(xi)) &= pdens\_mol\_vap(Tf(xi),p,water.y) \text{waterlist;} \\
\end{align*}
\]

\[
\begin{align*}
rho\_mix(xi) &= hydrogen.rho(xi)*molf2\_h2(xi) + water.rho(xi)*molf2\_h2o(xi) + \\
& carbonmonoxide.rho(xi)*molf1\_co(xi) + carbondioxide.rho(xi)*molf1\_co2(xi);
\end{align*}
\]
\[ v_{\text{cp mix}}(x_i) = \text{hydrogen}.v_{\text{cp}}(x_i) \times \text{molf}_2.h_2(x_i) + \]
\[ \text{water}.v_{\text{cp}}(x_i) \times \text{molf}_2.h_2o(x_i) + \text{carbon monoxide}.v_{\text{cp}}(x_i) \times \text{molf}_1.co(x_i) + \]
\[ \text{carbon dioxide}.v_{\text{cp}}(x_i) \times \text{molf}_1.co_2(x_i); \]

\[ k_{\text{solid}}(x_i) = 5.50072 + 1.65535e-3 \times T_s(x_i); \]

\[ (\text{area}_{\text{conv}}.h_2^*h_f(x_i)) \times (T_s(x_i) - T_f(x_i)) = \]
\[ ((\text{rho}_{\text{mix}}(x_i) \times v_{\text{cp mix}}(x_i) \times u_f^2) \times (T_f(x_i).d/dx)); \]
\[ (\text{area}_{\text{conv}}.o_2^*h_a(x_i)) \times (T_s(x_i) - T_a(x_i)) = \]
\[ ((\text{rho}_{\text{mix}}(x_i) \times v_{\text{cp mix}}(x_i) \times u_o_2) \times (T_a(x_i).d/dx)); \]

\[ \text{mol wt avg } a(x_i) = (2 \times \text{molf}_2.h_2(x_i) + 18 \times \text{molf}_2.h_2o(x_i) + 44 \times \text{molf}_1.co(x_i) + 28 \times \text{molf}_1.co_2(x_i))/((\text{molf}_1.co(x_i) + \text{molf}_1.co_2(x_i) + \text{molf}_2.h_2(x_i) + \text{molf}_2.h_2o(x_i)); \]
\[ \text{mol wt avg } c(x_i) = (32 \times \text{molf}_o_2(x_i) + 28 \times \text{molf}_n_2(x_i)); \]
\[ \alpha_{h_2}(x_i) = 1 - \sqrt{2/\text{mol wt avg } a(x_i)}; \]
\[ \alpha_{h_2o}(x_i) = 1 - \sqrt{18/\text{mol wt avg } a(x_i)}; \]
\[ \alpha_{co_2}(x_i) = 1 - \sqrt{44/\text{mol wt avg } a(x_i)}; \]
\[ \alpha_{co}(x_i) = 1 - \sqrt{28/\text{mol wt avg } a(x_i)}; \]
\[ \alpha_{o_2}(x_i) = 1 - \sqrt{32/\text{mol wt avg } c(x_i)}; \]
\[ \alpha_{n_2}(x_i) = 1 - \sqrt{28/\text{mol wt avg } c(x_i)}; \]

\[ T_{n_{h_2.h_2o}}(x_i) = T_s(x_i)/\sqrt{\text{le jones pot } h_2 \times \text{le jones pot } h_2o}; \]
\[ T_{n_{h_2.co}}(x_i) = T_s(x_i)/\sqrt{\text{le jones pot } h_2 \times \text{le jones pot } co}; \]
\[ T_{n_{h_2.co_2}}(x_i) = T_s(x_i)/\sqrt{\text{le jones pot } h_2 \times \text{le jones pot } co_2}; \]
\[ T_{n_{co.co_2}}(x_i) = T_s(x_i)/\sqrt{\text{le jones pot } co \times \text{le jones pot } co_2}; \]
\[ T_{n_{co.h_2o}}(x_i) = T_s(x_i)/\sqrt{\text{le jones pot } co \times \text{le jones pot } h_2o}; \]
\[ T_{n_{co_2.h_2o}}(x_i) = T_s(x_i)/\sqrt{\text{le jones pot } co_2 \times \text{le jones pot } h_2o}); \]
\[ T_{n_{o_2.n_2}}(x_i) = T_s(x_i)/\sqrt{\text{le jones pot } o_2 \times \text{le jones pot } n_2}; \]
\[ \text{sigma}_d\text{-h2-h2o(xi)} = \left( \frac{a}{\text{sigmd}(T_n\text{-h2-h2o(xi)} \cdot b_{\text{sigma}})} + (c_{\text{sigma}}/\exp(d_{\text{sigma}} \cdot T_n\text{-h2-h2o(xi)})) + (e_{\text{sigma}}/\exp(f_{\text{sigma}} \cdot T_n\text{-h2-h2o(xi)})) + (g_{\text{sigma}}/\exp(h_{\text{sigma}} \cdot T_n\text{-h2-h2o(xi)})) \right); \]

\[ \text{sigma}_d\text{-h2-co(xi)} = \left( \frac{a}{\text{sigmd}(T_n\text{-h2-co(xi)} \cdot b_{\text{sigma}})} + (c_{\text{sigma}}/\exp(d_{\text{sigma}} \cdot T_n\text{-h2-co(xi)})) + (e_{\text{sigma}}/\exp(f_{\text{sigma}} \cdot T_n\text{-h2-co(xi)})) + (g_{\text{sigma}}/\exp(h_{\text{sigma}} \cdot T_n\text{-h2-co(xi)})) \right); \]

\[ \text{sigma}_d\text{-h2-co2(xi)} = \left( \frac{a}{\text{sigmd}(T_n\text{-h2-co2(xi)} \cdot b_{\text{sigma}})} + (c_{\text{sigma}}/\exp(d_{\text{sigma}} \cdot T_n\text{-h2-co2(xi)})) + (e_{\text{sigma}}/\exp(f_{\text{sigma}} \cdot T_n\text{-h2-co2(xi)})) + (g_{\text{sigma}}/\exp(h_{\text{sigma}} \cdot T_n\text{-h2-co2(xi)})) \right); \]

\[ \text{sigma}_d\text{-co-h2o(xi)} = \left( \frac{a}{\text{sigmd}(T_n\text{-co-h2o(xi)} \cdot b_{\text{sigma}})} + (c_{\text{sigma}}/\exp(d_{\text{sigma}} \cdot T_n\text{-co-h2o(xi)})) + (e_{\text{sigma}}/\exp(f_{\text{sigma}} \cdot T_n\text{-co-h2o(xi)})) + (g_{\text{sigma}}/\exp(h_{\text{sigma}} \cdot T_n\text{-co-h2o(xi)})) \right); \]

\[ \text{sigma}_d\text{-co2-h2o(xi)} = \left( \frac{a}{\text{sigmd}(T_n\text{-co2-h2o(xi)} \cdot b_{\text{sigma}})} + (c_{\text{sigma}}/\exp(d_{\text{sigma}} \cdot T_n\text{-co2-h2o(xi)})) + (e_{\text{sigma}}/\exp(f_{\text{sigma}} \cdot T_n\text{-co2-h2o(xi)})) + (g_{\text{sigma}}/\exp(h_{\text{sigma}} \cdot T_n\text{-co2-h2o(xi)})) \right); \]

\[ \text{sigma}_d\text{-co2-co(xi)} = \left( \frac{a}{\text{sigmd}(T_n\text{-co2-co(xi)} \cdot b_{\text{sigma}})} + (c_{\text{sigma}}/\exp(d_{\text{sigma}} \cdot T_n\text{-co2-co(xi)})) + (e_{\text{sigma}}/\exp(f_{\text{sigma}} \cdot T_n\text{-co2-co(xi)})) + (g_{\text{sigma}}/\exp(h_{\text{sigma}} \cdot T_n\text{-co2-co(xi)})) \right); \]

\[ \text{sigma}_d\text{-o2-n2(xi)} = \left( \frac{a}{\text{sigmd}(T_n\text{-o2-n2(xi)} \cdot b_{\text{sigma}})} + (c_{\text{sigma}}/\exp(d_{\text{sigma}} \cdot T_n\text{-o2-n2(xi)})) + (e_{\text{sigma}}/\exp(f_{\text{sigma}} \cdot T_n\text{-o2-n2(xi)})) + (g_{\text{sigma}}/\exp(h_{\text{sigma}} \cdot T_n\text{-o2-n2(xi)})) \right); \]

\[ \text{diff}_{\text{-h2-h2o(xi)}} = \frac{0.001858 \cdot \left( T_s(xi)^{1.5} \right) \cdot \left( \frac{20}{2 \cdot 32} \right)^{0.5}}{1 \cdot \left( \left( \frac{\text{dia-h2+dia-h2o}}{2} \right)^2 \right) \cdot \text{sigma}_d\text{-h2-h2o(xi)}}; \]

\[ \text{diff}_{\text{-o2-n2(xi)}} = \frac{0.001858 \cdot \left( T_s(xi)^{1.5} \right) \cdot \left( \frac{60}{28 \cdot 32} \right)^{0.5}}{1 \cdot \left( \left( \frac{\text{dia-o2+dia-n2}}{2} \right)^2 \right) \cdot \text{sigma}_d\text{-o2-n2(xi)}}; \]

\[ \text{diff}_{\text{-co-h2o(xi)}} = \frac{0.001858 \cdot \left( T_s(xi)^{1.5} \right) \cdot \left( \frac{46}{28 \cdot 18} \right)^{0.5}}{1 \cdot \left( \left( \frac{\text{dia-co+dia-h2o}}{2} \right)^2 \right) \cdot \text{sigma}_d\text{-co-h2o(xi)}}; \]

\[ \text{diff}_{\text{-co2-h2o(xi)}} = \frac{0.001858 \cdot \left( T_s(xi)^{1.5} \right) \cdot \left( \frac{62}{44 \cdot 18} \right)^{0.5}}{1 \cdot \left( \left( \frac{\text{dia-co2+dia-h2o}}{2} \right)^2 \right) \cdot \text{sigma}_d\text{-co2-h2o(xi)}}; \]
\[
\text{diff\_co\_co2}(\xi) = (0.001858*(T_s(\xi)^{1.5})*(72/(28*44))^{0.5})/(1*(((\text{dia\_co}+\text{dia\_co2})/2)^2)\times\text{sigma\_d\_co\_co2}(\xi));
\]
\[
\text{diff\_h2\_co}(\xi) = (0.001858*(T_s(\xi)^{1.5})*(20/(2*28))^{0.5})/(1*(((\text{dia\_h2}+\text{dia\_co})/2)^2)\times\text{sigma\_d\_h2\_co}(\xi));
\]
\[
\text{diff\_h2\_co2}(\xi) = (0.001858*(T_s(\xi)^{1.5})*(46/(2*46))^{0.5})/(1*(((\text{dia\_h2}+\text{dia\_co2})/2)^2)\times\text{sigma\_d\_h2\_co2}(\xi));
\]
\[
\text{diff\_h2\_m}(\xi) = (1-\text{mol}_f(\text{h}_2(\xi)))/(\text{mol}_f(\text{h}_2(\xi))/\text{diff\_h2\_h}_2(\xi));
\]
\[
\text{diff\_eff\_h2\_m}(\xi) = (\text{porosity}\times\text{diff\_h2\_m}(\xi))/((1-\text{mol}_f(\text{h}_2(\xi))\times\text{alpha\_h}_2(\xi))\times\text{torosity});
\]
\[
\text{diff\_o2\_m}(\xi) = (1-\text{mol}_f(\text{o}_2(\xi)))/(\text{mol}_f(\text{o}_2(\xi))/\text{mol}_f(\text{dia\_h2}\_\xi));
\]
\[
\text{diff\_eff\_o2\_m}(\xi) = (\text{porosity}\times\text{diff\_o2\_m}(\xi))/((1-\text{mol}_f(\text{o}_2(\xi))\times\text{alpha\_o}_2(\xi))\times\text{torosity});
\]
\[
\text{h\_a}(\xi) = 3.66\times\text{K\_solid}(\xi)/\text{equiv\_dia\_o}_2; // \text{KJ/m}_2\text{.K.hr};
\]
\[
\text{h\_f}(\xi) = 3.66\times\text{K\_solid}(\xi)/\text{equiv\_dia\_h}_2; // \text{KJ/m}_2\text{.K.hr};
\]
end for

for \( \xi \) in \( x.\text{interior} \)

// Calling dynamic viscosity, entropy, enthalpy, gibbs-free energy;

call (hydrogen.h(\xi)) = \text{penth\_mol}(\text{tf}(\xi),p,\text{hydrogen.y}) \text{hydrogenlist};

call (hydrogen.s(\xi)) = \text{pentr\_mol\_vap}(\text{tf}(\xi),p,\text{hydrogen.y}) \text{hydrogenlist};

call (hydrogen.gibb(\xi)) = \text{pgibbs\_mol\_vap}(\text{tf}(\xi),p,\text{hydrogen.y}) \text{hydrogenlist};

call (water.h(\xi)) = \text{penth\_mol\_vap}(\text{tf}(\xi),p,\text{water.y}) \text{waterlist};

call (water.s(\xi)) = \text{pentr\_mol\_vap}(\text{tf}(\xi),p,\text{water.y}) \text{waterlist};

call (water.gibb(\xi)) = \text{pgibbs\_mol\_vap}(\text{tf}(\xi),p,\text{water.y}) \text{waterlist};
call (carbonmonoxide.h(xi)) = penth_mol_vap(tf(xi),p,carbonmonoxide.y) carbonmonoxidelist;
call (carbonmonoxide.s(xi)) = pentr_mol_vap(tf(xi),p,carbonmonoxide.y) carbonmonoxidelist;
call (carbonmonoxide.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,carbonmonoxide.y) carbonmonoxidelist;

call (carbondioxide.h(xi)) = penth_mol_vap(tf(xi),p,carbondioxide.y) carbondioxidelist;
call (carbondioxide.s(xi)) = pentr_mol_vap(tf(xi),p,carbondioxide.y) carbondioxidelist;
call (carbondioxide.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,carbondioxide.y) carbondioxidelist;

call (oxygen.h(xi)) = penth_mol(ta(xi),p,oxygen.y) oxygenlist;
call (oxygen.s(xi)) = pentr_mol_vap(ta(xi),p,oxygen.y) oxygenlist;
call (oxygen.gibb(xi)) = pgibbs_mol_vap(ta(xi),p,oxygen.y) oxygenlist;

//governing equations of heat transfer;
(volume-solid*ksolid(xi))*(Ts(xi).d2dx2) = (((area_conv_o2*h_a(xi))*(Ts(xi)-Ta(xi)))+((area_conv_h2*h_f(xi))*(Ts(xi)-Tf(xi)))) - (Qsource(xi)/x(l));

//delta_enthalpy_total:
htotal(xi) = water.h(xi) - hydrogen.h(xi) - 0.5*oxygen.h(xi);

//gibbs_free_energy_total:
gtotal(xi) = water.g(xi) - hydrogen.g(xi) - 0.5*oxygen.g(xi);

//delta_gibbs_table:
gt(xi) = water.gibb(xi) - hydrogen.gibb(xi) - 0.5*oxygen.gibb(xi);
//delta_enthropy_total:
stotal(xi) = water.s(xi) - hydrogen.s(xi) - 0.5*oxygen.s(xi);

//delta_enthalpy_total_shift:
htotal_shift(xi) = carbondioxide.h(xi) - water.h(xi) + hydrogen.h(xi) - carbonmonoxide.h(xi);

//gibbs_free_energy_total_shift:
gtotal_shift(xi) = carbondioxide.gibb(xi) - water.gibb(xi) + hydrogen.gibb(xi) - carbonmonoxide.gibb(xi);

//delta_gibbs_shift:
gt_shift(xi) = carbondioxide.g(xi) -water.g(xi) + hydrogen.g(xi) - carbonmonoxide.g(xi);

//delta_enthropy_total_shift:
stotal_shift(xi) = carbondioxide.s(xi) - water.s(xi) + hydrogen.s(xi) - carbonmonoxide.s(xi);

//delta_gibbs_table:
gtotal_co(xi) = carbondioxide.gibb(xi) - carbonmonoxide.gibb(xi) - 0.5*oxygen.gibb(xi);

//gibbs_each_component:
hydrogen.g(xi) = hydrogen.h(xi) - (((Tf(xi)+273.15)*(hydrogen.s(xi)))/1E06);
oxygen.g(xi) = oxygen.h(xi) - (((Tf(xi)+273.15)*(oxygen.s(xi)))/1E06);
water.g(xi) = water.h(xi) - (((TF(xi)+273.15)*(water.s(xi)))/1E06);
carbonmonoxide.g(xi) = carbonmonoxide.h(xi) - (((TF(xi)+273.15)*(carbonmonoxide.s(xi)))/1E06);
carbondioxide.g(xi) = carbondioxide.h(xi) - 
(((TF(xi)+273.15)*(carbondioxide.s(xi)))/1E06);

// resistance ;

ASR(xi) = (1.253e-5 * exp(11156 / (Ts(xi)+273))) + 0.02396 + (9.364e-5 * Ts(xi)) - 
(1.384e-8 * (Ts(xi)^2));
resist(xi) = ASR(xi)/(area_cell*10000);

// current;
zh2(xi) = 3.6*curn_h2(xi)/(2*96485);
zo2(xi) = 0.5*zh2(xi);
zh2o(xi) = zh2(xi) + z_ih2o(xi-1);
z2h2o(xi) = zh2(xi) + z2h2o(xi-1);
yco(xi) = 3.6*curn_co(xi)/(2*96485);
yo2(xi) = 0.5*yco(xi);
yco2(xi) = yco(xi);

// mole fraction:
h2_moles_left(xi) = h2_moles_left1(xi-1) - zh2(xi);
h2_moles_left2(xi) = h2_moles_left1(xi-1) - zh2(xi);
o2_moles_left(xi) = o2_moles_left1(xi-1) - zo2(xi) - yo2(xi);

molf_h2(xi) = h2_moles_left2(xi)/(h2_moles_left2(xi) + z2h2o(xi));
molf_h2o(xi) = z2h2o(xi)/(h2_moles_left2(xi) + z2h2o(xi));

// assuming air as the input to cathode;
molf_o2(xi) = (o2_moles_left(xi)/mol_air_in);
molf_n2(xi)=1-molf_o2(xi);
//ideal voltage:
idlvoltxi = ((-1)*gt(xi)*1000000)/(2*96485)+((8.314*(ts(xi)+273.15))/(2*96485))*loge((molf1_h2(xi)*molf_o2(xi)*0.5)/molf_h2o(xi)*P^0.5)+((8.314*(ts(xi)+273.15))/(4*96485))*loge(P);
idlvolt1(xi) = ((-1)*gt(xi)*1000000)/(2*96485);

mol_co2(xi) = mol2_co2(xi-1);
mol_co_eq(xi) = mol2_co_eq(xi-1);
molf1_h2(xi) = h2_moles_left(xi)/mol_f2_in;
molf1_h2o(xi) = zh2o(xi)/mol_f2_in;
molf_co(xi) = mol_co_eq(xi)/mol_f2_in;
molf_co2(xi) = mol_co2(xi)/mol_f2_in;

// equilibrium constant calculation;
equi_const_shift(xi) = exp((((-1)*gt_shift(xi)*1000000)/(R*(Ts(xi)+273.15)));
equi_const(xi) = exp((4276/(Ts(xi) + 273.15))-3.961);
equi_const_shift(xi)*((molf_co(xi)*100000)-z(xi))*((molf1_h2o(xi)*100000)-z(xi))= ((molf1_h2(xi)*100000)+z(xi))*((molf_co2(xi)*100000)+z(xi));

if (z(xi) > 0.0005) and (z(xi) < 1E05) then
z_shift(xi) = (z(xi)*(h2_moles_left(xi) + zh2o(xi)+ mol_co_eq(xi) + mol_co2(xi)))/1E05;
else
z_shift(xi) = 0.25*zh2(xi);
endif

zlh2o(xi) = zh2o(xi) - z_shift(xi);
h2_moles_left1(xi) = h2_moles_left(xi) + z_shift(xi);
mol1_co2(xi) = mol_co2(xi) + z_shift(xi);
mol1_co_eq(xi) = mol_co_eq(xi) - z_shift(xi);
molf2_h2(xi) = h2_moles_left1(xi)/mol_f2_in;
molf2_h2o(xi) = z1h2o(xi)/mol_f2_in;
molf1_co(xi) = mol1_co_eq(xi)/mol_f2_in;
molf1_co2(xi) = mol1_co2(xi)/mol_f2_in;
mol2_co2(xi) = mol1_co2(xi) + yco2(xi);
mol2_co_eq(xi) = mol1_co_eq(xi) - yco(xi);
molf2_co(xi) = mol2_co_eq(xi)/mol_f2_in;
molf2_co2(xi) = mol2_co2(xi)/mol_f2_in;

current_conc_loss_c(xi) = (4*96485*(molf_o2(xi)*1)*diff_eff_o2_m(xi))/((1-molf_o2(xi))*r*(ts(xi)+273)*l_cathode);
current_conc_loss_a(xi) = ((2*96485*(molf2_h2(xi)*1)*diff_eff_h2_m(xi))/(r*(ts(xi)+273)*l_anode));

//idealvoltage:
volt_idl_act(xi) = (((-1)*gt(xi)*1000000)/(2*96485))+((8.314*(ts(xi)+273.15))/(2*96485))*loge((molf2_h2(xi)*molf_o2(xi)^0.5)/molf2_h2o(xi))*P^0.5+((8.314*(ts(xi)+273.15))/(4*96485))*loge(P_t);
volt_co(xi) = (((-1)*gtotal_co(xi)*1000000)+(8.314*(ts(xi)+273.15)))*loge((molf2_co(xi)*molf_o2(xi)^0.5)/molf2_co2(xi)))/(2*96485);
current_dens = current (xi)/(area_cell*10000);

r_curr_cs(xi) = (r*ts(xi)*loge(1-(current_dens/current_conc_loss_c(xi))))/(4*96485);
r_curr_as(xi) = (r*ts(xi)*loge(1-(curr_dens/current_conc_loss_a(xi))))/(2*96485)-(r*ts(xi)*loge(1+(molf2_h2(xi)*current_dens)/(molf2_h2o(xi)*current_conc_loss_a(xi))))/(2*96485);
\[ \text{curr}_{\text{h2}}(\xi) \times \text{resist}_{\text{h2-actl}}(\xi) = \text{volt}_{\text{idl-act}}(\xi) - \text{net}_{\text{op-volt}}(\xi) - (\text{current}(\xi) \times \text{resist}(\xi)); \]
\[ \text{volt}_{\text{idl-act}}(\xi) - \text{volt}_{\text{co}}(\xi) = (\text{curr}_{\text{h2}}(\xi) - \text{curr}_{\text{co}}(\xi)) \times \text{resist}_{\text{h2-actl}}(\xi); \]
\[ \text{current}(\xi) = \text{curr}_{\text{co}}(\xi) + \text{curr}_{\text{h2}}(\xi); \]

\[ \text{volt}_{\text{conc-loss}}(\xi) = \text{volt}_{\text{idl-act}}(\xi) - \text{volt}_{\text{act}}(\xi) - \text{act-loss}(\xi); \]
\[ \text{act-loss}(\xi) = \text{curr}_{\text{h2}}(\xi) \times \text{resist}_{\text{h2-actl}}(\xi); \]

\[ \text{resist}_{\text{h2-actl}}(\xi) = (8.314 \times (\text{T}(\xi) + 273) \times (96485 \times \text{ex}_\text{curr} \times \text{area-cell} \times 10000) + (8.314 \times (\text{T}(\xi) + 273) \times (96485 \times \text{ex}_\text{curr-c} \times \text{area-cell} \times 10000); \]
\[ \text{resist}_{\text{co-actl}}(\xi) = (8.314 \times (\text{T}(\xi) + 273) \times (96485 \times \text{ex}_\text{curr-c} \times \text{area-cell} \times 10000); \]

\[ \text{volt}_{\text{act}}(\xi) = \text{volt}_{\text{idl-act}}(\xi) - \text{curr}_{\text{h2}}(\xi) \times \text{resist}_{\text{h2-actl}}(\xi); \]
\[ \text{r} \_ \text{curr}_{\text{cs}}(\xi) + \text{r} \_ \text{curr}_{\text{as}}(\xi); \]
\[ \text{pow}_\text{dens}(\xi) = \text{net}_{\text{op-volt}}(\xi) \times \text{current}_\text{dens}; \]
\[ \text{ohm}_\text{loss}(\xi) = \text{current}(\xi) \times \text{resist}(\xi); \]

// heat of reaction;
\[ \text{Qsource}_{\text{shift}}(\xi) = (-1)(\text{T}(\xi) + 273.15) \times \text{stotal}_{\text{shift}}(\xi) \times \text{zh}_{\text{shift}}(\xi) \times n_{2}; \]
\[ \text{Qsource}_{\text{h2}}(\xi) = (-1)(273.15 + \text{T}(\xi)) \times \text{stotal}(\xi) \times \text{zh}_{\text{h2}}(\xi) \times n_{2} + \text{Qsource}_{\text{shift}}(\xi) + \text{Qsource}_{\text{co}}(\xi); \]
\[ \text{Qsource}_{\text{co}}(\xi) = (-1)(273.15 + \text{T}(\xi)) \times \text{stotal}_{\text{co}}(\xi) \times \text{y}_{\text{co}}(\xi) \times n_{2}; \]

\[ \text{rate}_{\text{co}}(\xi) = 3.528 \times 10^{10} \times (\exp(-33092/(8.314 \times (\text{T}(\xi) + 273.15)))) \times (\text{molfl}_{\text{co}}(\xi)^{-0.1}) \times (\text{molf}_{\text{o2}}(\xi)^{0.5}) \times \text{vol}_\text{solid}(\text{l}/\text{n}); \]
\[ \text{curr}_{\text{co-r}}(\xi) = (\text{rate}_{\text{co}}(\xi) \times 2 \times 96485); \]

endfor

End
**APPENDIX I: Variable Assignment for dynamic state models:**

1 as realparameter (0.1016);
n as integerparameter (24);
k_s as realvariable(fixed,7.3); // KJ/hr.m.k
area_air_cs_channel as realvariable;
area_fuel_cs_channel as realvariable;
x as lengthdomain (highestorderderivative:2,length:1,
 spacingpreference:l/n, discretizationmethod:"BFD2");
Tin as temperature(fixed,850);
T_stack_in as temperature(fixed,750);
p as pressure(fixed,1.0);
Pt as pressure(fixed,1.0);
uh2 as velocity(fixed,0.175); // Volumetric flow: m3/hr;
uo2 as velocity(fixed,2.625); // Volumetric flow: m3/hr;
mol_h2_in as realvariable ;//Kmol/hr;
mol_n2_in as realvariable;
mol_f_in as realvariable;
mol_o2_in as realvariable ;
mol_air_in as realvariable ;
mol_co2 as realvariable(lower:0.000000000001);
mol_co_eq as realvariable(lower:0.000000000001);
mol1_co2 as realvariable(lower:0.000000000001);
mol1_co_eq as realvariable(lower:0.000000000001);
molf_co2([0:n]) as mole_fraction;
molf_co([0:n]) as mole_fraction;
molf1_co2 as mole_fraction;
molf1_co as mole_fraction;
h_a,h_f as realvariable ; // KJ/m2.hr.k;
Ts
of temperature;

Tf
of temperature;

Ta
of temperature;

v viscosity

v cp([0:n])

v cp mix([0:n])

v cp mix 1([1:n])

rhomv

rho([0:n])

rho mix([0:n])

re o2

re h2

pr

y(component list)

molf o2

molf h2

molf h2o

molf n2

molf o2

of mole fraction;
molf h2

of mole fraction;
molf h2o

of mole fraction;
molf co

of mole fraction;

as distribution 1D(xdomain is x, highest order derivative: 2)
as distribution 1D(xdomain is x, highest order derivative: 1)
as distribution 1D(xdomain is x, highest order derivative: 1)
as visc_vap; // mPa-s;
as cp mol; // KJ/Kmol/k;
as cp mol;
as cp mol;
as cp mol;
as dens_mass; // Kg/m3;
as dens mol; // Kmol/m3

as dens mol; // Kmol/m3

as reynolds no;
as reynolds no;
as real variable(fixed, 0.7);
as mole fraction(fixed, 1.0);
as mole fraction;
as mole fraction;
as mole fraction;
as mole fraction; // bar

as mole fraction;
as mole fraction;
as distribution 1D(xdomain is x, highest order derivative: 1)
as distribution 1D(xdomain is x, highest order derivative: 1)
as distribution 1D(xdomain is x, highest order derivative: 1)
as distribution 1D(xdomain is x, highest order derivative: 1)
molfco2 

of mole_fraction;
molf1_h2([0]) 
as mole_fraction;
molf1_h2o([0]) 
as mole_fraction;
molf2_h2([0]) 
as mole_fraction;
molf2_h2o([0]) 
as mole_fraction;
molf2_h2o([0]) 
as mole_fraction;
molfn2([0:n]) 
as mole_fraction;
net_molf_o2([0:n]) 
as mole_fraction;
net_molf_h2([0:n]) 
as mole_fraction;
net_molf_h2o([0:n]) 
as mole_fraction;
net_molf2_h2 
as mole_fraction;
net_molf2_h2o 
as mole_fraction;
net_molf1_h2([0]) 
as mole_fraction;
net_molf1_h2o([0]) 
as mole_fraction;
net_molf_n2([0:n]) 
as mole_fraction;
z([0:n]) 
as realvariable(upper:700,lower:0.0,value:100);
z_shift([0:n]) 
as realvariable(upper:0.5,lower:0.0,value:0.000005);
z_shift1([0:n]) 
as realvariable(upper:0.5,value:0.000000005);
mol_co_in 
as realvariable;
molf_co_in 
as realvariable;
gtotal([0:n]) 
as enth_mol; // MJ/mol;
gt([0:n]) 
as enth_mol; // MJ/mol;
htotal([0:n]) 
as enth_mol; // MJ/mol 
g([0:n]) 
as enth_mol; // MJ/mol 
h([0:n]) 
as enth_mol; // MJ/mol 
gibb([0:n]) 
as gibbs_mol_vap; // MJ/mol; 
stotal_shift([0:n]) 
as entr_mol; 
htotal_shift([0:n]) 
as enth_mol; 
gt_shift([0:n]) 
as enth_mol; 
gtotal_shift([0:n]) 
as enth_mol;
s([0:n]) as entr_mol; // KJ/Kmol.K;
stotal([0:n]) as entr_mol; // KJ/Kmol.K;
id1volt([0]) as voltage;
netvolt_act as voltage;
netvolt as voltage;
volt_act([0:n]) as voltage;
Qsource([0:n]) as realvariable(value:100,lower:0.0); // KJ/Kmol;
Qsource_shift([0:n]) as realvariable(value:0.5,lower:0.0); // KJ/Kmol;
Qsource_total([0:n]) as realvariable(value:0.5,lower:0.0); // KJ/Kmol;
Vol_solid1 as realvariable(fixed,0.0000048996); // m3,
area_conv1_h2 as realvariable(fixed,0.008567); // m2;
area_conv1_o2 as realvariable(fixed,0.007804); // m2;
equiv_dia_o2 as realvariable ; // m;
equiv_dia_h2 as realvariable ; // m;
equi_const([0:n]) as realvariable (lower:0.0);
equi_const1([(1:n)] as realvariable (lower:0.0);
equi_const_shift([0:n]) as realvariable (lower:0.0);
R as realvariable(fixed,8.314) ;// KJ/Kmol.K;
current([0]) as realvariable(lower:0.0); // amperes;
current_act([0:n]) as realvariable(lower:0.0); // amperes;
net_current as realvariable(lower:0.0); // amperes;
net_current_dens as realvariable(lower:0.0);
net_current_dens_chan as realvariable(lower:0.0);
current_conc_loss_a([0:n]) as realvariable; // amperes;
current_conc_loss_c([0:n]) as realvariable; // amperes;
resist([0:n]) as realvariable(lower:0.0) ; // ohm;
ASR([0:n]) as realvariable (lower:0.0); //ohm-cm2;
temp_asr as realvariable ;
resist_temp as realvariable;
zh2 as realvariable; // Kmol/hr;
zo2 as realvariable;
zh2o as realvariable;
rh2([0:n]) as realvariable; // Kmol/hr;
ro2([0:n]) as realvariable;
rh2o([0:n]) as realvariable(lower:0.0);
trans_current([0:n]) as realvariable(lower:0.0);
trans_volt([0:n]) as realvariable(lower:0.0);
trans_volt1 as realvariable;
volt_conc_loss_c([0:n]) as realvariable;
volt_conc_loss_a([0:n]) as realvariable;
net_volt_cell([0:n]) as realvariable(lower:0.0);
net_h2_con as realvariable(lower:0.0);
net_h2_out as realvariable(lower:0.0);
h2_moles_present([0:n]) as realvariable(lower:0.0);
h2_moles_present1 as realvariable;
o2_moles_present([0:n]) as realvariable(lower:0.0);
h2o_moles_present([0:n]) as realvariable(lower:0.0);
h2o_moles_present1 as realvariable;
co2_moles_present([0:n]) as realvariable(lower:0.0);
co_moles_present([0:n]) as realvariable(lower:0.0);
h2_moles_reacn([0:n]) as realvariable(value:0.000005,lower:0.0);
h2_moles_reacn1([0]) as realvariable(value:0.000005);
o2_moles_reacn([0:n]) as realvariable(value:0.000005,lower:0.0);
h2o_moles_reacn([0:n]) as realvariable(value:0.000005,lower:0.0);
h2o_moles_reacn1([0]) as realvariable(value:0.000005);
c02_moles_reacn([0:n]) as realvariable(value:0.000005,lower:0.0);
c0_moles_reacn([0:n]) as realvariable(value:0.000005,lower:0.0);
mol_air_present([0:n]) as realvariable(lower:0.0);
k_solid([0:n]) as realvariable(lower:0.0);
current_dens as realvariable(lower:0.0, fixed, 0.5);
op_volt([0:n]) as voltage(value:0.7);
n1 as realvariable;
n2 as realvariable;
area_air_cs_channel1 as realvariable(fixed,0.000002393);
area_fuel_cs_channel1 as realvariable(fixed,0.000003589);
Vol_solid as realvariable; // m3,
area_conv_h2 as realvariable; // m2;
area_conv_o2 as realvariable; // m2;
area_cell as realvariable; // m2;
area_exposed as realvariable;
Ea as realvariable (fixed, 12384.98);
rho_solid as realvariable (fixed, 6600);
V_cp_solid as realvariable (fixed, 0.382);
net_fuel_util as realvariable;
net_fuel_util_co as realvariable;
pow_dens([0:n]) as realvariable;
net_pow_dens as realvariable;
net_pow_dens_chan as realvariable;
T_cell_avg as realvariable;
net_op_volt as realvariable;
net_co_con as realvariable;

n1 = 16; // no. of channels
n2 = 16; // no. of channels
area_cell = (0.005714*(0.1016/(n)));

//Kmol of fuel & oxygen entering in per hr;
mol_o2_in = (p*100*uo2*0.21)/(n1*R*(Tin+273.15));
mol_air_in = (p*100*uo2)/(n1*R*(Tin+273.15));
mol_f2_in = (p*100*uf2)/(n1*R*(Tin+273.15));
APPENDIX J: Main Programs for the dynamic models

Main Iteration loop for Hydrogen oxidation model in dynamic mode:

// initial condition of mass conservation;

molfh2(x.interior): initial;
molfh2o(x.interior): initial;

molfh2(0) = molf_h2;
molf02(0) = molf_o2;
molfh2o(0) = molf_h2o;
molfn2(0) = 1-molf02(0);

for xi in x.interior + x.endnode do

// Calling specific heat, density;

call (hydrogen.v_cp(xi)) = pcp_mol_vap(Tf(xi),p,hydrogen.y) hydrogenlist;
call (hydrogen.rho(xi)) = pdens_mol_vap(Tf(xi),p,hydrogen.y) hydrogenlist;

call (oxygen.rho(xi)) = pdens_mol_vap(Ta(xi),p,oxygen.y) oxygenlist;
call (oxygen.v_cp(xi)) = pcp_mol_vap(Ta(xi),p,oxygen.y) oxygenlist;

call (water.v_cp(xi)) = pcp_mol_vap(Tf(xi),p,water.y) waterlist;
call (water.rho(xi)) = pdens_mol_vap(Tf(xi),p,water.y) waterlist;

call (nitrogen.rho(xi)) = pdens_mol_vap(Ta(xi),p,nitrogen.y) nitrogenlist;
\[ \rho_{\text{mix}}(\xi) = \text{hydrogen.}\rho(\xi) \times \text{net}\_\text{molf}_h2(\xi) + \text{water.}\rho(\xi) \times \text{net}\_\text{molf}_h2o(\xi); \]

\[ v_{\text{cp}}_{\text{mix}}(\xi) = \text{hydrogen.}v_{\text{cp}}(\xi) \times \text{net}\_\text{molf}_h2(\xi) + \text{water.}v_{\text{cp}}(\xi) \times \text{net}\_\text{molf}_h2o(\xi); \]

// governing equations of heat transfer;

\[(\text{area}\_\text{conv}_h2\_h\_f) \times (T_s(\xi) - T_f(\xi)) + \text{vol}\_\text{solid} \times \rho_{\text{mix}}(\xi) \times v_{\text{cp}}_{\text{mix}}(\xi) \times (\$T_f(\xi)) =
\left( \rho_{\text{mix}}(\xi) \times v_{\text{cp}}_{\text{mix}}(\xi) \times u_{\text{h}2}(\xi) \right) \times (T_f(\xi). \text{d}x); \]

\[(\text{area}\_\text{conv}_o2\_h\_a) \times (T_s(\xi) - T_a(\xi)) + \text{vol}\_\text{solid} \times \rho_{\text{mix}}(\xi) \times v_{\text{cp}}_{\text{mix}}(\xi) \times (\$T_a(\xi)) =
\left( \text{oxygen.}\rho(\xi) \times \text{oxygen.}v_{\text{cp}}(\xi) \times u_{\text{o}2}(\xi) \right) \times (T_a(\xi). \text{d}x); \]

// hydrogen gas;

\[ \$\text{molfh}_2(\xi) = (-(u_{\text{h}2}/\text{area\_fuel\_cs\_channel}) \times (\text{molfh}_2(\xi). \text{d}x)) +
(r_{\text{h}2}(\xi)) \times ((r\times t_f(\xi))/(p \times 100 \times \text{vol}\_\text{solid})); \]

// steam;

\[ \$\text{molfh}_2o(\xi) = (-(u_{\text{h}2}/\text{area\_fuel\_cs\_channel}) \times (\text{molfh}_2o(\xi). \text{d}x)) +
(r_{\text{h}2o}(\xi)) \times ((r\times t_f(\xi))/(p \times 100 \times \text{vol}\_\text{solid})); \]

// oxygen gas;

\[ \$\text{molfo}_2(\xi) = (-(u_{\text{o}2}/\text{area\_air\_cs\_channel}) \times (\text{molfo}_2(\xi). \text{d}x)) +
(r_{\text{o}2}(\xi)) \times ((r\times t_a(\xi))/(p \times 100 \times \text{vol}\_\text{solid})); \]

// nitrogen;

\[ \text{molfn}_2(\xi) = 1 - \text{molfo}_2(\xi); \]

\[ k\_\text{solid}(\xi) = 5.50072 + 1.65535e-3 \times T_s(\xi); \]
for xi in x.interior do

// Calling dynamic viscosity, entropy, enthalpy, gibbs-free energy;

call (hydrogen.h(xi)) = penth_mol(tf(xi),p,hydrogen.y) hydrogenlist;
call (hydrogen.s(xi)) = pentr_mol_vap(tf(xi),p,hydrogen.y) hydrogenlist;
call (hydrogen.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,hydrogen.y) hydrogenlist;

call (oxygen.h(xi)) = penth_mol(tf(xi),p,oxygen.y) oxygenlist;
call (oxygen.s(xi)) = pentr_mol_vap(tf(xi),p,oxygen.y) oxygenlist;
call (oxygen.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,oxygen.y) oxygenlist;

call (water.h(xi)) = penth_mol_vap(tf(xi),p,water.y) waterlist;
call (water.s(xi)) = pentr_mol_vap(tf(xi),p,water.y) waterlist;
call (water.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,water.y) waterlist;

//governing equation of heat transfer;

(vol_solid*k_solid(xi))*(Ts(xi).d2dx2)- (vol_solid*rho_solid*v_cp_solid*(dTsvs(x))) = (((area_conv_o2*h_a)*(Ts(xi)-Ta(xi)))+((area_conv_h2*h_f)*(Ts(xi)-Tf(xi)))) - (Qsource(xi)/x(1));

//delta_enthalpy_total:
htotal(xi) = water.h(xi) - hydrogen.h(xi) - 0.5*oxygen.h(xi);

//gibbs_free_energy_total:
gtotal(xi) = water.g(xi) - hydrogen.g(xi) - 0.5*oxygen.g(xi);

//delta_gibbs_table:
\[
\Delta_{\text{entropy\_total}} = \text{stotal}(\xi) = \text{water.s}(\xi) - \text{hydrogen.s}(\xi) - 0.5\times\text{oxygen.s}(\xi);
\]

\[
\text{mol\_air\_present}(\xi) = \text{mol\_n2\_in} + \text{o2\_moles\_present}(\xi);
\]

if \((\text{h2\_moles\_present}(\xi-1) > \text{h2\_moles\_reacn}(\xi-1))\) then
\[
\text{h2\_moles\_present}(\xi) = \text{h2\_moles\_present}(\xi-1) - \text{h2\_moles\_reacn}(\xi);
\]
\[
\text{h2\_moles\_reacn}(\xi) = (\text{molfh2o}(\xi))\times\text{mol\_h2\_in};
\]
else
\[
\text{h2\_moles\_present}(\xi) = 0.000000001;
\]
\[
\text{h2\_moles\_reacn}(\xi) = 0.00000000001;
\]
endif

if \((\text{h2o\_moles\_present}(\xi-1) < (\text{mol\_f\_in}-(2\times0.000000001)-\text{h2o\_moles\_reacn}(\xi-1)))\) then
\[
\text{h2o\_moles\_present}(\xi) = \text{h2o\_moles\_present}(\xi-1) + \text{h2o\_moles\_reacn}(\xi);
\]
\[
\text{h2o\_moles\_reacn}(\xi) = \text{molfh2o}(\xi)\times\text{mol\_h2\_in};
\]
else
\[
\text{h2o\_moles\_present}(\xi) = \text{mol\_f\_in}-(2\times0.000000001);
\]
\[
\text{h2o\_moles\_reacn}(\xi) = 0.00000000001;
\]
endif

if \((\text{o2\_moles\_present}(\xi-1) > \text{o2\_moles\_reacn}(\xi-1))\) then
\[
\text{h2o\_moles\_present}(\xi) = \text{h2o\_moles\_present}(\xi-1) - \text{h2o\_moles\_reacn}(\xi);
\]
\[
\text{h2o\_moles\_reacn}(\xi) = (\text{molfh2o}(\xi))\times\text{mol\_h2\_in};
\]
else
\[
\text{h2o\_moles\_present}(\xi) = 0.000000001;
\]
\[
\text{h2o\_moles\_reacn}(\xi) = 0.00000000001;
\]
endif
\[ o_2 \text{ moles present}(xi) = o_2 \text{ moles present}(xi-1) - o_2 \text{ moles reacn}(xi); \]
\[ o_2 \text{ moles reacn}(xi) = (0.5 \times h_2 \text{ moles reacn}(xi)); \]

else

\[ o_2 \text{ moles present}(xi) = 0.000000001; \]
\[ o_2 \text{ moles reacn}(xi) = 0.00000000001; \]
endif

\[ \text{net molf o}_2(xi) = \frac{o_2 \text{ moles present}(xi)}{\text{mol air present}(xi)}; \]
\[ \text{net molf n}_2(xi) = 1 - \text{net molf o}_2(xi); \]
\[ \text{net molf h}_2(xi) = \frac{h_2 \text{ moles present}(xi)}{\text{mol f in}}; \]
\[ \text{net molf h}_2o(xi) = \frac{h_2o \text{ moles present}(xi)}{\text{mol f in}}; \]

// heat of reaction;
\[ Q_{\text{source}}(xi) = \left( (T_s(xi)+273.15) \times \text{stotal}(xi) \times rh_2(xi) \times n_2; \right) \]
\[ \text{current dens} = \frac{\text{trans current}(xi)}{(\text{area cell} \times 10000)}; \]

// transient case;
\[ rh_2(xi) = (-1 \times \text{trans current}(xi) \times 3.6/(2 \times 96485)); \]
\[ ro_2(xi) = (0.5 \times rh_2(xi)); \]
\[ rh_2o(xi) = -1 \times rh_2(xi); \]

\[ \text{trans current}(xi) = \frac{(\text{trans volt}(xi) - v_{op}(xi))}{\text{resist}(xi)}; \]
\[ \text{trans volt}(xi) = ((-1) \times gt(xi) \times 1000000)/(2 \times 96485) \]
\[ +((8.314 \times (ts(xi)+273.15)) \times \text{loge}((\text{net molf h}_2(xi) \times \text{net molf o}_2(xi)^0.5)/\text{net molf h}_2o(xi)^P^0.5))/(2 \times 96485) +((8.314 \times (ts(xi)+273.15))/(4 \times 96485)) \times \text{loge}(Pt); \]
\[ \text{pow dens}(xi) = \text{current dens} \times v_{op}(xi); \]

// resistance ;
ASR(xi) = (1.253e-5 \times \exp(a\_energy / (Ts(xi)+273)) + 0.02396 + (9.364e-5 \times Ts(xi)) - (1.384e-8 \times (Ts(xi)^2));
resist(xi) = ASR(xi)/(area\_cell*10000);

endfor

//Calculations:

// net_voltage:
netvolt = (sigma(trans\_volt))/(n+1) ;
// net current;
net\_current\_dens = current\_dens;
// net hydrogen consumed;
net\_h2\_con = sigma(h2\_moles\_reacn);
net\_h2\_out = mol\_h2\_in - net\_h2\_con;
//fuel utilisation;
fuel\_util = net\_h2\_con/mol\_h2\_in ;
//temperature calculation:
t\_avg = (sigma(ts))/(n+1);
total\_temp\_inc = (ts(x.endnode)-ts(0));
// net_voltage:
net\_v\_op = (sigma(v\_op))/(n+1) ;
net\_pow\_dens = (sigma(pow\_dens))/(n+1);

End
**Main iteration loop with water-shift reaction model:**

// initial conditions for dynamic model with water-shift reaction;
molfh2(0) = net_molf_h2(0);
molfh2o(0) = net_molf_h2o(0);
molfo2(0) = net_molf_o2(0);
molfn2(0) = 1-molfo2(0);
molfo(0) = molf1_co;
molfo2(0) = molf1_co2;

molfh2(x.interior): initial;
molfh2(x.interior).value: molfh2(0);
molfo2(x.interior): initial;
molfo2(x.interior).value: molfo2(0);
molfh2o(x.interior): initial;
molfh2o(x.interior).value: molfh2o(0);
molfo(x.interior): initial;
molfo(x.interior).value: molfo(0);
molfo2(x.interior): initial;
molfo2(x.interior).value: molfo2(0);

for xi in x.interior + x.endnode do

// Calling specific heat,density;

call (hydrogen.v_cp(xi)) = pcp_mol_vap(Tf(xi), p, hydrogen.y) hydrogenlist;
call (hydrogen.rho(xi)) = pdens_mol_vap(Tf(xi), p, hydrogen.y) hydrogenlist;

call (oxygen.rho(xi)) = pdens_mol_vap(Ta(xi), p, oxygen.y) oxygenlist;
call (oxygen.v_cp(xi)) = pcp_mol_vap(Ta(xi), p, oxygen.y) oxygenlist;
call (water.v.cp(xi)) = pcp_mol_vap(Tf(xi), p, water.y) waterlist;
call (water.rho(xi)) = pdens_mol_vap(Tf(xi), p, water.y) waterlist;

call (nitrogen.rho(xi)) = pdens_mol_vap(Ta(xi), p, nitrogen.y) nitrogenlist;

call (carbonmonoxide.v.cp(xi)) = pcp_mol_vap(Tf(xi), p, carbonmonoxide.y) carbonmonoxidelist;
call (carbonmonoxide.rho(xi)) =
  pdens_mol_vap(Tf(xi), p, carbonmonoxide.y) carbonmonoxidelist;

call (carbondioxide.v.cp(xi)) = pcp_mol_vap(Tf(xi), p, carbondioxide.y) carbondioxidelist;
call (carbondioxide.rho(xi)) = pdens_mol_vap(Tf(xi), p, carbondioxide.y) carbondioxidelist;

rho_mix(xi) = hydrogen.rho(xi)*net_molf_h2(xi) +
  water.rho(xi)*net_molf_h2o(xi) +
  carbonmonoxide.rho(xi)*molf_{co}(xi) +
  carbondioxide.rho(xi)*molf_{co2}(xi);

v_cp_mix(xi) = hydrogen.v.cp(xi)*net_molf_h2(xi) +
  water.v.cp(xi)*net_molf_h2o(xi) +
  carbonmonoxide.v.cp(xi)*molf_{co}(xi) +
  carbondioxide.v.cp(xi)*molf_{co2}(xi);

v_cp_mix1(xi) = (hydrogen.v.cp(xi)*net_molf_h2(xi))/2 +
  (water.v.cp(xi)*net_molf_h2o(xi))/18 +
  (carbonmonoxide.v.cp(xi)*molf_{co}(xi))/28 +
  (carbondioxide.v.cp(xi)*molf_{co2}(xi))/44;

//governing equations of heat transfer;
(area_conv_h2*h_f)*(Ts(xi)-Tf(xi)) +
  vol_solid*rho_mix(xi)*v_cp_mix(xi)*($Tf(xi)) =
  ((rho_mix(xi)*v_cp_mix(xi)*uh2)*(Tf(xi).ddx));
(area_conv_o2*h_a)*(Ts(xi)-Ta(xi)) +
  vol_solid*rho_mix(xi)*v_cp_mix(xi)*($Ta(xi)) =
  ((oxygen.rho(xi)*oxygen.v.cp(xi)*uo2)*(Ta(xi).ddx));
// conservation of mass: hydrogen gas;
$molf_h2(x_i) = -(uh2/area_{fuel\_cs\_channel})*(molf_h2(x_i).ddx)) + (rh2(x_i)+z\_shift(x_i))*((r*tf(x_i))/(p*100*vol\_solid));

// conservation of mass: steam;
$molf_h2o(x_i) = -(uh2/area_{fuel\_cs\_channel})*(molf_h2o(x_i).ddx)) + (rh2o(x_i)-z\_shift(x_i))*((r*tf(x_i))/(p*100*vol\_solid));

// conservation of mass: carbonmonoxide gas;
$molf_co(x_i) = -(uh2/area_{fuel\_cs\_channel})*(molf_co(x_i).ddx)) + (-z\_shift(x_i))*((r*tf(x_i))/(p*100*vol\_solid));

// conservation of mass: carbondioxide gas;
$molf_co2(x_i) = -(uh2/area_{fuel\_cs\_channel})*(molf_co2(x_i).ddx)) + (z\_shift(x_i))*((r*tf(x_i))/(p*100*vol\_solid));

// conservation of mass: oxygen gas;
$molf_o2(x_i) = -(uo2/area_{air\_cs\_channel})*(molf_o2(x_i).ddx)) + (ro2(x_i))*((r*tf(x_i))/(p*100*vol\_solid));

// conservation of mass: nitrogen;
molf_n2(x_i) = 1 - molf_o2(x_i);

endfor

for xi in x.interior do

// Calling dynamic viscosity,entropy,enthalpy,gibbs-free energy;
call (hydrogen.h(xi)) = penth_mol(tf(x_i),p,hydrogen.y) hydrogenlist;

call (hydrogen.s(xi)) = pentr_mol_vap(tf(xi),p,hydrogen.y) hydrogenlist;
call (hydrogen.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,hydrogen.y) hydrogenlist;

call (oxygen.h(xi)) = penth_mol(ta(xi),p,oxygen.y) oxygenlist;
call (oxygen.s(xi)) = pentr_mol_vap(ta(xi),p,oxygen.y) oxygenlist;
call (oxygen.gibb(xi)) = pgibbs_mol_vap(ta(xi),p,oxygen.y) oxygenlist;

call (water.h(xi)) = penth_mol_vap(tf(xi),p,water.y) waterlist;
call (water.s(xi)) = pentr_mol_vap(tf(xi),p,water.y) waterlist;
call (water.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,water.y) waterlist;

call (carbonmonoxide.h(xi)) = penth_mol_vap(tf(xi),p,carbonmonoxide.y) carbonmonoxidelist;
call (carbonmonoxide.s(xi)) = pentr_mol_vap(tf(xi),p,carbonmonoxide.y) carbonmonoxidelist;
call (carbonmonoxide.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,carbonmonoxide.y) carbonmonoxidelist;

call (carbondioxide.h(xi)) = penth_mol_vap(tf(xi),p,carbondioxide.y) carbondioxidelist;
call (carbondioxide.s(xi)) = pentr_mol_vap(tf(xi),p,carbondioxide.y) carbondioxidelist;
call (carbondioxide.gibb(xi)) = pgibbs_mol_vap(tf(xi),p,carbondioxide.y) carbondioxidelist;

//molfo2(xi) + molfn2(xi) = 1;

k_solid(xi) = 5.50072 + 1.65535e-3 * Ts(xi);

//delta_enthalpy_total:
htotal(xi) = water.h(xi) - hydrogen.h(xi) - 0.5*oxygen.h(xi);
//gibbs_free_energy_total:
gtotal(xi) = water.g(xi) - hydrogen.g(xi) - 0.5*oxygen.g(xi);

//delta_gibbs_table:
gt(xi) = water.gibb(xi) - hydrogen.gibb(xi) - 0.5*oxygen.gibb(xi);

//delta_entropy_total:
stotal(xi) = water.s(xi) - hydrogen.s(xi) - 0.5*oxygen.s(xi);

//delta_enthalpy_total_shift:
htotal_shift(xi) = carbondioxide.h(xi) - water.h(xi) + hydrogen.h(xi) - carbonmonoxide.h(xi);

//gibbs_free_energy_total_shift:
gtotal_shift(xi) = carbondioxide.gibb(xi) - water.gibb(xi) + hydrogen.gibb(xi) - carbonmonoxide.gibb(xi);

//delta_gibbs_shift:
gt_shift(xi) = carbondioxide.g(xi) - water.g(xi) + hydrogen.g(xi) - carbonmonoxide.g(xi);

//delta_entropy_total_shift:
stotal_shift(xi) = carbondioxide.s(xi) - water.s(xi) + hydrogen.s(xi) - carbonmonoxide.s(xi);

//gibbs_each_component:
hydrogen.g(xi) = hydrogen.h(xi) - (((Tf(xi)+273.15)*(hydrogen.s(xi)))/1E06);
oxygen.g(xi) = oxygen.h(xi) - (((Tf(xi)+273.15)*(oxygen.s(xi)))/1E06);
water.g(xi) = water.h(xi) - (((TF(xi)+273.15)*(water.s(xi)))/1E06);
carbonmonoxide.g(xi) = carbonmonoxide.h(xi) - (((TF(xi)+273.15)*(carbonmonoxide.s(xi)))/1E06);
carbon dioxide.g(xi) = carbon dioxide.h(xi) - 
(((TF(xi)+273.15)*(carbon dioxide.s(xi)))/1E06);

//governing equation of heat transfer;

(vol solid*k solid(xi))*(Ts(xi).d2dx2)-(vol solid*rho solid*v Cp solid*(Ts(xi)))) = 
(((area conv_o2*h_a)*(Ts(xi)-Ta(xi))+((area conv_h2*h_f)*(Ts(xi)-Tf(xi))))-
(Qsource total(xi)/x(1));

// equilibrium constant calculation;
equi_const(xi) = exp((-1)*gtotal shift(xi)*1000000)/(R*(Ts(xi)+273.15));
equi_const_shift(xi) = exp((4276/(Ts(xi)+273.15))-3.961);

// mole conservation;
mol air present(xi) = mol n2 in + o2 moles present(xi-1);

h2o moles reacn(xi) = molfh2o(xi)*mol f in;
h2 moles reacn(xi) = molfh2o(xi)*mol f in;
/h2o moles reacn1(xi) = molf h2o(xi)*mol f in;
/h2 moles reacn1(xi) = molf h2o(xi)*mol f in;
o2 moles reacn(xi) = (0.5*h2o moles reacn(xi));
co moles reacn(xi) = molfco2(xi)*mol f in;
c02 moles reacn(xi) = molfco2(xi)*mol f in;

h2o moles present(xi) = h2o moles present(xi-1)+ h2o moles reacn(xi);
h2 moles present(xi) = h2 moles present(xi-1) - h2 moles reacn(xi);
o2 moles present(xi)=o2 moles present(xi-1) - o2 moles reacn(xi);
co moles present(xi) = co moles present(xi-1) -co moles reacn(xi);
c02 moles present(xi) = co2 moles present(xi-1) +co2 moles reacn(xi);
net_molf_o2(xi) = o2_moles_present(xi)/mol_air_present(xi);
net_molf_n2(xi) = 1 - net_molf_o2(xi);
net_molf_h2(xi) = h2_moles_present(xi)/(mol_f_in);
net_molf_h2o(xi) = h2o_moles_present(xi)/(mol_f_in);
molf_co(xi) = co_moles_present(xi)/mol_f_in;
molf_co2(xi) = co2_moles_present(xi)/mol_f_in;

// transient case;
rh2(xi) = (-1*trans_current(xi)*3.6/(2*96485));
ro2(xi) = (0.5*rh2(xi));
rh2o(xi) = -1*rh2(xi);
current_dens=trans_current(xi)/(area_cell*10000);

//trans_volt(xi) = ((-1)*gt(xi)*1000000)/(2*96485)
+((8.314*(ts(xi)+273.15))/(2*96485))*loge(((molf_l_h2o(xi)*net_molf_o2(xi)^0.5)/molf_l_h2o(xi)))*p^0.5)+((8.314*(ts(xi)+273.15))/(4*96485))*loge(Pt);

current_conc_loss_c(xi) = (4*96485*(net_molf_o2(xi)*1)*diff_eff_o2_m(xi))/((1-net_molf_o2(xi))*r*(ts(xi)+273)*1_cathode);
current_conc_loss_a(xi) = ((2*96485*(net_molf_h2o(xi)*1)*diff_eff_h2_m(xi))/(r*(ts(xi)+273)*1_anode));

equi_const(xi) =
((net_molf_h2o(xi)*1000)+z(xi))*)((molf_co2(xi)*1000)+z(xi))/((molf_co2(xi)*1000)-z(xi))*((net_molf_h2o(xi)*1000)+z(xi));

if (z(xi) > 0) and (z(xi) < 1E03) and (z(xi) < ((h2_moles_present(xi)*1e3)/mol_f_in)) then
z_shift1(xi) = (z(xi)*(h2_moles_present(xi) + h2o_moles_present(xi) + co_moles_present(xi) + co2_moles_present(xi)))/1E03;
else
z_shift1(xi) = h2_moles_reacn(xi);
endif

if (z(xi)<=0) then
  z_shift(xi)=0.000005;
else
  z_shift(xi)=z_shift1(xi);
endif

// heat of reaction;
Qsource(xi) = ((Ts(xi)+273.15)*stotal(xi)*rh2(xi)*n2);
Qsource_shift(xi) = ((-1)*(Ts(xi)+273.15)*stotal_shift(xi)*z_shift(xi)*n2);
Qsource_total(xi) = Qsource(xi) + Qsource_shift(xi);

trans_volt(xi) = ((-1)*gt(xi)*1000000)/(2*96485) +((8.314*(ts(xi)+273.15))/(2*96485))*loge(((net_molf_h2(xi)*net_molf_o2(xi)^0.5)/net_molf_h2o(xi)*P^0.5)+((8.314*(ts(xi)+273.15))/(4*96485))*loge(Pt));
op_volt(xi)=trans_volt(xi)-trans_current(xi)*resist(xi);

// resistance;

ASR(xi) = (1.253e-5 * exp(Ea/ (Ts(xi)+273)))+ 0.02396 + (9.364e-5 * Ts(xi)) - (1.384e-8 * (Ts(xi)^2));
resist(xi) = ASR(xi)/(area_cell*10000);
endfor

//Calculations:

// net current;
net_current_dens_chan = current_dens;
net_current = ((sigma(trans_current))/(n+1));
net_current_dens = net_current_dens_chan*n1;

// net hydrogen and CO consumed;
net_h2_con = (sigma(h2_moles_reacn));
net_h2_out = ((mol_h2_in - net_h2_con));
net_co_con = sigma(co_moles_reacn);

// fuel utilization;
net_fuel_util = (net_h2_con)/mol_h2_in;
net_fuel_util_co = (sigma(co_moles_reacn))/mol_co_in;

// power density, voltage;
net_pow_dens_chan = current_dens*net_op_volt;
net_pow_dens = net_pow_dens_chan*n1;
net_op_volt = (sigma(op_volt))/(n+1);
netvolt = (sigma(trans_volt))/(n+1);

// temperature;
T_cell_avg = (sigma(Ts))/(n+1);

End
**Appendix K: Experimental ASR values with N₂-H₂ fuel gas from SOFCO, Alliance**

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<th>Time</th>
<th>ASR</th>
<th>Time</th>
<th>ASR</th>
<th>Time</th>
<th>ASR</th>
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