Modeling of the Kinetic Factors in Flame-Assisted Fuel Cells

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Abstract: Despite the significant experimental work in flame-assisted fuel cells (FFCs), a detailed model of FFC polarization losses does not exist in the literature. This paper thus presents a combination of theoretical and empirical models to describe the performance of FFCs. Previous models for solid oxide fuel cell (SOFC) polarization losses typically assumed values of the charge transfer coefficient ($\alpha$) of 0.5 and a Nernst diffusion layer thickness ($\delta$) equal to the anode thickness. The theoretical model developed in this work, parametrized in $\alpha$ and $\delta$, is empirically fitted to the experimental polarization curves to understand the variation of these parameters while the FFC operates with different fuel partial pressures. Model results indicate that at low fuel concentrations ($C_{R,0}$), the current density of the fuel cell ($j$) is limited by mass transfer limitations. As $C_{R,0}$ increases, $j$ is then limited by activation due to the limited number of activation sites in the fuel cell. Activation loss ($\eta_{act}$) remains constant at low $C_{R,0}$ (concentration limited) and increases rapidly with an increase in $C_{R,0}$ under activation-limited conditions. The value of $\alpha$, which varies significantly from 0.5, under concentration-limited conditions remains constant at ~0.24 and decreases rapidly with $C_{R,0}$ under activation-limited conditions. The value of $\delta$, which is much smaller than anode thickness, remains constant at ~10 $\mu$m under concentration-limited conditions and increases to a constant value of ~17.5 $\mu$m under activation limitations. Overcoming activation losses under high $C_{R,0}$ conditions requires further investigation of FFCs.

Keywords: flame-assisted fuel cells; solid oxide fuel cells; charge transfer coefficient; diffusion layer thickness; syngas

1. Introduction

Solid oxide fuel cells (SOFCs) electrochemically convert the chemical energy of fuels, such as H$_2$, CO and CH$_4$, into electricity. Despite the potential for low emissions [1–3], several inherent challenges with the traditional dual chamber solid oxide fuel cells (DC-SOFCs) have limited their commercial success [4,5]. The development of direct flame fuel cells (DFFCs) [6–9] replaced the stringent sealing requirements associated with DC-SOFCs and simplified the reformer [10]. The DFFC setup places the SOFC in direct contact with a fuel-rich flame, which then electrochemically converts the syngas generated during partial oxidation into electricity while maintaining the high temperature required (~1073 K) for the SOFC operation [11,12]. Though DFFCs considerably simplify the SOFC setup, they report low conversion efficiency (<1%) [13–15] and low power density [8,16,17]. Poor thermal management of the partially premixed combustion exhaust leads to large heat losses and low fuel utilization and ultimately causes poor overall efficiency [9,18].

Flame-assisted fuel cells (FFCs) exhibit higher SOFC power density compared to DFFCs by improving the thermal management of the combustion exhaust [19]. Similar to DFFCs, FFCs utilize fuel-rich combustion (i.e., partial oxidation) for fuel reforming [20–22]. Fuel-rich combustion of a hydrocarbon fuel produces syngas (CO+H$_2$), which is electrochemically oxidized in the SOFC [23]. Operating at high equivalence ratios is desirable to enhance the syngas production. The use of a fuel-rich burn, fuel cell, quick mix, fuel-lean burn (RFQL) setup in FFC research shows the potential to improve the electrical...
efficiency and fuel utilization [24]. FFCs report much higher fuel utilization than DF-
FCs, thereby improving the design while retaining most of the desired benefits of DFCCs. Milcarek et al. [25] and Ghotkar et al. [26] report fuel utilization efficiencies ($\epsilon_{FU}$) up to
50.7% and 75%, respectively. Despite the increase in syngas concentration, in both of these
studies, the SOFC $\epsilon_{FU}$ decreases with an increase in the combustion equivalence ratio. All
of the previous FFC studies were experimental, with no known attempts in the literature
at modeling the kinetic losses during polarization. Milcarek et al. provided a model for
the reversible cell potential of FFCs, but did not model the polarization losses [25]. An
experimentally supported FFC kinetic model of polarization losses is needed to understand
the connections between fuel-rich combustion and SOFC performance. Such a model can
help explain the limitations in $\epsilon_{FU}$ and performance at high equivalence ratios. A model
for the FFC polarization losses is developed in this study to fill this gap in the literature.

Since FFC performance depends strongly on SOFC performance, it is important
to understand the SOFC modeling literature before developing the FFC model. A re-
view of numerical and mathematical SOFC models is provided by Kakac et al. [27] and
Hajimolana et al. [28], respectively. The primary zeroth order model of SOFC operation is
well established in the literature but does not model the polarization losses explicitly [10,29].
SOFC polarization models accounting for multi-dimensional mass transport with experi-
mental validation provide useful and reliable insights into SOFC kinetics. Several studies
have utilized these models, as follows. Costamagna et al. proposed the concept of electro-
chemical effectiveness to search for the best electrode microstructure [30], but their
model assumes a linear local current-overpotential ($i$-$\eta$) relationship, which is valid only
for low current densities. Shin and Nam resolve this limitation by considering a nonlinear $i$-
$\eta$relationship with symmetric Butler–Volmer kinetics [31]. The diffusion of species through
the porous media was modeled by Yakabe et al. [32]. Their study provides the details
of Knudsen diffusion characteristics for fuel diffusion into the anode. Gebregergis et al.
presented a lumped and distributed parameter model for real-time evaluation and control
of SOFCs [33]. In their study, they used fuel cell exit species partial pressures for calculation
of fuel cell losses. Chan et al. provided a model for anode-supported and electrolyte-
supported fuel cells using detailed mass transfer models [34]. Their study shows the benefit
of using an anode-supported fuel cell over an electrolyte-supported fuel cell to minimize
concentration losses.

Though the previously proposed models describe different aspects of SOFC operation,
all of these models have a few key assumptions, such as a constant charge transfer coeffi-
cient ($\alpha$), usually 0.5, and a constant Nernst diffusion layer thickness ($\delta$), equal to the anode
thickness. $\alpha$ and $\delta$ are important parameters affecting the activation loss and concentration
loss and influencing the $\epsilon_{FU}$. Other independent studies have shown that $\alpha$ can vary signif-
ically from 0.5, depending on the reaction conditions [10]. The parameter $\alpha$ varies with
the slope of polarization ($j$-$V$) curve, while both $j$ and $V$ vary with fuel concentration [35].
Assuming $\alpha$ is constant can pose problems for understanding the dependence of FFC kinet-
ic on reaction conditions. The assumption of $\delta$ equal to the electrode thickness also poses
problems, because $\delta$ varies significantly from the electrode thickness as it depends on the
diffusivity of the reactants [36]. Instead of a completely theoretical model, a combination of
theory and an empirical model can provide deeper understanding of several key kinetic
parameters under different FFC reaction conditions. Initial efforts at developing such a
kinetic model were presented in Ghotkar et al. and compared to previously published
experimental data [37]. The scope of that study was limited, since several key experimental
parameters were unknown. The conclusions only indicate a need to investigate $\alpha$ and limit
current density ($j_L$) as potential design parameters for understanding FFC kinetics [37].

This paper provides a novel theoretical FFC polarization model, parameterizing $\alpha$
and $\delta$ to better understand the kinetics of the SOFC operation in FFC setup. This model
empirically calculates $\alpha$ and $\delta$ values in the SOFC model by fitting them to the experimental
polarization curves. This removes all assumptions about $\alpha$ and $\delta$, and this study investigates
how they change at different FFC inlet conditions, with a focus on high equivalence ratios.
This helps identify the effect of $\alpha$ and $\delta$ and the associated activation and concentration polarization on FFC performance and indicates key shortcomings in SOFC operation at high equivalence ratios.

2. Materials and Methods

This section contains the details of the FFC model. In this model, all gases are assumed to obey the ideal gas law. While this paper presents the model for an entire FFC, a large section of the methods is dedicated to modeling and understanding the SOFC polarization losses while operating in the FFC setup.

2.1. Operating Principle of FFC

This section describes the operating principle of FFCs. As mentioned earlier, FFCs use fuel-rich combustion as a fuel reformer to generate syngas that is electrochemically converted in the fuel cell. Figure 1 shows the different reaction zones in the FFC. The FFC employs a 2-stage combustion process called Rich-burn, Fuel Cell, Quick-mix, Lean-burn (RFQL) for its operation. In the fuel-rich combustion chamber, incoming hydrocarbon fuel is partially oxidized under an O$_2$-deficient environment to produce syngas (CO+H$_2$) and trace quantities of CO$_2$ and H$_2$O. This syngas mixture from the fuel-rich combustion then diffuses into the anode, where it is electrochemically oxidized using air or oxygen. The O$^2-$ ions coming from the air on the cathode side are transported to the triple boundary layer for oxidation. After the fuel cell, excess air is rapidly mixed with unreacted fuel from the fuel cell, making the mixture fuel-lean. The fuel-lean mixture auto-ignites in the fuel-lean combustion chamber. The heat from the fuel-lean combustion is used to maintain the high temperature of the FFC and can be used for pre-heating. The external air on the cathode side is used in electrochemical and fuel-lean oxidation and can be used for FFC temperature control. The fuel-lean exhaust contains mainly CO$_2$, H$_2$O, and N$_2$.

![Figure 1. Schematic of the tubular FFC showing the different reaction zones.](image)

A mixture of a hydrocarbon fuel and air is sent to the fuel-rich combustion chamber. The fuel/air composition going to the fuel-rich combustion chamber is characterized in terms of equivalence ratio ($\Phi$), as shown in Equation (1). $\Phi$ is the ratio of the fuel/air ratio ($n_{\text{fuel}}/n_{\text{air}}$) of the gas composition to the fuel/air ratio of the mixture at stoichiometry ($n^3_{\text{fuel}}/n^3_{\text{air}}$). Thus $\Phi > 1$ represents fuel-rich combustion and $\Phi < 1$ represents fuel-lean combustion, whereas $\Phi = 1$ represents combustion at stoichiometric conditions.

$$\Phi = \frac{n_{\text{fuel}}/n_{\text{air}}}{n^3_{\text{fuel}}/n^3_{\text{air}}}$$

The SOFC in the FFC setup consists of porous electrodes and a dense electrolyte layer sandwiched between the cathode and the anode. Nickel is commonly used as the anode material, and LSCF (La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{1-y}$O$_3$) is commonly used as the cathode material [38,39]. The electrodes have high electronic and ionic conductivity, whereas the
electrolyte has high ionic but ideally no electronic conductivity to prevent an internal short circuit [40]. Thus, materials like Yttria Stabilized Zirconia (YSZ) and Samaria Doped Ceria (SDC) are used to make the electrolyte, as they have high O\textsuperscript{2-} ion conductivity at the target temperature (~1073 K).

In the next few sections, the operating principles of the fuel-rich combustion, the SOFC, and the fuel-lean combustion are outlined. In this paper, modeling efforts mainly focus on the SOFC, since the fuel-rich and fuel-lean combustion models are well established in the literature and are largely independent of the fuel cell. More details of fuel-rich and fuel-lean combustion models can be found in a previous study [37].

2.2. Fuel-Rich Combustion

Fuel-rich combustion in the FFC setup performs the function of a typical fuel-reformer, such as a steam or water gas shift reactor used for DC-SOFC. This is the first step of the FFC operation, and it is responsible for generating syngas for the fuel cell to electrochemically oxidize. A fuel-rich mixture of a hydrocarbon fuel (e.g., CH\textsubscript{4}) is sent to the fuel-rich combustion chamber, where partial oxidation of the fuel forms syngas (CO+H\textsubscript{2}) and smaller quantities of CO\textsubscript{2} and H\textsubscript{2}O, as shown in Equation (2). In Equation (2), a–e are the mole fractions of the respective species in the fuel-rich combustion exhaust.

\[
\Phi CH_4 + 2(O_2 + 3.76N_2) \rightarrow a CO + b H_2 + c CO_2 + d H_2O + e N_2
\] (2)

The element balance for the fuel-rich combustion reaction is dependent on \( \Phi \), as shown in Equations (3)–(6).

\[
C: a + c = \Phi
\] (3)
\[
H: 2b + 2d = 4 \Phi
\] (4)
\[
O: a + 2c + d = 4
\] (5)
\[
N: e = 7.52
\] (6)

The total enthalpy released in the fuel-rich combustion reaction (\( \Delta H_{RC} \)) can be calculated using the molar flow rate (\( n \)) for each species and the molar specific enthalpy for each species. In Equation (7), \( T_{in,RC} \) and \( T_{out,RC} \) are the temperatures of the species at the inlet and outlet of the fuel-rich combustion chamber.

\[
\Delta H_{RC} = n_{CO}h_{CO} (T_{out,RC}) + n_{CO_2}h_{CO_2} (T_{out,RC}) + n_{H_2O}h_{H_2O} (T_{out,RC}) + n_{H_2}h_{H_2} (T_{out,RC}) + n_{N_2}h_{N_2} (T_{out,RC}) - n_{CH_4}h_{CH_4} (T_{in,RC}) - n_{O_2}h_{O_2} (T_{in,RC}) - n_{N_2}h_{N_2} (T_{in,RC})
\] (7)

Fuel-rich combustion increases the temperature of the products, allowing the fuel cell to operate at the target temperature (~1073 K). A common method of simulating the fuel-rich combustion exhaust uses chemical equilibrium to estimate the composition at operating conditions [41]. Programs such as NASA Chemical Equilibrium and Applications (NASA CEA) are typically used for this purpose. The software approximates the products at equilibrium by minimizing the Gibbs’ free energy of the composition at a given \( \Phi \) and temperature for one mole exhaust [41]. NASA CEA provides a good approximation of the fuel-rich combustion exhaust and has been used in previous FFC literature [22]. Thus, NASA CEA software can be used to obtain the values of a–e in Equation (2) for one mole of fuel after fuel-rich combustion.

2.3. Fuel Cell
2.3.1. Fuel Cell Potential

The exhaust from the fuel-rich combustion passes through the fuel cell to generate heat and electricity. Only the CO and H\textsubscript{2} from the fuel-rich exhaust are used as fuel.
The electrochemical reactions of CO and H\textsubscript{2} that occur at the boundary of the anode and electrolyte are shown in Equations (8) and (9).
\[
\begin{align*}
H_2 + O^{2-} & \rightarrow H_2O + 2e^- \quad (8) \\
CO + O^{2-} & \rightarrow CO_2 + 2e^- \quad (9)
\end{align*}
\]

The overall fuel cell reaction, including all the products of combustion in the exhaust, thus follows, as shown in Equation (10).
\[
a \text{CO} + b \text{H}_2 + c \text{CO}_2 + d \text{H}_2O + e \text{N}_2 + \gamma(\text{O}_2 + 3.76\text{N}_2) \\
\rightarrow (a + c) \text{CO}_2 + (b + d) \text{H}_2O + (3.76\gamma + e)\text{N}_2 \quad (10)
\]

Considering only the species taking part in the electrochemical reaction and dividing Equation (10) by the total moles of syngas (a+b) leads to Equation (11).
\[
\frac{a}{a+b} \text{CO} + \frac{b}{a+b} \text{H}_2 + \frac{\gamma}{a+b} \text{O}_2 \rightarrow \frac{a}{a+b} \text{CO}_2 + \frac{b}{a+b} \text{H}_2O \quad (11)
\]

Note that one mole of syngas uses 1/2 mole of \text{O}_2 at stoichiometry. Due to this, the coefficient of \text{O}_2 in Equation (2) is $\frac{\gamma}{a+b} = \frac{1}{2}$.

2.3.2. Standard State Thermoneutral Potential

Equations (10) and (11) are used to calculate the thermodynamic potential of the fuel cell. First, the standard state (298 K and 1 atm) thermal neutral potential ($E_\text{th}$) is calculated using the molar specific enthalpy change ($\Delta h^{0\text{FC}}$) in the fuel cell reaction and the coefficients of species in Equation (11). This is shown in Equation (12), where $h^0_i$ are the molar specific enthalpies of species ‘i’ at the operating temperature.
\[
\Delta h^{0\text{FC}} = \frac{a}{a+b} h_{\text{CO}_2} + \frac{b}{a+b} h_{\text{H}_2O} - \frac{a}{a+b} h_{\text{CO}} - \frac{b}{a+b} h_{\text{H}_2} - \frac{1}{2} h_{\text{O}_2} \quad (12)
\]

From Equation (12), the $E_\text{th}$ follows as shown in Equation (13), where $n_e$ is the number of electrons exchanged in the reaction (i.e., 2 per mole of syngas) and F is Faraday’s constant.
\[
E_\text{th} = -\frac{\Delta h^{0\text{FC}}}{n_e F} \quad (13)
\]

2.3.3. Standard State Reversible Potential

The reversible cell potential at reaction temperature ($E_{\text{rev}}$) is the theoretically predicted thermodynamic potential of the fuel cell at the fuel cell temperature. $E_{\text{rev}}$ contains two main parts under constant pressure conditions, as shown in Equation (14). In Equation (14), $E_{\text{rev}}^0$ is the reversible potential at the operating temperature of the fuel cell, and $E_C$ is the concentration correction factor.
\[
E_{\text{rev}} = E_{\text{rev}}^0 - E_C \quad (14)
\]

The $E_{\text{rev}}$ of the fuel cell for reaction in Equation (10) is calculated similar to $E_\text{th}$, but uses the molar specific Gibbs’ free energy of the species involved ($g_i$) instead of $h_i$. Thus, the total molar specific Gibbs’ energy change in the fuel cell is given by Equation (15).
\[
\Delta g^{\text{FC}} = \frac{a}{a+b} g_{\text{CO}_2} + \frac{b}{a+b} g_{\text{H}_2O} - \frac{a}{a+b} g_{\text{CO}} - \frac{b}{a+b} g_{\text{H}_2} - \frac{1}{2} g_{\text{O}_2} \quad (15)
\]

Thus, $E_{\text{rev}}$ of the fuel cell is given by Equation (16).
\[
E_{\text{rev}} = -\frac{\Delta g^{\text{FC}}}{n_e F} \quad (16)
\]
EC arises from dilution of the fuel with inert or unreactive species. EC is calculated as shown in Equation (17).

$$EC = \frac{RT_F}{n_e F} \log(K)$$ \hspace{1cm} (17)

In Equation (17), R is the universal gas constant, and K is the equilibrium constant of the fuel cell reaction. K for the reaction in Equation (11) is calculated as shown in Equation (18), where [i] is the concentration of the species ‘i’. The model only uses the species taking part in the fuel cell reaction (CO, H₂, O₂) for the calculation of K.

$$K = [CO]^{a+b} \cdot [H_2]^{b} \cdot [O_2]^{-1/2}$$ \hspace{1cm} (18)

In Equation (18), [i] is the coefficient of the species ‘i’ in Equation (10) if the coefficient is also the mole fraction of each species. Thus, Equation (18) can be converted to Equation (19), assuming the O₂ concentration in air as 21%.

$$K = (a)\frac{b}{a+b} \cdot (b)\frac{b}{a+b} \cdot 0.21^{-1/2}$$ \hspace{1cm} (19)

Experimentally, Errev remains close to the experimental value of the open circuit voltage (OCV). Irreversibilities in the fuel cell at equilibrium lead to small deviations from the theoretical value.

2.4. Fuel Cell Kinetic Losses

When current is generated in the fuel cell, several losses or overpotentials (η) occur, causing a drop in the fuel cell potential. The three main losses in the fuel cell are activation loss, ohmic loss, and concentration loss. Each of these losses are discussed in the following sections.

2.4.1. Activation Loss

When current starts flowing from the fuel cell, a portion of the cell overpotential is provided for overcoming the activation barriers of the fuel oxidation and oxygen reduction reactions. This leads to a loss of the cell potential, called activation loss (ηact). ηact is calculated using the Tafel equation [10], as shown in Equation (20). In Equation (20), α is the charge transfer coefficient, j₀ is the exchange current density of the reaction, and j is the actual current density of the reaction.

$$\eta_{act} = \frac{RT_F}{\alpha n_e F} \log \left( \frac{j}{j_0} \right)$$ \hspace{1cm} (20)

As the Tafel equation works well only for j > 4j₀, this method provides large errors for j < 4j₀ and is negative for j < j₀. Thus, instead of Equation (20), an approximation of Equation (20) with inverse hyperbolic sine is used to calculate activation loss at all current densities, as shown in Equation (21) [33].

$$\eta_{act} = \frac{RT_F}{\alpha n_e F} \sinh^{-1} \left( \frac{j}{2j_0} \right)$$ \hspace{1cm} (21)

where j₀ is the current density that exists when the forward and reverse reaction rates are equal, i.e., at equilibrium. j₀ results from the equal number of oxidation and reduction reactions, with no current actively being extracted from the fuel cell. j₀ can be experimentally calculated as the x-intercept of the Tafel equation.

Activation losses also depend upon α, the charge transfer coefficient. α is a kinetic parameter that determines the symmetry of the activation barrier and always ranges from 0 to 1 [10]. This parameter determines how the electrical potential changes the sizes of the oxidation and reduction activation barriers. α varies linearly with the parameter \( \frac{d}{dt} \ln|I_a| (1 - \alpha \text{ with } \frac{d}{dt} \ln|I_c|) \), where I_a is the partial anodic current [35].
2.4.2. Ohmic Loss

Ohmic loss occurs due to resistance to the motion of electrons and ions by electrode and electrolyte materials. Most fuel cells operate in the ohmic region where the concentration losses are near minimum. The ohmic loss ($\eta_{\text{ohm}}$) is calculated using Ohm’s law, as shown in Equation (22) [10].

\[
\eta_{\text{ohm}} = j \sum \rho_{\text{k}} \frac{A_{\text{FC}}}{\delta_{\text{k}}}
\] (22)

In Equation (22), $\rho_{\text{k}}$ is the temperature-dependent electrical resistivity (or ionic resistivity for electrolyte) of the material, $A_{\text{FC}}$ is the active area of the fuel cell (connected to current collector), and $\delta_{\text{k}}$ is the thickness of the respective layer ‘k’ ($k = \text{anode, cathode, electrolyte}$). Generally, in anode-supported fuel cells (like the one used in this study), anode resistance is significantly higher than the cathode or electrolyte due to its much larger thickness compared to the cathode and electrolyte.

2.4.3. Concentration Loss

The concentration loss ($\eta_{\text{conc}}$) arises from the finite rate of mass transport of the fuel and oxidant. At high current densities, the given flow rate of the species cannot match the increased fuel consumption rate. This causes large kinetic losses and a decrease in the cell potential. $\eta_{\text{conc}}$ can be calculated as shown in Equation (23).

\[
\eta_{\text{conc}} = \frac{RT}{n_{e}F} \left(1 + \frac{1}{\alpha} \right) \ln \left( \frac{j_{L}}{j_{L} - j} \right)
\] (23)

In Equation (23), $j_{L}$ is the limiting current density of the fuel cell. Assuming the concentration of reactants at the activation sites ($C_{R,0}$) to be constant, according to Fick’s law, in the Nernst diffusion layer, $j_{L}$ can be calculated as shown in Equation (24), where $\epsilon$ is the porosity and $\tau$ is the tortuosity of the anode.

\[
j_{L} = n_{e}F D_{i} \frac{C_{R,0}}{\delta} \frac{\epsilon}{\tau}
\] (24)

In Equation (24), $D_{i}$ is the effective self-diffusivity of the fuel, and $\delta$ is the thickness of the Nernst diffusion layer. For simplicity, $C_{R,0}$ is assumed to be equal to the bulk channel reactant concentration.

In calculating $D_{i}$, the first step is the binary diffusivity of each pair of gases in the incoming mixture, using the kinetic theory of gases as shown in Equation (25) [10].

\[
D_{ij} = \frac{a}{p_{\text{total}}} \left( \frac{T}{T_{c,i} T_{c,j}} \right)^{\frac{b}{2}} \left( p_{c,i} p_{c,j} \right)^{\frac{1}{2}} \left( T_{c,i} T_{c,j} \right)^{\frac{1}{2}} \left( \frac{1}{M_{i}} + \frac{1}{M_{j}} \right)^{\frac{1}{2}}
\] (25)

In Equation (25), $a = 3.640 \times 10^{-4}$ and $b = 2.334$ if the pair $ij$ contains polar molecules, and $a = 2.745 \times 10^{-4}$ and $b = 2.334$ if the pair contains non-polar molecules only. $T_{c}$ is the critical temperature, $p_{c}$ is the critical pressure, $p$ is the total operating pressure, and $M$ is the molecular weight of species $i$ and $j$, respectively. The self-diffusion coefficient of species ‘$i$’ in a multicomponent system (e.g., CO+H$_2$+CO$_2$+H$_2$O) is calculated using the Maxwell–Stefan equation, as shown in Equation (26) [28,42].

\[
D'_{i} = \frac{1 - X_{i}}{X_{i} D_{ii} + \frac{X_{i}}{D'_{ii}} + \frac{X_{j}}{D'_{ij}} + \cdots}
\] (26)

In Equation (26), $D'_{i}$ is the self-diffusivity and $X$ is the mole fraction of the respective species. Thus, from Equations (25) and (26), the self-diffusivity of the specific fuel mixture containing CO and H$_2$ can be calculated as shown in Equation (27).
\[ D_f = X_{H_2}D'_{H_2} + X_{CO}D'_{CO} \]  

(27)

The Nernst diffusion layer is a virtual layer within which the gradient of ion concentration is constant and equal to the true gradient at the electrode–electrolyte interface. The thickness of this diffusion layer (\( \delta \)) depends on the diffusivity of reactants [36], which, as established by Equation (24), depends on the reactant concentration. With an \( O^{2-} \) conducting electrolyte, this diffusion layer is present at the boundary of the anode and electrolyte. This model assumes no change in the fuel concentration from the bulk channel concentration to the anode-diffusion layer boundary.

The operating voltage of the fuel cell at an arbitrary current density \( j \) (\( E_j \)) is thus given by Equation (28). Equation (28) represents the main governing equation of the proposed parametric SOFC model.

\[ E_j = E_{\text{rev}} - n_{\text{act},j} - n_{\text{ohm},j} - n_{\text{conc},j} \]  

(28)

Since the values of \( \alpha \) and \( \delta \) are not calculated theoretically, the parametric model (30), parameterized in \( \alpha \) and \( \delta \), is used to fit the experimental polarization curves, as shown in Equation (29), where \( j_L \) is a function of \( \delta \).

\[ E_j = E_{\text{rev}} - \frac{RT}{\alpha n_e F} \sinh^{-1} \left( \frac{j}{2j_0} \right) - \frac{j}{\delta} \sum \rho_{k} A_{\text{FC}} \frac{RT}{n_e F} \left( 1 + \frac{1}{\alpha} \right) \ln \left( \frac{j}{j_L - j} \right) \]  

(29)

Fitting Equation (29) to the experimental polarization curves can provide values of \( \alpha \) and \( \delta \). Consequently, the operating power density of the fuel cell at an arbitrary current density \( j \) (PD\(_j\)) is given by Equation (30).

\[ \text{PD}_j = jE_j \]  

(30)

2.5. Fuel Cell Efficiencies

Due to various losses and kinetic limitations in the fuel cell, not all fuel that is supplied to the fuel cell will participate in the electrochemical reaction. Of the fuel that actually participates in the electrochemical reaction, the fuel cell converts the available chemical energy into heat and electricity. The fuel utilization efficiency (\( \epsilon_{FU} \)) and fuel cell efficiency (\( \epsilon_{FC} \)) help characterize these conversions.

2.5.1. Fuel Utilization Efficiency

The total current density (\( j_{\text{max}} \)) available in the incoming fuel can be calculated as shown in Equation (31). In Equation (31), \( A_{\text{FC}} \) is the active area of the fuel cell, and \( n_0 \) is the molar flow rate of fuel supplied to the fuel cell.

\[ j_{\text{max}} = \frac{n_0 n_e F}{A_{\text{FC}}} \]  

(31)

\( \epsilon_{FU} \) results from all the kinetic losses of the fuel cell. The limitations of fuel cell kinetics result in a reduction of the total fuel oxidized compared to the total fuel available in the bulk flow stream. \( \epsilon_{FU} \) is defined as the ratio of the actual current density (\( j \)) generated by the fuel cell to the total available current density that could be generated by the fuel mixture if all the fuel oxidizes (\( j_{\text{max}} \)). The \( \epsilon_{FU} \) at any voltage (\( \epsilon_{FU,V} \)) is defined in Equation (32), where \( j_V \) is the current density measured at that voltage.

\[ \epsilon_{FU,V} = \frac{j_V}{j_{\text{max}}} \]  

(32)

2.5.2. Fuel Cell Efficiency

\( \epsilon_{FC} \) results from the inability of the fuel cell to convert all the fuels’ chemical energy into electrical power. It is defined as the ratio of the total electrical power produced in the
fuel cell to the total chemical energy available in the utilized fuel. In Equation (33), \( \Delta h_f \) is the mole specific enthalpy of the fuel.

\[
\varepsilon_{\text{FC}} = \frac{P_{D,j} A_{\text{FC}}}{n \cdot \Delta h_f}
\]  

(33)

2.6. Fuel-Lean Combustion

Unreacted fuel from the fuel cell is combusted in an excess oxygen (fuel-lean) environment to generate heat to maintain the fuel cell temperature. The total heat generated in the fuel-lean combustion is shown in Equation (34), where \( \bar{n}_j \) represents the remaining moles of the reactant species after the fuel cell reaction, and \( T_{\text{in/out,LC}} \) represents the inlet and outlet temperatures of the species, respectively.

\[
\Delta H_{\text{LC}} = \bar{n}_{\text{H}_2\text{O}}h_{\text{H}_2\text{O}}(T_{\text{out,LC}}) + \bar{n}_{\text{CO}_2}h_{\text{CO}_2}(T_{\text{out,LC}}) + \bar{n}_{\text{N}_2}h_{\text{N}_2}(T_{\text{out,LC}}) - \bar{n}_{\text{H}_2}h_{\text{H}_2}(T_{\text{in,LC}}) - \bar{n}_{\text{CO}}h_{\text{CO}}(T_{\text{in,LC}}) - \bar{n}_{\text{O}_2}h_{\text{O}_2}(T_{\text{in,LC}}) - \bar{n}_{\text{N}_2}h_{\text{N}_2}(T_{\text{in,LC}})
\]  

(34)

3. Experimental Setup

Experiments were conducted on a tubular fuel cell and polarization curves under a wide range of FFC operating conditions. Figure 2 shows the schematic of the experimental fuel cell setup. In the experiment, gas compositions containing CO, H\(_2\), N\(_2\), and CO\(_2\) were mixed and sent to a tubular fuel cell placed inside a furnace at 1073 K. Air for oxidation was taken from the environment. The details of the experimental flow rate calculations and the fuel cell details are provided in the following sections.

![Figure 2. Schematic of the experimental setup used for understanding the kinetic parameters.](image)

3.1. Species Flow Rate

The experiment was conducted with N\(_2\), CO\(_2\), H\(_2\), and CO\(_2\) as the composition of the model dry exhaust of methane partial oxidation in air at 1073 K [45]. The species mole fractions were based on chemical equilibrium calculations from NASA CEA. Along with the model dry exhaust, a few custom compositions were used to understand the impact of the fuel concentration on the FFC operation. The fuel compositions used in the FFC experiment and their respective identifiers are shown in Table 1.

In Table 1, the gas compositions are chosen to include a wide variety of different fuel concentrations that can be present in the FFC. C\(_{\text{H}_2}\) and C\(_{\text{N}_2}\) were chosen to isolate the effects of the fuel (i.e., CO and H\(_2\)) from CO\(_2\). Since the fuel cell operates under model dry exhaust, \( X_{\text{N}_2} \) is the sum of both \( X_{\text{H}_2\text{O}} \) and \( X_{\text{N}_2} \) from the NASA CEA predictions to maintain the level of fuel dilution. The experiment was conducted under a constant fuel-rich exhaust flow rate of 150 sccm at 298 K and 1 atm. The volumetric flow rate of species ‘\( i \)’ is thus
the product of the total flow rate and $X_i$. To meter the gas flows, mass flow controllers were used.

**Table 1.** Mole fractions of the gas species used in the experiment.

| Experiment Identifier | $X_{CO}$ | $X_{H2}$ | $X_{CO2}$ | $X_{N2}$ |
|-----------------------|----------|----------|-----------|----------|
| $C_{H2}$              | 0        | 0.1      | 0         | 0.9      |
| $C_{CO}$              | 0.1      | 0        | 0         | 0.9      |
| $\Phi = 1.4$          | 0.07     | 0.06     | 0.046     | 0.81     |
| $\Phi = 1.8$          | 0.11     | 0.14     | 0.032     | 0.72     |
| $\Phi = 2.2$          | 0.13     | 0.21     | 0.027     | 0.63     |
| $\Phi = 2.6$          | 0.15     | 0.27     | 0.025     | 0.55     |
| $\Phi = 3$            | 0.16     | 0.32     | 0.024     | 0.49     |

3.2. Measurement Techniques

The model dry exhaust gases were mixed and sent to the fuel cell placed inside a furnace at 1073 K. The current density and the voltage were measured using a sourcemeter (Keithley 2460) connected to both the cathode and anode via current collectors using the four-probe technique. In the four-probe technique, a high impedance current source supplies current through two outer probes, while a voltmeter measures the voltage across the two inner probes [43]. Flame arrestors were placed in line with the CO and H$_2$ lines to avoid flashback. Air for oxidation came from the environment, as shown in Figure 2.

3.3. Fuel Cell Fabrication

The details of the fabrication technique for fuel cell anode, NiO + YSZ ($Y_2O_3$)$_{0.08}$($ZrO_2$)$_{0.92}$, and electrolyte, YSZ, were reported previously in the literature [14]. The anode was pre-fired at 1373 K. The electrolyte was dip-coated on the anode and sintered, with a final thickness of ~22 µm. The final inner and outer diameter of the tubular fuel cell was 2.2 mm and 3.3 mm, respectively. A buffer layer of Sm$_{0.20}$Ce$_{0.80}$O$_{2−x}$ (SDC) was sprayed onto the electrolyte to prevent adverse reactions between the cathode and electrolyte. The fuel cell was then dried and sintered at 1673 K for 4 h. A cathode made of SDC + LSCF ($La_{0.60}Sr_{0.40}$)$_{0.95}$Co$_{0.20}$Fe$_{0.80}$O$_{3−x}$ was dip-coated onto the buffer layer, dried, and sintered at 1373 K for 2 h. A silver wire and silver paste were used as a current collector on the cathode and anode. The total active cell area after these modifications was 4.14 cm$^2$. The porosity ($\varepsilon$) of the fuel cell anode measured using scanning electron microscopy (SEM) was 6.34%. The $\tau$ of the SOFC Ni-YSZ anode was taken as 2 from the literature [44].

3.4. Experimental Error and Reproducibility

The main experimental parameters include voltage, current, and flowrate measurements. A Keithley 2460 sourcemeter has a maximum error of ±5.58 mA or ±1.33 mA/cm$^2$ for the current source at the maximum current (~900 mA/cm$^2$). For the voltage source, the maximum error is ±0.00165 V or 0.165% at the maximum voltage of around 1 V. A bubble-meter was used to verify the factory-calibrated flow meters, and the error was found to be within ±3% of the species flow rates. Since these errors are small, previously published results have not displayed them on j-V curves of the fuel cell. In regard to reproducibility, all polarization curves were measured five different times, with comparable results across all measurements. Factory-calibrated flow meters were used in the recommended ranges of the flow rates. The calibration was further verified multiple times.

4. Results and Discussion

This section starts with a comparison of experimental and model-predicted polarization curves for the fuel cell. The polarization curves are then broken down into several relevant kinetic factors. The dependence of the kinetic factors with the composition of inlet gas is then used to draw conclusions about the effect of gas composition on the FFC performance. Figure 3 shows the experimental data and model-predicted polarization curves for
different gas compositions. The model is able to predict the experimental results to a high degree of accuracy (>95%) at all values of \( j \). The experiment is terminated at \( V \approx 0.1 \) V to prevent anode reoxidation. The \( j \) at the termination of the experiment is termed \( j_T \). In the experiment, the fuel cell had a lower \( j_T \) for the \( \text{C}_2\text{H}_2 \) than the \( \text{C}_\text{CO} \) fuel composition. Since \( \text{CO} \) and \( \text{H}_2 \) represent the fuel in the FFC gas composition, we define \( C_{R,0} = X_{\text{CO}} + X_{\text{H}_2} \), which increases from the lowest concentration (for \( \text{C}_2\text{H}_2 \) and \( \text{C}_\text{CO}, C_{R,0} = 0.1 \)) to the highest concentration (for \( \Phi = 3, C_{R,0} = 0.48 \)) tested in these experiments.

![Figure 3. Experimental and model-predicted polarization curves for different gas compositions.](image)

Figure 3 shows that \( j_T \) increases with \( C_{R,0} \). The slope of the curves at low \( j \) values is almost equal, indicating that \( n_{\text{ohm}} \) varies linearly with \( j \) and does not change with \( C_{R,0} \). \( n_{\text{ohm}} \) only depends on \( \rho_{\text{ohm}} \), which is a function of \( T_{\text{FC}} \) (which is constant at 1073 K) and does not depend on \( C_{R,0} \). The next few sections discuss several factors that contribute to the results in Figure 3.

### 4.1. Dependence of Cell Potentials on Fuel Concentration

Figure 4 shows the variation of experimental open circuit voltage (OCV) and \( E_{\text{rev}} \) with \( C_{R,0} \). The results show that \( E_{\text{rev}} \) is able to approximate the OCV well. After the initial dip at \( \Phi = 1.4, E_{\text{rev}} \) increases with an increase in \( C_{R,0} \). The results confirm that addition of \( \text{CO}_2 \) at \( \Phi = 1.4 \) decreases \( E_{\text{rev}} \) compared to lower concentrations. As \( \Phi \) increases above 1.4, an increase in fuel concentration and decrease in \( \text{CO}_2 \) concentration leads to an increase in \( E_{\text{rev}} \).

### 4.2. Dependence of Activation Losses on Fuel Concentration

Figure 5 shows the dependence of \( n_{\text{lact}} \) on \( j \) at different \( C_{R,0} \). Figure 5 shows that for low values of \( C_{R,0} \) (up to \( \Phi = 1.4 \)) \( n_{\text{lact}} \) is constant and low at the same \( j \) values. This happens because at low \( C_{R,0} \), the available reaction sites in the fuel cell can activate most of the available fuel in the gas composition. As \( C_{R,0} \) increases, the limited number of reaction sites cannot accommodate the arbitrarily increasing fuel \( C_{R,0} \) in the limited residence time in the fuel cell. The fuel cell thus has a larger \( n_{\text{lact}} \). \( n_{\text{lact}} \) depends on the number of reaction sites, which vary with porosity, tortuosity, surface roughness, dimensions of the fuel cell, etc. [10]. Thus, modifying any of these parameters should theoretically affect \( n_{\text{lact}} \). More experimental work in FFCs is required to confirm this hypothesis. Thus, care needs to be taken while designing the FFC to account for the range of \( C_{R,0} \) that the FFC is expected to operate under and to minimize the effect of activation limitations. When the \( j_T \) is limited by high \( n_{\text{lact}} \), the fuel cell is considered activation-limited.
A decrease in the sites are available to activate a significant portion of available fuel, i.e., not lead to a significant rise in the transfer losses due to available excess inactivated fuel. This reduction in faster than CO, as observed in the literature [45], R,0 for similar j values with an increase in C

4.3. Dependence of Concentration Loss on Fuel Concentration

Figure 6 shows the dependence of \( \eta_{\text{conc}} \) on j at various values of \( C_{R,0} \). \( \eta_{\text{conc}} \) decreases for similar j values with an increase in \( C_{R,0} \). Since \( H_2 \) electrochemically oxidizes much faster than CO, as observed in the literature [45], \( \eta_{\text{conc}} \) is much higher for \( C_{H2} \) than \( C_{CO} \). As \( C_{R,0} \) increases, a smaller portion of the overpotential is needed to overcome the mass transfer losses due to available excess inactivated fuel. This reduction in \( \eta_{\text{conc}} \) thus does not lead to a significant rise in the \( j_T \) and does not indicate improvement in fuel cell kinetics. A decrease in \( \eta_{\text{conc}} \) increases the fuel cell current density only if a large number of reaction sites are available to activate a significant portion of available fuel, i.e., \( \eta_{\text{act}} \) is low. When the \( j_T \) is limited by high \( \eta_{\text{conc}} \), the fuel cell is considered concentration-limited.
4.4. Dependence of Fuel Utilization Efficiency on Fuel Concentration

ε_{FU} is calculated at the termination of the experiment to observe the effect of all the fuel cell losses. Figure 7 shows that ε_{FU} decreases with an increase in C_{R,0}. The ε_{FU} of C_{CO} is higher than C_{H2} because C_{H2} experiences larger i_{conc} than C_{CO}, as described earlier. Observing the trends in i_{act} and i_{conc}, at low C_{R,0} up to Φ = 1.4, ε_{FU} is limited by i_{conc} (concentration limited), and beyond Φ = 1.4, ε_{FU} is limited by i_{act} (activation limited). This difference is also apparent in Figure 3, where for C_{R,0} up to Φ = 1.4, a rapid drop in j at low voltages indicates high i_{conc}. The drop in j with V at low voltages in Figure 3 is much more gradual for Φ ≥ 1.8. The results suggest that the optimum value of C_{R,0}, where the activation limitations and concentration limitations are simultaneously low, lies between Φ = 1.4 and Φ = 1.8 for this experimental fuel cell.

4.5. Dependence of Exchange Current Density on Fuel Concentration

Figure 8 shows the variation of j_0 with C_{R,0}. The values of j_0 shown in Figure 8 are calculated using the x-intercept of the Tafel plot, as described in earlier sections. Since j_0
depends on the $C_{R,0}$, as the $C_{R,0}$ increases, $j_0$ increases because more total fuel is available in the gas composition. Though $j_0$ is inversely related to $\eta_{\text{act}}$, this increase in $j_0$ does little to reduce the $\eta_{\text{act}}$ at higher $j$ values as $C_{R,0}$ increases. Thus, an increase in $j_0$ is not a sufficient indicator of the improvement in fuel cell activation kinetics.

![Figure 8](image1)

**Figure 8.** Dependence of exchange current density ($j_0$) on fuel concentration ($C_{R,0}$).

### 4.6. Dependence of Charge Transfer Coefficient on Fuel Concentration

Figure 9 shows the dependence of $\alpha$ on $C_{R,0}$. As shown, $\alpha$ is much smaller compared to the normally assumed value of 0.5 for all values of $C_{R,0}$. This indicates the syngas oxidation reaction is not symmetric and favors the reduction reaction in FFCs. Under concentration-limited conditions, $\alpha$ remains constant at ~0.24. This is the primary reason for the similar $\eta_{\text{act}}$ for $C_{\text{H}_2}$, $C_{\text{CO}}$, and $\Phi = 1.4$ shown in Figure 5.

![Figure 9](image2)

**Figure 9.** Dependence of charge transfer coefficient ($\alpha$) on fuel concentration ($C_{R,0}$).

As $C_{R,0}$ further increases, the activation limitations set in and lead to a rapid drop in $\alpha$ with $C_{R,0}$. This decrease in $\alpha$ indicates worsening activation kinetics and leads to a rapid rise in $\eta_{\text{act}}$ and a decrease in $\varepsilon_{\text{FU}}$ at higher $C_{R,0}$. The results thus suggest that strategies to reduce $\eta_{\text{act}}$ will increase $\alpha$, thereby improving fuel cell kinetics.
4.7. Dependence of Nernst Diffusion Layer Thickness on Fuel Concentration

Figure 10 shows the dependence of $\delta$ on $C_{R,0}$. First, the model results show that $\delta$ is much smaller than the thickness of the anode (~400 µm). Under concentration-limited conditions, $\delta$ remains constant at ~10 µm. Under activation-limited conditions, $\delta$ increases to ~17.5 µm. This variation in $\delta$ indicates reaction kinetics differ significantly between concentration-limited and activation-limited conditions. Slower reactions at higher $C_{R,0}$ values create larger diffusion layers, which rapidly reduce $\epsilon_{FU}$.

![Figure 10](image)

**Figure 10.** Dependence of Nernst diffusion layer thickness ($\delta$) on fuel concentration ($C_{R,0}$).

4.8. Model Sensitivity

Since these results are based on fitted parameters, it is important to check the sensitivity of the model to $\alpha$ and $\delta$. A high parameter sensitivity is better for ensuring that no other value of $\alpha$ and $\delta$ also match the experiment, potentially causing conflicting results. Figure 11 shows that the model is sensitive to change in the values of these parameters. As an example, we consider the case of $\Phi = 2.2$. Figure 11 shows the variation of the $j$-$V$ curves at a constant $\delta$ of 18.2 µm but varying $\alpha$. The cell voltage at $j > 0$ increases with an increase in $\alpha$ due to reduction in $\eta_{act}$. As only one value of $\alpha$ (0.157) over a wide range (0.1 < $\alpha$ < 0.3) matches the experimental curve, the results provide confidence in the model.

![Figure 11](image)

**Figure 11.** Polarization curves for $\Phi = 2.2$ with varying charge transfer coefficient ($\alpha$) and constant Nernst diffusion layer thickness ($\delta$).
Similar to $\alpha$, the model is very sensitive to $\delta$, as can be seen in Figure 12. The cell voltage at $j > 0$ decreases with an increase in $\delta$ due to an increase in $r_{\text{conc}}$. Only $\delta = 18.2 \, \mu m$ correctly matches the experimental result.

![Polarization curves for $\Phi = 2.2$ with varying Nernst diffusion layer thickness ($\delta$) and constant charge transfer coefficient ($\alpha$).](image)

Figure 12. Polarization curves for $\Phi = 2.2$ with varying Nernst diffusion layer thickness ($\delta$) and constant charge transfer coefficient ($\alpha$).

5. Conclusions

A model for describing the FFC operation at different fuel concentrations is provided in this paper. The model is parametrized in $\alpha$ and $\delta$ and then empirically fitted to the experimental SOFC polarization curves. The model fitted experimental results to >95% accuracy at all values of current density. The results show $\alpha$ is much lower than the normally assumed value of 0.5, indicating asymmetric syngas reaction kinetics, and $\delta$ is much smaller than the anode thickness. The high $\epsilon_{\text{FU}}$ (>70%) at lower fuel concentration values ($C_{R,0}$) up to $\Phi = 1.4$ is mainly a result of low activation losses, where the FFC current density is mainly concentration-limited. The $\epsilon_{\text{FU}}$ at higher $\Phi$ decreases rapidly with $C_{R,0}$ due to the onset of activation limitations, which prevents activation of a large portion of the fuel in the limited residence time. Activation-limited fuel cells thus have a much lower $\epsilon_{\text{FU}}$ than concentration-limited fuel cells. Thus, the model suggests that increasing the number of activation sites should decrease the activation losses and should lead to an increase in fuel utilization and power density under similar current densities. These experiments thus indicate future directions for further validating this model. The charge transfer coefficient is almost constant at ~0.24 for concentration-limited conditions and decreases with $C_{R,0}$ at the onset of activation limitations. The value of $\delta$ remains constant at ~10 $\mu m$ for concentration-limited conditions and increases to ~17.5 $\mu m$ under activation-limited conditions, indicating worsening of reaction kinetics under activation-limited conditions. Care should be taken to operate FFC under fuel concentrations where activation and concentration losses are simultaneously low. The results indicate that such a point lies between $\Phi = 1.4$ and $\Phi = 1.8$ for the experimental fuel cell under the given operating conditions.

Author Contributions: Conceptualization, R.G. and R.J.M.; data curation, R.G.; formal analysis, R.G.; funding acquisition, R.J.M.; investigation, R.G.; methodology, R.G. and R.J.M.; project administration, R.J.M.; resources, R.J.M.; software, R.G.; supervision, R.J.M.; validation, R.J.M.; visualization, R.G.; writing—original draft, R.G.; writing—review and editing, R.G. and R.J.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.
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