NUMERICAL MODELING OF AN ANODE SUPPORTED BUTTON SOFC

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RESUMEN
Un modelo numérico tridimensional para Celdas de Combustible de Óxido Sólido (SOFC) se ha desarrollado con la finalidad de simular el desempeño de este tipo de celdas operando con gas de síntesis. Las reacciones de reformado de metano y la conversión de monóxido de carbono a hidrógeno catalizadas con níquel son consideradas en el modelo mediante un mecanismo de reacción global. La oxidación simultánea de hidrógeno y monóxido de carbono también es tomada en cuenta. El modelo cinético químico fue verificado y el modelo de la celda de combustible fue validado con datos experimentales. El funcionamiento de la SOFC fue estimado y comparado con los datos experimentales. En ambos casos se observó que la velocidad de la reacción de conversión de monóxido de carbono a hidrógeno es lo suficientemente rápida para equilibrar la composición del combustible. El efecto de la oxidación electroquímica del monóxido de carbono en el desempeño de la celda fue cuantificado y se concluyó que este proceso de oxidación no puede ser simplemente despreciado.

ABSTRACT
A three-dimensional numerical model for Solid Oxide Fuel Cells (SOFCs) has been developed in order to simulate the performance of this type of cells operating on clean coal syngas. The steam methane reforming and water gas shift reactions catalyzed by nickel are considered to take place in the anode through a global reaction mechanism. Simultaneous electrochemical oxidation of hydrogen and carbon monoxide is also taken into account. The reforming kinetics model was verified and the fuel cell model was also validated with experimental data. The SOFC performance was predicted and compared with fuel compositions at equilibrium and non-equilibrium conditions. In both cases, it was observed that the water gas shift reaction rate is high enough to equilibrate the fuel composition. Also the effect of the carbon monoxide electrochemical oxidation on the cell performance was assessed and it was concluded that this oxidation process can not be simply neglected.

INTRODUCTION
One of the most promising technologies for energy conversion are the fuel cells, specifically the SOFCs because of its range of power generation and fuel flexibility. The operating conditions, primarily the operating temperature and the electrode materials used in SOFCs give the capability to this type of fuel cell to use fuels such as coal syngas, methanol, ethanol and biofuels in general. In this study the efforts are directed on the use of coal syngas as fuel. However, coal syngas is known to be a ‘dirty’ gas containing a wide range of impurities in addition to methane, hydrogen, carbon monoxide, carbon dioxide and nitrogen. Research in this area [1, 2, 3, 4] is being focused on determining the effect of various coal impurities on the performance of the anode and understanding the underlying mechanisms of degradation. Such knowledge would be necessary to develop new anode materials that can withstand coal syngas impurities. To expedite this new research, detailed numerical simulation tools are needed for modeling fuel cells operating on coal syngas.

With this background, a three-dimensional CFD code (DREAM-SOFC) [5, 6] has been modified to include the main species commonly found in coal syngas such as CH4, H2, CO, CO2, H2O and N2 [7]. Due to the presence of nickel as a catalyst on the anode and the species mentioned above the steam methane reforming reaction and the water gas shift reaction are accounted for in the code through a chemical kinetics model of these species.
two reactions explicitly. Although many researchers consider the water gas shift reaction to be at equilibrium [8, 9, 10, 11] since it is faster than the methane reforming reaction, in this study no equilibrium assumption is made for any of the reactions. Unlike many models where only \( \text{H}_2 \) oxidation is considered [12, 13, 14] in this study an electrochemistry model has been implemented based on the model used by Nishino et al. [15] for simultaneous hydrogen and carbon monoxide electrochemical oxidation. The activation overpotentials for hydrogen, carbon monoxide and oxygen are calculated by using the Butler-Volmer equation instead of the empirical relations like those proposed by Achenbach [16]. The computational domain consists of the anode and cathode electrodes as well as the electrolyte. Each of the electrodes consists of two layers, the diffusion and catalyst layers, in which each layer has a particular porosity. Flow channels are not included in the model but their influence on the performance of the fuel cell is introduced as boundary conditions at the electrode surfaces.

**NUMERICAL MODEL**

The mathematical model used in this study is described briefly in this section. A more detailed description can be found in [6]. The three-dimensional governing conservation equations solved by the numerical model inside the porous electrodes and electrolyte are charge conservation equation, specie conservation equation and energy conservation equation given respectively by:

\[
\frac{\partial}{\partial x} \left( \sigma \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial y} \left( \sigma \frac{\partial \phi}{\partial y} \right) + \frac{\partial}{\partial z} \left( \sigma \frac{\partial \phi}{\partial z} \right) = S_e \tag{1}
\]

\[
\frac{\partial}{\partial t} \left( \rho \phi X_j \right) = V \cdot \left( \rho \phi D_0^e \nabla X_j \right) + \epsilon S_{e,\text{react}} + \epsilon S_{e,\text{electrochem,react}} \tag{2}
\]

\[
\frac{\partial}{\partial t} \left( \rho C T \right) = \frac{\partial}{\partial x} \left( k \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( k \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial z} \right) + S_T \tag{3}
\]

In the equations \( \phi \) is the electrical or electronic conductivity, \( \phi \) is the electric potential, \( \epsilon \) represents the porosity of the electrode, \( \rho \) is the density of the gas mixture inside the electrode, \( D_0^e \) is the “corrected” effective diffusivity of specie \( j \) and \( X_j \) is the mass fraction of the species \( j \), \( C \) is the specific heat, \( T \) is the temperature and \( k \) is the thermal conductivity. When solving for the electrodes, the thermal conductivity represents the effective thermal conductivity of the porous media. The last two terms on the right hand side of Eq. (2) are the net production of species \( j' \) due to bulk reactions inside the anode and electrochemical reactions near the active interfaces, respectively. Similarly the source term in Eq. (3) represents net heat generation from ohmic heating, bulk reactions and electrochemical reactions. Following, some of the sub-models are briefly described.

**Diffusivity**

Inside both electrodes, convection is neglected; therefore the only species transport mechanism is diffusion. The flux of each species in the multi-component mixture is modeled using Fick’s law along with an effective multi-component diffusivity as done by Yakabe et al. [19]. The effective diffusivity of the \( i \)th species is given by

\[
D_{eff}^i = \frac{\epsilon}{\tau} \left( \frac{1 - \alpha_k X_i}{D_{i,m}} + \frac{1}{D_k^e} \right)^{1-\epsilon} \tag{4}
\]

where \( \tau \) is the tortuosity of the porous anode, \( Y_i \) represents the molar fraction of the species \( i \), \( D_k^e \) is the Knudsen diffusivity and \( D_{i,m} \) the molecular diffusivity which depends on the binary diffusivity. A corrected effective diffusivity is used in the species transport equation. The applied correction to the effective diffusivity is similar to that proposed by Cayan et al. [20] and given by

\[
D_{eff}^i = \left( 1 + \frac{i}{i_{ref}} \right)^n D_{eff}^i \tag{5}
\]

For more detailed information on the diffusion model see [17].

**Electrochemistry**

Hydrogen and carbon monoxide can both be electrochemically oxidized inside a SOFC. The direct electrochemical oxidation reactions of hydrogen and carbon monoxide at the anode-electrolyte triple phase boundary are given by:

\[
\text{H}_2 + \text{O}^+ \rightarrow \text{H}_2\text{O} + 2e^- \tag{6}
\]

\[
\text{CO} + \text{O}^+ \rightarrow \text{CO}_2 + 2e^- \tag{7}
\]

At the cathode/electrolyte interface, the oxygen reduction reaction is given by:

\[
\text{O}_2 + 4e^- \rightarrow 2\text{O}^+ \tag{8}
\]

Therefore the overall redox reactions can be identified according to the two oxidation reactions shown above, resulting in

\[
\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} \tag{9}
\]
In DREAM-SOFC simultaneous electrochemical oxidation of hydrogen and carbon monoxide was implemented. This was done following the methodology proposed by Achenbach [16] and Nishino et al. [15] based on the constraint that the net potential difference should be the same for both electrochemical oxidation reactions. The previous statement allows us to determine the current produced by each of these reactions. The Butler-Volmer equation was used to calculate the hydrogen, carbon monoxide and oxygen activation overpotentials. The exchange current densities for these species were obtained by fitting the experimental data from [18] for hydrogen and carbon monoxide and from [19] for oxygen, resulting in the following equations:

\[
\begin{align*}
    \theta^*_{i, H_2} &= e \frac{Y_{H_2}}{Y_{H_2, ref}} \exp \left( -\frac{E_{act,H_2}}{RT} \right) \\
    \theta^*_{i, CO} &= e \frac{Y_{CO}}{Y_{CO, ref}} \exp \left( -\frac{E_{act,CO}}{RT} \right) \\
    \theta^*_{i, O_2} &= \frac{e}{(T-279.1757)} \left( \frac{Y_{O_2}}{Y_{O_2, ref}} \right) \exp \left( -\frac{E_{act,O_2}}{RT} \right)
\end{align*}
\]

**Internal reforming**

In composite Ni-YSZ anodes commonly used in SOFCs and under the operating conditions such as temperature and fuel composition, the methane steam reforming and water gas shift reactions take place. Internal reforming is modeled using two reversible reactions; namely the methane steam reforming and water gas shift reactions given respectively by

\[
\begin{align*}
    CH_4 + H_2O \leftrightarrow CO + 3H_2 \\
    CO + H_2O \leftrightarrow CO_2 + H_2
\end{align*}
\]

The kinetics of these catalyzed reactions is modeled with the rate constants determined experimentally by Lehnert et al. [20], fitted to Arrhenius type curves by Haberman and Young [21] and used in a modified form by Gemmen and Trembly [7]. The forward rate constants in a pressure basis (mol/m^3-Pa^-s) for the methane steam reforming reaction and the water gas shift reaction are given respectively by

\[
k_{mr,p}^f = 0.0203 \exp \left( \frac{-103191}{RT} \right)
\]

where the subscripts \textit{mr} and \textit{wgs} stand for methane reforming and water gas shift reaction respectively. The backward rate constants are related to the forward rate constants through the equilibrium constant.

**Electrical conductivities**

The electrodes of the commercial button cell are made up of two layers. In the anode, the two layers are the anode interlayer and the anode support both consisting of a Ni-YSZ composite, with thicknesses of around 20μm and 760μm respectively. The cathode consists of an LSM-YSZ interlayer (~20μm) and an LSM current collector (~180μm). For these materials, the dependence of the electrical conductivity with respect to temperature is linear and has the general form

\[
\sigma = aT + b
\]

where \(\sigma\) is the electronic conductivity in (S/m) and \(T\) is the temperature in (K). The linear trend is as those reported by Kim et al. [22], by Zhang et al. [23] and by Tsai and Barnett [24] for the composite Ni-YSZ, LSM-YSZ and LSM electrodes, respectively. The constants \(a\) and \(b\) do not correspond to the values obtained from the fitting to the measured conductivities [22, 23, 24]. They were scaled to represent the values reported by Zhao and Virkar [25]. The constants used in this study are listed in Table 1.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Ni-YSZ</th>
<th>LSM-Y5</th>
<th>LSM</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>-0.38</td>
<td>0.0254</td>
<td>2.9058</td>
</tr>
<tr>
<td>(b)</td>
<td>824.97</td>
<td>-1.7542</td>
<td>-1080.1</td>
</tr>
</tbody>
</table>

The ionic conductivity of the thin (~20μm) dense YSZ electrolyte has the form and activation energy as reported by Achenbach [26] and Janardhanan [12]. A small correction in the pre-exponential coefficient was performed to represent the ionic conductivity at 800°C reported in [25]. The modified relation is expressed by

\[
\sigma_{YSZ} = A \exp \left( -\frac{E_a}{RT} \right)
\]
where the pre-exponential coefficient $A$ and the activation energy are 61456 and 85634.2 J/mol respectively.

RESULTS

Verification of the Reforming Kinetics Model

An indirect verification of the reforming kinetics model implemented in this study is done by comparing the results reported by Lehnert et al. [21]. The study of Lehnert et al. [20] is based on a one-dimensional model whose computational domain consisted only of the anode electrode whereas the model developed in this study is a transient three-dimensional model that considers the whole cell. However, since the model is applied to a button cell where almost negligible radial and angular distributions are observed, it is fair to use it for verification purposes. In Lehnert’s et al. [20] simulation, a 2 mm thick anode operates isothermally at 850°C supporting a current density of 0.3 A/cm$^2$. The fuel composition (by volume) is considered to be that resulting from 30% pre-reformed methane resulting in 17.1% CH$_4$, 49.3% H$_2$O, 26.3% H$_2$, 2.9% CO and 4.4% CO$_2$. The same operating conditions were prescribed in DREAM-SOFC. The comparison of the predicted net molar production rates with those reported in literature [20] is shown in Figure 1. As it can be seen, the two models compare well along the thickness of the anode where the largest differences are observed close to the anode-electrolyte interface.

![Figure 1 Net production rates of a CH$_4$-H$_2$-H$_2$O-CO-CO$_2$ mixture](image)

Validation

The validation case consists of a button cell operating on simulated clean syngas, a mixture of H$_2$-CO-CO$_2$-H$_2$O with concentrations of 30%-23%-21%-26% by volume, respectively. The validation was performed by comparing the data obtained from numerical simulations and experiments [27]. The operating cell temperature is 800°C. A more detailed description of the experiments can be found in [27]. In Figure 2 the experimentally measured cell potential with time under a load of 0.5 A/cm$^2$ is presented. Once the cell potential becomes more stable (after around 20 hours) the average cell voltage is approximately 0.622 V. Therefore, it is evident that experimental uncertainty is present in the data.

![Figure 2 Time history of the cell potential under a load of 0.5 A/cm$^2$](image)

The V-i curve was obtained experimentally at 40 hrs, 90 hrs and 110 hrs of operation. From these data, the mean at each current loaded experimentally was calculated and the uncertainty was estimated using the standard deviation of the mean. The calculated experimental uncertainties varied from 1 mV at low current densities to 9 mV at high current densities which represent approximately 0.2% and 8% respectively. The experimental error bars are shown in Figure 3 along with the average experimental V-i curve.

The comparison between the V-i and power density curves from experiments and numerical predictions (validation of the model) is shown in Figure 4. The numerically predicted V-i curve for the cell operating on clean syngas compares well with the experimental V-i curve and predicting closely the limiting current.
Syngas Composition at Non-Equilibrium Conditions

A button cell operating at 800°C on clean syngas whose fuel concentration (5% H₂, 48% CO, 6% CO₂, 41% H₂O by volume) is high in carbon monoxide and not at equilibrium is simulated using DREAM-SOFC and its predicted performance is compared to that of the validation case (fuel composition at equilibrium). Comparing both cases, it can be realized that the total amount of fuel (H₂ and CO) is the same in both fuel streams. The predicted performance of the button cell at these operating conditions is shown in Figure 5. As it can be observed, the cell operating on syngas at equilibrium delivers a higher performance and a higher limiting current than the syngas composition which is not at equilibrium.

The major losses of potential in both cases (equilibrium and non-equilibrium fuel concentrations) were caused by hydrogen and carbon monoxide activation overpotentials followed by oxygen activation, concentration and ohmic overpotentials. Comparing the non-equilibrium case with the equilibrium concentration case, the cause of decline in the cell performance is attributed to a considerable increase in the anode activation overpotentials (hydrogen and carbon monoxide which are very similar) and concentration overpotential as shown in Figure 6. Ohmic and oxygen activation overpotentials remained basically the same (not shown for the sake of brevity) with a small decrease in the case of non-equilibrium fuel concentration due, presumably, to an increase in the cell temperature. Thus though the total fuel concentration (sum of H₂ and CO concentration) is the same for the two cases, the one with more hydrogen and less carbon monoxide shows better performance due to relatively lower activation and concentration losses associated with hydrogen oxidation.

The change in cell temperature (T_{cell} – T_{op}) is larger in the case of operation under non-equilibrium syngas concentration as shown in Figure 7. The cell running on non-equilibrium fuel concentration heats up more as a consequence of a higher rate of the exothermic water gas shift reaction as shown by the overall heat from this reaction in Figure 8a. Also heat is produced by water gas shift reaction even at open circuit condition and as a result the cell temperature increases by about 6°C even when the cell is not producing any current.
For the non-equilibrium composition case, the water gas shift reaction always proceeds forward whereas the case with equilibrium composition proceeds forward only at high currents as shown in Figure 8a. The methane reforming reaction proceeds in the reverse direction in both cases although the heat generated by this reaction is negligible when compared with heat from the water gas shift reaction (see Figure 8b). From Figure 8c, it can be seen that the entropic heat is higher for the non-equilibrium case as a consequence of a higher cell temperature. The ohmic heat is slightly lower in the non-equilibrium case also due to a higher cell temperature which decreases the cell ohmic resistance.

The splitting of the total current supported by hydrogen and carbon monoxide is shown in Figure 9 where the ratio of the two is presented as a function of the current density. For the non-equilibrium case, the ratio increases from around 0.6 to 2.2 for low currents to high currents whereas in the equilibrium composition case, it decreases for low to high currents from 6 to 5.2 approximately. It is shown that the partition of the current between hydrogen and carbon monoxide is dependent on the fuel concentrations and not constant as used in other studies [7]. Also, with these results, it is evident that the CO electrochemical oxidation can not be neglected [12, 13].

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Figure 7 Cell temperature change ($T_{\text{cell}}-T_{\text{op}}$) for equilibrium and non-equilibrium fuel composition

Figure 6 Comparison of overpotentials between the equilibrium and non-equilibrium fuel concentration (a) CO activation overpotential, (b) O$_2$ activation overpotential and (c) concentration overpotential
Figure 8 Heat sources from (a) water gas shift reaction, (b) methane reforming reaction and (c) entropic heat.

Figure 9 Ratio of the current generated by hydrogen oxidation to carbon monoxide oxidation.

From the case of syngas fuel at equilibrium can be observed that there is only one limiting current even though two fuels can be oxidized simultaneously (see Figure 10). The existence of one limiting current could be explained by the fact that the concentrations equilibrate through the water gas shift reaction. It is interesting to note that this still holds true for operation of the cell on inlet fuel concentrations which are far from equilibrium. This can be seen from Figure 10 where the concentration of hydrogen and carbon monoxide at the active interface tend to zero at around same cell current. This suggests that the water gas shift reaction is fast enough to equilibrate the concentrations even when the inlet syngas fuel concentration is far from equilibrium.

Figure 10 Hydrogen and carbon monoxide mass fraction at the anode-electrolyte interface for fuel concentrations at equilibrium and non-equilibrium conditions.
The concentration profiles along the thickness of the anode are not expected to be linear since the fuel composition is not at equilibrium and therefore the water gas shift reaction is taking place. The curvature of the concentration profiles is caused by the source term, otherwise these profiles would be basically linear. From Figure 11 it can be seen that the water gas shift reaction proceeds in the forward direction and that the rate of the reaction increases as the current density increases. This behavior is caused because the higher the current density the higher the temperature and the water concentration in the anode.

Effect of CO Electrochemical Oxidation

The effect of carbon monoxide electrochemistry on the cell performance was investigated. An anode supported button cell operating on coal syngas at the same conditions as the equilibrium concentrations case but with carbon monoxide electrochemistry artificially disabled was simulated. The results from these simulations are compared with those from the equilibrium concentrations case which considered carbon monoxide electrochemistry. The predicted V-i and power density curves for these two cases are shown in Figure 12. From the figure it is evident that though the fuel is the same for the two cases, the cell voltage is lower when CO electrochemistry is neglected. The small decline in performance when carbon monoxide electrochemistry is neglected is caused by an increase in the hydrogen activation overpotential since the total current is supported only by hydrogen and also by the decrease of hydrogen concentration at the anode-electrolyte interface which reduces the hydrogen exchange current density which depends on hydrogen concentration.

The overall heat produced from the water gas shift reaction plotted in Figure 13 shows that the net water gas shift reaction always proceeds in the forward direction for the case where carbon monoxide oxidation is neglected whereas it proceeds in the backward direction at low currents for the other case. Therefore, as expected, a small increase in the cell temperature is observed when carbon monoxide oxidation is not considered. Also, the water gas shift reaction rate is much higher when carbon monoxide electrochemistry is neglected. This implies that though carbon monoxide is not directly supporting the current production, it is indirectly contributing by augmenting the hydrogen supply through the water gas shift reaction.

The local carbon monoxide concentration at the anode/electrolyte interface as a function of the current density supported by the cell is presented in Figure 14. This figure shows that carbon monoxide concentration decreases faster near the limiting current even though it is not involved in the electrochemistry, probably caused by the increase of water concentration and temperature which increase the reaction rate of the water gas shift reaction. Summarizing, if carbon monoxide electrochemistry is not taken into account as done by some researchers [12, 28, 29] the computations will incur errors due to overprediction of water gas shift reaction rates and resulting heat generation. Moreover incorrect
prediction of carbon monoxide concentration distribution may lead to wrong conclusions with respect to carbon deposition and similar phenomenon.

![Figure 13 Net heat generation from water gas shift reaction](image)

When CO electrochemical oxidation is neglected, it was observed that the predicted cell performance decreased about 5% at the maximum power density conditions. In addition, the dynamics of the water gas shift reaction are quite different for cases with and without carbon monoxide electrochemistry.

**CONCLUSIONS**

The chemical kinetics model of the methane reforming and water gas shift reactions was verified by comparing the 3D model used in this study with a 1D model reported in the literature. The CFD model was also validated with experimental data through the V-i and power density curves when the SOFC operates on clean coal syngas (equilibrium composition) at 800°C.

The numerical model considers the H₂ and CO simultaneous electrochemical oxidation. It was found that the splitting of the total current between the two species shows a dependence on fuel composition and total current density. Also, the model predicts only one limiting current irrespective of whether the inlet fuel stream composition is close to equilibrium or not. Apparently, the water gas shift reaction is fast enough that equilibrates these two fuels.

**REFERENCES**

fuel cell,” Journal of Power Sources, 161, pp 1084-1095