SOFC OPERATION WITH SYNGAS FUELS: EXPERIMENTS AND MODEL VALIDATION

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ABSTRACT

An isothermal model of an SOFC operating with syngas fuel based on button-cell geometry is presented. The model considers momentum and multi-component mass transport coupled with electrochemical reactions (H₂ and CO oxidation at the anode as well as O₂ reduction at cathode) and chemical reaction (water-gas shift reaction at anode). The model agrees well with experimental performance data for various syngas compositions for isothermal operation at 900°C but not as well for operation at 800°C, where the model underestimates cell voltage. It was observed both experimentally and with the model results that the presence of CO does not affect significantly the cell performance. However, if CO₂ is present without CO, the cell performance decreases rapidly compared to that with pure hydrogen.

INTRODUCTION

Fuel flexibility is one of the major advantages of SOFC operation in addition to high efficiency and long term stability (1). A wide range of hydrocarbon-based fuels or their syngas derivatives, such as natural gas, biomass and coal can potentially be used to power an SOFC. The use of syngas derived from biomass and coal has received much more attention in recent years (1-4) since biomass and coal are more abundant than natural gas. When used with syngas, the cell performance strongly depends on operating conditions and on syngas composition. Therefore, it is very important to develop a modelling tool to predict the effect of operating conditions such as syngas feed composition and operating temperature on SOFC performance. In this work, an isothermal model of an SOFC for syngas operation based on the button cell geometry is developed. It takes into account momentum transport and multi-component mass transport coupled with electrochemical (oxidation and reduction) and chemical (water-gas shift) reactions. The model is validated using experimental cell performance for various syngas compositions at operating temperatures of 800°C and 900°C.
EXPERIMENTAL

The electrochemical cells used in this study were Electrolyte Supported Cells (ESC) supplied by Innovative Dutch Electro Ceramics, InDEC B.V. The ESC consists of an approximately 150 μm thick TZ3Y electrolyte (3 mol % yttria-stabilized zirconia) made by tape casting. After sintering, a 50 μm thick Ni/8YSZ anode and 50 μm thick La0.7Sr0.2MnO3-δ (LSM) were applied by screen printing. The area of the electrolyte is 25 cm² (5x5 cm²). The active area of each electrode is 16 cm² (4x4 cm²).

The fuel gases, H2, CO, CO2 and N2 were mixed using a gas mixing station. Gas concentration could be varied by controlling the flow rate of each gas through separate mass flow controllers. Thereafter, the gas mixture was humidified to desired levels by passing through a humidifier prior to entering the anode side of the electrochemical cell. The extent of gas humidification was controlled by a temperature bath. The exit gas from the anode side was discharged to the atmosphere through a fume hood. Air was fed directly into the cathode either from a cylinder or by direct exposure to the ambient atmosphere. Gas sampling lines located at the inlet and outlet of the experimental setup were connected to a gas chromatograph to measure gas concentrations.

The cell performance was characterized by measuring the cell voltage as a function of the current density for various gas compositions and operating temperatures. The cell voltage and current were recorded only when the response had remained unchanged for at least 3 minutes at each load resistance setting. In this study, the influences of N2 and CO2 dilution, H2/CO composition ratio and simulated syngas composition (mixture of H2, CO, CO2 and N2) on the cell performance were investigated at operating temperatures of 800°C and 900°C.

MATHEMATICAL MODEL

Modeling Geometry

The test rig is based on a button cell and includes an anode feed tube, air channel, fuel channel and an electrochemical cell as displayed in Figure 1. The cell in this model geometry consists of the electrolyte layer and electrode layers. Since the electrodes are very thin (50 μm), mass transport and ohmic resistances at electrode layers are insignificant and, therefore, the governing equations of mass transport are considered at the fuel and air channels while charge transport is taken into account at the electrolyte subdomain. Also, the electrode reactions are assumed to take place at the interfaces of cathode and electrolyte, and anode and electrolyte. The fuel gas is supplied to the anode side through an anode feed tube. After impinging on the anode layer, it then flows backward to the gas outlet channel. Air diffuses through the air channel to the cathode side of the cell.

Governing Equations

The governing equations are summarized in Table I. The momentum and mass transport equations for the fuel channel are solved simultaneously to determine the velocity of the fuel stream and concentration profile of each gas. Fuel gases considered in the model are

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H₂, CO, CO₂, H₂O and N₂. Only charge transport is considered within the electrolyte subdomain to determine the potential distribution and calculate the ohmic overpotential. Mass transport and electrical resistances of the very thin electrode layers are ignored. Only mass transport of O₂ is considered within the air channel.

**Boundary Conditions**

In order to solve the systems of transport equations simultaneously, the related boundary conditions are specified as follows: along the symmetry line, i.e., r = 0: \( \mathbf{n} \cdot \mathbf{N}_i = 0 \) (\( \mathbf{N}_i \) = molar flux of each gas species), \( \partial v / \partial r = 0 \), \( \partial u / \partial r = 0 \), where \( i = \text{H}_2, \text{H}_2\text{O}, \text{CO} \) and \( \text{CO}_2 \) and \( \text{O}_2 \). At the fuel inlet, i.e., \( z = 0 \) and \( r < r_a \) (3 mm), the conditions are prescribed to be the inlet velocity and species mole fractions. The inlet mole fraction of \( \text{O}_2 \) is also prescribed at \( z = L \). At the outlet of the fuel channel, the outlet pressure is specified for momentum transport, i.e., \( p_f = 101.35 \text{ kPa} \) and \( \partial v / \partial z = 0, \partial u / \partial z = 0 \); and for mass transport \( \mathbf{n} \cdot \mathbf{N}_i = 0 \). At the anode/electrolyte layer, i.e., \( z = z_a \), the rate of consumption and production of participating gas components can be determined by the rate of their electrochemical and water-gas shift reactions (RWGS), i.e., \( \mathbf{n} \cdot \mathbf{N}_\text{H}_2\text{O} = \text{R}_{\text{WGS}} J_\text{a,HD}/2F \), \( \mathbf{n} \cdot \mathbf{N}_\text{H}_2 = J_\text{a,HD}/2F+\text{R}_{\text{WGS}} \), \( \mathbf{n} \cdot \mathbf{N}_\text{CO} = -J_\text{a,CO}/2F+\text{R}_{\text{WGS}} \), and \( \mathbf{n} \cdot \mathbf{N}_\text{CO}_2 = J_\text{a,CO}_2/2F+\text{R}_{\text{WGS}} \). For boundary conditions of charge transport through the electrolyte, \( \mathbf{n} \cdot \mathbf{i} = J_\text{a,HD}+J_\text{a,CO} \). At the cathode/electrolyte layer, i.e., \( z = z_c \); \( \mathbf{n} \cdot \mathbf{N}_\text{O}_2 = -J_c/4F \) for mass transport and \( \mathbf{n} \cdot \mathbf{i} = -J_c \) for charge transport. At \( r = r_b \), \( u_f = 0 \), \( v_f = 0 \), \( \mathbf{n} \cdot \mathbf{N}_i = 0 \).

![Figure 1. Modelling geometry of the test rig (not to scale). Due to symmetry, only half of the cell is shown and used in the model.](image-url)
Table I. Governing Equations.

| Subdomain | Variables: $v_f$, $u_f$, $p_f$ and $c_i$ |
|-----------|---------------------------------------------|
| Fuel channel | Overall mass $\frac{\partial v_f}{\partial z} + \frac{1}{r} \frac{\partial (r u_f)}{\partial r} = 0$ [1] |
| Momentum $r$ direction $\rho \frac{\partial (v_f u_f)}{\partial z} + \frac{1}{r} \frac{\partial (r u_f)}{\partial r} = - \frac{\partial p_f}{\partial z} + \frac{\partial}{\partial z} \left( \mu_f \frac{\partial v_f}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( \mu_f \frac{\partial u_f}{\partial r} \right)$ [2] |
| Momentum $z$ direction $\rho \frac{\partial (v_f u_f)}{\partial z} + \frac{1}{r} \frac{\partial (r u_f)}{\partial r} = - \frac{\partial p_f}{\partial z} + \frac{\partial}{\partial z} \left( \mu_f \frac{\partial v_f}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( \mu_f \frac{\partial u_f}{\partial r} \right) - \frac{2 \mu_f u_f}{r^2}$ [3] |
| Species $\frac{\partial (c_i v_f)}{\partial z} + \frac{1}{r} \frac{\partial (r c_i u_f)}{\partial r} = \frac{\partial}{\partial z} \left( D_i \frac{\partial c_i}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r D_i \frac{\partial c_i}{\partial r} \right)$ [4] |

where $i = H_2, H_2O, CO$ and $CO_2$ and $u_f$ the fuel velocity in $r$ and $z$ direction.

Electrolyte Variables: $\phi_i$

| Ion | \( \frac{1}{r} \frac{\partial (r \partial \phi_i / \partial r)}{\partial r} + \frac{\partial^2 \phi_i}{\partial z^2} = 0 \) [5] |

Air channel Variables: $c_{O2}$

| Mass | \( \frac{\partial (c_{O2} v_f)}{\partial z} + \frac{1}{r} \frac{\partial (r c_{O2} u_f)}{\partial r} = \frac{\partial}{\partial z} \left( D_{O_2-H_2} \frac{\partial c_{O2}}{\partial z} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r D_{O_2-H_2} \frac{\partial c_{O2}}{\partial r} \right) \) [6] |

The current densities, $J_{a,H_2}$, $J_{a,CO}$ and $J_e$ are the rates of electrochemical reactions for $H_2$ oxidation, $CO$ oxidation and $O_2$ reduction, respectively. They depend on the cathode and anode overpotentials ($\eta$) as follows:

\[
J_e = -\frac{10000RT}{4F} s_e \left\{ \exp \left( \frac{2F \eta_e}{RT} \right) - \exp \left( -\frac{2F \eta_e}{RT} \right) \right\} \quad [7]
\]

\[
J_{a,H_2} = \frac{1000RT}{3F} s_{a,H_2} \left\{ \exp \left( \frac{2F \eta_{a,H_2}}{RT} \right) - \exp \left( -\frac{2F \eta_{a,H_2}}{RT} \right) \right\} \quad [8]
\]

\[
J_{a,CO} = \frac{1000RT}{8F} s_{a,CO} \left\{ \exp \left( \frac{2F \eta_{a,CO}}{RT} \right) - \exp \left( -\frac{2F \eta_{a,CO}}{RT} \right) \right\} \quad [9]
\]

\[
\eta_{a,H_2} = \phi_a - \phi_s (z_a, r) - E^{0}_{a,H_2} (z_a, r) \quad [10]
\]
\[
\eta_{a,CO} = \phi_a - \phi_s (z_a, r) - E^0_{a,CO} (z_a, r) \quad [11]
\]
\[
\eta_e = \phi_e - \phi_s (z_c, r) - E^0_e (z_c, r) \quad [12]
\]

where, \(s_{a,H2}, s_{a,CO}\) and \(s_e\) are the interface conductivities of the electrode reactions. \(\phi_a\) and \(\phi_e\) are potentials at the anode and the cathode, respectively. \(E^0_{a,H2}, E^0_{a,CO}\) and \(E^0_e\) are the reversible cell voltages for the half-cell reactions of H2 oxidation, CO oxidation and O2 reduction, respectively. The coefficient "8" in the denominator of Eq. 9 has been chosen so that the ratio \(J_{a,H2}/J_{a,CO}\) is between 2 and 3, specifically 2.7 here, as observed by Matsuzaki and Yasuda (5).

### Numerical Implementation

The momentum, mass and ion transports were solved simultaneously using FEMLAB version 3.0a. To calculate the cell performance, the cell voltage \((V_{cell} = \phi_e - \phi_a)\) was specified and the current density distribution along the anode surface \((r = 0 \text{ to } r = 18 \text{ mm})\) was determined. Thereafter, the averaged current density was estimated by integrating the current density along the anode surface \((I_{avg} = \text{total current/area})\), i.e.,

\[
I_{avg} = 2\pi \int_0^b r (J_{a,H2} + J_{a,CO}) dr \quad [13]
\]

The effect of the contact resistance between current collector and electrode coatings was incorporated into the developed model as follows:

\[
V_{load} = (\phi_e - \phi_a) - I_{avg} R_{contact} \quad [14]
\]

where \(V_{load}\) is the voltage delivered to the external load. \(R_{contact}\) is the contact resistance determined by fitting the model to experimental data. Since \(R_{contact}\) should only be a function of operating temperature, it was fitted using the experimental performance data for pure H2 feed at 800°C and 900°C. Once so determined, the values of \(R_{contact}\) were used for all other gas feed compositions for the model simulations at the two temperatures.

### RESULTS AND DISCUSSION

In this work, cell performances obtained from the developed model are compared with the experimental data at both 800 and 900°C. The fitted values of \(R_{contact}\) are found to be 1.6 and 1.2 \(\Omega\) cm\(^2\) at 800 and 900°C, respectively.

#### Effect of N2 Dilution

Figure 2 shows the experimental and modelling results for the cell performance when mixtures of either H2/N2 or CO/N2 are used. From Fig. 2(a), the model predictions agree reasonably well with the experimental data obtained at both 800 and 900°C for various H2/N2 mixtures. Although the open circuit voltages (OCVs) do not change much over the wide range of inlet H2 concentrations, the cell performance declines when H2 concentration is reduced. However, in the range of current density considered here, the impact of N2 dilution is not large since the cell performance decreases only about 15% when the H2 concentration is reduced from 100% to 10%. From Fig. 2(b), the model results agree well with the experimental data only at 900°C. At 800°C, large discrepancies are observed particularly at high current density.
Figure 2. Experimental data and model predictions of cell performances for various H₂/N₂ (a) and CO/N₂ (b) compositions at 800°C and 900°C; symbols: experiment; lines: model.

Effect of CO₂ Dilution

From Fig. 3, both model and experimental curves show that the effect of dilution by CO₂ is more pronounced than that by N₂. From Fig. 3(a), a reduction in H₂ concentration from 100 to 20% results in 20 and 26% decreases of the OCV at 800 and 900°C, respectively. This is likely due to the impact of the water-gas shift reaction (WGS). In the presence of H₂ and CO₂, CO and H₂O are generated via the WGS reaction thereby reducing OCV (6). The model prediction is accurate at 900°C, but slightly underestimates the voltage at 800°C.

From Fig. 3(b), it is evident that the model predictions show similar trends as the experimental data at high CO concentration. However, at high current densities and low CO concentration a drop in cell performance is observed experimentally, but is not predicted by the model. Evidently, the model is not accounting for some phenomenon that becomes increasingly important at high current densities. Both OCVs and cell voltage decrease as the extent of CO₂ dilution increases.
Figure 3. Experimental data and model prediction of cell performances for various H₂/CO₂ (a) and CO/CO₂ (b) compositions at 800 and 900°C.

Effect of H₂/CO ratio

Fig. 4 shows the experimental data and model predictions of cell performance for various feed compositions of H₂/CO gas mixtures. The interesting result from this figure, in particular the experimental data, is that the cell performance achieved in pure CO is only slightly lower than that obtained using pure H₂. This implies that the slower electrochemical reaction kinetics of CO oxidation does not play an important role in determining the overall cell performance. This is not surprising since the cathodic overpotential is much larger than the anodic overpotential. The model underestimates the results at both temperatures.

Effect of Syngas Composition

The impact of simulated syngas composition on the cell performance is exhibited in Fig. 5. Experiments and model simulations were carried out at the 6 gas compositions given in Table II. For most of the syngas compositions, the model results agree well with the experimental data at 900°C but underestimate the cell voltage at 800°C. Fuel F1 provides
1.2

Figure 4. Experimental data and model prediction of cell performances for various H₂/CO compositions at (a) 800°C and (b) 900°C.

the highest performance since the fuel contains moist H₂ only. Fuel F6 which contains 20% H₂ and 20% CO, provides slightly better performance than diluted H₂ (F2). This indicates that CO is a useful fuel for an SOFC. Fuel F3 contains H₂, CO₂ and N₂ whereas fuels F4 and F5 are examples of biomass syngas compositions typically obtained from air and oxygen gasifiers (7), respectively. It is observed that the OCVs of F3, F4 and F5 are less than those of F1, F2 and F6. This is likely due to the effect of the WGS that becomes operative due to the presence of CO₂, as previously described. The cell performance for F5 is slightly better than that of F4 because of its higher fuel concentration and lower N₂ dilution. However, considering the cost of syngas production, syngas fuel, F4 may be the most appropriate for an SOFC. F3 fuel yields the lowest cell performance because of lower fuel concentration and the presence of significant amounts of CO₂ and N₂ in the feed stream. If CO₂ is removed before the syngas enters the SOFC, the cell performance increases. On the other hand, the presence of CO₂ might help to prevent carbon formation. Thus, a trade-off between these effects must be made to optimize both cell performance and its lifetime.

Table II. Simulated syngas compositions.

| Fuel no. | H₂ | H₂O | CO | CO₂ | N₂ |
|----------|----|-----|----|-----|----|
| F1       | 97 | 3   | -  | -   | -  |
| F2       | 20 | 3   | -  | -   | 80 |
| F3       | 20 | 3   | -  | 14  | 63 |
| F4       | 20 | 3   | 20 | 14  | 43 |
| F5       | 32 | 3   | 45 | 15  | 3  |
| F6       | 20 | 3   | 20 | 0   | 57 |
CONCLUSIONS

An isothermal mechanistic model based on a button cell geometry was validated using experimental performance data for various syngas compositions at 800 and 900°C. The results showed that the model predictions agree reasonably well with the experimental data at 900°C while it yields slightly lower cell voltage at 800°C. Although the oxidation rate of CO is less than that of H₂, it has only a very small effect on the overall cell performance. Thus, syngas may serve as an effective fuel for an SOFC, although possible carbon deposition in the presence of large amount of CO should be looked at in more details. This model has enabled us to gain a better understanding of SOFC performance when syngas is used as a fuel and should be invaluable for purposes of determining optimal cell design and operating conditions.

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